APPENDIX.

LIST OF NOTES & PAPERS

BY

B.N.DESAI AND CO-WORKERS

ALONG WITH

REPRINTS.

Notes and papers
by
B. N. Desai & co-workers.

PHYSICAL CHEMISTRY (P)

Notes & papers.

* 1. Note on the influence of hydrolysed gelatine on the precipitation of silver chromate by T.R.Bolam and B.N.Desai, Trans. Faraday Soc., 24, 50, 1928.

* 2. The Kinetics of coagulation by B.N.Desai, Trans. Faraday Soc., 24, 181, 1928.

* 3. The coagulation of thrium hydroxide by electrolytes by B.N.Desai, Kolloidchem. Beihefte, 26,357, 1928.

* 4. Studies in ceric oxide sol and gel by B.N.Desai, Kolloidchem. Beihefte, 26, 422, 1928.

* 5. The Kinetics of coagulation by A.M.Patel and B.N. Desai, Trans. Faraday Soc., 26, 128, 1930.

* 6. Effect of non-electrolytes on the precipitation of thorium hydroxide from its salt solution in presence of alkali by A.M.Patel and B.N.Desai, J.Indian Chem. Soc., 7, 161, 1930.

* 7. Sensitisation by non-electrolytes in the presence and absence of electrolytes of colloidal thorium hydroxide dialysed to different extents by A.M.Patel and B.N.Desai, Kolloid Zeit.,51, 318, 1930.

* 8. The influence of hydrolysed gelatine on the precipitation of silver chromate by B.N.Desai and G.M.Nabar, Trans. Faraday Soc., 28, 449, 1932.

* 9. Studies in the influence of non-electrolytes containing different number of hydroxyl groups on the precipitation of thorium hydroxide from solution of thorium nitrate on addition of caustic soda by G.M. Nabar, A.M. Patel and B.N.Desai, Kolloid Zeit., 57, 173, 1931.

10. Relation between charge and stability of colloidal gold by G.M.Nabar and B.N.Desai, Nature, 127, 666, 1931.

11. Condition of silver chromate in gelatine by G.M.Nabar and B.N.Desai, Nature, 127, 628, 1931.

12. Condition of sparingly soluble substances in gelatine by B.N.Desai, Nature, 128, 222, 1931.

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* Reprints submitted.

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*13. A note on the liesegang rings of silver chromate in gelatine by B.N.Desai and G.M.Nabar, J.Indian Chem. Soc., 9, 141, 1932.

*14. Relation between charge and stability of colloidal solutions of gold and ferric hydroxide dialysed to different extents by B.N.Desai, G.M.Nabar and P.M. Barve, J.Indian Chem.Soc,9, 463, 1932.

15. Coagulation of colloids by electrolytes by B.N.Desai and P.M.Barve, Nature, 128, 907, 1931.

16. Relation between charge and viscosity of colloidal solutions by B.N.Desai, Current Science, 1,37,1932.

17. Importance of dialysis in the study of colloids by B.N.Desai, Current Science, 1, 125, 1932.

*18. The importance of dialysis in colloid chemistry - Behaviour of colloids towards electrolytes and non-electrolytes with progress of dialysis by B.N.Desai, Special Number of J. Indian Chem.Soc.,37, 1933.

*19. A note on the existence of critical potential characteristic of coagulation of a colloid by an electrolyte by B.N.Desai, J. Bombay Univ.,1, Part II, 25, 1932.

*20. Influence of acidity of gelatine solution on its inhibitive power and on the solubility of silver chromate by B.N.Desai and G.M.Nabar, J.Bombay Univ., 1, Part II, 28, 1932.

21. Influence of wall effect on the nature of coagulation process by B.N.Desai, Current Science, 1, 376, 1933.

*22. Importance of dialysis in the study of colloids - Part I - Colloidal ferric hydroxide by B.N.Desai and S.K.Borkar, Trans. Faraday Soc.,29, 1269, 1933.

23. Negative viscosity of solutions by H.N.Desai, D.B.Naik and B.N.Desai, Current Science, 2, 206, 1933.

*24. Importance of dialysis in the study of colloids - Part II - Colloidal thorium hydroxide by B.N.Desai and A.K.Desai, Trans. Faraday Soc., 30, 265, 1934.

*25. Condition of silver chloride, silver iodide and lead iodide in gelatine by B.M.Naik, H.N.Desai and B.N. Desai, J.Indian Chem.Soc., 11, 45, 1934.

*26. Influence of acidity of gelatine on the Liesegang rings of silver chromate and silver iodide. by B.N. Desai and B.M.Naik, J.Indian Chem.Soc.,11, 59,1934.

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* Reprints submitted.

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*27. Inhibitive power of gelatine by B.N.Desai and B.M. Naik, J.Bombay Uinv.,2, Part II, 90, 1933.

*28. Importance of dialysis in the study of colloids, by B.N.Desai, J.Bombay Univ., 2, Part II, 265,1933.

29. Changes in charge on colloidal particles during dialysis of sols by B.N.Desai, Current Science, 2, 473, 1934.

*30. Conductivity measurements of some chlorides, iodides and nitrates of Alkalis and Alkaline earths in water and methyl, ethyl and n-propyl alcohols by H.N.Desai, D.B.Naik and B.N.Desai, Indian Journal of Physics, 8, Part IV, 323, 1934.

31. Changes in charge, conductivity, stability and composition of colloidal arsenious sulphide on exposure to light by C.B.Joshi, P.M.Barve and B.N. Desai, Current Science, 3, 105, 1934.

32. Inhibitive power of agar by B.N.Desai and collaborators, Current Science, 3, 172, 1934.

*33. Viscosity of moderately and highly concentrated solutions of some salts in water and methyl, ethyl and n-propyl alcohols by H.N.Desai, D.B.Naik and B.N.Desai, J.Bombay Univ., 3, Part II, 109, 1934.

*34. Importance of dialysis in the study of colloids - Part III - Colloidal prussian blue by G.F.Mankodi, P.M.Barve and B.N.Desai, Proc.Ind.Acad.Sci.,4(4), 480, 1936.

*35. Condition of sparingly soluble substances in gels - Part I - Silver chromate in gelatine by R.R. Khanolkar, P.M.Barve and B.N.Desai, Proc.Ind.Acad. Sci., 4(4), 468, 1936.

*36. Conductivity and cataphoretic speed measurements of Benzopurpurin 4 B, Congo Red and Sky Blue F.F. by B.N.Acharya, A.M.Patel and B.N.Desai, Proc.Ind.Acad. Sci., 4(5), 503, 1936.

*37. Importance of dialysis in the study of colloids - Part IV - Colloidal arsenious sulphide by C.B.Joshi, P.M.Barve and B.N.Desai, Proc. Ind.Acad.Sci.,4(5), 590, 1936.

*38. A discussion of conductivity and cataphoretic speed measurements of colloidal prussian blue and arsenious sulphide from the point of view of origin of charge on colloidal particles by G.F.Mankodi,C.B.Joshi,P.M. Barve and B.N.Desai, J.Bombay Univ.,5, Part II, 53, 1936.

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* Reprints submitted.

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39. Liesegang rings and the influence of media on their formation by B.N.Desai, Current Science, 5, 584, 1937.

40. Mutual coagulation of colloidal solutions. Part I - Interaction between ferric hydroxide and prussian blue sols by P.M.Barve, Y.S.Paranjpe and B.N.Desai, In course of publication in the journal of the Bombay University.

P.T.O.

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METEOROLOGY (M)

Notes & papers.

* 1. A study of thunderstorms in Poona in 1930 by B.N.Desai India Met.Dept.Scientific Notes, Vol.3, No.27.

* 2. A study of the structure of the Bay storm of November 1926 by S.Mal and B.N.Desai, India Met.Dept. Scientific Notes, Vol.4, No.39.

* 3. Nocturnal atmospheric radiation at Poona - A discussion of measurements made during the period Jan. 1930 to Feb. 1931 by K.R.Ramanathan and B.N.Desai, Gerlands Beitr. z. Geophysik, 35, 68, 1932.

4. Structure and development of temperature inversions by S.Mal, S.Basu and B.N.Desai, Nature, 129, 97, 1932.

* 5. Structure and development of temperature inversions in the atmosphere by S.Mal, S.Basu and B.N.Desai, Beitr. z. Physik d.f. Atmos., 20, 56, 1932.

* 6. Evidence in favour of non-symmetrical structure in the inner storm area of cyclones in the Indian Seas by B.N.Desai and S.Basu, Gerlands Beitr, z. Geophysik, 40, 1, 1933.

* 7. Vertical structure of the surface of discontinuity between the continental and the monsoon air masses in the pre-monsoon period by B.N.Desai and S. Mal, Gerlands Beitr. z. Geophysik, 40, 12, 1933.

* 8. A discussion of structure of inner storm area of some Indian cyclones by S. Basu and B.N.Desai, Gerlands Beitr. z. Geophysik, 42, 353, 1934.

* 9. Colloids in the Atmosphere by B.N.Desai, J.Bombay Univ., 3, Part II, 195, 1934.

10. A discussion of the mechanism of the development of thundery conditions over Karachi between 24th June and 2nd July, 1936 with reference to upper air temperature ascents by S. Mal and B.N.Desai. In course of publication in the Quarterly Journal of the Royal Meteorological Soc., London.

11. Thundersqualls of Bengal by B.N.Desai and S.Mal. In course of publication in Gerlands Beiträge zur Geophysik.

12. A discussion of some aeroplane ascents at Drigh Road (Karachi) on the days of dust-raising winds, duststorms and thunderstorms by B.N.Desai and S.Mal. In course of publication as a Scientific Note in the India Meteorological Dept.

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* Reprints submitted.

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METEOROLOGY (m) 6

Books.

1. Meteorology and climate of Gujarat (in Gujarati) by B.N.Desai and M.V.Unakar. Published by Gujarati Forbes Sabha, Bombay - 1936.

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Reprinted from the *Transactions of the Faraday Society*, No. 80,
Vol. XXIV., Part 1, January, 1928.

NOTE ON THE INFLUENCE OF HYDROLYSED GELATIN ON THE PRECIPITATION OF SILVER CHROMATE

NOTE ON THE INFLUENCE OF HYDROLYSED GELATIN ON THE PRECIPITATION OF SILVER CHROMATE.

By T. R. Bolam and B. N. Desai.

Received 4th November, 1927.

It has been shown[1, 2] that gelatine has to a marked degree the power of retarding the separation of silver chromate from aqueous mixtures of silver nitrate and potassium chromate. With sufficient gelatin the mixture will remain clear and yellow for 72 hours, although the solution is strongly supersaturated with silver chromate.

No experiments seem to have been carried out to determine quantitatively how the inhibitive influence is affected by hydrolysis of the gelatin. It may be mentioned that Liesegang[4] states that the solubility of silver chromate in "gelatose" alone is less than in mixtures of "gelatose" with gelatin.

The gelatin was hydrolysed by heating a solution (3 per cent. or 6 per cent.) on the water-bath or by gentle boiling. For these operations it was placed in a fused silica flask fitted with a water-cooled ground-in fused silica condenser. The flask and its contents were weighed before and after each period of heating and any loss in weight, always small, made good by the addition of water.

In all experiments, 5 c.c. $N/100$ K_2CrO_4 + 3·8 c.c. 3 per cent. gelatin was added to 5 c.c. $N/100$ $AgNO_3$ + 3·8 c.c. 3 per cent. gelatin. Gelatin B[2] and pure salts were used and all solutions were made up with con-

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[1] Williams and MacKenzie, *J.C.S.*, **117** (1920), 844.

[2] Bolam and MacKenzie, *Trans. Far. Soc.*, **221** (1926), 151, 162.

ductivity water. The reacting solutions were prepared in pyrex test-tubes, brought to approximately 25° C., mixed by pouring from tube to tube several times, and then immediately placed in a 25° C. thermostat. The time required for the appearance of a definite red colour was taken as the measure of the inhibition.

The p_H of the gelatin at the various stages of hydrolysis was determined colorimetrically, using brom-cresol-purple as indicator and Sörenson's phosphate mixtures as standards. The gelatin was considerably diluted for this purpose.[2]

The following are the figures for three entirely independent series of experiments. :—

Treatment.	(t) Time for appearance of precipitate (mins.).			p_H.
	1.	2.	3.	
3 per cent. gelatin heated on water-bath for :—				
1 hour	43	41	39	5·9
2 hours	44	42	42	5·9
2 hours + 1 hour boiling.	70	57	62	5·9-5·95
,, ,, + 2 hours ,,	47	52	56	5·95
,, ,, + 3 ,, ,,	57	50	42	5·95
,, ,, + 5 ,, ,,	59	52	—	5·95
,, ,, + 7 ,, ,,	41	—	—	5·95-6·0

For comparison "t" was determined for the unhydrolysed gelatin (dispersed at 30° to 35° C.) and found to have the following values in four independent experiments: 146, 130, 134, 161 mins. The p_H of the unhydrolysed material proved to be 5·75 and the question arises whether the marked loss in effect on hydrolysis is not due simply to decrease in acidity.[2] To test this, 6 per cent. gelatin was heated on the water-bath for one hour and then diluted to 3 per cent. with acetic acid of such strength that the p_H of the gelatin was brought back to approximately its original value. Also 3 per cent. unhydrolysed gelatin was prepared containing the same amount of acetic acid. Whereas in the case of the latter "t" underwent a large increase (t = 220 and 251 mins. : indep. expts.), the inhibitive capacity of the hydrolysed gelatin was not affected (t = 38 and 35 mins. : indep. expts.).

It was found that the hydrolysis of the gelatin produced considerable changes in the formation and appearance of the precipitate, which may be broadly summarised as follows :—

Unhydrolysed gelatin.	*Hydrolysed gelatin.*
1. Precipitation localised at certain points.	Precipitate appears uniformly in all parts.
2. Mixture becomes turbid red.	Mixture becomes clear red.
3. Precipitate settles much more rapidly than in the case of hydrolysed gelatin.	

The hydrolysis thus increases the degree of dispersion of the precipitate, which is in agreement with the work of Ganguly [3] and is, as pointed out by him, due to a stronger "protective" action.

While the data given above are rather approximate, owing, probably, to the simple method of mixing and to inadequate control of temperature

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[3] Ganguly, *Quart. J. Indian Chem. Soc.*, 3 (1926), 177.

during hydrolysis, there is clear indication of a maximum in the value of "*t*" at a certain stage.

Liesegang[4] found that for the formation of periodic structures of silver chromate in gelatin a certain proportion of the hydrolysis products of the latter is necessary. In view of the weak inhibitive power of "gelatose" this is surprising, and suggests that the inhibitive influence of a mixture of gelatin and gelatose is greater than might be expected from the behaviour of its constituents.

From the foregoing it will be seen that the decrease in inhibitive capacity on hydrolysis is due to the fundamental changes produced in the gelatin. Further, it is obvious that inhibition and protection *do not go hand in hand.* It must be remembered that there is a difference in function. In the case of the first the gelatin operates by opposing the formation or growth of crystallisation centres or nuclei. Svedberg's[5] work on the reduction of gold chloride in the presence of gelatin, and that of Marc[6] on the crystallisation of K_2SO_4 in the presence of certain dyestuffs, provide examples of similar action. On the other hand "protection" prevents the aggregation of small particles to larger masses.

[4] Liesegang, *Koll. Z.*, **2** (1907), 70; *Z. physik. Chem.*, **88** (1914), 1.
[5] Svedberg, *Koll. Z.* **5** (1909), 318.
[6] Marc, *Z. physik. Chem.*, **67** (1909), 470.

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THE KINETICS OF COAGULATION.

By B. N. Desai.

Received 5th September, 1927.

(*Communicated by* Sir James Walker, K.B.E., F.R.S.).

Within the last few years attempts have been made to derive an equation which will truly represent the changes which take place when an electrolyte is added to a sol. Smoluchowski[1] has proposed an equation to represent the kinetics of rapid coagulation on the assumptions that on the addition of an electrolyte (1) the potential of the micellae is instantaneously changed, (2) the charge on the miscellae is completely neutralised and hence there is no repulsive force opposing the coalescence, (3) the collisions are inelastic, *i.e.*, every collision between the particles results in the formation of an aggregate.

Smoluchowski's equation for rapid coagulation has the form

$$\theta = \frac{1}{\mathrm{K}v_0} = \frac{1}{4\pi \mathrm{D}rv_0} \quad . \quad . \quad . \quad . \quad (1)$$

where θ is the specific coagulation time, K the velocity constant, v_0 the number of particles at the beginning, r the radius of the sphere of attraction round each discharged particle, and D the diffusion coefficient.

This expression has been confirmed by Zsigmondy,[2] Westgren and Reitstötter,[3] and Kruyt and van Arkel.[4]

According to Smoluchowski[1] the slow coagulation can be distinguished from the rapid by the fact that in the former case all the encounters between the micellae are not effective, but only a proportion which depends upon the electrolyte concentration. Thus, the expression for slow coagulation will be

$$\theta_1 = \frac{1}{\mathrm{K}_1v_0} = \frac{1}{8\pi \mathrm{D}rxv_0} \quad . \quad . \quad . \quad . \quad (2)$$

where x is the fraction by which K, the velocity constant for rapid coagulation, must be multiplied. If this theory is correct, we should be able to pass from a coagulation velocity curve of rapid coagulation to one of slow coagulation at a lower electrolyte concentration by multiplying the times t by a certain numerical factor, *i.e.* the curves of coagulation velocity must be related to one another. This expression for slow coagulation has been confirmed by Westgren.[5]. Mukherjee,[6] on the other hand, has shown that it is valid only up to a certain stage of coalescence.

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[1] *Physikal Z.*, 1916, **17**, 557, 583; *Z. physik. Chem.*, 1917, **92**, 129.

[2] *Ibid.*, 1918, **92**, 600.

[3] *Ibid.*, 1918, **92**, 750.

[4] *Rec. Trav. Chim.*, 1920, **39**, 656.

[5] *Ark. Matem. Astron. Fys.*, 1918, **13**, 14.

[6] *J. Chem. Soc.*, 1924, **125**, 794.

Miyazawa,[7] Ishizaka,[8] Paine,[9] Gann,[10] Lottermoser,[11] Weigner,[12] and Galecki[13] have shown that the rate of coagulation over the sensitive range of electrolyte concentration may not be a simple reaction, as postulated by Smoluchowski. According to them, the rate of slow coagulation has an autocatalytic character and the reaction velocity can be represented by the equation :—

$$\frac{dx}{dt} = \mathrm{K}(1 + bx)(1 - x) \quad . \quad . \quad . \quad . \quad (3)$$

where K and b are constants and x the amount of change in time t.

The purpose of this investigation is to test the validity of the above two theories of the kinetics of coagulation by a very accurate method.

Methods of following the Course of Coagulation.

Various methods have been used to follow the course of coagulation, but none of them has proved to be free from all defects.

Paine[9] has determined the velocity of coagulation of a copper (or copper oxide) sol by electrolytes by estimating the amount of uncoagulated copper at different intervals. He separated the coagulated coarser particles from the uncoagulated ones by stirring, dissolved the uncoagulated copper by adding a known amount of nitric acid and then estimated the excess of the acid. The defect of the method lies in the fact that while stirring has an extremely small effect in the beginning on the already coagulated but still small particles of the amicronic and submicronic size, it might affect them to a very high degree as soon as they have become considerably larger in course of time. Therefore, it is possible that the apparent autocatalytic course observed by Paine might have been due to this stirring effect.

Miyazawa,[7] Ishizaka,[8] and Gann[10] have followed the coagulation velocity by observing the change in viscosity of the sol. Now, as the viscosity depends upon the total volume of the particles, alteration of the "hydration" of the colloid particles might affect the viscosity measurements, especially in the later stages of coagulation.[14] Therefore, in the later measurements of viscosity a considerable increase might be found due to this hydration effect, and hence the apparent autocatalytic nature of the reaction.

Zsigmondy[2] and Kruyt and van Arkel[4] have followed the changes in a sol after addition of the electrolyte by means of an ultramicroscope. Undoubtedly, this is one of the best methods as the decrease in the number of particles is directly observed, but the method has its own drawbacks. First, very dilute sols have to be used in order to count the number of particles successfully and, therefore, it is possible that the autocatalytic nature of the reaction might not be observed. This can be observed markedly in fairly concentrated sols which contain a considerably larger number of particles, because sufficiently large multiple particles can be formed in them. Secondly, the walls of the cell containing the colloid might have also some effect on the course of the reaction. There is a possibility of greater percentage error with dilute sols—which alone can be used with this method—than with concentrated ones, owing to this effect. Thirdly, the particles of amicronic size

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[7] *J.C.S. Tokio*, 1912, **33**, 1179.

[8] *Z. physik. Chem.*, 1913, **83**, 97.

[9] *Kolloidchem. Beih.*, 1912, **4**, 24.

[10] *Ibid.*, 1916, **8**, 65.

[11] *Koll. Z.*, 1914, **15**, 145.

[12] *Ibid.*, 1911, **8**, 227.

[13] *Z. anorg. Chem.*, 1912, **74**, 174.

[14] Freundlich, *Colloid and Capillary Chemistry*, 1922, 440.

will not at first be visible, but make their appearance suddenly in the later stages of coagulation when they reach submicronic size. Fourthly, a sufficient number of readings might not be obtained for each experiment, because of the limited number of particles studied.

Hatschek[15] has developed the wedge method for gold sols in which colour changes in the coagulating sol are compared with the standard red and blue from time to time. The percentage of red remaining gives the amount of the uncoagulated sol. The method seems to be very simple and easy to carry out, but it is limited to gold sols where the colour changes are very marked. Moreover, the assumption that the red colour is due to primaries requires that all the particles in the sol must be of the same size. It is well known that gold sols contain particles varying from amicronic to submicronic size. If this be the case, the amicrons are sure to play an important part in the later stages of coagulation and might be taken as showing the absence of the autocatalytic nature of the reaction. It is, however, possible to prepare gold sols containing particles of fairly uniform size by the methods developed by Zsigmondy and others, but the fact remains that the above-mentioned defect ought to be taken into consideration. Again, the human eye may make considerable error in comparing the colour of the coagulated sol with the standards.

Mukherjee and Papaconstantinou[16] have measured the coagulation velocity of gold sols spectrophotometrically. They have also utilised the colour change in the coagulating sol as their criterion in calculating the coagulation velocity from the spectrophotometric measurements. The method though very accurate is subject to the same criticism as the Hatschek wedge method, so far as the assumption that the red colour of the sol is due to the primaries alone is concerned. Moreover, the method can be used only to follow the changes in the coagulating sol from the range—red to blue and is not applicable when the limit of absorption has been reached. This is an important point which must be borne in mind while estimating the exactness of the method.

The velocity of coagulation may be best studied by utilising a property which varies only with the increase in the size of the particles. Such a property is the scattering of light by the particles, which is directly proportional to their size. Therefore, the intensity of the transmitted light will decrease with the increase in the size of the particles. The use of this property in measuring the rate of coagulation has one fundamental advantage, in that it reveals the properties of the dispersed phase without disturbing its delicate equilibrium. The intensity of the transmitted light can be measured under suitable conditions, with the least possible difficulty, very accurately. In fact this property—the scattering of light—is so characteristic and extremely sensitive that it has been applied with success to the study of gaseous systems.

Mukherjee and Majumdar[17] have utilised this property to measure the velocity of coagulation of an arsenious sulphide sol when coagulators are added to it. The light from a source was allowed to pass through the cell containing the colloid + electrolyte and the intensity of the transmitted light was measured by allowing it to fall on a very sensitive thermopile connected with a galvanometer, which gave a deflection proportional to the intensity of the transmitted light falling on the thermopile. Unfortunately, adequate provision was not made to cope with all the difficulties that are likely to

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[15] *Trans. Faraday Soc.*, 1921, **17**, 499.

[16] *J. Chem. Soc.*, 1920, **117**, 1563.

[17] *Ibid.*, 1924, **125**, 794.

arise and, therefore, the initial slow coagulation phenomena, which have been observed even with not very refined methods, seem to have escaped their notice. First, they overlooked the fact that the colour of the arsenious sulphide particles might vary with the increase in their size, although Mukherjee and Papaconstantinou[16] used this very property to follow the course of coagulation of gold sols. Thus it will be seen that there is a probability of error in their measurements. Such an error can easily be obviated by using a suitable colour filter which will from the beginning cut off, before it passes through the cell containing the reaction mixture, the light of all wave-lengths which might be absorbed most by the coagulated particles during the increase in their size. Such an error seems to have been partly responsible for the non-observance of the initial slow coagulation velocity, because of the probability of the transmitted light having been deprived of some waves by absorption by the larger coagulated particles. Such a secondary effect seems to be the cause of a comparatively greater initial decrease in deflection.

Further, Freundlich and Nathansohn[18] have investigated the effect of light on arsenious sulphide sol. According to them, the sol becomes turbid when exposed to a Nitra lamp and its flocculation value by electrolytes is lowered. The same thing has also been observed by the writer. A sample of arsenious sulphide sol when exposed to sunlight for five to ten minutes became turbid, with a simultaneous change in colour. It seems that a complex sulphide compound is formed because of this photochemical change, with simultaneous formation of fine colloidal sulphur. In the light of these facts, it is very probable that, in the beginning of the process of coalescence, the galvanometer deflection observed by Mukherjee and Majumdar[17] was larger than that due solely to the action of the added electrolyte and, therefore, they could note the initial slow coagulation phenomenon.

It is preferable to use a photo-electric cell rather than a thermopile, for the former is decidedly more sensitive and reliable, as it is much easier to eliminate stray light than stray heat which may be emitted from all parts of the apparatus. Objections have, however, frequently been raised to photo-electric cells on the score of short life, fragility and change of sensitivity, but experience has proved otherwise. The cell used by Dobson, Griffith, and Harrison[19] though employed for nearly eight years was in perfect working order, although no special precaution was taken. Moreover, it is now possible to get photoelectric cells of great reliability and accuracy and, therefore, there are no grounds for the above criticisms.

Lottermoser[11] seems to have used a photoelectric cell to measure the velocity of coagulation of tungstic acid sol. However, he used the method in its crude form and at a time when the cells were not very reliable; consequently it has not received due attention from workers in the field. Freundlich[14] has, however, criticised the method as follows: "The possibility exists, however, that as in the case of increase in viscosity, the larger flakes appearing in the later stages of coagulation exert a stronger influence upon the appearance than the double and triple particles at first formed." Assuming, however, that the particles are hydrated, there is no possibility that the measurements will be affected in the same manner as the viscosity of the sol. The amount of transmitted light will not be reduced by surrounding the particles with a water envelope. It is well known that dust-free water does not scatter light to

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[18] *Kolloid Z.*. **28**, 1921, 258.

[19] *Photographic Photometry*, 1926, 61 f.

an appreciable extent and, therefore, the effect on the transmitted light of the water envelope round the colloid particle will be the same as if it had to pass through dust-free water.[20] The scattering of the light will be only proportional, in the circumstances, to the actual size of the colloid particles without the water envelope. Moreover, this effect will be further reduced because the size of the particles is greater than the wave-length of the light employed. If there is any effect of hydration on the transmitted light at all, it will be in the beginning when the particles are not large as in the later stages of coagulation. This will affect the transmitted light in the opposite sense to that in which it affects the viscosity measurements. Thus, a greater decrease in the deflection will be observed in the initial stages of coagulation and, hence, the slow coagulation should not be observed.

Apparatus.

The light from a gas-filled Osram lamp (60 watts-30 volts) enclosed in a wooden box lined inside with asbestos and having a glass window ($r = 2$cms). is first allowed to pass through a condenser ($f = 9$ cms.) to obtain a parallel beam of light. This is allowed to pass from a window (4×6 cm.^{2}) through 4 per cent. $Cu(NO_3)_2$ solution contained in a rectangular optical glass cell (30 c.c. capacity). The light is thus deprived of ultraviolet rays and is rich in light waves from the violet to yellow range only. In this way any effect of light of short wave-lengths is eliminated. After passing through an optical glass colloid cell (100 c.c. capacity) the light then falls on a photo-electric cell, enclosed in a box, through a glass window ($r = 1$ cm.). The $Cu(NO_3)_2$ solution cell as well as the colloid cell are placed in a tank (12 cms. wide externally) with two glass windows (4×6 cm.^{2} and $2{\cdot}5 \times 1{\cdot}5$ cm.^{2}) for the passage of light as mentioned above. The tank is maintained at 25° C. by means of a 10 per cent. $CaCl_2$ solution thermoregulator. Thus the distance between the photo-electric cell and the source of light is 21 cms. Arrangement is made to keep the water in the tank running continuously, thus avoiding as far as possible the accumulation of dust particles which might scatter some light. The water is first passed through a glass-wool filter.

The vacuum photo-electric cell (supplied by G.E.C.) contains potassium as the sensitive material. The cell has a large window (specially designed to work with diffuse light) and contains a central plate cathode, while the silvered surface of the bulb is the anode. This type of cell is rather more sensitive than the one with a small window when exposed to diffused light; its main advantage is that it gives a more accurate proportionality between the photo-electric current and illumination. Its sensitivity is independent of temperature within atmospheric limits.

The photo-electric cell is connected to a very sensitive "Broca" galvanometer supplied with a lamp and scale. The figure of merit of the galvanometer is determined every day before each set of experiments and a suitable correction applied to the readings for any variation in the sensitivity of the galvanometer. A high tension Exide battery (Type W.J.) of 40 volts and a Mullard resistance of 180,000 ohms are also introduced in the circuits, the negative pole of the battery being connected to the cathode of the photo-electric cell. The high tension battery amplifies the photo-electric current while the large resistance serves to protect the photo-electric cell and the galvanometer in case too large a potential is accidentally applied. If the voltage varies during an experiment, a suitable

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[20] *Cf.* Kraemer and Dexter, *J. physical Chem.*, 1927, **31**, 779.

correction can be applied from the photo-electric current-voltage curve for the particular photo-electric cell used.

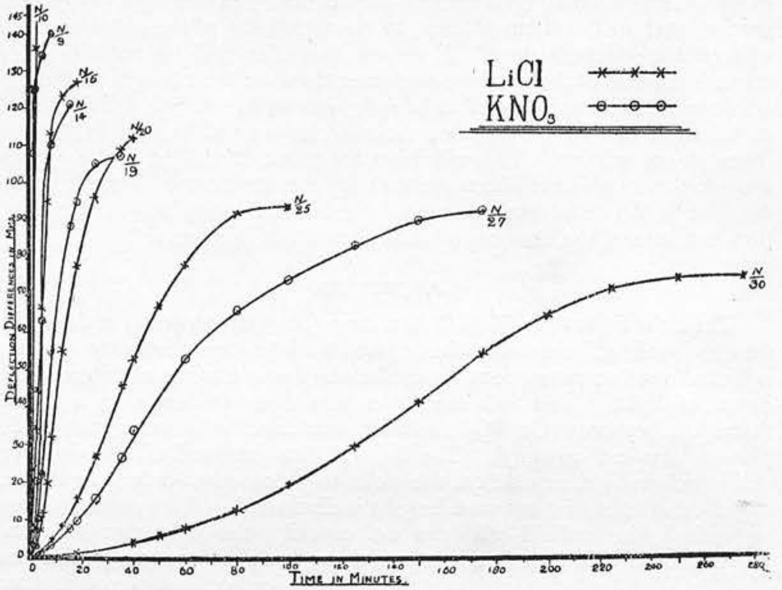

FIG. 1.

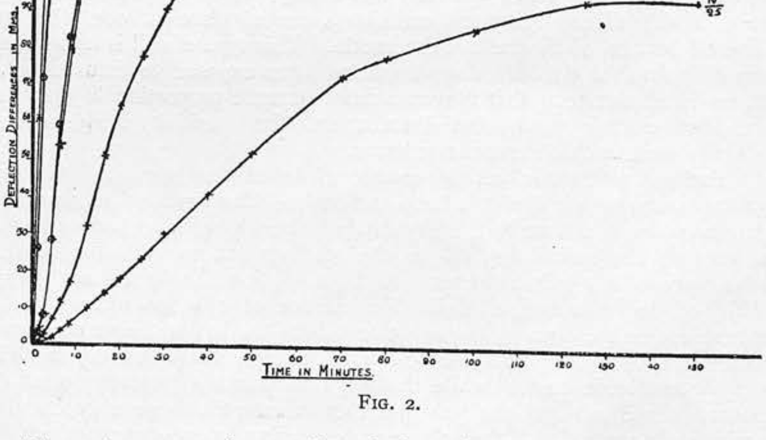

FIG. 2.

The galvanometer is so adjusted that with water alone in the colloid cell, a deflection of 335 mm. on the scale is produced. With 20 c.c. of water and 20 c.c. of colloid, the deflection is 328 mm.; this gives the zero reading, *i.e.* the initial transparency before coagulation sets in. A blank experiment, with the colourless electrolytes employed in the investigation in the colloid cell, showed that the galvanometer reading, *viz.* 335 mm. is not at all affected by them. When taking readings 20 c.c. of the sol (at 25° C.) and 20 c.c. of the electrolyte (at 25° C.) are first mixed in a test-tube by adding the electrolyte to the sol along the wall of the test-tube and pouring the mixture back into the electrolyte-tube, the method of mixing being maintained uniform throughout. The mixture is immediately transferred to the colloid cell. The time of mixing is carefully noted. The photo-electric cell is exposed to the light at intervals of a few minutes by means of a sliding asbestos screen interposed between the source of light and the condenser. The intensity of the light at its source is checked by means of an ammeter reading to 1/20 of an ampere. Further the ammeter scale is read by means of a microscope with a scale inside (1 division of the ammeter = 50 divisions of microscope scale). Before each experiment, the correction to be applied for the variation of the current by 1 division of the microscope scale is determined and the readings of the galvanometer are accordingly corrected for the variation of the illumination during each set of experiments. If there is great variation during an experiment, the current is brought to the original reading by means of a sliding resistance which is introduced in the light circuit. The distances between the light source and various cells are permanently fixed.

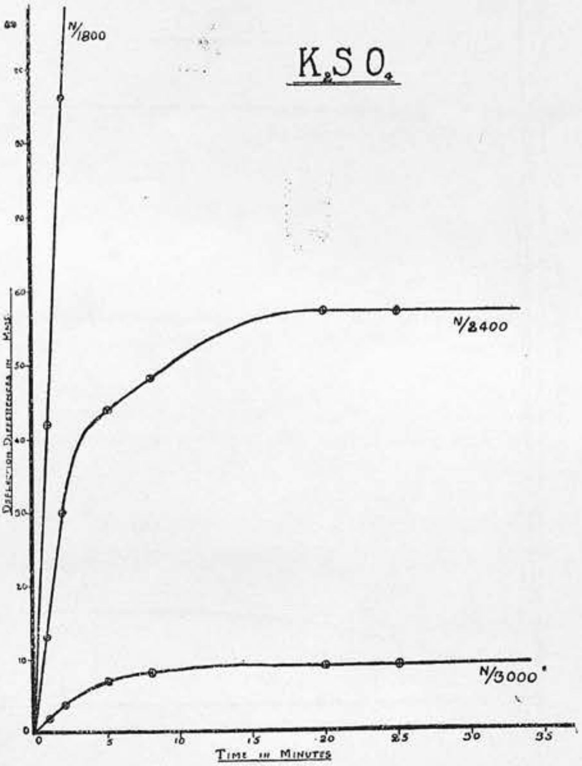

Fig. 3.

As the size of the particles increases with the progress of coagulation, the galvanometer deflection decreases. It reaches a minimum in all cases, then (with concentrated electrolytes) it begins to increase while (with dilute electrolytes) it remains constant for a time and then begins to increase. The height of the box in which the photo-electric cell is contained is adjusted in such a way that with 40 c.c. of the mixture in the colloid cell, the level of the surface of the mixture in the cell forms a tangent to the top of the circular window ($r = 1$ cm.) of the photo-electric cell box. Thus the settling of the coagulum as a whole or its separation into big flakes, when the coagulation is over, is observed immediately without any difficulty. The increase in the deflection of the galvanometer shows that sedimentation has set in.

Preparation of the Sol.

Thorium oxide sol was investigated as it has not been much studied. Several methods of preparation are known. The condensation method of Biltz[21] was not chosen as much thorium passes out during dialysis and hence a sol of any desired concentration could not be prepared. It was decided to utilise Muller's method,[22] by which a sol of any desired concentration can be prepared, as almost all the thorium is in colloidal condition of ThO_2 from the beginning and hence no thorium passes out during dialysis.

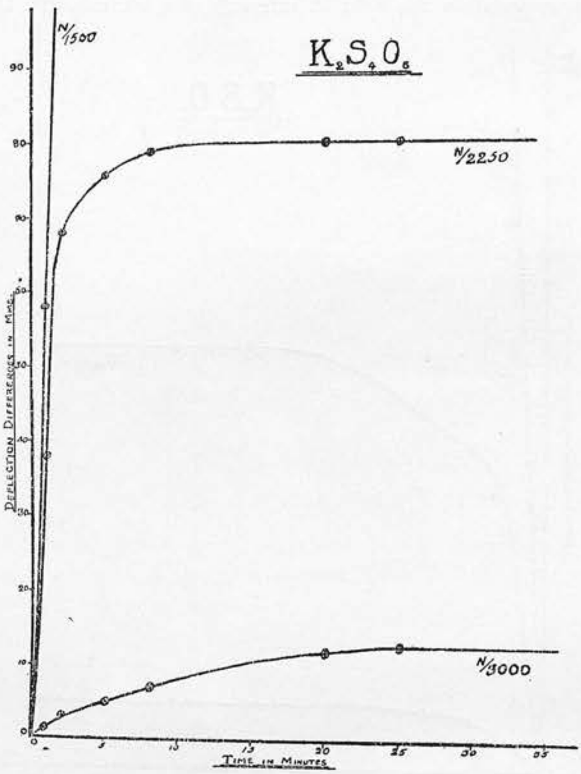

FIG. 4.

Twenty-five g. of thorium nitrate were dissolved in about 300 c.c. of warm distilled water and the hydroxide precipitated by adding excess of ammonia. The precipitate was rapidly washed with hot water till free from ammonia and suspended in two litres of water. The suspension was heated nearly to the boiling-point and $N/20$ HCl was added in quantities of 2 c.c. at intervals. The evaporated water was replaced from time to time. After adding nearly 320 c.c. of HCl and heating for nearly 7 hours, an opalescent sol was obtained. This was transferred to a parchment bag suspended from the rim of a rectangular trough. Distilled water was allowed to flow through the trough at the rate of one litre per hour while the dialysate was run out at the same rate. The sol was removed to a resistance glass flask after dialysis. During the dialysis practically no thorium passed out in the dialysate.

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[21] *Ber.*, 1902, 45, 4431-4438.
[22] *Allgemeine Chemie der Kolloid*, 1907.

The glass ware used in this investigation was of resistance glass and it was cleaned every time with the usual precautions. The conductivity of the water used in making up solutions varied from – 1·0 to 2·0 × 10 $^{-6}$ mhos. The electrolytes were prepared from "B.D.H., A.R." salts which were further twice recrystallised from conductivity water under suitable conditions.

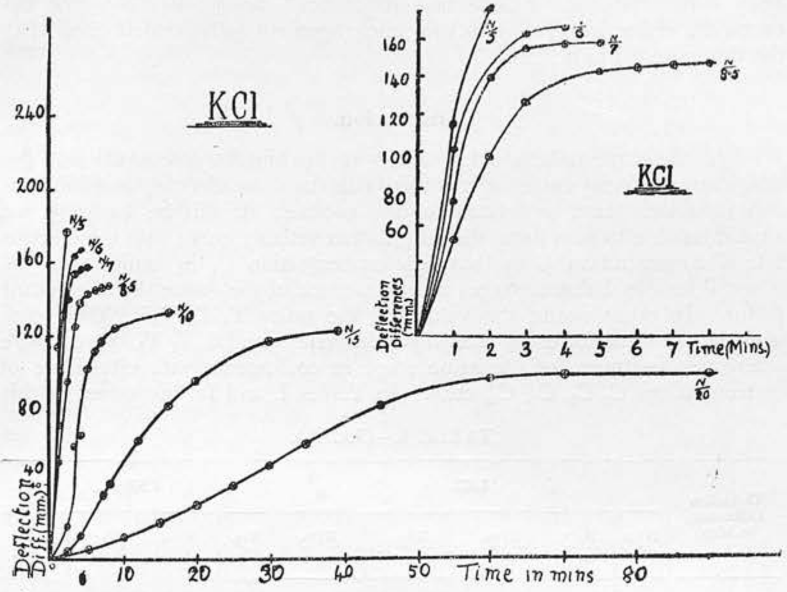

FIG. 5.

Results.

The coagulation experiments were carried out as already described. A blank experiment with ThO_2 sol, showed that it was not sensitive to light even when exposed for nearly two hours. Each experiment was duplicated and the results of the two experiments did not vary beyond 2 to 3 per cent. These values were plotted and an average curve for each electrolyte concentration obtained.

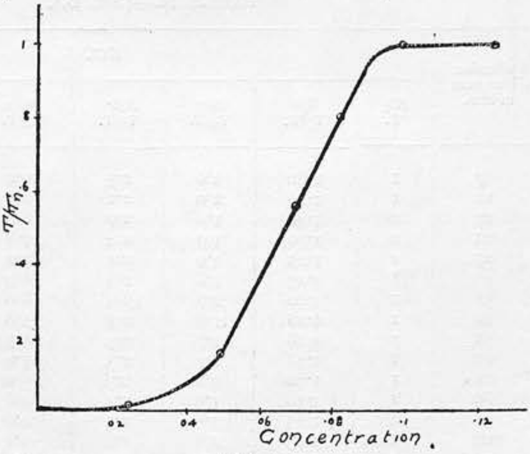

FIG. 6.

The curves are shown in Figs. 1 to 5. Figs. 1 to 4 apply to a sol (A) dialysed for 7 days and Fig. 5 to a sol

(B) dialysed for 6 days. Sol A contained 4·95 g. and sol B, 4·90 g. ThO_2/litre respectively. The concentrations given are those of the electrolytes before mixing. "Deflection difference" means the difference between the deflection (328 mms.) for unchanged sol and the deflection after the time interval indicated.

Discussion.

According to Smoluchowski's theory of the kinetics of coagulation,[1] the coagulation velocity curves of a colloid with the same electrolyte of different concentrations must be related to one another. If this be the case, we should be able to pass from the coagulation velocity curve with the electrolyte of concentration C to that with concentration C_1 by multiplying the times T for the different stages of coalescence of the former by a constant factor. In other words, the values of the ratios T_1/T, T_2/T, T_3/T, etc., must be the same for every electrolyte concentration (T, T_1 T_2, T_3, etc., are the respective times for the same stage in coalescence with electrolyte of concentrations C, C_1, C_2, C_3, etc.). In Tables I. and I*a*. the values of this

TABLE I.—(Sol A.).

Deflection Differences in Mm.	LiCl.					KNO$_3$.			
	N/10 T.	*N*/15 T_1/T.	*N*/20 T_2/T.	*N*/25 T_3/T.	*N*/30. T_4/T.	*N*/9. T.	*N*/14 T_1/T.	*N*/19 T_2/T.	*N*/27 T_3/T.
3	1	6·3	25·0	155·00	875·0	1	13·3	33·3	233·0
8	1	5·0	25·0	100·00	500·0	1	13·3	25·3	200·0
18	1	4·2	20·2	74·10	365·4	1	11·5	19·4	154·3
28	1	4·5	17·5	60·25	300·0	1	9·5	17·8	141·2
48	1	4·6	15·7	52·14	228·6	1	7·5	15·5	120·0
68	1	4·4	15·5	52·20	210·0	1	6·3	15·2	136·0
88	1	4·3	16·8	56·50	—	1	5·5	18·6	175·7
108	1	4·4	21·2	—	—	1	7·6	—	—

TABLE I*a*.—(Sol B.).

Deflection Differences in Mm.	KCl.						
	N/5 T.	*N*/6 T_1/T.	*N*/7 T_2/T.	*N*/8·5 T_3/T.	*N*/10 T_4/T.	*N*/15 T_5/T.	*N*/20 T_6/T.
7	1	1·60	2·6	2·5	10·0	54·0	140·0
12	1	1·40	2·0	2·1	8·1	38·0	105·0
17	1	1·40	1·9	2·0	8·0	33·6	100·0
22	1	1·30	1·9	2·4	7·8	30·6	90·0
27	1	1·25	1·9	2·4	7·0	26·6	84·3
32	1	1·25	1·8	2·4	6·9	25·2	81·5
37	1	1·20	1·7	2·4	6·0	23·4	75·0
42	1	1·18	1·6	2·3	5·8	22·2	70·1
52	1	1·18	1·7	2·3	5·5	21·7	67·8
62	1	1·18	1·7	2·3	5·0	21·3	64·8
72	1	1·20	1·6	2·3	5·0	21·3	62·7
82	1	1·16	1·6	2·4	4·8	22·0	62·5
92	1	1·15	1·6	2·5	4·6	23·0	66·1
102	1	1·15	1·6	2·7	5·4	25·0	—
112	1	1·20	1·7	3·0	6·5	27·3	—
132	1	1·20	1·7	—	—	—	—

ratio for some of the electrolytes are calculated by taking the values of T for the same stage in coalescence from the respective coagulation velocity curves.

It will be seen from the tables that the value of the ratio T_n/T is nearly constant for $N/15$ LiCl, but that for other LiCl concentrations, the values vary greatly with the advance in the stage of coalescence, the variation becoming more and more with the increase in dilution of the electrolyte. The same is the case with KNO_3. In case of KCl the values of the ratio are nearly constant for concentrations $N/6$, $N/7$, and $N/8{\cdot}5$. For $N/10$, $N/15$, and $N/20$ KCl, the values vary as in the case of LiCl and KNO_3.

The reciprocal of the value of the ratio T_n/T will be proportional to the coagulation velocity. It will be seen from Fig. 6 that the velocity is greatly reduced with increase in dilution of the coagulator; at very great dilutions the velocity will be reduced to zero. Further, at higher concentrations a limiting value is reached. This is in agreement with Freundlich's [23] theory of coagulation.

According to Gann [10] and others, the coagulation process resembles an autocatalytic reaction. He has calculated the value of the velocity constant K according to the equation,

$$\frac{dx}{dt} = K(1 + bx)(1 - x).$$

The value of b was taken from the ordinates of the point of inflection on the $\frac{dx}{dt} - t$ curve.

In Tables II. and II*a*. are given the values of the velocity constant K

TABLE II.—(Sol A.).

Electrolyte.	Conc.	*b*.	*t* (Mins.).	K		
				Max.	Min.	Mean.
LiCl*	$N/20$	0·015	9 to 30	0·0276	0·0230	0·0264
,,	$N/25$	0·005	35 ,, 80	0·00805	0·00736	0·0755
,,	$N/30$	0·0007	150 ,, 250	0·00195	0·00161	0·00184
KCl*	$N/15$	0·027	8 ,, 15	0·0660	0·0621	0·0639
,,	$N/20$	0·0116	16 ,, 40	0·0200	0·0184	0·0192
,,	$N/25$	0·005	30 ,, 100	0·0062	0·0051	0·00585
KNO_3**	$N/14$	0·55	63 ,, 110	0·126	0·115	0·121
,,	$N/19$	0·033	5 ,, 18	0·043	0·036	0·040
,,	$N/27$	0·0035	40 ,, 125	0·0058	0·0051	0·0053
$BaCl_2$*	$N/15$	0·02	6 ,, 12	0·069	0·051	0·065

TABLE II*a*.—(Sol B.).

Electrolyte.	Conc.	*b*.	*t* (Mins.).	K		
				Max.	Min.	Mean.
KCl***	$N/10$	0·0515	3 to 7	0·165	0·138	0·155
,,	$N/15$	0·0166	12 ,, 30	0·0488	0·0452	0·0471
,,	$N/20$	0·007	15 ,, 45	0·0133	0·0073	0·0103

* Maximum deflection difference for concentrated solutions = 200 mm.
** ,, ,, ,, = 180 ,,
*** ,, ,, ,, = 180 ,,

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[23] *Kolloid Z.*, 1918, 23, 163.

calculated according to this equation, x being put equal to − deflection difference at time t/maximum deflection. The fourth column gives the limits within which the calculation was applied.

The values of K for any one electrolyte concentration are fairly constant in many cases, which justifies the belief that the nature of the coagulation process is autocatalytic.

It will be seen that the values of the velocity constant for $N/20$ and $N/25$ LiCl are greater than those for $N/20$ and $N/25$ KCl (Table II.) respectively. This is due to the greater stabilising power of K ion as compared with Li ion. The exact manner in which this influence affects the course of coagulation as well as the conditions under which it makes itself most conspicuous will be dealt with elsewhere.

According to Paine,[9] $T_n/T = (c/c_n)^P$

or $\log T_n - \log T = P(\log c - \log c_n)$.

In Tables III and III*a*. are calculated the values of P for different values of c.

TABLE III.—(Sol A.).

(Average values of T_n/T taken from Table II.)

Value of T for $N/10$ LiCl as Standard.			Value of T for $N/9$ KNO_3 as Standard.		
T_n/T.	C/C_n.	P.	T_n/T.	C/C_n.	P.
4·7	1·5	3·82	9·34	1·555	5·06
19·6	2·0	4·29	20·73	2·111	4·05
78·6	2·5	4·76	165·74	3·000	4·65
413·1	3·0	5·48	—	—	—

TABLE III*a*.—(Sol B.).

(Average values T_n/T taken from Table II*a*.)

Value of T for $N/5$ KCl as Standard.			Value of T for $N/10$ KCl as Standard.		
T_n/T.	C/C_n.	P.	T_n/T.	C/C_n.	P.
1·25	1·2	1·34	0·160	0·500	2·6
1·79	1·4	1·73	0·197	0·600	3·2
2·40	1·7	1·65	0·275	0·700	3·6
6·43	2·0	2·68	0·411	0·855	5·6
27·70	3·0	3·02	3·880	1·510	3·3
82·30	4·0	3·18	11·300	2·000	3·5

Paine found the value of P for univalent coagulating ions to be between 5 and 6; Hatschek[15] on the other hand, found 12. From the above tables it will be seen that the value varies with the dilution and also with the concentration of the electrolyte taken as standard.

Freundlich[14] has derived an empirical equation connecting the velocity constant K with concentration C which has the form

$$K = \text{const } K \times C^P$$

$$\text{or } \frac{K}{K_n} = \left(\frac{C}{C_n}\right)^P$$

$$\text{or } \log K - \log K_n = P(\log C - \log C_n)$$

In the following Tables IV. and IV*a*. are calculated the values of P for different concentrations, the value of the velocity constant being the average taken from Tables II. and II*a*.

TABLE IV.—(Sol A.).

K for *N*/30 LiCl as Standard.			K for *N*/25 LiCl as Standard.			K for *N*/20 LiCl as Standard.		
K/K*n*.	C/C*n*.	P.	K/K*n*.	C/C*n*.	P.	K/K*n*.	C/C*n*.	P.
14·340	1·5	6·4	3·496	1·200	6·8	0·2859	0·800	5·6
4·103	1·2	7·7	0·2438	0·833	7·7	0·0700	0·666	6·4

K for *N*/25 KCl as Standard.			K for *N*/27 KNO_3 as Standard.		
K/K*n*.	C/C*n*.	P.	K/K*n*.	C/C*n*.	P.
10·923	1·666	4·7	20·940	1·93	4·6
3·282	1·250	5·3	7·547	1·42	5·7

According to Freundlich the value of P varies from 2 to 7. It will be seen from the above tables that the variation is practically within these limits.

TABLE IV*a*.—(Sol B.).

K for *N*/20 KCl as Standard.		
K/K*n*.	C/C*n*.	P.
15·050	2·000	3·9
4·572	1·333	5·3

A possible explanation of the "S" shaped curves may be arrived at by extending Freundlich's theory of coagulation. This is based on the fact that coagulation commences though the colloid is still far from the iso-electric point and postulates that the velocity of coagulation is a function of the electrokinetic *P.D.* between the particles and the dispersion medium. If now we assume that the decrease in *P.D.* may under certain circumstances take place at a relatively slow rate we should get in those cases a gradual acceleration of the coagulation at first and hence an "S" shaped curve. The observations of Powis[24] on oil emulsions show that the establishment of ionic equilibrium in such disperse systems may take considerable time. On the other hand when the electrolyte is of such a nature or at such a concentration that the *P.D.* is reduced immediately to its new value the velocity of coagulation will reach its maximum value at once. This apparently happens at high concentrations of univalent ions (Figs. 1, 2, and 5), and at all concentrations of bivalent ions[10] (Figs. 3 and 4). The behaviour of the latter may be related to their great adsorbability.[25]

Another factor which may account, at least in part, for the change from slow to rapid coagulation when the electrolyte is sufficiently dilute is indicated in the experiments of Wiegner[12] and Galecki[13] who found from ultramicroscopic observations with gold sols that the small particles showed a greater

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[24] *Z. physikal. Chemie.*, 1915, **89**, 179.

[25] Freundlich, *Kolloid Z.*, 1907, **1**, 321; Bancroft, *J. physical Chem.*, 1915, **19**, 349; Weiser, *J. physical Chem.*, 1919, **23**, 205.

tendency to coalesce with larger ones than with one another. The same thing has also been observed by the writer with gum dammer suspension. Equal volumes of *N* KCl and gum dammer were mixed in a test-tube and the mixture transferred to a rectangular cell. After the addition of KCl hundreds of small particles were observed in the mixture. On allowing it to stand for a time it was observed without difficulty that smaller particles settled on larger ones and after an hour only four big particles remained suspended in the liquid. These four settled without any further coalescence and the supernatant liquid did not contain any colloidal gum dammer. If this be the case we should expect acceleration of the coagulation velocity as the degree of coalescence increases.

Odén[26] found that the ultimate size of the aggregates in a coagulated $BaSO_4$ suspension depended upon the concentration of the coagulator. The same thing apparently applies to ThO_2 sol, for, as will be seen from Figs. 1 to 5, the maximum deflection decreases as the electrolyte becomes more dilute. The viscosity measurements of Gann[10] show a similar effect. The amount of light scattered when the limiting stage of coalescence is reached is less for bivalent than for univalent coagulating ions. This may be connected with the large difference in the rates of coagulation, the coagulation process being thus comparable with crystallisation from solution as far as crystal size is concerned.

Summary.

1. The velocity of coagulation of colloidal thorium oxide has been measured by a very accurate optical method.

2. It has been shown that the constancy of the ratio T_n/T demanded by Smoluchowski's theory is maintained only up to a certain coagulator concentration.

3. The view that the nature of the coagulation process is autocatalytic is supported by these experiments. The velocity constant K has been calculated according to the equation $\frac{dx}{dt} = K(1 + bx)(1 - x)$, the value of b being equal to $\frac{dx}{dt}$ at a point of inflection of the $x - t$ curve. A fairly constant value is obtained.

4. Reasons for the non-observance of the "slow coagulation" region by many workers have been advanced.

5. It is found that the value of P according to the equations of Paine and Freundlich varies with the dilution and depends upon the electrolyte concentration which is taken as standard.

6. The difference in the value of K for corresponding concentrations of LiCl and KCl is explained as due to the influence of the ion carrying the same charge as the colloid.

7. The theory developed by Freundlich for rapid as well as slow coagulation is supported and extended.

8. The observance of the decrease in the maximum deflection difference with the increase in dilution of the electrolyte supports the results of Odén on $BaSO_4$ suspension, showing that the ultimate size of the particles varies with the concentration of the coagulator. The peculiar behaviour of bivalent ions is explained on the basis of their great adsorbability and the consequent initial rapid rate of coagulation.

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[26] *Koll. Z.*, 1920, **26**, 160; *Ark. Kem. Mineral Geol.*, 1920, **26**, 7.

I have great pleasure in thanking Professor Sir James Walker for his constant interest in the work and for the facilities in carrying it out. My thanks are also due to Mr. T. R. Bolam and Dr. E. B. Ludlam for some valuable suggestions.

The University,
Edinburgh.

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Die Koagulation von Thoriumhydroxydsol durch Elektrolyte.

Von B. N. Desai, Edinburgh.[1])

(Mit 1 Diagramm und 25 Figuren.)

(Eingegangen am 24. Oktober 1927.)

I. Teil.

Kinetik der Koagulation.

Theoretisches.

In den letzten Jahren sind mehrfach Versuche unternommen worden, die Vorgänge, die sich abspielen, wenn zu einem Sol ein Elektrolyt gegeben wird, durch eine Gleichung zu erfassen. So hat v. Smoluchowski[2]), um die Kinetik einer raschen Koagulation darzustellen, eine Gleichung vorgeschlagen auf Grund folgender Erwägungen:

Bei Zusatz eines Elektrolyten wird 1. sofort das Potential der Micellen geändert, 2. die Ladung der Micellen neutralisiert und so die einer Koagulation entgegenwirkende Kraft beseitigt, 3. werden die Zusammenstöße der Teilchen unelastisch, d. h. es bilden sich beim Zusammentreffen Teilchenaggregate.

Smoluchowskis Gleichung für rasche Koagulation lautet:

$$\Theta = \frac{1}{\mathrm{K}\mathrm{v}_0} = \frac{1}{4\pi \mathrm{D}\mathrm{r}\mathrm{v}_0}, \qquad (1)$$

wo Θ die spezifische Koagulationszeit, K die Geschwindigkeitskonstante, v_0 die Teilchenzahl zu Beginn der Reaktion, r den Radius der Anziehungssphäre um jedes entladene Teilchen und D den Diffusionskoeffizienten bedeutet.

Diese Gleichung ist durch R. Zsigmondy[3]), Westgren und Reitstötter[4]) und von K. Kruyt und van Arkel[5]) bestätigt worden.

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[1]) Übersetzt von W. Rödiger, Leipzig.

[2]) v. Smoluchowski, Physik. Zeitschr. **17**, 557, 583 (1916); Zeitschr. f. phys. Chem. **92**, 129 (1917).

[3]) R. Zsigmondy, Zeitschr. f. phys. Chem. **92**, 600 (1918).

[4]) Westgren u. Reitstötter, Zeitschr. f. phys. Chem. **92**, 750 (1918).

[5]) K. Kruyt u. van Arkel, Rec. trav. chim. **39**, 656 (1920).

Das Potential der Micellen sinkt indessen nicht augenblicklich auf Null, wenn die Elektrolytkonzentration unter einem gewissen Werte bleibt[1]), und mithin wird auch nicht in allen Fällen die Koagulationsgeschwindigkeit von Anfang an schon sehr groß sein. Nach v. Smoluchowski (loc. cit.) unterscheidet sich die allmähliche Koagulation von der raschen dadurch, daß im ersten Falle nicht alle Micellen miteinander zusammentreffen werden, sondern nur ein gewisser Bruchteil, der abhängig ist von der Elektrolytkonzentration. So lautet also der Ausdruck für die langsame Koagulation

$$\Theta = \frac{1}{K_1 v_0} = \frac{1}{8 \pi D r x v_0}, \tag{2}$$

wo x den Bruchteil bedeutet, mit dem K, die Geschwindigkeitskonstante für rasche Koagulation, multipliziert werden muß. Wenn diese Theorie den Tatsachen entspricht, müßte es möglich sein, von einer Geschwindigkeitskurve rascher Koagulation zu einer Kurve langsamer Koagulation bei geringerer Elektrolytkonzentration zu gelangen durch einfache Multiplikation der Zeit t mit einem gewissen Zahlenfaktor, d. h. die Koagulationsgeschwindigkeitskurven müssen miteinander in Beziehung stehen. Obige Formel für langsame Koagulation ist durch Westgren[2]) bestätigt worden. Anderseits hat Mukherjee[3]) gezeigt, daß sie nur in einer gewissen Annäherung gültig ist.

Weiter haben S. Miyazawa[4]), N. Ishizaka[5]), L. Paine[6]), J. A. Gann[7]), A. Lottermoser[8]), G. Wiegner[9]) und Galecki[10]) nachgewiesen, daß die Koagulation bei verschiedenen Elektrolytkonzentrationen nicht nach einem einfachen Reaktionsschema verläuft, wie v. Smoluchowski voraussetzt.

Nach diesen Autoren hat langsame Koagulation einen autokatalytischen Charakter, und die Reaktionsgeschwindigkeit läßt sich durch die Gleichung ausdrücken:

$$\frac{dx}{dt} = K(1 + bx)(1 - x), \tag{3}$$

wo K und b Konstanten sind und x die in der Zeit t umgewandelte Menge ist.

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[1]) F. Powis, Zeitschr. f. phys. Chem. **89**, 186 (1915).

[2]) Westgren, Ark. f. Matem. Artron. Och. Fys. **13**, 14 (1918).

[3]) Mukherjee, Journ. Chem. Soc. Trans. **125**, 794 (1924).

[4]) S. Miyazawa, J. C. S. Tokio **33**, 1179 (1912).

[5]) N. Ishizawa, Zeitschr. f. phys. Chem. **83**, 97 (1913).

[6]) L. Paine, Kolloidchem. Beih. **4**, 24 (1912).

[7]) J. A. Gann, Kolloidchem. Beih. **8**, 65 (1916).

[8]) A. Lottermoser, Koll.-Zeitschr. **15**, 145 (1914).

[9]) G. Wiegner, Koll.-Zeitschr. **8**, 227 (1911).

[10]) Galecki, Zeitschr. f. anorg. Chem. **74**, 174 (1912).

Der Zweck vorliegender Untersuchung ist, die Geltung der beiden obigen Theorien über die Kinetik der Koagulation mittels einer sehr genauen Methode zu prüfen.

Methoden zur Verfolgung des Verlaufs der Koagulation.

Verschiedene Methoden sind angewandt worden, um den Verlauf der Koagulation verfolgen zu können; aber keine davon hat sich als völlig fehlerfrei erwiesen.

L. Paine (loc. cit.) hat die Geschwindigkeit der Koagulation von Kupfer- (oder Kupferoxyd-) Sol mit Elektrolyten dadurch gemessen, daß er von Zeit zu Zeit die Menge des nichtkoagulierten Kupfers bestimmt hat. Er hat die koagulierten gröberen Teilchen von den nichtkoagulierten durch Schütteln getrennt, das nichtkoagulierte Kupfer durch Zugabe einer bekannten Menge Salpetersäure gelöst und die nicht umgesetzte Säure bestimmt. Der Fehler in der Methode liegt darin, daß im Anfang die Menge des abgetrennten Kupfers extrem klein sein wird, weil zwar schon Teilchen koaguliert, aber noch von der Größenordnung von Amikronen oder Submikronen sein werden, im Laufe der Zeit aber mit Zunahme der Teilchengröße immer größer werden wird. Dadurch könnte der von Paine beobachtete autokatalytische Verlauf vorgetäuscht sein.

Miyazawa (loc. cit.), Ishizaka (loc. cit.) und Gann (loc. cit.) haben die Koagulationsgeschwindigkeit verfolgt durch Messung der Viskositätsänderungen des Sols. Da nun die Viskosität vom Gesamtvolumen der Teilchen abhängig ist, würde eine Änderung in der Hydratation der Kolloidteilchen die Viskositätsmessungen stark beeinflussen, besonders in den späteren Stadien.¹) Man würde bei den späteren Messungen ein starkes Anwachsen der Viskosität feststellen und daraus schon auf einen autokatalytischen Reaktionsverlauf schließen.

R. Zsigmondy (loc. cit.) und K. Kruyt und van Arkel (loc. cit.) haben die Zustandsänderungen in einem Sol nach Zugabe von Elektrolyten mit Hilfe des Ultramikroskopes verfolgt. Das ist ohne Zweifel eine der besten Methoden, da die Abnahme der Teilchenzahl direkt beobachtet werden kann; aber auch diese Methode hat ihre Nachteile. Erstlich haben die Autoren verdünnte Sole verwandt, um die Teilchen gut zählen zu können, und dadurch ist es möglich, daß man einen autokatalytischen Verlauf nicht hat feststellen können. Den kann man ja nur deutlich in ziemlich konzentrierten Solen beobachten, die beträchtlich mehr Teilchen enthalten als die verdünnten, weshalb sich auch viel mehr zu größeren Aggregaten zusammenfinden können. Zweitens

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¹) H. Freundlich, Colloid and Capillary Chemistry (1926), 440.

können auch die Wände der Küvette, in der sich das Sol befindet, von Einfluß auf den Verlauf der Reaktion sein. Natürlich ist dann der mögliche Fehler bei verdünnten Solen, die allein für diese Methode in Frage kommen, prozentual bedeutend größer als bei konzentrierten. Drittens sind im Anfang die Teilchen von Amikronengröße nicht sichtbar, sie treten erst im späteren Verlaufe der Reaktion plötzlich in Erscheinung, sobald sie die Größe von Submikronen erreichen.

Hatschek¹) hat für Goldsole die Keilmethode entwickelt, wobei die Farbänderungen im koagulierten Sol von Zeit zu Zeit mit der roten und blauen Standardlösung verglichen werden. Der Prozentgehalt an zurückbleibendem Rot ergibt dann die Menge des nichtkoagulierten Sols. Die Methode scheint sehr einfach und leicht ausführbar zu sein, aber sie ist nur auf Goldsole beschränkt, wo die Farbänderung sehr deutlich hervortritt. Überdies erfordert die Voraussetzung, daß die rote Farbe von den Primärteilchen herrührt, daß alle Teilchen im Sol von gleicher Größenordnung sind. Es ist allgemein bekannt, daß Goldsol Teilchen verschiedener Größenordnung enthält, Amikronen sowohl wie Submikronen, und es ist sicher, daß im späteren Verlauf der Reaktion die Amikronen eine wichtige Rolle spielen; das könnte wieder zu der Annahme führen, daß die Reaktion nicht autokatalytisch erfolgt. Es ist nun allerdings möglich — nach dem Vorgange von Zsigmondy und anderen —, Goldsole mit ziemlich gleichen Teilchen herzustellen, aber die Tatsache bleibt bestehen, daß die oben erwähnte Fehlerquelle zu berücksichtigen ist. Übrigens kann sich auch das menschliche Auge beim Vergleich der Farben des koagulierten Sols mit den Standardlösungen sehr irren.

Mukherjee und Papaconstantinou²) haben die Koagulationsgeschwindigkeit von Goldsolen spektrophotometrisch gemessen. Sie haben also ebenfalls den Farbumschlag des koagulierenden Sols als Kriterium bei der Berechnung der Koagulationsgeschwindigkeit aus den spektrophotometrischen Messungen verwandt. Diese Methode, obwohl sehr genau, unterliegt doch denselben Bedenken wie die Keilmethode von Hatschek, soweit die Voraussetzung, daß die rote Farbe des Sols allein den Primärteilchen zuzuschreiben ist, in Frage kommt. Weiterhin ist die Methode nur brauchbar, um den Umschlag rot in blau zu verfolgen, und versagt, wenn die Absorptionsgrenze erreicht ist. Das ist ein wichtiger Punkt, der bei der Beurteilung der Exaktheit der Methode im Auge zu behalten ist.

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¹) Hatschek, Trans. Faraday Soc. **17**, 499 (1921).

²) Mukherjee u. Papaconstantinou, Journ. Chem. Soc. **117**, 1563 (1920).

Die Koagulationsgeschwindigkeit kann am besten studiert werden unter Benutzung einer Eigenschaft, die sich nur mit Zunahme der Teilchengröße ändert. Eine derartige Eigenschaft ist die Lichtzerstreuung der Teilchen, die ihrer Größe direkt proportional ist. Es wird also die Intensität des durchfallenden Lichtes mit der Zunahme der Teilchengröße abnehmen. Die Verwendung dieser Eigenschaft bei der Messung des Koagulationsgrades hat den grundwichtigen Vorteil, daß sie gestattet, Untersuchungen über den Zustand des dispersen Anteils durchzuführen, ohne das empfindliche Gleichgewicht zu stören. Die Intensität des durchfallenden Lichtes kann unter passenden Bedingungen ohne die geringste Schwierigkeit sehr genau gemessen werden. In der Tat ist diese Eigenschaft — die Lichtzerstreuung — so charakteristisch und subtil, daß sie bereits mit Erfolg beim Studium von Gassystemen verwandt worden ist.

Mukherjee und Majumdar[1]) haben diese Eigenschaft bei der Messung der Koagulationsgeschwindigkeit an Arsensulfidsol verwandt. Man ließ das Licht einer Lichtquelle die Zelle passieren, die Kolloid + Elektrolyt enthielt; die Intensität des durchfallenden Lichtes wurde dadurch gemessen, daß man es auf eine empfindliche Thermosäule lenkte, die mit einem Galvanometer verbunden war, das dann einen Ausschlag proportional dem durchfallenden Licht anzeigte. Unglücklicherweise sind keine entsprechenden Vorkehrungen getroffen worden, um den möglicherweise entstehenden Schwierigkeiten zu begegnen, und so sind denn die schwachen Anfangserscheinungen bei der Koagulation, zumal die Beobachtung nach nicht eben besonders verfeinerten Methoden geschah, ihrem Augenmerk entgangen. So haben sie den Umstand übersehen, daß die Farbe der Arsensulfidteilchen mit der Zunahme der Teilchengröße sich ändert, obwohl Mukherjee und Papaconstantinou (loc. cit.) gerade diese Eigenschaft benutzt haben, um den Verlauf der Koagulation an Goldsolen zu verfolgen. So könnte sich ein Fehler in ihre Messungen eingeschlichen haben. Abhilfe läßt sich leicht schaffen durch Verwendung eines Farbfilters, welches das Licht aller Wellenlängen ausscheidet, die besonders leicht durch die koagulierenden Teilchen während ihrer Größenzunahme absorbiert werden, bevor es die Zelle mit dem Reaktionsgemisch passiert. Im anderen Falle kann leicht die geringe Anfangsgeschwindigkeit der Koagulation übersehen werden, da die Möglichkeit besteht, daß dem durchfallenden Licht einige Wellen infolge Absorption durch die koagulierten bereits etwas größer gewordenen Teilchen entzogen werden und so die

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[1]) Mukherjee u. Majumdar, Journ. Chem. Soc. **125**, 785 (1924).

Abnahme der Lichtzerstreuung im Anfang verhältnismäßig größer erscheint.

Ferner haben H. Freundlich und Nathansohn[1]) den Einfluß des Lichtes auf Arsensulfidsol untersucht. Darnach wird das Sol trübe, wenn es einer Nitralampe ausgesetzt wird, und sein Flockungswert gegenüber Elektrolyten sinkt. Bolam hat beobachtet, daß Arsensulfidsol bei Tageslicht trübe wird (Priv. Mitteilung). Dasselbe hat Verfasser ebenfalls beobachtet. Eine Probe eines Arsensulfidsols, die 5—10 Minuten dem Sonnenlicht ausgesetzt wurde, wurde trüb; gleichzeitig trat Farbänderung ein. Es scheint, daß sich durch diese photochemische Umsetzung eine komplexe Sulfidverbindung bildet unter gleichzeitiger Abscheidung von feinverteiltem kolloiden Schwefel. Im Lichte dieser Tatsachen ist es durchaus wahrscheinlich, daß der von Mukherjee und Majumdar beobachtete Galvanometerausschlag größer war, als der zugesetzten Elektrolytmenge entsprach, und so der allmähliche Beginn der Koagulation von ihnen nicht entdeckt werden konnte.

Es ist zweckmäßiger, an Stelle einer Thermosäule eine photoelektrische Zelle zu verwenden; letztere ist entschieden empfindlicher und zuverlässiger als erstere. Lindemann[2]) äußert sich darüber folgendermaßen: „Es gibt grundsätzlich nur zwei Wege, um die Lichtintensität zu messen. Das Prinzip des einen liegt darin, die durch Lichtabsorption an einem schwarzen Körper hervorgerufene Temperatursteigerung zu bestimmen. Der zweite beruht auf der Messung der Zahl der durch Licht aus ihren festen Bahnen im Atom geworfenen Elektronen. Die erstere Methode ist im Prinzip die allgemeinere, sie gestattet eine direkte Bestimmung der Energie. Die zweite ist aber entschieden eleganter, da sie auf eine Bestimmung der Quantenzahlen hinausläuft. In der Praxis hat sich denn auch allgemein die zweite durchgesetzt. Denn während die erste den Ausschluß der geringsten Temperaturschwankung erfordert, genügt bei der zweiten die Fernhaltung fremden Lichtes." Das allein schon erklärt den Vorteil der photoelektrischen Zelle, denn es ist naturgemäß leichter, diffuses Licht fernzuhalten, als Wärme.

Man hat auch gegen photoelektrische Zellen Einwände erhoben wegen ihrer kurzen Lebensdauer, Zerbrechlichkeit und Empfindlichkeitsschwankungen. Die Erfahrung hat das Gegenteil gelehrt. Die von Dobson, Griffith und Harrison benutzte Zelle (Fußnote S. 61 loc. cit.) arbeitete nach achtjährigem Gebrauch noch tadellos, obwohl man

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[1]) H. Freundlich u. Nathansohn, Koll.-Zeitschr. **28**, 258 (1921).

[2]) Lindemann, Introduction to Photographic Photometry by Dobson, Griffith and Harrison (Aufl. 1926).

keine besondere Vorsicht hatte walten lassen. Überdies ist es jetzt möglich, photoelektrische Zellen von großer Zuverlässigkeit und Exaktheit in der Ausführung zu erhalten, so daß kein Grund zu Beanstandungen vorliegt.

Lottermoser (loc. cit.) scheint bei der Messung der Koagulationsgeschwindigkeit von Wolframsäuresol schon eine photoelektrische Zelle verwandt zu haben. Allerdings hat er sie in roher Form benutzt; es war überdies damals nicht möglich, präzise arbeitende Zellen zu erhalten. H. Freundlich¹) kritisiert die Methode folgendermaßen: „Die Möglichkeit besteht, daß — im Falle eines Anwachsens der Viskosität — die in den späteren Stadien der Koagulation auftretenden größeren Flocken von unverhältnismäßig größerer Wirkung sind als die im Anfang sich bildenden doppelt und dreifach zusammengesetzten Teilchen.“ Das ist indessen nicht der Fall. Zugegeben, die Teilchen wären hydratisiert, so könnte das unmöglich die Messungen in gleicher Weise wie die Viskosität beeinflussen. Die Menge des durchfallenden Lichtes wird nicht dadurch reduziert, daß die Teilchen von einer Wasserhülle umgeben sind. Bekanntlich zerstreut optisch leeres Wasser das Licht nicht merklich, und der Effekt ist derselbe, ob das Licht nun die Wasserhüllen der Kolloidteilchen durchdringt oder reines Wasser.²)

Die Lichtzerstreuung wird nur proportional der Größe der Kolloidteilchen ohne Wasserhülle sein. Überdies würde der Effekt noch weiter dadurch eingeschränkt, daß die Teilchengröße die Wellenlänge des verwandten Lichtes übertrifft. Wenn überhaupt ein Einfluß der Hydratation auf das durchfallende Licht sich bemerkbar macht, so nur im Anfang, wo die Teilchengröße im Verhältnis zu den späteren Stadien der Koagulation noch gering ist. Dadurch würde das durchfallende Licht in entgegengesetztem Sinne beeinflußt als die Viskosität, d.h. es würde eine stärkere Abnahme der Zerstreuung festzustellen sein; in diesem Falle wäre eine langsame Koagulation nicht zu beobachten.

Im Hinblick auf die vielen Vorteile, die die photoelektrische Zelle bietet, entschied ich mich für sie, um den Koagulationsverlauf beobachten zu können. Bei der Wahl geeigneter Mittel ist es möglich, zu sehr exakten Ergebnissen zu gelangen.

Beschreibung der Apparatur (Fig. 1).

Das Licht einer gasgefüllten Osramlampe (60 Watt — 30 Volt) S, die sich in einem mit Asbest ausgekleideten mit einem Glasfenster (r = 2 cm) versehenen Holzkasten befindet, wird durch einen Kondensor

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¹) H. Freundlich, Colloid and Capillary Chemistry (1926), 440.

²) cf. Kraemer and Dexter, Journ. Phys Chem. **31**, 779 (1927); cf. des Verfassers Arbeit über Ceroxydsol und -gel, Beob. 17 u. Diskussion.

(f = 9 cm) L parallel gerichtet. Von dort tritt der Lichtstrahl durch ein Fenster (4×6 cm^2) in ein rechtwinklig geschliffenes optisches Gefäß (50 ccm) C_1 mit 4prozentiger $Cu(NO_3)_2$-Lösung. Auf diese Weise werden die ultravioletten Strahlen entfernt und das Licht ist nur noch reich an Wellen von Violett bis Gelb. So wird ein eventueller Einfluß des kurzwelligen Lichts ausgeschaltet. Nach dem Passieren einer optischen Zelle C (100 ccm), die das Kolloid enthält, fällt das Licht auf eine photoelektrische Zelle P, die sich in einem mit einem Glasfenster (r = 1 cm) versehenen Kasten befindet. Die Gefäße mit der Kolloid- und $Cu(NO_3)_2$-Lösung befinden sich in einem Thermostaten von 12 cm äußerer Weite mit 2 Glasfenstern (4×6 cm^2 und $2{,}5 \times 1{,}5$ cm^2) für den Lichtdurchtritt, wie oben erwähnt. Der Thermostat wird mit Hilfe einer 10prozentigen $CaCl_2$-Lösung als Thermoregulator auf 25° erhalten. Das Wasser wird täglich gewechselt, das frische wird vor dem Einfüllen durch Glaswolle filtriert und dann in steter Bewegung gehalten, um Staubanhäufungen, die Licht zerstreuen könnten, zu verhindern.

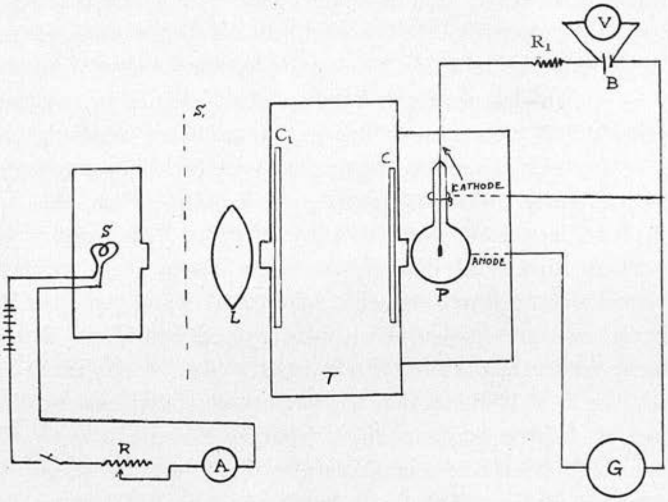

Fig. 1. Anordung der Apparatur.

Die photoelektrische Vakuumzelle (geliefert von der G. E. C.) enthält Kalium als sensitives Material. Sie besitzt ein breites Fenster (speziell für diffuses Licht bestimmt) und enthält eine Platinelektrode in der Mitte des Kolbens. Diese wirkt als Kathode, während die versilberte Oberfläche des Lampenkolbens als Anode dient. „Dieser Zellentyp ist gegenüber diffusem Licht stärker empfindlich als solche mit schmalem Fenster. Ihr Hauptvorzug ist genauere Proportionalität zwischen photoelektrischem Strom und Belichtung. Sie ist daher für sehr exakte Arbeiten geeignet."[1]) Die Empfindlichkeit der Zelle ist unabhängig von der Temperatur innerhalb der atmosphärischen Grenzen.

Die photoelektrische Zelle ist mit einem hochempfindlichen „Broca"-Galvanometer G verbunden, das mit Lampe und Skala versehen ist. Täglich vor jeder Versuchsreihe wurde der Ausschlag des Galvanometers geprüft und bei Empfindlichkeitsschwankungen an den Ablesungen eine entsprechende Korrektur angebracht. Eine Hochspannungs-(Exide-) Batterie (Type W. J.) B von 40 Volt und ein Mullard-Widerstand von 180 000 Ω R_1 wurden so in den Stromkreis geschaltet, daß der negative Pol der Batterie mit der Kathode der photoelektrischen Zelle verbunden war. Die Hochspannungsbatterie verstärkt den photoelektrischen Strom, während der große Widerstand dazu dient, photoelektrische Zelle und Galvanometer zu schützen, wenn einmal ein zu hohes Potential angewandt wird und spontane Funkenentladung erfolgt. Die Spannung der Batterie bleibt lange Zeit praktisch konstant; sollte sich sie während eines Versuches etwas ändern, so kann eine entsprechende Korrektur mittels der photoelektrischen Stromspannungskurve der benutzten photoelektrischen Zelle angebracht werden.

Das Galvanometer wurde so justiert, daß mit Wasser allein in der „Kolloidzelle" auf der Skala ein Ausschlag von 335 mm erfolgte. Mit 20 ccm Wasser + 20 ccm Kolloid betrug er 328 mm. Diese Ablesung von 328 mm stellt die Nullablesung dar, d. h. die Anfangslichtdurchlässigkeit, bevor Koagulation einsetzt. Ein Blindversuch mit dem farblosen Elektrolyten, der bei den Untersuchungen in der Kolloidzelle verwandt wurde, ergab keine Änderung des Galvanometerausschlages von 335 mm. Für die Ablesungen wurden zuerst 20 ccm des Sols (Temperatur 25°) mit 20 ccm des Elektrolyten (25°) im Reagenzglase derart vermischt, daß man den Elektrolyten an der Glaswand in das Sol laufen ließ und das Gemisch in das Gefäß zurückgab, das den Elektrolyten enthalten hatte; von da wurde es unverzüglich in die Kolloidzelle gegeben. Diese Methode wurde bei allen Versuchen gleichmäßig angewandt. Der Zeitpunkt der Vermischung wurde sorgfältig notiert. Die photoelektrische Zelle wurde dann dem Lichte in kurzen Abständen mit Hilfe eines Asbestgleitschirmes S_1 ausgesetzt, der sich zwischen Lichtquelle und Kondensor befand. Die Intensität des Lichtes an seiner Quelle wurde mittels eines Amperemeters A bis auf $^1/_{20}$ Amp. genau bestimmt, überdies wurde die Amperemeterskala noch mit Hilfe eines Mikroskops

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[1]) Flugschrift, herausgegeben vom Untersuchungslaboratorium der General-Electric-Company Wembley, Mai 1924.

mit Skala (1 Teilstrich des Amperemeters = 50 Teilstriche der Mikroskopskala) abgelesen. Vor jedem Versuch wurde die Korrektur, die bei Änderung des Stromes um einen Teilstrich der Mikroskopskala anzubringen war, bestimmt und entsprechend die Galvanometerablesungen bei Lichtschwankungen innerhalb des Versuches korrigiert. Wenn die Lichtschwankungen während des Versuches zu groß wurden, wurde der Strom mit Hilfe eines Gleitwiderstandes R, der in den Lichtstromkreis eingeschaltet war, wieder auf die Originalablesung gebracht. Die Abstände zwischen Lichtquelle und den verschiedenen Zellen wurden für dauernd fixiert.

Mit der Zunahme der Teilchengröße mit dem Fortschreiten der Koagulation wird der Galvanometerausschlag geringer. Er erreicht in allen Fällen ein Minimum, wird in einigen Fällen (bei konz. Elektrolyten) wieder größer und bleibt in anderen (bei verdünnten Elektrolyten) für eine Zeit konstant und steigt dann erst wieder. Die Höhe des Kastens, in dem sich die photoelektrische Zelle befindet, ist so bemessen, daß bei einem Inhalt von 40 ccm in der Kolloidzelle die Ebene der Oberfläche dieses Gemisches eine Tangente zum höchsten Punkt des runden Glasfensters (r = 1 cm) des photoelektrischen Zellkastens bildet. So ist das Absetzen des Koagulums als Ganzes oder seine Trennung in dicke Flokken, wenn die Koagulation vorüber ist, unmittelbar ohne Schwierigkeit zu sehen. Die Zunahme des Galvanometerausschlages zeigt an, daß die Sedimentation eingesetzt hat.

Herstellung des Sols.

Uns schien zur Untersuchung Thoriumoxydsol geeignet, zumal es noch wenig studiert worden ist. Es gibt verschiedene Herstellungsmethoden. Die Kondensationsmethode nach W. Biltz[1]) war in unserem Falle unzweckmäßig, da während der Dialyse viel Thorium ausfiel und deswegen ein Sol von gewünschter Konzentration nicht herzustellen war. Es wurde deshalb die Methode von Müller[2]) gewählt, die ein Sol jeder gewünschten Konzentration herzustellen gestattete.

25 g Thoriumnitrat wurden in etwa 300 ccm warmen destillierten Wassers gelöst und daraus das Hydroxyd mit einem Überschuß von Ammoniak gefällt. Der Niederschlag wurde sofort mit heißem Wasser ausgewaschen, bis er frei von Ammoniak war und in zwei Liter Wasser suspendiert. Die Suspension wurde bis fast zum Sieden erhitzt und von Zeit zu Zeit je 2 ccm $\frac{n}{20}$ HCl zugesetzt. Das verdampfende Wasser wurde

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[1]) W. Biltz, Ber. d. d. chem. Ges. **35**, 4431 (1902).

[2]) Allgemeine Chemie der Kolloide (1907).

regelmäßig ersetzt. Nach etwa siebenstündigem Erhitzen und Zugabe von etwa 320 ccm Salzsäure wurde ein opaleszierendes Sol erhalten.

Dieses Sol wurde in einen Pergamentbeutel gebracht, der in einen Trog mit destilliertem Wasser gehängt war, das durch ständigen Zu- und Abfluß (1 Liter pro Stunde) immer erneuert wurde. Nach der Dialyse wurde das Sol in eine Widerstandsglasflasche gebracht. Wie festgestellt wurde, war während der Dialyse praktisch kein Thorium in das Dialysat übergegangen.

Die Gefäße, die bei den Versuchen benutzt wurden, waren aus Widerstandsglas und wurden jedesmal sorgfältigst gereinigt. Die Leitfähigkeit des zu den Lösungen verwandten Wassers schwankte zwischen $1-2 \cdot 10^{-6}$. Die Elektrolyte wurden aus B. D. H. A. R.-Salzen durch zweimaliges Umkristallisieren aus Leitfähigkeitswasser unter geeigneten Bedingungen hergestellt.

Die Koagulationsversuche wurden wie oben beschrieben ausgeführt. Ein Blindversuch mit ThO_2-Sol ergab, daß es nicht lichtempfindlich war, selbst wenn es etwa zwei Stunden dem Licht ausgesetzt wurde. Die Resultate der Parallelversuche differierten um höchstens 2—3 Proz. Aus diesen Werten wurde für jeden Elektrolyten eine Kurve gezeichnet. Daraus sind die in Tabelle I und Ia enthaltenen Werte interpoliert.

Tabelle I.

Konzentration des Sols = 4,95 g ThO_2 pro Liter (7 Tage dialysiert).

Die in der Kolumne „Ausschlagsdifferenz“ enthaltenen Werte sind die Differenzen zwischen ursprünglichem Ausschlag und Ausschlag zur Zeit t.

K_2SO_4				$K_2S_4O_6$			
Zeit in Minuten	Ausschlagsdifferenz			Zeit in Minuten	Ausschlagsdifferenz		
	$\frac{n}{1800}$	$\frac{n}{2400}$	$\frac{n}{3000}$		$\frac{N}{1500}$	$\frac{N}{2250}$	$\frac{N}{3000}$
0	0	0	0	0	0	0	0
1	42	13	2	1	58	38	1
2	36	30	4	2	112	68	3
5	48	44	7	5	48	76	5
8	18	48	8	8	7	79	7
20	—	57	9	20	—	80	12
25	—	57	9	25	—	80	13
40	—	57*)	9**)	40	—	61	13
60	—	—	—	60	—	54	13**)

*) Setzt nach 2 Stunden noch nicht ab.

**) Verändert sich nach 4 Stunden noch nicht.

Tabelle I (Fortsetzung).

LiCl*)						BaCl$_2$*)		
Zeit in Minuten	Ausschlagsdifferenz					Zeit in Minuten	Ausschlagsdifferenz	
	$\frac{N}{10}$	$\frac{N}{15}$	$\frac{N}{20}$	$\frac{N}{25}$	$\frac{N}{30}$		$\frac{N}{10}$	$\frac{N}{15}$
0	0	0	0	0	0	0	0	0
2	136	34	4	—	—	1	28	3
3	150	44	7	—	—	2	72	8
4	148	66	12	—	—	4	102	28
6	128	95	20	2	—	6	121	59
8	94	113	32	4	—	8	132	83
12	13	123	55	8	—	12	141	115
18	—	127	78	16	1	16	136	126
25	—	118	96	27	—	20	104	125
35	—	97	109	46	—	25	4	125
40	—	84	112	53	4	30	—	112
50	—	52	111	67	6	40	—	18
60	—	7	92	78	8	50	—	—
80	—	—	54	92	13			
100	—	—	46	93	20			
125	—	—	—	—	30			
150	—	—	—	—	42			
175	—	—	—	—	55			
200	—	—	—	—	65			
225	—	—	—	—	72			
250	—	—	—	—	75			
275	—	—	—	—	76†)			

*) Die maximale Ausschlagsdifferenz betrug 200 mm bei $\frac{n}{25}$ Elektrolyt.

†) Beginnt nach 5 Stunden sich als Ganzes abzusetzen.

KCl*)					KNO$_3$**)				
Zeit in Minuten	Ausschlagsdifferenz in Millimeter				Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	$\frac{N}{10}$	$\frac{N}{15}$	$\frac{N}{20}$	$\frac{N}{25}$		$\frac{N}{9}$	$\frac{N}{14}$	$\frac{N}{19}$	$\frac{N}{27}$
0	0	0	0	0	0	0	0	0	0
1	61	4	1	—	1	108	8	3	—
2	104	8	3	—	2	125	20	10	—
4	137	28	7	2	4	134	63	22	1
6	145	54	12	4	8	140	110	55	3
8	143	80	17	6	15	69	121	88	8
12	98	110	32	10	18	28	120	95	10
16	20	120	51	14	25	—	98	105	16

Tabelle I (Fortsetzung).

KCl*)					KNO **)				
Zeit in Minuten	Ausschlagsdifferenz in Millimeter				Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	$\frac{N}{10}$	$\frac{N}{15}$	$\frac{N}{20}$	$\frac{N}{25}$		$\frac{N}{9}$	$\frac{N}{14}$	$\frac{N}{19}$	$\frac{N}{27}$
20	4	124	65	18	35	—	16	107	27
25	—	125	78	23	40	—	—	106	34
30	—	120	91	30	60	—	—	38	53
40	—	33	104	41	80	—	—	25	66
50	—	—	109	52	100	—	—	—	74
70	—	—	109	72	125	—	—	—	83
80	—	—	108	78	150	—	—	—	90
100	—	—	87	86	175	—	—	—	92
125	—	—	—	94	200	—	—	—	91†)
150	—	—	—	94					
180	—	—	—	94					
200	—	—	—	75†)					

*) Die maximale Ausschlagsdifferenz war dieselbe wie bei LiCl und $BaCl_2$.

**) Die maximale Ausschlagsdifferenz mit $\frac{n}{3}$ KNO_3 betrug 180 mm.

†) Setzt sich als Ganzes ab.

Tabelle Ia.

Konzentration des Sols 4·90 g. ThO_2 pro Liter (6 Tage dialysiert).

Zeit in Minuten	KCl Ausschlagsdifferenz in Millimeter						
	$\frac{N}{5}$ *)	$\frac{N}{6}$	$\frac{N}{7}$	$\frac{N}{8,5}$	$\frac{N}{10}$	$\frac{N}{15}$	$\frac{N}{20}$
0	0	0	0	0	0	0	0
1	114	100	72	52	—	—	—
2	177	—	140	97	16	2	—
3	136	164	155	126	61	—	—
4	88	167	157	138	86	12	—
5	—	—	158	143	103	—	4
6	—	155	—	145	113	—	—
7	—	—	104	146	117	34	—
8	—	—	—	148	—	41	—
9	—	—	—	—	124	—	—
10	—	27	—	142	—	—	11
12	—	—	—	—	—	64	—
15	—	—	17	—	—	—	19
16	—	—	—	—	132	83	—

Tabelle Ia (Fortsetzung).

Zeit in Minuten	KCl Ausschlagsdifferenz in Millimeter						
	$\frac{N}{5}$ *)	$\frac{N}{6}$	$\frac{N}{7}$	$\frac{N}{8,5}$	$\frac{N}{10}$	$\frac{N}{15}$	$\frac{N}{20}$
18	—	—	—	10	—	—	—
20	—	—	—	—	27	98	29
25	—	—	—	—	—	—	39
30	—	—	—	—	—	118	50
35	—	—	—	—	—	—	62
39	—	—	—	—	—	122	—
45	—	—	—	—	—	106	82
60	—	—	—	—	—	—	97
70	—	—	—	—	—	—	99
90	—	—	—	—	—	25	99**)

*) $\frac{N}{4}$ KCl ergibt auch dieselben Ablesungen, die maximale Ausschlagsdifferenz betrug 180 mm.

**) Setzt als Ganzes sich ab.

Diskussion.

Nach der Theorie von Smoluchowski über die Kinetik der Koagulation (loc. cit.) müssen die Koagulationsgeschwindigkeitskurven eines Kolloids mit dem gleichen Elektrolyten verschiedener Konzentration miteinander in Beziehung stehen. In diesem Falle würde es möglich sein, von der Koagulationsgeschwindigkeitskurve mit dem Elektrolyten von der Konzentration C zu der mit dem Elektrolyten von der Konzentration C_1 zu kommen durch Multiplikation der Zeiten t des ersteren für die verschiedenen Stadien der Koaleszenz mit einem konstanten Faktor. Mit anderen Worten: der Wert der Verhältnisse $\frac{T_1}{T}$, $\frac{T_2}{T}$, $\frac{T_3}{T}$ usw. muß für alle Elektrolytkonzentrationen der gleiche sein (T_1, T_2, T_3, T usw. sind die entsprechenden Zeiten für den gleichen Zustand der Koaleszenz mit Elektrolyten der Konzentrationen C, C_1, C_2, C_3 usw.). Der reziproke Wert der Verhältnisse wird dann proportional der

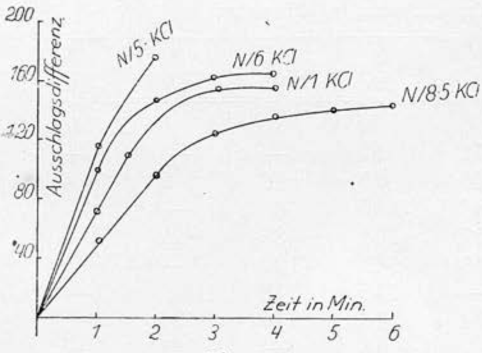

Fig. 2.

Koagulationsgeschwindigkeit sein. In Tabelle II und IIa sind die Werte dieses Verhältnisses für einige Elektrolyten berechnet, wobei die T-Werte für den gleichen Grad der Koaleszenz aus den entsprechenden Koagulationsgeschwindigkeitskurven sich ergeben.

Tabelle II.

Ausschlagsdifferenz in Millimeter	LiCl					KNO$_3$			
	$\frac{N}{10}$ T	$\frac{N}{15}$ $\frac{T_1}{T}$	$\frac{N}{20}$ $\frac{T_2}{T}$	$\frac{N}{25}$ $\frac{T_3}{T}$	$\frac{N}{30}$ $\frac{T_4}{T}$	$\frac{N}{9}$ T	$\frac{N}{14}$ $\frac{T_1}{T}$	$\frac{N}{19}$ $\frac{T_2}{T}$	$\frac{N}{27}$ $\frac{T_3}{T}$
3	1	6,3	25,0	155,00	875,0	1	13,3	33,3	233,0
8	1	5,0	25,0	100,00	500,0	1	13,3	25,3	200,0
18	1	4,2	20,2	74,10	365,4	1	11,5	19,4	154,3
28	1	4,5	17,5	60,25	300,0	1	9,5	17,8	141,2
48	1	4,6	15,7	52,14	228,6	1	7,5	15,5	120,0
68	1	4,4	15,5	52,20	210,0	1	6,3	15,2	136,0
88	1	4,3	16,8	56,50	—	1	5,5	18,6	175,7
108	1	4,4	21,2	—	—	1	7,6	—	—

Tabelle IIa.

Ausschlagsdifferenz in Millimeter	KCl						
	$\frac{N}{5}$ T	$\frac{N}{6}$ $\frac{T_1}{T}$	$\frac{N}{7}$ $\frac{T_2}{T}$	$\frac{N}{8,5}$ $\frac{T_3}{T}$	$\frac{N}{10}$ $\frac{T_4}{T}$	$\frac{N}{15}$ $\frac{T_5}{T}$	$\frac{N}{20}$ $\frac{T_6}{T}$
7	1	1,60	2,6	2,5	10,0	54,0	140,0
12	1	1,40	2,0	2,1	8,1	38,0	105,0
17	1	1,40	1,9	2,0	8,0	33,6	100,0
22	1	1,30	1,9	2,4	7,8	30,6	90,0
27	1	1,25	1,9	2,4	7,0	26,6	84,3
32	1	1,25	1,8	2,4	6,9	25,2	81,5
37	1	1,20	1,7	2,4	6,0	23,4	75,0
42	1	1,18	1,6	2,3	5,8	22,2	70,1
52	1	1,18	1,7	2,3	5,5	21,7	67,8
62	1	1,18	1,7	2,3	5,0	21,3	64,8
72	1	1,20	1,6	2,3	5,0	21,3	62,7
82	1	1,16	1,6	2,4	4,8	22,0	62,5
92	1	1,15	1,6	2,5	4,6	23,0	66,1
102	1	1,15	1,6	2,7	5,4	25,0	—
112	1	1,20	1,7	3,0	6,5	27,3	—
132	1	1,20	1,7	—	—	—	—

Wie aus den Tabellen ersichtlich, ist der Wert für das Verhältnis T_n/T für $\frac{n}{15}$ LiCl ungefähr konstant, variiert dagegen bei den anderen LiCl-Konzentrationen beträchtlich mit einer Änderung im Zustand der Koaleszenz; die Abweichungen werden mit zunehmender Verdünnung des Elektrolyten immer größer. Das gleiche ist bei KNO_3 der Fall. Bei KCl sind die Werte konstant für die Konzentrationen $\frac{n}{6}$, $\frac{n}{7}$ und $\frac{n}{8,5}$. Für $\frac{n}{10}$, $\frac{n}{15}$ und $\frac{n}{20}$ KCl ergaben sich dieselben Schwankungen wie bei LiCl und KNO_3.

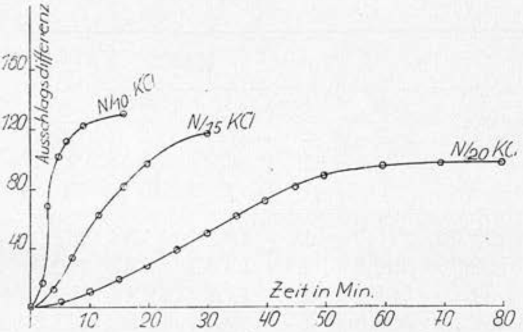

Fig. 3.

Mukherjee und Majumdar (loc. cit.) glauben, daß diese Änderung des Wertes für das Verhältnis T_n/T bei verdünnten Elektrolyten darauf beruht, daß ein Grenzzustand der Koaleszenz da erreicht ist, wo die Mengen der sich bildenden und der zerfallenden Aggregate gleich geworden sind. Demgemäß übersteigt im Bereich der raschen Koagulation der Betrag der sich bildenden Aggregate den der zerfallenden, aber im Laufe der Zeit gleicht sich letzterer dem ersteren an, und in diesem Punkte versagt die Theorie Smoluchowskis. Diesen Argumenten vermag man nicht unbedenklich zuzustimmen.

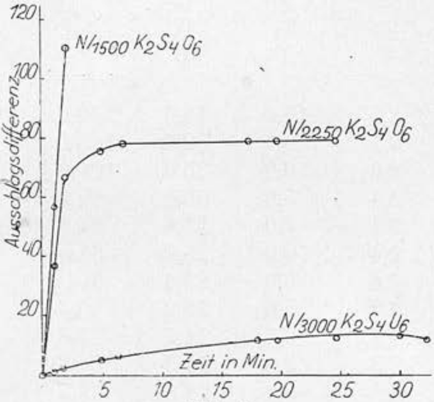

Fig. 4.

Folgende Deutung scheint dagegen einleuchtend.

Die Koagulationsgeschwindigkeitskurven für konzentrierte Elektrolyte sind gerade Linien (Fig. 2), ihre Richtung bleibt die gleiche, und demgemäß sind auch die Werte für das Verhältnis T_n/T — wie Smoluchowskis Theorie erfordert — konstant. Bei verdünnten Elektrolyten zeigt sich deutlich der langsame Koagulationsverlauf, die Kurvenrichtung ändert sich beständig und damit auch das Verhältnis T_n/T.

Nach Smoluchowski ist die „langsame Koagulation" nicht wesenseigentümlich, sondern beruht auf sekundären Faktoren. Bei der Betrachtung der Koagulationsgeschwindigkeitskurven springt bei verdünnten Elektrolyten sofort der S-förmige Verlauf (Fig. 3) ins Auge. Das Fehlen der S-förmigen Kurven bei konzentrierten Elektrolyten erklärt sich daraus, daß die Potentialdifferenz in der Doppelschicht sofort auf Null sinkt und daher die Koagulationsgeschwindigkeit von Anfang an sehr groß ist. F. Powis (loc. cit.) hat dargetan, daß die Koagulation beginnt, sobald das kritische Potential (H. Freundlichs erstes kritisches Potential) erreicht ist. Die langsame Koagulation geht in die rasche über, wenn die Potentialdifferenz Null wird (Freundlichs zweites kritisches Potential). Im Bereich der langsamen Koagulation tritt nicht beim Zusammenstoß aller Teilchen Koaleszenz ein, sondern nur in den Fällen, wo die Geschwindigkeit der Teilchen einen gewissen Wert überschreitet. Mit dem Absinken der Potentialdifferenz unter den kritischen Wert werden die abstoßenden Kräfte zwischen den Teilchen kleiner und kleiner und verschwinden beim isoelektrischen Punkte schließlich vollkommen. Im isoelektrischen Punkte werden alle Teilchenstöße von Wirkung sein trotz der Tatsache, daß die Geschwindigkeit, mit der die Teilchen sich bewegen, bisweilen sehr gering sein dürfte. Zwischen kritischem Potential und isoelektrischem Punkt muß die Geschwindigkeit der Teilchen stets einen gewissen Betrag übersteigen, um die infolge unvollständiger Neutralisation ihrer Ladung noch vorhandenen einander abstoßenden Kräfte zu überwinden.

Daraus folgt, daß bei konzentrierten Elektrolyten der Bereich der langsamen Koagulation nur klein sein wird (in Sekunden), weil die Zeit für den Übergang vom kritischen Potential zum isoelektrischen Punkte nur kurz sein wird. Deshalb wird es — bei den jetzigen Methoden zur Beobachtung des Koagulationsverlaufes — sehr schwer sein, den Bereich der langsamen Koagulation bei konzentrierten Elektrolyten zu messen. Das wird indessen bei verdünnten Elektrolyten nicht zutreffen, wo die Potentialdifferenz sich nur langsam verringert und sich deshalb der langsame Koagulationsverlauf über mehrere Minuten erstreckt (vgl. Powis, loc. cit.). Daraus resultiert die S-förmige Kurve. Die Gründe dafür, daß viele Fachgenossen den Bereich der langsamen Koagulation selbst bei verdünnten Elektrolyten nicht haben beobachten können, sind im ersten Abschnitt genügend auseinandergesetzt worden.

Tabelle IIb.

Konzentration von KCl in Mol/Liter in der Mischung	$\frac{T}{T_n}$
0,125	1,000
0,100	1,000
0,083	0,800
0,071	0,558
(0,058	0,417) ?
0,050	0,155
0,033	0,035
0,025	0,012

Der reziproke Wert des Verhältnisses T_n/T wird der Koagulationsgeschwindigkeit proportional sein. Aus Tabelle IIb geht hervor, daß die Geschwindigkeit mit steigender Verdünnung des Koagulators stark abnimmt; bei sehr großer Verdünnung wird die Geschwindigkeit gleich Null. Bei höheren Konzentrationen wird schließlich ein Grenzwert erreicht. Die Kurve aus Geschwindigkeit und Konzentration ist also S-förmig (Fig. 5). Das steht im Einklang mit der Theorie von H. Freundlich[1]), die sowohl auf langsame wie auf rasche Koagulation anwendbar ist.

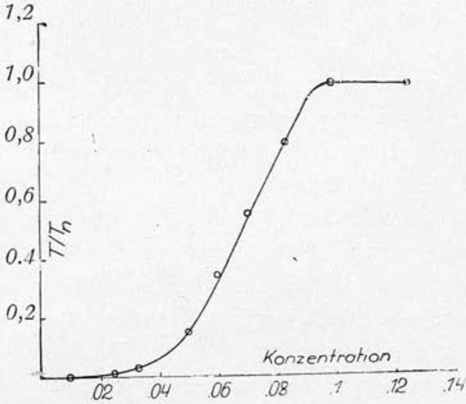

Fig. 5.

Ein anderer Faktor, der — wenigstens teilweise — bei dem Übergang von langsamer zu rascher Koagulation bei genügend verdünnten Elektrolyten mitsprechen mag, wird erkennbar in den Versuchen von Wiegner (loc. cit.) und Galecki (loc. cit.). Diese Autoren fanden bei ultramikroskopischen Beobachtungen an Goldsolen, daß die kleinen Teilchen eine größere Tendenz zeigten, sich mit größeren zu aggregieren als miteinander. Dasselbe ist vom Verfasser an Dammarharzsuspensionen beobachtet worden. Gleiche Volumina $\frac{1}{1}$ n KCl und Dammarharz wurden in einem Reagenzglas gemischt und von da in eine Küvette gebracht. Nach Zugabe von KCl ließen sich Hunderte kleiner Teilchen

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[1]) H. Freundlich, Koll.-Zeitschr. **23**, 163 (1918).

in der Mischung beobachten. Wenn man letztere einige Zeit stehen ließ, erkannte man deutlich, wie sich kleinere Teilchen an größere ansetzten, und nach Verlauf einer Stunde waren nur noch vier große Teilchen in der Lösung suspendiert. Diese vier setzten sich ohne weitere Koaleszenz ab und die überstehende Flüssigkeit war frei von kolloidem Dammarharz. In diesem Falle ist also mit zunehmender Koaleszenz auch eine Beschleunigung der Koagulationsgeschwindigkeit zu erwarten.

Aus obigen Betrachtungen ergibt sich, daß die langsame Koagulation eine Wesenseigentümlichkeit ist und nicht von sekundären Faktoren abhängt, wie Smoluchowski meint. Daß sie sich bei konzentrierten Koagulatoren nicht beobachten ließ, liegt an der Unzulänglichkeit der Meßmethoden.

Bei der Betrachtung der Kurvenbilder der zweiwertigen koagulierenden Ionen ergibt sich, daß S-förmige Kurven selbst in großer Verdünnung nicht zu erhalten sind. (Fig. 5.) Gann (loc. cit.) hat mit mehrwertigen Ionen die gleichen Ergebnisse erhalten. Die Zweiwertigkeit des koagulierenden Ions und seine größere Adsorbierbarkeit gegenüber dem einwertigen koagulierenden Ion[1]) lassen diese Anomalie erwarten. F. Powis (loc. cit.) hat gezeigt, daß die Menge eines zweiwertigen Ions, die nötig ist, um das elektrokinetische Potential auf einen gewissen Betrag herabzusetzen, bedeutend geringer ist als die eines einwertigen Ions. Das ist bedingt durch die stärkere Adsorbierbarkeit des zweiwertigen Ions, weil die Herabsetzung der Potentialdifferenz auf einer Störung des Gleichgewichtes in der Doppelschicht beruht. Demzufolge wird, wenn überhaupt mit verdünnten Elektrolyten eine Herabsetzung des Potentials erfolgt, dies gleich zu Beginn in weitem Ausmaße erfolgen und daher auch der Grad der Koaleszenz sehr hoch sein. Bei sehr großen Verdünnungen wird die Koagulation nicht fortschreiten, da nicht genügend Elektrolyt vorhanden ist, um das Potential weiter herabzusetzen. Die Koagulation wird in diesen Fällen nur partiell sein. In der Tat zeigten kataphoretische Versuche, daß ein größerer Betrag unkoagulierten Sols in der Mischung verblieben war. In den Fällen, wo vollständige Koagulation statt hat (bei konzentrierteren Elektrolyten), wird die Zeit für den Potentialabfall vom kritischen zum isoelektrischen Punkt so gering sein, daß es unmöglich ist, das Phänomen der langsamen Koagulation zu beobachten analog den Erscheinungen bei konzentrierten Lösungen einwertiger Ionen. Somit ergibt sich, daß das Fehlen der

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[1]) H. Freundlich, Koll.-Zeitschr. **1**, 321 (1907; W. D. Bancroft, Journ. of Physical Chem. **19**, 349 (1915); B. Weiser, Journ. of Physical Chem. **23**, 205 (1919).

S-Kurven bei verdünnten zweiwertigen Elektrolytlösungen eine Folge sekundärer Effekte und nicht dadurch bedingt sein kann, daß die langsame Koagulation nicht eine Wesenseigentümlichkeit ist.

Da die Adsorptionsfähigkeit des zweiwertigen koagulierenden Ions größer ist als die eines einwertigen Ions und damit das Potential verhältnismäßig stärker herabgesetzt wird, wird eine größere Anzahl Teilchen zur Koaleszenz neigen, d. h. die Koagulationsgeschwindigkeit wird von Beginn an verhältnismäßig groß sein. Die Bedingungen in einem Gemisch Kolloid + Elektrolyt mit mehrwertigem koagulierenden Ion lassen sich recht gut mit denen in einer übersättigten Lösung vergleichen — was die Größe der Kristalle betrifft. Infolge des raschen Koagulationsverlaufs ist die Möglichkeit zur Bildung größerer Aggregate selbst mit verdünnten Lösungen begrenzter als bei einwertigen Ionen. Die Zerstreuung des Lichts wird also in beiden Fällen verschieden sein; denn sie wird ja im wesentlichen durch die Teilchengröße bestimmt (Intensität des zerstreuten Lichts $= x\frac{v^2}{\lambda^4}$, wo x eine Konstante und v des Volumen eines Teilchens ist). Eine geringere Lichtzerstreuung im Falle der zweiwertigen Ionen beweist also, daß die endgültige Größe der Aggregate bei vollständiger Koaleszenz geringer ist als bei einwertigen Ionen. Anfänglich langsame Koagulation, die nach einer Zeit in rasche übergeht, kann nur bei den Elektrolyten auftreten, deren koagulierende Ionen die Potentialdifferenz nur wenig vermindern und wo das Wachstum der Teilchen von Beginn an nicht sehr lebhaft ist.

Nach Gann (loc. cit.) und anderen ist der Koagulationsvorgang keine einfache Reaktion, wie Smoluchowski annimmt, sondern ähnelt einer autokatalytischen Reaktion.

Gann hat den Wert für die Geschwindigkeitskonstante K nach der Gleichung

$$\frac{dx}{dt} = K(1 + bx)(1 - x)$$

berechnet. Der Wert für b ergab sich aus den Ordinaten des Wendepunktes der $\left(\frac{dx}{dt};\ t\text{-}\right)$ Kurve.

In den Tabellen III und IIIa sind die Werte für die Geschwindigkeitskonstante K — berechnet nach obiger Formel — eingetragen. Die Werte für b wurden in allen Fällen gleich $\frac{dx}{dt}$ im Wendepunkte der x; t-Kurve gesetzt.

Tabelle III.

$\frac{N}{20}$ LiCl*) b = 0,015				$\frac{N}{25}$ LiCl b = 0,005			
t in Minuten	Ausschlagsdifferenz in Millimeter	x	k	t in Minuten	Ausschlagsdifferenz in Millimeter	x	k
0	38	0,190	0,0230	25	27	0,135	(0,00575)
12	55	0,275	0,0276	30	37	0,185	0,00667
15	68	0,340	0,0276	35	46	0,230	0,00736
18	78	0,390	0,0276	40	53	0,265	0,00759
22	91	0,455	0,0276	50	67	0,335	0,00805
30	104	0,520	0,0276	60	78	0,390	0,00805
40	112	0,560	(0,0206)	80	92	0,460	0,00759
	Im Durchschnitt		0,0264		Im Durchschnitt		0,00755

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*) Der maximale Galvanometerausschlag betrug bei LiCl, KCl und $BaCl_2$ in konzentrierten Lösungen 200 mm, und dieser Betrag wurde für $x = 1$ in die Berechnung des K-Wertes für diese Elektrolyten eingesetzt.

$\frac{N}{30}$ LiCl b = 0,0007				$\frac{N}{15}$ $BaCl_2$ b = 0,02			
t in Minuten	Ausschlagsdifferenz in Millimeter	x	k	t in Minuten	Ausschlagsdifferenz in Millimeter	x	k
80	13	0,065	(0,00082)	4	28	0,140	(0,038)
100	20	0,100	(0,00103)	5	45	0,225	(0,051)
125	30	0,150	(0,00129)	6	59	0,295	0,058
150	42	0,210	0,00161	7	73	0,365	0,064
175	55	0,275	0,00186	8	83	0,415	0,062
200	65	0,325	0,00195	9	92	0,460	0,067
225	72	0,360	0,00195	10	102	0,510	0,069
150	75	0,375	0,00184	12	115	0,575	0,069
	Im Durchschnitt		0,00184		Im Durchschnitt		0,065

Tabelle III (Fortsetzung).

$\frac{N}{15}$ KCl		b = 0,027		$\frac{N}{20}$ KCl		b = 0,0116	
t in Minuten	Ausschlagsdifferenz in Millimeter	x	k	t in Minuten	Ausschlagsdifferenz in Millimeter	x	k
4	28	0,14	(0,0377)	10	28	0,140	(0,0150)
6	54	0,27	(0,0329)	16	51	0,255	0,0185
8	80	0,40	0,0621	20	65	0,325	0,0196
10	100	0,50	0,0660	25	78	0,390	0,0200
12	110	0,55	0,0640	30	91	0,455	0,0197
15	118	0,59	0,0628	40	104	0,520	0,0184
	Im Durchschnitt		0,0639		Im Durchschnitt		0,0192

$\frac{N}{25}$ KCl		b = 0,005		$\frac{N}{14}$ KNO_3*)		b = 0,55	
t in Minuten	Ausschlagsdifferenz in Millimeter	x	k	t in Minuten	Ausschlagsdifferenz in Millimeter	x	k
30	30	0,150	0,0053	2	20	0,111	(0,0628)
40	41	0,205	0,0051	3	38	0,211	(0,0759)
50	52	0,260	0,0062	4	63	0,350	0,126
60	64	0,320	0,0062	5	85	0,472	0,126
70	72	0,360	0,0060	6	94	0,522	0,120
80	78	0,390	0,0060	7	104	0,577	0,120
100	86	0,430	0,0056	8	110	0,611	0,115
	Im Durchschnitt		0,00585		Im Durchschnitt		0,121

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*) Der maximale Ausschlag bei KNO_3 in konzentrierter Lösung betrug 180 mm, und dieser Betrag wurde für x = 1 in die Berechnung des K-Wertes für diesen Elektrolyten eingesetzt.

Tabelle III (Fortsetzung).

$\frac{N}{19}$ KNO_3 b = 0,033				$\frac{N}{27}$ KNO_3 b = 0 0035			
t in Minuten	Ausschlagsdifferenz in Millimeter	x	k	t in Minuten	Ausschlagsdifferenz in Millimeter	x	k
5	30	0,166	0,036	25	16	0,088	(0,00368)
6	39	0,216	0,039	35	27	0,150	0,00460
8	55	0,305	0,043	40	34	0,188	0,00529
10	66	0,366	0,043	60	53	0,294	0,00575
15	88	0,488	0,043	80	66	0,366	0,00575
18	95	0,527	0,037	100	74	0,411	0,00529
	Im Durchschnitt		0,040	125	83	0,461	0,00506
					Im Durchschnitt		0,0053

Tabelle IIIa.

$\frac{N}{10}$ KCl*) b = 0,0415				$\frac{N}{15}$ KCl b = 0,0166			
t in Minuten	Ausschlagsdifferenz in Millimeter	x	k	t in Minuten	Ausschlagsdifferenz in Millimeter	x	k
3	61	0,338	0,138	8	41	0,228	(0,0301)
4	86	0,477	0,161	12	64	0,335	0,0463
5	103	0,571	0,165	16	83	0,461	0,0484
6	113	0,627	0,161	20	98	0,543	0,0488
7	117	0,650	0,149	30	118	0,655	0,0452
	Im Durchschnitt		0,155		Im Durchschnitt		0,0471

$\frac{N}{20}$ KCl b = 0 007			
t in Minuten	Ausschlagsdifferenz in Millimeter	x	k
10	11	0,061	(0,0052)
15	19	0,105	0,0073
20	29	0,161	0,0085
25	39	0,216	0,0098
30	50	0,277	0,0108
35	62	0,344	0,0122
45	82	0,455	0,0133
		Im Durchschnitt	0,0103

*) Der maximale Ausschlag betrug für KCl in konzentrierter Lösung 180 mm, welcher Wert für $x = 1$ in die Berechnung des K-Wertes für diesen Elektrolyten eingesetzt wurde.

Aus Tabelle III und IIIa geht hervor, daß die K-Werte für die verschiedenen Elektrolyten ziemlich konstant sind. Die Konstanz von K rechtfertigt die Annahme, daß der Koagulationsprozeß autokatalytisch verläuft. Dagegen sind die K-Werte für die verschiedenen Elektrolyten untereinander verschieden; so sind sie für KCl kleiner als die entsprechenden Werte für LiCl. Das erklärt sich aus der im Vergleich zum $Li^{\cdot}$-Ion stärker stabilisierenden Wirkung des $K^{\cdot}$-Ions. Genauere Untersuchungen über derartige Beeinflussungen des Koagulationsverlaufs sowie über die Bedingungen, unter denen derartige Erscheinungen am deutlichsten auftreten werden, folgen (Teil II und III).

Nach H. Paine (loc. cit.) ist

$$\frac{T_n}{T} = \left(\frac{c}{c_n}\right)^p \quad \text{oder} \quad \log T_n - \log T = p\,(\log c - \log c_n).$$

In den Tabellen IV und IVa sind die Werte von p für die verschiedenen c-Werte ausgerechnet.

Tabelle IV.

Die Werte für $\frac{T_n}{T}$ sind der Tabelle II entnommene Durchschnittswerte.

T-Wert für $\frac{n}{10}$ LiCl als Normalwert			T-Wert für $\frac{n}{9}$ KNO_3 als Normalwert		
$\frac{T_n}{T}$	$\frac{C_n}{C}$	p	$\frac{T_n}{T}$	$\frac{C}{C_n}$	p
4,7	1,5	3,82	9,34	1,555	5,06
19,6	2,0	4,29	20,73	2,111	4,05
78,6	2,5	4,76	165,74	3,000	4,65
413,1	3,0	5,48			

Tabelle IVa.

Die Werte für $\frac{T_n}{T}$ sind der Tabelle IIa entnommene Durchschnittswerte.

T-Wert für $\frac{n}{5}$ KCl als Normalwert			T-Wert für $\frac{n}{10}$ KCl als Normalwert		
$\frac{T_n}{T}$	$\frac{C}{C_n}$	p	$\frac{T_n}{T}$	$\frac{C}{C_n}$	p
1,25	1,2	1,34	0,160	0,500	2,6
1,79	1,4	1,73	0,197	0,600	3,2
2,40	1,7	1,65	0,275	0,700	3,6
6,43	2,0	2,68	0.411	0,855	5,6
27,70	3,0	3,02	3,880	1,510	3,3
82,30	4,0	3,18	11,300	2,000	3,5

H. Paine fand den Wert p für einwertige koagulierende Ionen zwischen 5 und 6 liegend. Hatschek (loc. cit.) fand p zu 12. Obige Tabellen lehren, daß p mit der Verdünnung schwankt und damit auch mit der Konzentration des Elektrolyten, der als Normalwert zur Berechnung von p gedient hat.

H. Freundlich hat eine empirische Formel, die die Geschwindigkeitskonstante K mit der Konzentration C in Beziehung bringt, in folgender Form abgeleitet:

$$K = \text{const. } C^p$$

oder

$$\frac{K}{K_n} = \left(\frac{C}{C_n}\right)^p$$

oder

$$\log K - \log K_n = p\,(\log C - \log C_n).$$

In den Tabellen V und Va sind die Werte für p für die verschiedenen Konzentrationen berechnet, der Wert für K ist ein den Tabellen III und IIIa entnommener Durchschnittswert.

Tabelle V.

K für $\frac{N}{30}$ LiCl als Normalwert			K für $\frac{N}{25}$ LiCl als Normalwert			K für $\frac{N}{20}$ LiCl als Normalwert		
$\frac{K}{K_n}$	$\frac{C}{C_n}$	p	$\frac{K}{K_n}$	$\frac{C}{C_n}$	p	$\frac{K}{K_n}$	$\frac{C}{C_n}$	p
14,340	1,5	6,4	3,496	1,200	6,8	0,2859	0,800	5,6
4,103	1,2	7,7	0,2438	0,833	7,7	0,0700	0,666	6,4

K für $\frac{N}{25}$ KCl als Normalwert			K für $\frac{N}{27}$ KNO_3 als Normalwert		
$\frac{K}{K_n}$	$\frac{C}{C_n}$	p	$\frac{K}{K_n}$	$\frac{C}{C_n}$	p
10,923	1,666	4,7	20,940	1,93	4,6
3,282	1,250	5,3	7,547	1,42	5,7

Tabelle Va.

K für $\frac{N}{20}$ KCl als Normalwert.

$\frac{K}{K_n}$	$\frac{C}{C_n}$	p
15,050	2,000	3,9
4,572	1,333	5,3

Nach H. Freundlich variiert der Wert für p zwischen 2 und 7. Obige Tabellen bestätigen das. Man kann annehmen, daß das Ion, das die gleiche Ladung trägt wie das Kolloid und dessen Einfluß natürlich mit der Koagulatorkonzentration variiert, irgendwie beim Koagulationsprozeß wirksam ist und diese Effekte hervorruft.[1]

Wie aus unseren Messungen hervorgeht, nimmt die maximale Ausschlagsdifferenz mit zunehmender Verdünnung ab. Das kommt daher, daß mit steigender Verdünnung des Elektrolyten die Koagulationsgeschwindigkeit abnimmt und demzufolge die Zeit, die zur Erreichung des gleichen Grades der Koaleszenz nötig ist, länger wird. Das hat zur Folge, daß der Absitzeffekt stärker in den Vordergrund tritt, und daher ist der erreichte Endzustand in der Koaleszenz nicht der gleiche. So hat Sven Odén[2]) gefunden, daß die erreichte Teilchengröße bei der Elektrolytkoagulation von der Konzentration des Koagulators abhängt. Die Viskositätsmessungen von Gann führten zu demselben Ergebnis (loc. cit.). Bei sehr verdünnten Koagulatorkonzentrationen ist die Koagulation nur partiell und mithin auch die Koaleszenz nicht weit fortgeschritten.

Bei zweiwertigen Ionen tritt die Abnahme des maximalen Ausschlages mit steigender Verdünnung deutlicher in Erscheinung als bei einwertigen Ionen. Nach H. Freundlich und Gann[3]) rührt das davon her, daß die Adsorbierbarkeit der zweiwertigen Ionen sehr groß ist; sie werden, wenn sie mit dem Kolloid gemischt werden, nahezu völlig adsorbiert. Verschiedene qualitative Versuche dieser Autoren ergaben, daß, nachdem das Koagulum sich gesetzt hatte, die überstehende Flüssigkeit kaum merkliche Mengen des koagulierenden Ions enthielt. Indessen sind ihre Beobachtungen nur teilweise durch gleiche Versuche mit $Th(OH)_4$ und verdünntem $K_2SO_4 \left(\frac{n}{200}\right)$ bestätigt worden. Es stellte sich heraus, daß in diesem Falle nach der Koagulation und dem Absitzen des Niederschlages eine wenn auch geringe Menge nichtadsorbierter SO_4''-Ionen in der überstehenden Flüssigkeit zurückgeblieben war. Es ist anzunehmen, daß die starke Abnahme des maximalen Ausschlagsdifferenz nicht einfach auf der vollständigen Adsorption der zweiwertigen Ionen beruht, wie H. Freundlich und Gann angeben, son-

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[1]) Wo. Ostwald, Koll.-Zeitschr. **26**, 79 (1920); Weiser u. Nicholas, Journ. of Physical Chem. **25**, 742 (1921); Mukherjee u. Chaudhuri, Journ. Chem. Soc. **125**, 794 (1924); Mukherjee u. Majumdar, loc. cit.

[2]) Sven Odén, Koll.-Zeitschr. **26**, 160 (1920); Ark. f. Kem. Mineral och. Geol. **7**, 26 (1920).

[3]) H. Freundlich u. Gann, Kolloidchem. Beih. **8**, 65 (1916).

dern es spielt doch die hohe Anfangskoagulationsgeschwindigkeit eine wichtige Rolle.

Zusammenfassung.

1. Die Koagulationsgeschwindigkeit von Thoriumoxyd wurde mittels einer sehr genauen optischen Methode messend verfolgt.

2. Es wurde gezeigt, daß die Konstanz des Verhältnisses $\frac{T_n}{T}$, die die Theorie von Smoluchowski verlangt, nur für eine gewisse Koagulatorkonzentration zutrifft und daß mit steigender Verdünnung diese Theorie nicht mehr anwendbar ist, der Bereich der „langsamen Koagulation" immer mehr hervortritt.

3. Die von H. Freundlich entwickelte Theorie für langsame und rasche Koagulation ließ sich annähernd bestätigen.

4. Es wurden die Gründe angegeben dafür, daß verschiedene Forscher die „langsame Koagulation" nicht beobachtet haben.

5. Das Fehlen einer S-förmigen Kurve bei mehrwertigen koagulierenden Ionen wurde mit ihrer raschen Adsorbierbarkeit erklärt.

6. Die Geschwindigkeitskonstante K wurde berechnet nach der Gleichung $\frac{dx}{dt} = K(1+bx)(1-x)$, wo b gleich $\frac{dx}{dt}$ ist im Wendepunkte der x; t-Kurve. Es wurden ziemlich konstante K-Werte erhalten. Dadurch wurde die Ansicht gestützt, daß die Koagulation ein autokatalytischer Vorgang ist.

7. Der Unterschied in den K-Werten für entsprechende Konzentrationen von KCl und LiCl wurde mit dem verschiedenen Einfluß der Ionen mit gleicher Ladung wie das Kolloid erklärt.

8. Es wurde festgestellt, daß die Werte für p nach der Formel von Paine und H. Freundlich mit der Verdünnung variieren und abhängen von der Elektrolytkonzentration, die man als Normalwert annimmt.

9. Die Beobachtung über die Abnahme des maximalen Galvanometerausschlages mit steigender Verdünnung des Elektrolyten bestätigt die Ergebnisse von S. Odén an $BaSO_4$-Suspensionen und zeigt, daß die schließlich erreichte Teilchengröße mit der Konzentration des Koagulators variiert. Das eigentümliche Verhalten zweiwertiger Ionen hinsichtlich dieser Eigenschaft wurde erklärt mit ihrer leichten Adsorbierbarkeit und der daraus folgenden Anfangsgeschwindigkeit der Koagulation.

II. Teil.

Über die Beziehung zwischen Reinheit des Sols und dem Einfluß von Ionen gleicher Ladung bei der Elektrolytkoagulation von $Th(OH)_4$-Sol.

Über den Einfluß der Verdünnung eines Sols auf seine Koagulierbarkeit durch Elektrolyten herrschen Meinungsverschiedenheiten. Im Hinblick auf die Tatsache, daß die Koagulation eines Sols durch Neutralisation seiner Ladung durch Zugabe eines Elektrolyten eingeleitet wird, sollte man erwarten, daß der Flockungswert für ein konzentriertes Sol höher ist als für ein verdünntes, da in ersterem eine größere Elektrolytenmenge zur Neutralisation der Solladung verbraucht wird als in letzterem. Das hat auch Gann[1]) für Al_2O_3-Sol festgestellt. Mukherjee[2]) und Mitarbeiter, K. Kruyt und van der Speck[3]), Burton[4]) und andere beobachteten das gleiche an As_2S_3-Sol bei Koagulationsversuchen mit mehrwertigen Ionen. Bei einwertigen Ionen ergab sich jedoch, daß zur Koagulation des konzentrierten Sols eine kleinere Elektrolytmenge notwendig war als bei dem verdünnten Sol.

Mukherjee (loc. cit.) zeigte auch, daß CuS, HgS und ähnliche Sole, die nur schwach adsorbieren, bei der Koagulation durch einwertige und mehrwertige Ionen in verdünnter Lösung mehr Elektrolyt benötigen als in konzentrierter. Diese Anomalie sucht er in folgender Weise zu erklären: Bei der Verdünnung vergrößert sich der Abstand der kolloiden Teilchen, und daher wird die Anzahl der in der Zeiteinheit zusammenstoßenden Teilchen kleiner werden. Daraus folgt, daß zur Erreichung desselben Grades von Koaleszenz im gleichen Zeitraum im Falle einer verdünnten Lösung mehr Elektrolyt notwendig ist als bei höherer Konzentration.

Burton und Mitarbeiter (loc. cit.) nehmen an, daß das gleichgeladene Ion bis zu einem gewissen Grade das Flockungsvermögen eines Elektrolyten beeinflußt. Weiter glauben Weiser und Nicholas[5]), daß die Adsorption des Ions mit gleicher Ladung für das anomale Verhalten des Sols bei der Verdünnung hauptsächlich verantwortlich zu machen ist. In einer neueren Abhandlung[6]) ändert Weiser indessen seine

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[1]) Gann, Kolloidchem. Beih. **8**, 64 (1916).

[2]) Mukherjee, Journ. Amer. Chem. Soc. **37**, 2024 (1915; Journ. Chem. Soc. **115**, 461 (1919); **117**, 350 (1920).

[3]) Kruyt u. van der Speck, Koll.-Zeitschr. **25**, 1 (1919).

[4]) Burton, Journ. of Physical Chem. **24**, 701; **25**, 517.

[5]) Weiser u. Nicholas, Journ. of Physical Chem. **25**, 742 (1921).

[6]) Weiser, Journ. of Physical Chem. **30**, 21 (1926).

Ansicht und legt nunmehr den Hauptwert auf die Vergrößerung der Distanz zwischen den Kolloidteilchen mit zunehmender Verdünnung.

N. R. Dhar) und Mitarbeiter[1]) sind auf Grund ihrer umfangreichen Versuche an verschiedenen Solen zu dem Schluß gekommen, daß die Verdünnungsregel — je höher die Konzentration eines Sols, desto größer auch die zu seiner Koagulation notwendige Elektrolytmenge — nur für solche Sole gültig ist, die aus dem koagulierenden Elektrolyten nicht merklich die Ionen zu adsorbieren vermögen, die die gleiche Ladung wie das Kolloid besitzen. Anderseits folgen die Sole, die Ionen mit gleicher Ladung bevorzugt adsorbieren, bei der Koagulation mit einwertigen koagulierenden Ionen der Verdünnungsregel nicht. Aus dieser Einteilung ergeben sich zwei streng voneinander geschiedene Gruppen von Solen. Zu den anomalen Kolloiden gehören z. B. As_2S_3, Sb_2S_3, Mastix, Berlinerblau, Dammarharz- und Gummiguttsole.

Beim Vergleich der Resultate von Weiser und Nicholas (loc. cit.) und N. R. Dhar und S. Ghosh[2]) für Berlinerblau zeigt sich, daß diese nicht übereinstimmen. Weiser und Nicholas finden, daß sich Berlinerblausol bei der Koagulation mit KCl normal verhält. S. Gosh und S. R. Dhar zeigten dagegen, daß eine ziemlich reine Probe des Sols sich gegenüber der Verdünnungsregel bei der Koagulation mit KCl anormal verhielt und daß diese Anomalie sich steigerte, wenn vor der Koagulation dem Sol etwas $K_4Fe(CN)_6$ zugesetzt wurde. Die anderen von N. R. Dhar als anomal aufgeführten Sole sind bis zu einem gewissen Grade hydrolytisch gespalten und enthalten somit eine gewisse Menge an peptisierendem Agens. Das läßt vermuten, daß die Anwesenheit eines Peptisators mit dem anomalen Verhalten des Sols in Zusammenhang stehen wird. Um dies zu entscheiden, wurde $Th(OH)_4$-Sol unter diesem Gesichtspunkt untersucht.

Experiment.

Sole verschiedener Konzentration, die getrennt voneinander hergestellt sind, lassen sich bei Verdünnungsversuchen nicht verwenden, da Teilchengröße und Gehalt an Verunreinigungen sicher verschieden sind, wenn auch die Herstellung unter scheinbar gleichen Bedingungen erfolgt. Der Unterschied im Gehalt an Verunreinigungen spielt, wie aus folgendem ersichtlich, eine wichtige Rolle; deswegen sind

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[1]) N. R. Dhar, Journ. of Physical Chem. **26**, 70 (1922); **28**, 313 (1924); **29**, 435 (1925); **29**, 659; **31**, 187 (1927); Koll.-Zeitschr. **34**, 262 (1924); **36**, 129 (1925).

[2]) S. Ghosh u. N. R. Dhar, Journ. of Physical Chem. **31**, 187 (1927).

für diese Experimente die Sole verschiedener Konzentration durch Verdünnung eines konzentrierten Sols bis zu bestimmtem Umfange hergestellt worden. Auch diese Darstellungsmethode birgt natürlich ihre Fehlerquellen insofern, als dem konzentrierten Sol zwecks Verdünnung das Dispersionsmittel zugesetzt und dadurch die Teilchengröße feiner wird, was die Stabilität des Sols erhöht. Die Konzentrationsabnahme an Verunreinigungen bei der Verdünnung dürfte ebenfalls bis zu gewissem Grade stabilitätssteigernd wirken, weil das Gleichgewicht im System gestört und die Ladung der Teilchen erhöht wird. Eine bessere Methode zur Herstellung verschieden konzentrierter Sole fand sich nicht, und so müssen die erwähnten Nachteile bei der Beurteilung der Resultate in Betracht gezogen werden.

N. R. Dhar und S. Ghosh (loc. cit.) stellten bei ihren Versuchen an Berlinerblausol zuerst eine fast reine Probe her und studierten dann an diesem Präparat den Verdünnungseffekt wie mit einem anderen Sol, dem vor Zugabe des Koagulators etwas $K_4Fe(CN)_6$ zugesetzt worden war. Diese Methode hat man nicht für völlig einwandfrei angesehen, da die Zeitspanne zwischen Zusatz des peptisierenden Agens und der Vermischung des verunreinigten Sols mit dem Koagulator auf die Stabilität des Sols von Einfluß sein könnte.[1]) Sole mit verschiedenem Gehalt an Peptisator wurden in diesem Falle erhalten durch verschieden lange Dialyse.

Thoriumhydroxydsol wurde auf zwei verschiedenen Wegen dargestellt, erstens nach W. Biltz[2]) und zweitens nach Müller[3]), um festzustellen, ob die gleichen Resultate zu erzielen sind; denn bekanntlich müssen auf verschiedene Methode hergestellte Sole nicht notwendig dasselbe Verhalten bei der Koagulation zeigen.

Zur Verfolgung des Koagulationsverlaufes kam die in Teil I für die Untersuchung der Kinetik der Koagulation beschriebene Methode zur Anwendung.

Tabellen I—VII enthalten die Versuchsergebnisse.

Die Angaben über Elektrolytkonzentrationen beziehen sich in allen Fällen auf die Elektrolytlösung vor der Zugabe und nicht auf die Konzentration im Gemisch Kolloid + Elektrolyt.

Die Leitfähigkeit der Sole bezieht sich in allen Versuchen auf die des Wassers als Norm, nämlich $1{,}5 \cdot 10^{-6}$. Und zwar soll sie ein Maß sein für die Reinheit des Sols mit fortschreitender Dialyse.

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[1]) A. Boutaric, Rev. gen. Colloides **5**, 450 (1927).

[2]) Ber. d. d. chem. Ges. **35**, 4431 (1902).

[3]) Allgemeine Chemie der Kolloide (1907).

Tabelle I.

Sol(Biltz) 4 Tage dialysiert;
Leitfähigkeit $> 2500 \cdot 10^{-6}$;
Konzentration
2,56 g ThO_2/Liter = Sol A.
$\frac{N}{240}$ K_2SO_4.*)

Zeit in Minuten	Auschlagsdifferenz in Millimeter	
	Sol A	Sol A/2
0	0	0
1	57	90
2	75	124
3	—	71
4	77	33
6	77	12
10	77	—

*) 2 n KCl koaguliert das Sol nicht.

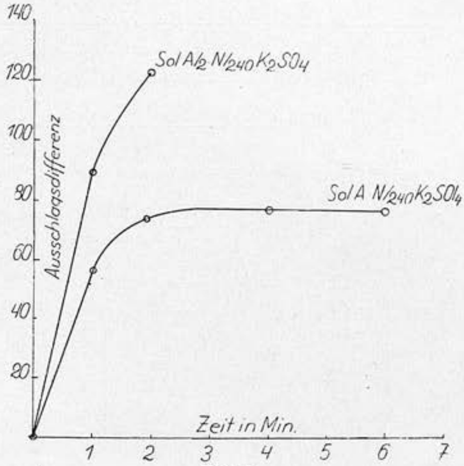

Fig. 1.

Tabelle II.

Sol (Biltz) 8 Tage dialysiert; Leitfähigkeit = $100-110 \cdot 10^{-6}$;
Konzentration = 2,11 g/Liter ThO_2 = Sol A.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	Sol A		Sol A/2	
	N · LiCl*)	N · KCl	N · LiCl	N · KCl
0	0	0	0	0
1	21	—	—	—
2	46	15	13	3
3	69	—	—	—
4	88	29	32	7
5	103	—	—	—
6	110	40	46	—
7	—	—	—	16
8	120	51	55	—
10	123	61	—	23
11	—	—	64	—
15	131	87	—	34
16	—	—	72	—
20	131	100	—	43
21	—	—	76	—
25	131	—	—	49

Tabelle II (Fortsetzung).

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	Sol A		Sol A/2	
	N · LiCl*)	N · KGl	N · LiCl	N · KCl
30	131	117	84	54
40	—	128	84	61
50	111	128	84	67
60	—	128	78	71
80	—	128	—	76
100	—	121	—	77
120	—	—	—	78
150	—	—	—	65

*, $\frac{n}{1}$ $BaCl_2$ koaguliert das Sol nicht.

$\frac{n}{400}$ K_2SO_4.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter	
	Sol A	Sol A/2
0	0	0
1	55	27
2	85	37
3	—	40
4	93	9
6	100	1
8	82	—
10	45	—
12	21	—

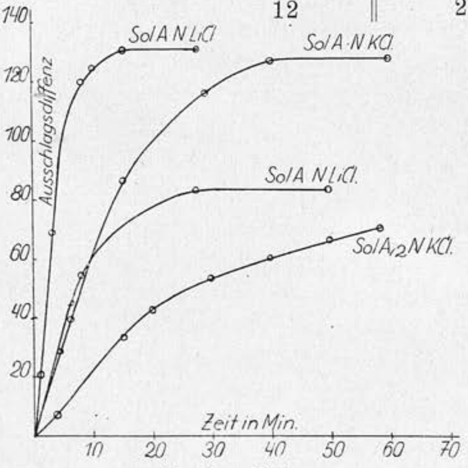

Fig. 2 und 3.

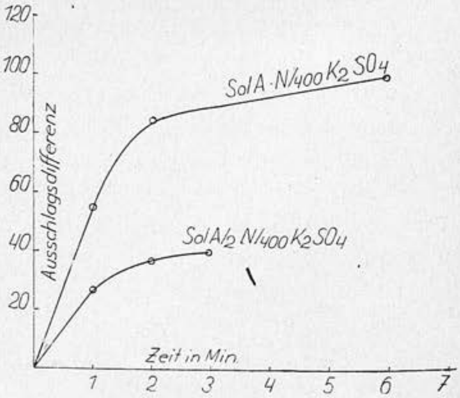

Fig. 4

Tabelle III.

Sol (Biltz) 16 Tage dialysiert; Leitfähigkeit $21 \cdot 10^{-6}$; Konzentration = 2,11 g ThO_2/Liter = Sol A.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter					
	Sol A			Sol A/2		
	$\frac{N}{3}$ LiCl	$\frac{N}{3}$ KCl	$\frac{N}{3}$ $BaCl_2$	$\frac{N}{3}$ LiCl	$\frac{N}{3}$ KCl	$\frac{N}{3}$ $BaCl_2$
0	0	0	0	0	0	0
1	50	40	—	10	—	—
2	102	75	50	24	12	10
3	128	100	—	—	—	—
4	137	117	98	42	23	19
6	150	137	—	59	38	—
8	154	143	116	—	51	34
9	—	—	—	75	—	—
10	158	—	—	—	63	—
11	—	148	—	—	—	—
12	—	—	—	84	—	—
13	160	—	129	—	—	—
14	—	—	—	—	—	48
15	—	154	—	—	75	—
16	—	—	—	90	—	—
18	162	—	—	—	—	—
20	—	158	—	93	82	—
21	—	—	—	—	—	59
24	162	—	142	—	—	—
25	—	—	—	95	—	—
30	135	160	142	95	90	—
31	—	160	142	95	—	70
35	—	—	—	87	—	—
40	—	158	142	—	91	—
41	—	—	—	—	—	74
50	—	99	142	—	92	—
60	—	—	142	—	86	76
80	—	—	135	—	—	76*)

*) Zeigt nach 3 Stunden noch keine Neigung, sich abzusetzen.

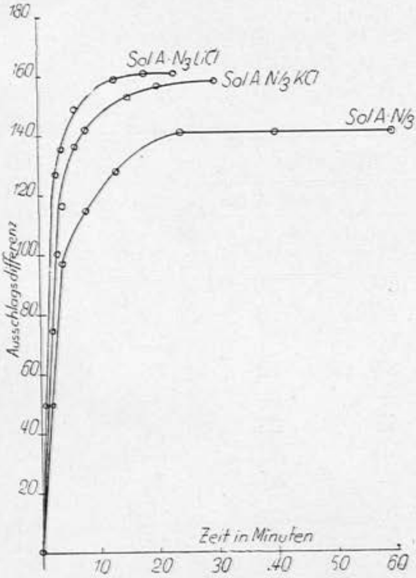

Fig. 5.

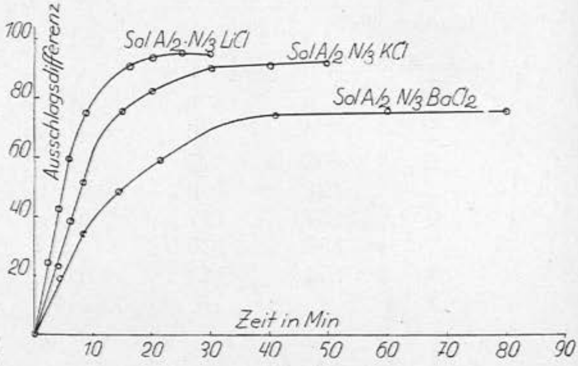

Fig. 6.

Tabelle IV.

Sol (Biltz) 24 Tage dialysiert; Leitfähigkeit = $14 \cdot 10^{-6}$;
Konzentration = 2,11 g ThO_2/Liter = Sol A.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	Sol A		Sol A/2	
	$\frac{N}{25}$ LiCl*)	$\frac{N}{25}$ $BaCl_2$	$\frac{N}{25}$ LiCl*)	$\frac{N}{25}$ $BaCl_2$
0	0	0	0	0
1	45	41	14	8
2	67	60	28	16
3	73	66	35	23
4	74	67	38	27
5	75	68	40	29
6	76	70	42	30
8	76	70	43	30
10	76	73	43	30
12	67	74	43	30
20	51	74	43	30
30	—	63	41	30**)

*) Die gleichen Ergebnisse wurden mit $\frac{n}{25}$ KCl erzielt.

**) Zeigt nach längerer Zeit noch keine Neigung, sich abzusetzen.

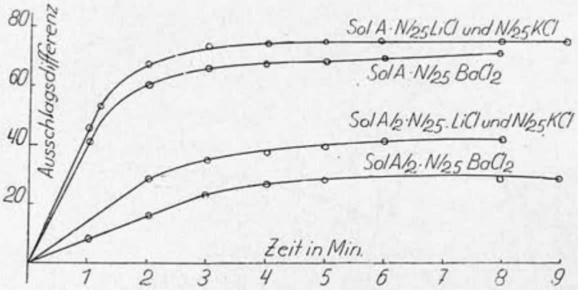

Fig. 7.

Tabelle V.

Sol (Müller) 2 Tage dialysiert; Leitfähigkeit = $130 \cdot 10^{-6}$;
Konzentration = 4,77 g ThO_2/Liter = Sol A.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	Sol A		Sol A/2	
	$\frac{N}{2}$ LiCl	$\frac{N}{2}$ $BaCl_2$	$\frac{N}{2}$ LiCl	$\frac{N}{2}$ $BaCl_2$
0	0	0	0	0
2	14	—	26	—
4	41	4	122	—
6	88	10	151	5
8	136	16	168	11
10	180	26	177	18
12	202	38	183	27
14	220	50	188	38
16	232	62	189	46
18	—	—	190	53
20	246	88	171	59
25	255	115	—	71
30	256	133	—	78
35	250	146	—	—
40	171	154	—	81
50	—	164	—	83
60	—	173	—	—
70	—	177	—	85
80	—	178	—	—
90	—	178	—	86
100	—	178	—	86

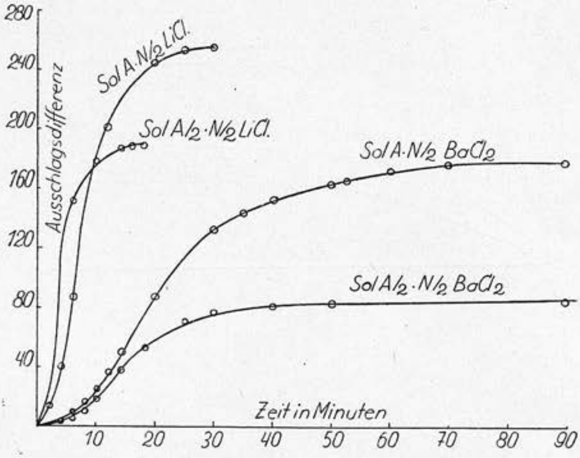

Fig. 8 und 9.

Tabelle VI.

Sol (Müller) 5 Tage dialysiert; Leitfähigkeit = $10 \cdot 10^{-6}$;
Konzentration = 4,77 g ThO_2/Liter = Sol A.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	Sol A		Sol A/2	
	$\frac{N}{10}$ LiCl	$\frac{N}{10}$ $BaCl_2$	$\frac{N}{10}$ LiGl	$\frac{N}{10}$ $BaCl_2$
0	0	0	0	0
2	50	28	60	30
4	112	60	110	66
6	175	100	154	95
8	197	134	168	119
10	208	154	174	134
12	217	171	177	146
14	—	—	180	156
15	222	190	—	—
17	—	—	161	165
20	226	204	—	170
25	228	214	—	174
30	197	220	—	176
35	—	224	—	177
40	—	226	—	177
45	—	—	—	143
50	—	228	—	—
55	—	207	—	—
60	—	153	—	—

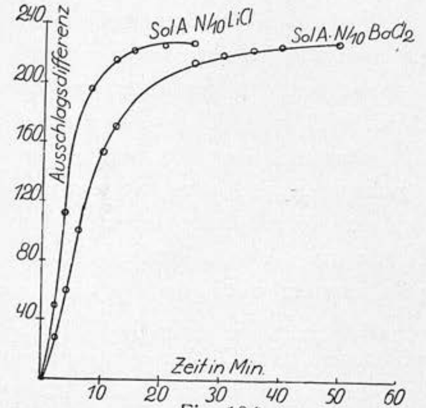

Fig. 10.

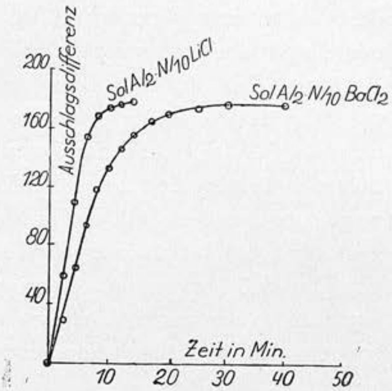

Fig. 11.

Tabelle VII.

Sol (Müller) 9 Tage dialysiert; Leitfähigkeit = $8 \cdot 10^{-6}$; Konzentration = 4,77 g ThO_2/Liter = Sol A.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	Sol A		Sol A/2	
	$\frac{N}{60}$ LiCl	$\frac{N}{60}$ $BaCl_2$	$\frac{N}{60}$ LiCl	$\frac{N}{60}$ $BaCl_2$
0	0	0	0	0
2	92	89	29	29
4	103	102	41	40
6	—	—	53	51
8	105	104	—	—
9	—	—	58	58
13	—	—	64	64
17	—	—	65	65
22	108	108	—	—
25	—	—	65	65
39	113	112	—	—
40	—	—	65	65
60	—	—	57	55
80	122	122	—	—
100	108	109	—	—

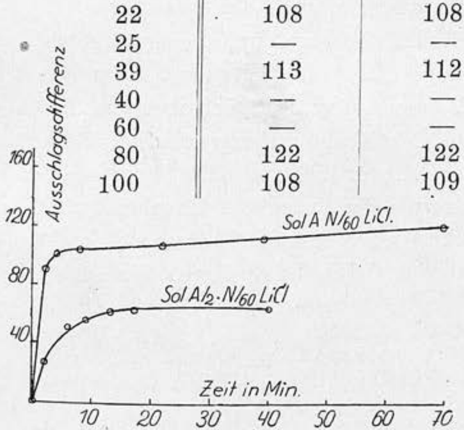

Fig. 12.

Diskussion.

Aus Tabelle I und Fig. 1 ist ersichtlich, daß ein konzentriertes Sol längere Zeit zu seiner Koagulation mit K_2SO_4 erfordert als ein verdünntes Sol, oder in anderen Worten: es ist eine größere Elektrolytmenge nötig, um ein konzentriertes Sol in derselben Zeit auszuflocken wie ein verdünntes. Das steht in Übereinstimmung mit der Verdünnungsregel.

Was das 8 Tage dialysierte und mit LiCl und KCl koagulierte Sol betrifft (Tabelle II und Fig. 2 und 3), so braucht dieses in verdünntem Zustande längere Zeit zu seiner Koagulation als in konzentriertem und zeigt damit, daß es bei der Flockung durch die erwähnten Elektrolyten gegenüber der Verdünnungsregel sich anormal verhält. Weiter geht aus Fig. 2 und 3 hervor, daß die Koagulationsgeschwindigkeitskurven für äquivalente Konzentrationen von LiCl und KCl nicht zusammenfallen, sondern daß die Koagulationsgeschwindigkeit bei KCl kleiner ist als bei LiCl, während $\frac{n}{1}$ $BaCl_2$ das Sol überhaupt nicht koagulieren würde. Das steht in Widerspruch zu der Forderung des Schulze-Hardy-Gesetzes: Die Zeit, die zur Koagulation eines Sols durch Elektrolyte, die ein gleiches Ion — mit der Solladung entgegengesetzter — Ladung enthalten, nötig ist, ist unabhängig von der Natur des Ions im Koagulator, das die gleiche Ladung trägt wie das Kolloid. Wo. Ostwald[1], W. D. Bancroft[2], Burton[3], Weiser und Nicholas[4] und N. R. Dhar[5] und Mitarbeiter sind der Meinung, daß keine Theorie die Resultate der Elektrolytkoagulation erschöpfend zu deuten vermag, wenn und solange nicht der Einfluß des Ions, das dieselbe Ladung wie das Kolloid führt, genügend Berücksichtigung findet.

Man sollte nach dem Verhalten des 8 Tage dialysierten Sols gegenüber KCl erwarten, daß es die gleichen Anomalien gegenüber der Verdünnungsregel auch bei der Koagulation mit K_2SO_4 aufweist. Tabelle II und Fig. 4 zeigt aber, daß das nicht der Fall ist, denn tatsächlich folgt das Sol der Regel. Wir werden das später eingehender diskutieren.

Eine Betrachtung der in Tabelle III und Fig. 5 und 6 eingetragenen Resultate lehrt, daß sich das 16 Tage dialysierte Sol zwar bei der Koagulation mit LiCl, KCl und $BaCl_2$ anormal verhält, sich aber von dem 8 Tage dialysierten unterscheidet. Die Koagulationsgeschwindigkeitskurven von Sol A fallen in letzterem Falle für LiCl und KCl (Fig. 2 und 3) nicht so eng zusammen wie bei ersterem (Fig. 5 und 6). Es scheint also, daß das 16 Tage dialysierte Sol A nicht so sehr in Widerspruch steht zum Schulze-Hardy-Gesetz wie das 8 Tage dialysierte. Wir sehen,

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[1] Wo. Ostwald, Koll-Zeitschr. **26**, 28 (1920).

[2] W. D. Bancroft, Second Coll. Chem. Report. Brit. Assoc. 2 (1918).

[3] Burton, Physical Properties of Coll. Solut. (1920), 187.

[4] Weiser u. Nicholas, loc. cit.

[5] N. R. Dhar, loc. cit.

daß die Kurven für Sol A bis zu einer Ausschlagdifferenz von 100 mm dicht nebeneinander verlaufen, während die Divergenz darüber hinaus etwas größer wird. Bei Sol $\frac{A}{2}$ ist das nur in beschränktem Maße feststellbar. Indessen sind diese Ergebnisse von großer Wichtigkeit hinsichtlich der Anwendbarkeit des Schulze-Hardy-Gesetzes, doch sollen sie erst bei einem Allgemeinüberblick über die gesamten Versuchsresultate näher besprochen werden.

Übergehend zu dem 24 Tage dialysierten Sol, bemerken wir, daß der Einfluß, der sich bei dem 16 Tage dialysierten bereits fühlbar machte, noch mehr in Erscheinung tritt, wie aus Tabelle IV und Fig. 7 zu entnehmen ist. Hier ist die Differenz zwischen LiCl und KCl völlig verschwunden, während sie zwischen LiCl und $BaCl_2$ viel geringer geworden ist.

Betrachten wir die zur Erreichung der maximalen Ausschlagsdifferenz erforderliche Zeit, die, als zur vollständigen Koagulation in jedem Falle notwendig, eine brauchbare Vergleichsgrundlage bildet, so können wir uns ein Bild von dem Verhalten der verschiedenen Sole gegenüber der Verdünnungsregel machen, wenn wir das Verhältnis der Koagulationszeiten T für Sol A und $\frac{A}{2}$ bilden. Tabelle VIII gibt die Werte für das Verhältnis $\frac{T_{\frac{A}{2}}}{T_A}$ für die verschiedenen Sole wieder.

Tabelle VIII.

Sole	$\frac{T_{\frac{A}{2}}}{T_A}$		
	LiCl	KCl	$BaCl_2$
8 Tage dialysiert . . .	2,0	3,0	—
16 " " . . .	1,4	1,65	2,5
24 " " . . .	1,3	1,3	0,6

Wie aus der Tabelle hervorgeht, sind die Werte für das 16 Tage dialysierte Sol kleiner als für das 8 Tage dialysierte. Das zeigt, daß mit fortschreitender Dialyse die Abweichung von der Verdünnungsregel zurückgeht. Bei dem 24 Tage dialysierten Sol sind die Werte für LiCl und KCl zwar kleiner als bei den 16 Tage dialysierten, sind aber größer als der $BaCl_2$-Wert. Das wird uns indes aus Tabelle IV klar, wo wir sehen, daß das Sol $\frac{A}{2}$ nicht in demselben Umfange koaguliert ist wie mit LiCl oder KCl. Die Werte zeigen auch, daß sich die Elektrolyte nach dem Grade ihrer Anomalie in der Reihenfolge $LiCl > KCl > BaCl_2$ einordnen. Da der Betrag an koagulierendem Ion überall der gleiche ist, dürften die Unterschiede nur der Natur des Ions zuzuschreiben sein, das die gleiche Ladung wie das Kolloid trägt.

Tabelle V und Fig. 8 und 9 zeigen das Verhalten eines 2 Tage dialysierten Müller-Sols bei der Koagulation mit LiCl und $BaCl_2$ in verschiedenen Verdünnungen. Dieses Sol folgt bei der Koagulation mit LiCl der Verdünnungsregel, nicht aber mit $BaCl_2$. Ferner fallen auch die Koagulationsgeschwindigkeitskurven für $\frac{n}{2}$ LiCl und $\frac{n}{2}$ $BaCl_2$ weder bei Sol A noch bei Sol $\frac{A}{2}$ zusammen. Die Divergenz der Kurven voneinander ist für Sol $\frac{A}{2}$ größer als für Sol A. Das zeigt klar, daß das Schulze-Hardy-Gesetz nicht überall anwendbar ist.

Die in Tabelle VI wiedergegebenen Resultate für Müller-Sol, 5 Tage dialysiert, zeigen, daß sich das Sol gegenüber LiCl und $BaCl_2$ normal verhält. Aus Fig. 10 und 11 ist auch zu sehen, daß der Abstand der Koagulationsgeschwindigkeitskurven voneinander sehr gering ist und daß das Schulze-Hardy-Gesetz hier zwar nicht exakt, aber in großer Annäherung gültig ist.

Das 9 Tage dialysierte Sol verhält sich, wie Tabelle VII und Fig. 12 angeben, bei der Koagulation mit LiCl und $BaCl_2$ gegenüber der Verdünnungsregel normal. Die Koagulationsgeschwindigkeitskurven für LiCl und $BaCl_2$ fallen zusammen; kleine Abweichungen in den Ausschlagsdifferenzen sind auf Versuchsfehler zurückzuführen. Es zeigt sich, daß hier der Forderung des Schulze-Hardy-Gesetzes genügt ist insofern, als die Zeit für die Koagulation des Sols durch äquivalente Mengen von LiCl und $BaCl_2$ unabhängig von der Natur des Kations ist und lediglich vom koagulierenden Ion abhängig ist.

In der folgenden Tabelle IX sind die Werte für das Verhältnis $\frac{T_{\frac{A}{2}}}{T_A}$ für die verschieden lange dialysierten Müller-Sole berechnet analog den Werten in Tabelle VIII für die Biltz-Sole.

Tabelle IX.

Sole	$\frac{T_{\frac{A}{2}}}{T_A}$	
	LiCl	$BaCl_2$
2 Tage dialysiert	0,6	1,12
5 ,, ,, ...	0,56	0,70
9 ,, ,, ...	0,21	0,21

Wie aus der Tabelle zu sehen ist, ist der Wert für LiCl in allen Fällen kleiner als 1. Bei $BaCl_2$ nimmt er auch ständig ab. Bei dem 9 Tage dialysierten Sol ist der Wert für LiCl und $BaCl_2$ gleich, was beweist, daß dem Schulze-Hardy-Gesetz Genüge geschieht.

Überblicken wir nun die Resultate für die Biltz- wie für die Müller-Sole und sehen wir, welche Folgerungen sich hieraus ableiten lassen.

Insoweit die Anwendbarkeit des Schulze-Hardy-Gesetzes in Frage kommt, so wurde an beiden Solen festgestellt, daß ein von Verunreinigungen noch nicht freies Sol dem Gesetz nicht gehorcht und daß mit fortschreitender Dialyse die Abweichung zurückgeht. Ein genügend gereinigtes Sol zeigt keine Abweichung mehr; äquivalente Mengen verschiedener Elektrolyte mit gleichem entgegengesetzt geladenen Ion koagulieren das Sol in gleicher Zeit.

In den Fällen, wo das Schulze-Hardy-Gesetz nicht anwendbar ist, dürfte die Abweichung von dem verschiedenen Charakter des gleichgeladenen Ions abhängen, weil Menge und Natur des koagulierenden Ions immer dieselbe ist und mithin auch das Sol in derselben Weise und in demselben Grade beeinflußt. Man findet in allen Fällen, daß bei der Koagulation des Sols LiCl wirksamer als KCl ist, das seinerseits wieder $BaCl_2$ weit übertrifft, mit anderen Worten: Ba-Ion widersetzt sich dem Einfluß des Cl'-Ions mehr als K˙ oder Li˙-Ion. Man sieht, daß das gleichgeladene Ion das Sol gegen die Einwirkung des koagulierenden Ions peptisiert oder schützt. Dieser Punkt wird in Teil III eingehender diskutiert werden, wo der Grad der Schutzwirkung für verschiedene gleichgeladene Ionen bestimmt worden ist.

Man ersieht aus den Ergebnissen bei beiden Solen, daß das abweichende Verhalten gegenüber der Verdünnungsregel mit fortschreitender Dialyse zurückgeht. Da der Einfluß des gleichgeladenen Ions mit fortschreitender Dialyse ebenfalls zurückgeht, so ist es nur natürlich, anzunehmen, daß zwischen anormalem Verhalten der Verdünnungsregel gegenüber und dem Einfluß des Ions, das die gleiche Ladung führt wie das Kolloid, eine Beziehung besteht. Burton[1]) hat gezeigt, daß die Geschwindigkeit bei der Kataphorese von nach der Methode von Bredig hergestelltem Kupfersol in erster Linie bei Zusatz geringer Quantitäten von KCl ansteigt, womit erwiesen ist, daß die Zunahme der Ladung auf der Adsorption gleichgeladener Ionen beruht. Burton und Bishop (loc. cit.) haben weiter dargetan, daß dieses Sol sich bei der Koagulation mit KCl anomal verhält. Es ist bekannt, daß die gleiche Menge eines Adsorbenten ein größeres Quantum eines Stoffes aus einer Lösung

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[1]) Burton, Phys. properties of col. solutions (1921), 167.

zu adsorbieren vermag, wenn letzterer in kleinen Portionen eingetragen wird, als wenn die Gesamtmenge auf einmal zur Anwendung kommt. Analog ist zu erwarten, daß, wenn Adsorption des Ions, das die gleiche Ladung trägt wie das Kolloid, durch letzteres stattfindet, proportional mehr durch ein verdünntes als durch ein konzentriertes Sol adsorbiert werden wird.

Die Adsorption eines Elektrolyten durch ein Sol ist teilweise elektrischer und teilweise chemischer Natur. Die elektrische Adsorption beruht auf einer Neutralisation der Ladung des Sols, und demgemäß wird in diesem Falle das entgegengesetzt geladene Ion adsorbiert werden. Das Ion mit gleicher Ladung wird durch das Sol adsorbiert infolge der chemischen Affinität zwischen beiden. S. Ghosh und N. R. Dhar (l. c.) haben kürzlich die Adsorption beider Ionen an einem positiv geladenen MnO_2-Sol gemessen, das sich gegenüber der Verdünnungsregel anormal verhält, wenn es durch $CuCl_2$ koaguliert wird. Sie fanden, daß eine verdünnte Probe dieses Sols proportional mehr an gleichgeladenem Ion adsorbierte als eine konzentrierte. Durch Adsorption des gleichgeladenen Ions nimmt aber die Stabilität des Sols zu infolge Anwachsens der Ladung; es wird demgemäß eine proportional größere Menge eines koagulierenden Ions bei der Flockung eines verdünnten als bei der Flockung eines konzentrierten Sols adsorbiert werden. N R. Dhar und S. Ghosh haben das indes nicht beobachten können; sie fanden nämlich, daß die Adsorption des entgegengesetzt geladenen Ions direkt proportional der Konzentration des Sols erfolgte und durch Zunahme der Adsorption des gleichgeladenen Ions mit steigender Verdünnung nicht beeinflußt wird. Das steht aber in Widerspruch zu Dhars Ansichten in einer früheren Arbeit.[1]) Hier sagt er bei der Beurteilung der Anwendbarkeit des Schulze-Hardy-Gesetzes, daß die Adsorption des koagulierenden Ions gleich sein muß der Summe aus dem zur Neutralisation der ursprünglichen Ladung nötigen Betrage und der Menge, die zur Neutralisation der Zuladung nötig ist, die auf den Kolloidteilchen durch Adsorption von Ionen, die die gleiche Ladung wie das Kolloid tragen, neu entstanden ist. Weiser[2]) stimmt in dieserFeststellung hinsichtlich der Adsorption des koagulierenden Ions mit N. R. Dhar überein. Es scheint daher ein Fehler in der Bestimmung des koagulierenden Ions bei der Flockung des positiv geladenen MnO_2-Sols mit $CuCl_2$-Lösung vorzuliegen.

Die Tatsache, daß mit zunehmender Menge des peptisierenden Agens im Sol die Abweichung des Sols von der Verdünnungsregel größer

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[1]) N. R. Dhar, Journ. of Physical Chem. **28**, 457 (1924).

[2]) Weiser, Journ. of Physical Chem. **28**, 232 (1924); **29**, 955 (1925).

wird, wird durch die Versuchsresultate an Biltz- und Müller-Solen erhärtet. Der Betrag an peptisierendem Agens nimmt mit fortschreitender Dialyse ab, da beobachtet wurde, daß von Beginn an im Dialysat stets HNO_3 und $Th(NO_3)_4$ beim Biltz-Sol und HCl beim Müller-Sol vorhanden war. Der Austritt von $Th(NO_3)_4$ ins Dialysat hörte beim Biltz-Sol nach 8tägiger Dialyse auf. Die Beträge an HNO_3 bzw. HCl im Dialysat wurden ständig geringer mit fortschreitender Dialyse. Von N. R. Dhar und S. Ghosh (loc. cit.) wurde beobachtet, daß die Anomalie von Berlinerblausol bei der Koagulation mit KCl mit steigender Zugabe von $K_4Fe(CN)_6$ zunimmt. Sie haben auch bei der Koagulation von Silberhydrosol mit KNO_3 beobachtet, daß dieses von der Verdünnungsregel um so mehr abweicht, je mehr OH'-Ionen zugegeben worden sind. Rossi und Marzari[1]) haben gezeigt, daß Berlinerblausol durch $Fe(CN)_6''''$-Ion stabiler wird. Überhaupt enthalten alle von N. R. Dhar und S. Ghosh als normal gefundenen Sole mehr oder weniger große Beträge an Peptisationsmitteln infolge unvollständiger Dialyse oder Hydrolyse. All das steht in Parallele zu unseren an ThO_2 gemachten Beobachtungen, das auch einen peptisierenden Stoff enthält.

Es sei hier erwähnt, daß die Anomalie des Sols gegenüber der Verdünnungsregel mit steigender Peptisatormenge nur bis zu einer gewissen Peptisatorkonzentration zunimmt, darüber hinaus findet keine weitere Stabilisierung statt, da ja zugleich auch die Menge des koagulierenden Ions gestiegen ist. Das von Weiser und Nicholas beobachtete normale Verhalten von Berlinerblausol bei der Koagulation mit KCl mag auf diesem Effekt beruhen.

Die Tatsache, daß die verschiedenen Sole durch das gleiche Peptisationsmittel nicht in gleichem Ausmaße stabilisiert werden, erklärt sich daraus, daß die adsorbierte Menge von Zustand und Art des Adsorbenten abhängt. Ist das Kolloid ein schwaches Adsorbens, so wird es auch nur wenig Ionen mit gleicher Ladung adsorbieren und daher der Verdünnungsregel gehorchen. Die Adsorption von Ionen gleicher Ladung kann auch bei einem sonst schwachen Adsorbenten gesteigert werden — doch darüber später.

Art und Wertigkeit eines peptisierenden Ions sind auch von Einfluß auf seine Adsorption durch ein Kolloid. Der stabilisierende Einfluß des gleichgeladenen Ions tritt stark hervor, wenn es mit einem Ion gleicher oder geringerer Valenz verbunden ist, das vor allem auch schwächer adsorbiert wird als das stabilisierende Ion. Das geht klar aus den Versuchen mit K_2SO_4 hervor, die in Tabelle I und II wiedergegeben sind.

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[1]) Rossi u. Marzari, Zymologica, Chim. Coll. Zucc. **2**, 25 (1927).

Bei dem 8 Tage dialysierten Sol (Tabelle II) wurde festgestellt, daß es sich anormal verhält, wenn es mit KCl, dagegen normal, wenn es mit K_2SO_4 koaguliert wurde. Dieser Unterschied erklärt sich daraus, daß die Adsorbierbarkeit des zweiwertigen SO_4''-Ions im Verhältnis zu der des einwertigen Cl'-Ions sehr groß ist und demgemäß die Menge des adsorbierten K'-Ions im ersten Falle viel geringer sein wird als im letzteren. Ist also z.T. das anomale Verhalten des Sols durch die Adsorption gleichgeladener Ionen bedingt, so wird anderseits, wenn die Adsorption des gleichgeladenen Ions durch ein stärkeres koagulierendes Ion eingeschränkt wird, das Sol normales Verhalten zeigen. Diese Annahme, daß die stärkere Adsorption eines mehrwertigen Ions die Adsorption des stabilisierenden Ions zurückdrängt, wird durch Messungen der Kataphorese-Geschwindigkeit von CuO-Sol in Gegenwart von KCl, K_2SO_4 und $K_4Fe(CN)_6$, die von Burton (loc. cit.) ausgeführt worden sind, gestützt. Er beobachtete bei Zugabe von wenig KCl ein Anwachsen der Ladung, während K_2SO_4 oder $K_4Fe(CN)_6$ diesen Effekt nicht hervorrief. Weitere Bestätigungen bedeuten die Resultate von S. Gosh und N. R. Dhar (loc. cit.). Nach diesen Autoren erwies sich ein positiv geladenes $Fe(OH)_3$-Sol als besser geschützt — infolge Adsorption des gleichgeladenen Ions —, wenn es mit $HCl + KCl$ als wenn es mit $HCl + K_2SO_4$ oder $HCl + K_4Fe(CN)_6$ koaguliert wurde. Diese Unterschiede in der peptisierenden Wirkung des H˙-Ions in den verschiedenen Kombinationen lassen sich nur aus der Mehrwertigkeit und Adsorbierbarkeit des SO_4''- bzw. $Fe(CN)_6''''$-Ions erklären.

Da die Anomalie mit steigender Menge Peptisationsmittel zunimmt, steht zu erwarten, daß das 4 Tage dialysierte Biltz-Sol eine größere Abweichung zeigen wird als das 8 Tage dialysierte. Ungünstigerweise ließ sich dieser Effekt nicht beobachten, da das Sol selbst durch eine konzentrierte KCl-Lösung sich nicht koagulieren ließ. Die Koagulationsversuche wurden mit K_2SO_4 ausgeführt, aber, wie nach den obigen Ausführungen erklärlich, wurde keine Anomalie beobachtet. Daß auch N. R. Dhar und S. Gosh (loc. cit.) bei $Th(OH)_2$-Sol (Biltz) keine Anomalie feststellen konnten, wird in diesem Falle auf das stärkere Koagulationsvermögen der BrO_3', SO_4'' und $Fe(CN)_6''''$-Ionen zurückzuführen sein.

Neben der Adsorption von Ionen gleicher Ladung dürfte auch die Vergrößerung des Abstandes zwischen den Kolloidteilchen für die Anomalien gegenüber der Verdünnungsregel verantwortlich sein. Das erkennt man aus Tabelle IV bei einem 24 Tage dialysierten Biltz-Sol. Obwohl der Einfluß des dieselbe Ladung führenden Ions verschwunden ist und das Sol dem Schulze-Hardy-Gesetz folgt, verhält es sich doch anomal bei der Koagulation mit LiCl und KCl. Die Verdünnung bewirkt Abstandsvergrößerung zwischen den Teilchen und verringert die Möglichkeit des Zusammenstoßes zwischen letzteren. Da der Koaleszenzanteil durch die gleichen Voraussetzungen bedingt wird, ist eine größere Menge von dem koagulierenden Ion notwendig, um das verdünnte, als um das konzentrierte Sol zu flocken.

Die Abweichung von der Verdünnungsregel tritt bei den verdünnten Solen stärker in Erscheinung als bei konzentrierten; das wird deutlich bei einem Vergleich der mit Biltz-Sol erhaltenen Resultate mit den mit Müller-Sol erhaltenen. Obwohl bei letzteren nach 9tägiger Dialyse ein Einfluß des gleichgeladenen Ions sich nicht mehr bemerkbar macht, ebenso wie bei einem Biltz-Sol nach 24 Tagen, besteht zwischen beiden in ihrem Verhalten gegenüber der Verdünnungsregel keine Anologie; das Müller-Sol verhält sich normal, das Biltz-Sol nicht. Der Grund für das unterschiedliche Verhalten ist die höhere Konzentration des Müller-Sols. Mukherjee (loc. cit.), K. Kruyt und van der Speck (loc. cit.) glauben deshalb auch nicht, daß abweichendes Verhalten gegenüber der Verdünnungsregel mit der Adsorption von Ionen gleicher Ladung zusammenhängt. Weiser (loc. cit.) nimmt an, daß beide Effekte für das anormale Verhalten verantwortlich sind. Daß N. R. Dhar (loc. cit.) an einem ziemlich reinen Berlinerblausol bei der Koagulation mit KCl anomales Verhalten beobachtet hat, dürfte auf die Verwendung eines verdünnten Sols zurückzuführen sein, was Dhar nicht beachtet hat. Die Distanzzunahme und die Verringerung der Möglichkeit des Zusammenstoßens und der Koaleszenz der Kolloidteilchen bei der Verdünnung wird bis zu einem gewissen Grade durch die größere Wirksamkeit eines mehrwertigen koagulierenden Ions aufgewogen, was die Neigung eines Sols zu anomalem Verhalten gegenüber der Verdünnungsregel verringert.

Nach den in dieser Arbeit gegebenen Daten muß als feststehend gelten, daß Adsorption von Ionen gleicher Ladung sowie die Vergrößerung des gegenseitigen Abstandes der Kolloidpartikeln bei der Verdünnung ein anomales Verhalten des Sols zur Folge haben und daß sich der erstgenannte Faktor als wirkungsvoller erweist. Daraus ergibt sich klar, daß man die Sole nicht in zwei Gruppen einteilen kann nach dem Vorgange von N. R. Dhar, denn $Th(OH)_4$-Sol zeigt normales oder anomales Verhalten, je nachdem man die Bedingungen variiert.

Man könnte annehmen, daß der Unterschied im Koagulationsvermögen von Elektrolyten gleicher Konzentration aber mit verschiedenem gleiche Ladung wie das Sol führendem Ion mit ihrem verschiedenen Dissoziationsgrad in Zusammenhang stünde. Auf den ersten

Blick scheint das gut möglich, aber bei einem vergleichenden Überblick über alle in diesen Versuchen verwandten Konzentrationen stellt sich sofort heraus, daß diese Erklärung ungenügend ist. Das Koagulationsvermögen der verschiedenen Elektrolyte wird nämlich unabhängig von der Art des Kations, mit dem das gleiche koagulierende Ion verbunden ist, bei einer Konzentration von $\frac{1}{25}$ norm für das Sol nach Biltz und $\frac{1}{60}$ norm für das Müller-Sol. Der Einfluß des gleichgeladenen Ions verschwindet also, obwohl man aus Leitfähigkeits- und anderen Messungen weiß, daß bei diesen Konzentrationen $\frac{n}{25}$ und $\frac{n}{60}$ der Dissoziationsgrad der verschiedenen Elektrolyte nicht gleich ist.

Es wäre noch daran zu denken, daß der Unterschied im Koagulationsvermögen von $LiCl$, KCl und $BaCl_2$ durch verschiedenen Dissoziationsgrad in Gegenwart von HCl bedingt wäre. Aus oben Gesagtem folgt aber, daß dieser Umstand nicht von großem Einfluß sein kann.

Die im folgenden entwickelte Erklärung scheint den tatsächlichen Verhältnissen am besten gerecht zu werden und ein Bild zu geben von den Bedingungen, unter denen infolge Anwesenheit eines peptisierenden Stoffes $Th(OH)_4$-Sol bei der Elektrolytkoagulation Abweichungen vom Schulze-Hardy-Gesetz zeigt.

Bei Zugabe des peptisierenden Agens (HCl) nimmt die Adsorption von $H^{\cdot}$-Ionen durch das Kolloid zu. Dadurch steigt die Ladung des Kolloids, was wiederum zur Folge hat, daß ein größerer Betrag an einwertigem koagulierenden Ion notwendig ist, um das Sol zu flocken. Dabei wird die Konzentration des Kations größer und deswegen nimmt seine Adsorption und auch sein Einfluß zu. Diese Kationenadsorption ist spezifisch für jedes Ion. In einem verhältnismäßig reinen Sol ist die Ladung geringer und demzufolge wird schon eine geringe Menge Elektrolyt das Sol koagulieren. Dabei wird aber auch eine geringere Menge des Ions mit gleicher Ladung in das Sol eingebracht, die Adsorption ist dementsprechend gering und sein Einfluß während der Koagulation nicht fühlbar. Daraus wird auch erklärlich, warum bei Elektrolyten mit mehrwertigem koagulierenden Ion der Einfluß des Ions mit gleicher Ladung sich nicht geltend macht, wenn jene zur Koagulation von Solen verwandt werden, die beträchtliche Mengen an peptisierendem Agens enthalten. Da das Koagulationsvermögen dieser Ionen sehr groß ist, können sie — selbst in geringerer Konzentration — ein Sol mit hoher Aufladung koagulieren. Dabei bleibt natürlich auch die Menge an stabilisierendem Ion gering, seine Adsorption ist unbedeutend, sein Einfluß nicht merkbar.

Die Salzsäure hat noch einen anderen Einfluß, nämlich den, daß, je höher die Konzentration ist, um so höher der Dispersitätsgrad der $Th(OH)_4$ und daher die spezifische Oberfläche um so größer sein wird. Der peptisierende Einfluß der Säure ist also das Resultat verschiedener möglicher Faktoren, von denen Abnahme der Oberflächenspannung und Zunahme der Ladung infolge Adsorption von $H^{\cdot}$ und $Th^{\cdot\cdot\cdot\cdot}$-Ionen erwähnt sei. Infolge vergrößerter Oberfläche wird die bevorzugte Adsorption von Ionen in Gegenwart eines peptisierenden Stoffes auffälliger. Mit fortschreitender Dialyse werden die abstoßenden Kräfte geringer infolge Entfernung des peptisierenden Stoffes, die Teilchen werden sich vereinigen, wobei die Gesamtoberfläche sich verringert und zugleich die bevorzugte Adsorption eines Ions aus der Lösung abnimmt. Das Schulze-Hardy-Gesetz ist dann anwendbar, wenn das Sol nur unbedeutende Mengen peptisierenden Stoffes enthält, weil dann der Einfluß des gleichgeladenen Ions zu vernachlässigen ist.

Rona und Michaelis[1]) haben gezeigt, daß die Adsorption von $H^{\cdot}$-Ion durch Holzkohle in Gegenwart von KCl größer ist als ohne dies und bei steigenden Mengen KCl einem Maximum zustrebt.[2]) Wenn also die Adsorptionswirkung von ThO_2 der von Holzkohle analog ist, werden die in Gegenwart von verschiedenen Chloriden adsorbierten Beträge an $H^{\cdot}$-Ion sehr wahrscheinlich verschieden sein und damit wird auch die Koagulationsgeschwindigkeit mit äquivalenten Mengen verschiedener Chloride nicht die gleiche sein. Dem Verfasser scheinen indes die beiden erstgenannten Möglichkeiten die wichtigsten Faktoren für die Wirkungsweise des peptisierenden Agens bei der Elektrolytkoagulation eines Sols zu sein.

Zusammenfassung.

1. Es wurde die Wirkung der Verdünnung bei der Koagulation von ThO_2-Hydrosol mit Elektrolyten studiert; dabei wurden hauptsächlich die bei fortschreitender Dialyse auftretenden Erscheinungen berücksichtigt.

2. Es wurde gefunden, daß bei Solen, die beträchtliche Mengen peptisierender Stoffe enthalten, die Koagulationsgeschwindigkeitskurven für äquivalente Mengen von LiCl, KCl und $BaCl_2$ nicht gleichlaufend sind; mit fortschreitender Dialyse gehorcht das Sol immer mehr dem Schulze-Hardy-Gesetz.

3. Die Abweichung der Geschwindigkeitskurven wird der verschiedenen Adsorption der Ionen mit gleicher Ladung durch das Sol zu-

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[1]) Rona und Michaelis, Biochem. Zeitschr. **97**, 85 (1919).

[2]) Vgl. Parks und Bartlett, Journ. Amer. Chem. Soc. **49**, 1698 (1927).

geschrieben. Die Wirkungsweise des peptisierenden Agens besteht wahrscheinlich darin, daß dadurch der Einfluß des gleichgeladenen Ions erweitert wird.

4. Die Abweichung von der Verdünnungsregel (zur Koagulation stärker konzentrierter Sole sind größere Mengen Elektrolyt notwendig) geht mit fortschreitender Dialyse zurück.

5. Die Anomalie gegenüber der Verdünnungsregel ist am deutlichsten bei einwertigen koagulierenden Ionen zu beobachten. Bei mehrwertigen koagulierenden Ionen verschwindet das anomale Verhalten des Sols infolge des stärkeren Koagulationsvermögens und der größeren Adsorbierbarkeit, wodurch die Adsorption der gleichgeladenen Ionen beträchtlich zurückgedrängt wird.

6. Die Annahme von N. R. Dhar, daß sich die Sole in zwei Klassen einteilen lassen, nämlich solche, die sich zur Verdünnungsregel normal und solche, die sich anormal verhalten, wird als irrtümlich festgestellt. Thoriumhydroxydsol zeigt unter passend gewählten Bedingungen sowohl normales als anomales Verhalten.

7. Es wird die Ansicht entwickelt, daß die Adsorption des gleichgeladenen Ions sowohl als auch die Abstandsvergrößerung der Kolloidteilchen untereinander mit der Verdünnung des Sols als Grund für das anormale Verhalten anzusehen sind und daß der erste der entscheidende Faktor ist.

III. Teil.

Die stabilisierende Wirkung von Alkali- und Erdalkaliionen.

Wie in Teil II dargelegt wurde, darf das Schulze-Hardy-Gesetz auf die Vorgänge bei der Elektrolytflockung von Kolloiden nur mit Vorsicht angewandt werden. Es ist auch gezeigt worden, daß in den Fällen, wo eine Einwirkung des Ions, das die gleiche Ladung wie das Kolloid trägt, zu beobachten ist, Ionen gleicher oder verschiedener Wertigkeit, die mit dem gleichen entgegengesetzt geladenen Ion verbunden sind, in ihrer Gegenwirkung gegenüber dem koagulierenden Ion verschieden sind. Verfasser hat es deshalb unternommen, die Schutzwirkung von Alkali- und Erdalkaliionen zu untersuchen und zu prüfen, ob sich irgendeine Gesetzmäßigkeit feststellen ließ.

Experiment.

In den im folgenden angeführten Versuchen wurde ein zwei Tage dialysiertes Müller-Sol verwandt, bei dem die Einwirkung des die gleiche Ladung wie das Sol führenden Ions besonders deutlich war. Die Methode zur Verfolgung des Koagulationsverlaufs war die gleiche, wie sie in Teil I beschrieben ist. Die Resultate sind in Tabelle I und II eingetragen und in Fig. 1 und 2 graphisch wiedergegeben. Die Konzentrationsangaben der Elektrolyte beziehen sich auf die Herstellungskonzentrationen. Die Konzentration des Sols betrug 4,77 g ThO_2/Liter (Sol A).

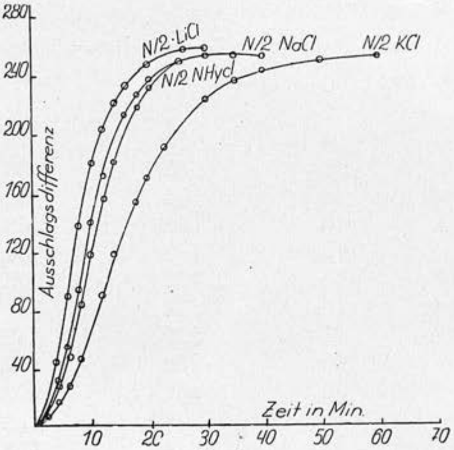

Fig. 1.

Tabelle I.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	$\frac{N}{2}$ LiCl	$\frac{N}{2}$ NaCl	$\frac{N}{2}$ KCl	$\frac{N}{2}$ NH_4Cl
0	0	0	0	0
2	14	13	6	13
4	44	32	16	28
6	88	54	28	48
8	136	94	46	84
10	180	137	66	118
12	202	170	90	156
14	220	197	118	181
16	231	212	135	204
18	239	226	153	219
20	246	236	170	231
23	252	244	191	244
26	255	249	207	249
30	256	252	221	252
35	239	253	235	253
40	—	253	244	253
50	—	203	251	211
60	—	—	252	—
70	—		246	—

Tabelle II.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	$\frac{N}{2}$ $MgCl_2$	$\frac{N}{2}$ $CaCl_2$	$\frac{N}{2}$ $SrCl_2$	$\frac{N}{2}$ $BaCl_2$
0	0	0	0	0
2	9	8	4	—
4	20	18	11	4
6	42	33	19	10
8	74	50	30	16
10	126	68	42	26
12	164	84	58	38
15	197	105	83	55
18	214	128	105	75
21	226	147	126	92
25	232	172	149	115
30	237	199	177	132
35	238	214	192	145
40	234	218	200	154
45	213	218	204	160
50	—	218	208	164
60	—	218	213	172
70	—	207	213	176
80	—	—	213	178
90	—	—	213	178
100	—	—	209	178
120	—	—	—	178

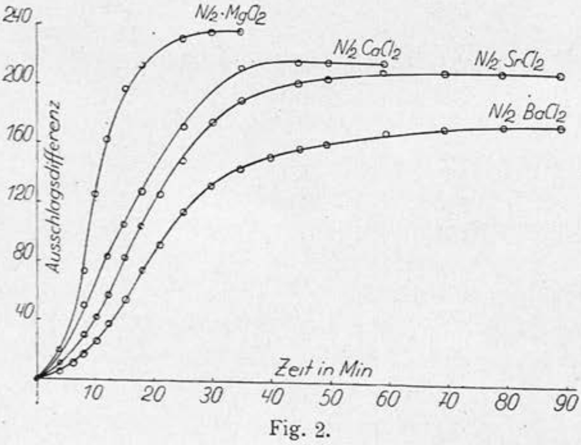

Fig. 2.

Diskussion.

Tabellen I und II zeigen, daß das Sol durch äquivalente Mengen der verschiedenen Chloride nicht in gleicher Zeit koaguliert wird. Das dürfte nach dem Schulze-Hardy-Gesetz nicht der Fall sein. In Teil II ist nun bereits darauf hingewiesen worden, daß in Gegenwart eines peptisierenden Agens das Gesetz keine Gültigkeit hat infolge des Einflusses des die gleiche Ladung wie das Kolloid führenden Ions.

Beim Vergleich der Kurven der Alkalichloride mit denen der Erdalkalien ergibt sich, daß letztere weiter entfernt von der y-Achse verlaufen als erstere. Das bedeutet, daß die Koagulationsgeschwindigkeit mit Erdalkalichloriden kleiner ist als mit Alkalichloriden, also der Einfluß der Erdalkaliionen größer ist als der der Alkalimetalle. Weiter geht daraus hervor, daß zwar die Koagulationsgeschwindigkeit bei den Alkalichloriden nicht ganz die gleiche ist, daß aber das schließlich erreichte Endstadium der Koaleszenz, und zwar in dem Moment, wo das Koagulum sich abzusetzen beginnt, immer dasselbe ist. Bei den alkalischen Erden ist das nicht der Fall. Die letzte maximale Ausschlagsdifferenz ist nicht die gleiche wie bei den Alkalien und vor allem ist der Grad der Koaleszenz, wie er durch die einzelnen Erdalkalichloride in dem Augenblick erreicht wird, wo der Niederschlag sich abzusetzen beginnt, nicht der gleiche. Das beweist schlagend, daß zweiwertige Ionen besser stabilisierend wirken als einwertige Ionen. Es erscheint möglich, daß der stabilisierende Einfluß auf ein Sol gleicher Ladung um so stärker ist, je höher die Wertigkeit ist.¹) Eine Stütze für diese Annahme bedeuten auch die Versuche von N. R. Dhar und S. Ghosh.²) Diese haben festgestellt, daß mehrwertige Ionen ein besseres Peptisationsmittel sind als einwertige. Die Messungen des elektrokinetischen Potentials in der Zwischenschicht Öl—Wasser durch L. Powis³) und Glas—Wasser von K. Kruyt⁴) zeigen, daß das Stabilisierungsvermögen eines Ions um so größer ist, je höherwertiger es ist.⁵) Die notwendige Folgerung daraus ist, daß das zweiwertige stabilisierende Ion stärker adsorbiert wird als das einwertige. Es sind also höhere Valenz und stärkere Adsorption maßgebend für hohes Stabilisierungsvermögen.

Der Koagulationsverlauf wäre, wie folgt, zu denken. Wird zu Beginn dem Kolloid Elektrolyt zugesetzt, so werden die entgegengesetzt

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¹) Weiser u. Nicholas, Journ. of Physical Chem. **25**, 752 (1927); Sen. ibid. **29**, 524 (1925).

²) N. R. Dhar u. S. Ghosh, Journ. of Physical Chem. **31**, 649 (1927).

³) L. Powis, Zeitschr. f. physik. Chem. **89**, 91 (1915).

⁴) K. Kruyt, Koll.-Zeitschr. **22**, 81 (1918).

⁵) H. Freundlich und Zeh, Zeitschr. f. physik. Chem. **114**, 65 (1924).

geladenen Ionen auf Grund ihrer elektrischen Affinität von den Kolloidteilchen adsorbiert und gleichzeitig die Ladung bis zu einem gewissen Grade neutralisiert. Insoweit wäre das Schulze-Hardy-Gesetz anwendbar, da der Einfluß des gleichgeladenen Ions auf das Kolloid sich noch nicht geltend macht. Die partiell neutralisierten Teilchen adsorbieren, während sie sich aggregieren, einige der gleichgeladenen Ionen infolge chemischer Affinität; und diese Adsorption ist spezifisch für jedes Ion. Die adsorbierten Ionen gleicher Ladung haben die Neigung, die partiell neutralisierten Teilchen wieder aufzuladen. Es ist dadurch mehr von dem entgegengesetzt geladenen Ion notwendig, um auch diese Zusatzladung zu neutralisieren. Da die Adsorbierbarkeit des stabilisierenden Ions eine spezifische Eigenschaft jedes Ions ist, so wird nicht jedes Ion in gleichem Ausmaße adsorbiert und ist infolgedessen die durch Adsorption herbeigeführte Aufladung in den einzelnen Fällen verschieden, woraus sich die verschiedenen Koagulationsgeschwindigkeiten erklären. Diese Ansicht über den Mechanismus der Koagulation teilen auch Weiser[1]) und N. R. Dhar.[2])

Sven Odén und Anderson[3]) haben gezeigt, daß die Reihenfolge in der Adsorption von Alkalimetallionen aus ihren NO_3'-Verbindungen durch Holzkohle die folgende ist: $Li < Na < K < Rb < NH_4$. Wenn wir annehmen, daß der Adsorptionsvorgang bei kolloidem ThO_2 der gleiche ist wie bei Holzkohle, sollten wir erwarten, daß das Koagulationsvermögen der verschiedenen Alkalichloride nicht das gleiche ist. Die Unterschiede in der Adsorption der Alkalimetallionen aus ihren Neutralsalzen durch Holzkohle sind indessen nicht sehr groß. Das mag der Grund davon sein, daß ein ziemlich reines Sol bei der Koagulation mit Alkalimetallsalzen durch gleichgeladene Ionen wenig beeinflußt wird. Vergrößern lassen sich die Unterschiede in der Adsorption jedoch durch Zugabe eines peptisierenden Stoffes, wobei sich zeigt, daß der Einfluß eines Ions mit gleicher Ladung merklich intensiver wird.

Die Alkali- und Erdalkalimetallionen ordnen sich nach ihrer Schutzwirkung gemäß Fig. 1 und 2 folgendermaßen ein:

$$Li < Na \leq NH_4 < K \text{ und } Mg < Ca < Sr < Ba.$$

Einstufung nach ihrem Hydratationsgrad ergibt folgende Reihe [nach Remy[4])]:

$$Li > Na > NH_4 > K \text{ und } Mg > Ca > Sr > Ba.$$

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[1]) Weiser, Journ. of Physical Chem. **28**, 232 (1924); **29**, 955 (1925).

[2]) N. R. Dhar, Journ. of Physical Chem. **28**, 457 (1924).

[3]) Sven Odén u. Anderson, Journ. of Physical Chem. **25**, 311 (1921).

[4]) Remy, Trans. Faraday Soc. 1927, Gen. Discussion.

Nach den Beweglichkeiten der Alkali- und Erdalkaliionen geordnet ergibt sich folgendes Bild [nach Ulich[1])]:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{NH_4} < \mathrm{K}$$
$$\mathrm{Mg} < \mathrm{Ca} = \mathrm{Sr} < \mathrm{Ba}.$$

Je größer die Beweglichkeiten der Ionen sind, desto größer ist die Möglichkeit, mit den Kolloidteilchen in der Lösung zusammenzutreffen und adsorbiert zu werden, und damit die Schutzwirkung. Demzufolge ist die Gegenwirkung gegenüber den koagulierenden Ionen bei $K^{\cdot}$- und $Ba^{\cdot\cdot}$-Ionen größer als bei $Li^{\cdot}$- und $Mg^{\cdot\cdot}$-Ionen. Ionenbeweglichkeiten und Schutzwirkung gehen also bei den Alkali- und Erdalkalimetallionen parallel. Wie Verfasser bereits weiter oben ausführte, ist nun auch die Schutzwirkung um so ausgeprägter (infolge stärkerer Adsorption), je höherwertiger das die gleiche Ladung wie das Kolloid führende Ion ist. Die Schutzwirkung der gleichgeladenen Ionen hängt also ab von Valenz und Ionenbeweglichkeit.

Zusammenfassung.

1. Die Koagulationsgeschwindigkeitskurven für $Th(OH)_4$-Sol (Müller) bei der Koagulation mit Alkali- und Erdalkalichloriden wurden aufgestellt. Dabei ergab sich, daß das Schulze-Hardy-Gesetz in diesem Falle keine Gültigkeit besitzt.

2. Es wurde beobachtet, daß die stabilisierende Wirkung der die gleiche Ladung wie das Sol führenden Ionen um so größer ist, je höher die Wertigkeit ist.

3. Die Alkali- und Erdalkaliionen reihen sich nach ihrer Schutzwirkung folgendermaßen ein:

$$\mathrm{Li} < \mathrm{Na} \leq \mathrm{NH_4} < \mathrm{K}$$
$$\text{und } \mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba}.$$

Die gleiche Reihenfolge gilt auch für die Ionenbeweglichkeiten, was besagt, daß die stabilisierende Wirkung wahrscheinlich eine Funktion von Valenz und Ionenbeweglichkeit ist.

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[1]) Ulich, Trans. Faraday Soc. 1927, Gen. Discussion.

IV. Teil.

Die Koagulation durch Elektrolytgemische.

Einleitung.

Die Frage der Koagulation von Solen durch Elektrolytgemische ist sehr verwickelt, und die bisher erhaltenen Resultate hat man in verschiedener Weise zu erklären versucht. In der Beurteilung der Fälle, wo die Flockungswerte bei Anwendung von Mischungen von Elektrolyten kleiner sind als bei den einzelnen Komponenten, gehen die Autoren in der Hauptsache einig, dagegen gehen die Meinungen über den in einigen Fällen beobachteten „Ionenantagonismus" weit auseinander.

H. Weiser[1]) meint, daß sich der „Ionenantagonismus" in den meisten Fällen mit einer verschiedenen Adsorbierbarkeit des koagulierenden Ions erklären läßt. H. Freundlichs[2]) Ansicht geht dahin, daß sich der Ionenantagonismus in beträchtlichem Ausmaße dann beobachten läßt, wenn eins der beiden koagulierenden Ionen stark hydratisiert ist, und dies ein Charakteristikum der hydrophilen Kolloide wäre.

N. R. Dhar[3]) und Mitarbeiter haben gezeigt, daß der Ionenantagonismus nicht auf einem Unterschied in der Adsorbierbarkeit des koagulierenden Ions beruht, wie B. Weiser annimmt, sondern auf der Adsorption des Ions mit gleicher Ladung wie das Kolloid. Sie haben dabei beobachtet, daß Anomalie gegenüber der Verdünnungsregel und Ionenantagonismus Hand in Hand gehen. Im folgenden ist die Koagulation von Th $(OH)_4$-Sol mit Mischungen je zweier Elektrolyte 1. mit gleichem koagulierenden Ion und verschiedenen Ionen gleicher Ladung wie das Sol und 2. mit gleichem peptisierenden Ion, aber verschiedenen koagulierenden Ionen untersucht worden.

Experiment.

Zu 10 ccm des Kolloids A wurde Elektrolyt in einer Menge zugesetzt, die ungenügend war, irgendeine Änderung hervorzurufen. In jedem Falle wurde auf ein Gesamtvolum von 20 ccm aufgefüllt und hierzu 20 ccm des anderen Elektrolyten zugesetzt. Im Falle der Koagulation mit $LiCl + BaCl_2$ wurde dadurch, daß die Anteile nach Äquivalenten berechnet wurden, erreicht, daß stets derselbe Gesamtbetrag

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[1]) H. Weiser, Journ. of Physical Chem. **28**, 232 (1924); **29**, 955 (1925); **30**, 20, 1527 (1926).

[2]) H. Freundlich, Colloid and Capillary Chemistry (Aufl. 1926), 461—462.

[3]) S. Ghosh u. N. R. Dhar, Journ. of Physical Chem. **30**, 830 (1926); **31**, 649 (1927); **29**, 435. 659 (1925).

an koagulierendem Ion vorhanden war. Zur Messung der Koagulationsgeschwindigkeit wurde die in Teil I beschriebene sehr exakte Methode angewandt.

Die Ergebnisse dieser Versuche sind in den Tabellen I und II wiedergegeben und in den Fig. 1 bis 7 graphisch dargestellt. Die Konzentrationsangaben der Elektrolyte beziehen sich auf die Konzentrationen bei der Herstellung der Lösungen und nicht auf die Endkonzentrationen im Gemisch Kolloid + Elektrolyt.

Tabelle I.

Müller-Sol, eine Woche dialysiert;
Konzentration = 4,95 g ThO_2/Liter.

$$\left(10\,\text{ccm Kolloid} + \frac{n}{60}\,KCl + H_2O = 20\,\text{ccm}\right) + 20\,\text{ccm}\,\frac{n}{2100}\,K_2SO_4 =$$

Gesamtvolum 40 ccm.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	0,0 ccm KCl	0,2 ccm KCl	1,0 ccm KCl	2 ccm KCl
0	0	0	0	0
1	44	48	60	89
2	68	78	87	108
3	71	83	91	89
4	73	84	83	51
6	73	85	69	—
8	73	85	—	—

$$\left(10\,\text{ccm Kolloid A} + \frac{N}{20}\,HCl + H_2O = 20\,\text{ccm}\right) + 20\,\text{ccm}\,\frac{N}{1080}\,K_2SO_4 =$$

Gesamtvolum 40 ccm.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter		
	0,0 ccm HCl	0,2 ccm HCl	0,5 ccm HCl
0	0	0	0
1	62	53	18
2	123	91	30
3	77	94	30
4	—	95	30
6	—	95	30
8	—	95	30

Tabelle I (Fortsetzung).

$$\left(10 \text{ ccm Kolloid A} + \frac{N}{4680} K_2SO_4 + H_2O = 20 \text{ ccm}\right) + 20 \text{ ccm} \frac{N}{25} KNO_3$$
$$= \text{Gesamtvolum 40 ccm.}$$

Zeit im Minuten	Galvanometerausschlag in Millimeter			
	0,0 ccm K_2SO_4	2,5 ccm K_2SO_4	5 ccm K_2SO_4	10 ccm K_2SO_4
0	0	0	0	0
1	1	3	6	28
2	3	9	14	61
4	8	18	32	101
6	15	30	53	109
8	21	39	69	113
10	28	49	80	115
12	34	57	88	97
16	49	73	100	—
20	62	84	105	—
25	77	95	108	—
30	89	102	109	—
40	100	108	85	—
50	104	95	—	—
60	105	—	—	—
70	99	—	—	—

$$\left(10 \text{ ccm Kolloid A} + \frac{N}{60} KCl + H_2O = 20 \text{ ccm}\right) + 20 \text{ ccm} \frac{N}{25} KNO_3 = \text{Gesamtvolum 40 ccm.}$$

Zeit im Minuten	Ausschlagsdifferenz in Millimeter			
	0,0 ccm KCl	2,5 ccm KCl	4 ccm KCl	10 ccm KCl
0	0	0	0	0
1	1	4	4	8
2	3	8	9	18
4	8	18	25	39
6	15	29	43	62
8	21	41	58	77
10	28	52	73	87
12	34	63	87	94
16	49	84	100	105
20	62	96	107	112
25	77	105	110	101
30	89	108	97	—
40	100	110	—	—
50	104	99	—	—
60	105	—	—	—
70	99	—	—	—

Tabelle I (Fortsetzung).

$\left(10\,\text{ccm Kolloid A} + \frac{N}{50}\,\text{HCl} + \text{H}_2\text{O} = 20\,\text{ccm}\right) + 20\,\text{ccm}\,\frac{N}{4{,}23}\,\text{KNO}_3 =$ Gesamtvolum 40 ccm.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter			
	0,0 ccm HCl	2 ccm HCl	2,5 ccm HCl	3 ccm HCl
0	0	0	0	0
1	80	13	4	—
2	200	27	8	2
4	111	70	20	3
6	—	124	38	5
8	—	159	59	7
10	—	179	83	9
13	—	192	122	13
17	—	197	158	23
21	—	200	177	37
26	—	177	189	59
30	—	—	194	77
35	—	—	195	99
40	—	—	195	118
50	—	—	181	140
60	—	—	—	157
80	—	—	—	178
100	—	—	—	182
120	—	—	—	182
140	—	—	—	179

$\left(10\,\text{ccm Kolloid A} + \frac{N}{25}\,\text{HCl} + \text{H}_2\text{O} = 20\,\text{ccm}\right) + 20\,\text{ccm}\,\frac{N}{4{,}5}\,\text{KCl} =$ Gesamtvolum 40 ccm.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter		
	0,0 ccm HCl	0,15 ccm HCl	0,3 ccm HCl
0	0	0	0
1	200	60	10
2	143	160	28
3	—	182	45
4	—	188	66
6	—	198	104
8	—	200	140
10	—	173	162
12	—	—	174
14	—	—	182
16	—	—	187
18	—	—	192
20	—	—	194
22	—	—	189

Tabelle II.

Müller-Sol, zwei Tage dialysiert;
Konzentration = 4,77 g ThO_2/Liter.
20 ccm Kolloid $\frac{A}{2} + \left(\frac{N}{2}\,LiCl + \frac{N}{2}\,BaCl_2 = 20\text{ ccm}\right)$.

Zeit in Minuten	Ausschlagsdifferenz in Millimeter				
	0.0 ccm $BaCl_2$	5 ccm $BaCl_2$	10 ccm $BaCl_2$	15 ccm $BaCl_2$	20 ccm $BaCl_2$
0	0	0	0	0	0
2	26	11	6	3	—
4	122	31	16	7	1
6	151	72	30	13	5
8	168	115	54	24	11
10	177	145	75	37	18
12	183	162	96	50	27
15	188	173	123	70	40
18	190	181	145	85	51
21	171	185	159	97	61
25	—	187	170	109	71
30	—	187	174	123	78
35	—	163	174	135	83
40	—	—	174	140	85
50	—	—	169	142	86
60	—	—	—	142	86
80	—	—	—	142	86
100	—	—	—	133	86

Diskussion.

Tabelle I und Fig. 1 zeigen den Einfluß der Zugabe von KCl zum Sol bei der Koagulation mit K_2SO_4. Der Winkel der Koagulationsgeschwindigkeitskurven zur X-Achse ist um so größer, je mehr KCl zugesetzt wird. Das bedeutet, daß die Koagulationsgeschwindigkeit in Gegenwart von KCl größer ist als ohne dies. Das stand zu erwarten, da durch eine größere Menge an koagulierendem Ion das elektrokinetische Potential entsprechend stärker herabgesetzt wird, wodurch die Koagulationsgeschwindigkeit steigt.

Aus Fig. 3 und 4 ersicht man die Wirkung eines Zusatzes von K_2SO_4 bzw. KCl bei der Koagulation mit KNO_3. Sowohl bei Zugabe von K_2SO_4 wie KCl wird die Koagulationsgeschwindigkeit erhöht.

Zugleich lehrt ein Blick auf Fig. 1, 3 und 4, daß die maximale Ausschlagsdifferenz mit zunehmender Menge an koagulierendem Ion ansteigt. Das stimmt mit unseren Beobachtungen in Teil I „Kinetik der

Koagulation" überein. Dort wurde festgestellt, daß mit zunehmender Verdünnung des Elektrolyten das Maximum des Ausschlages tiefer liegt und daß diese Abnahme des Maximums bei zweiwertigen Ionen beträchtlicher ist als bei einwertigen. Ein Vergleich von Fig. 3 und 4 zeigt ferner, daß, wenn man die Konzentration des einwertigen Hauptkoagulators beibehält und nun die Gesamtkonzentration an koagulierendem Ion durch Zugabe von Ionen verschiedener Wertigkeiten steigert, ein Ion höherer Valenz die maximale Ausschlagsdifferenz stärker erhöht als ein Ion niederer Wertigkeit. Dieses eigenartige Verhalten des zweiwertigen Ions beruht ebenfalls auf einer stärkeren Adsorbierbarkeit.

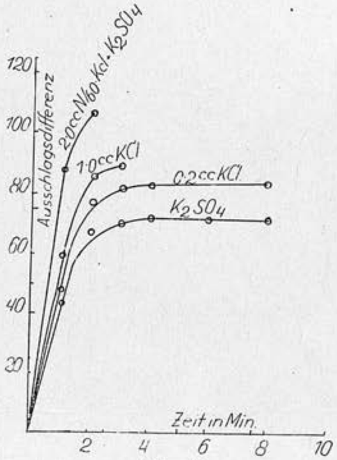

Fig. 1.

Alle diese Fälle bestätigen aber die allgemeine Regel, daß die Flockungswerte bei Anwendung eines Elektrolytgemisches geringer sind als bei einzelnen Elektrolyten, trotzdem Gemische von koagulierenden Ionen verschiedener Wertigkeiten angewandt wurden. Das dürfte nicht der Fall sein, wenn Weisers Standpunkt (loc. cit.) richtig wäre. Aus obigen Versuchen geht klar hervor, daß mit zunehmender Menge an koagulierendem Ion — mag es ein Gemisch von Ionen gleicher oder verschiedener Wertigkeiten sein — (solange nur das koagulierende Ion stark adsorbierbar ist) nur das Potential entsprechend stärker herabgesetzt und dadurch die Koagulationsgeschwindigkeit erhöht wird; Bedingung ist natürlich, daß das Ion, das die gleiche Ladung trägt wie das Sol, dasselbe bleibt und nicht stark adsorbiert wird (im Verhältnis zum koagulierenden Ion). Daß die Potentialdifferenz

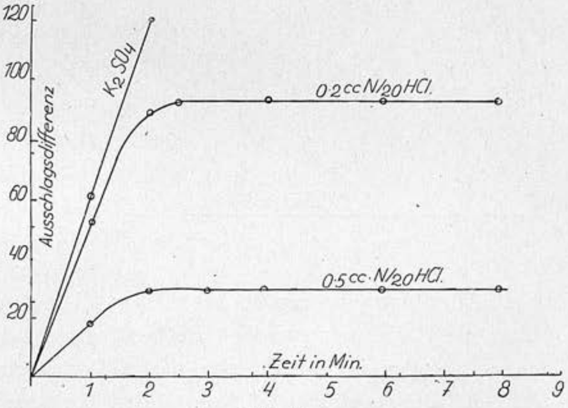

Fig. 2.

mit steigender Menge an koagulierendem Ion stärker zurückgeht, sieht man auch daraus (Fig. 3 und 4), daß die S-förmige Gestalt der Kurve verschwindet, d. h. der Bereich der langsamen Koagulation eingeengt wird; es nimmt also die Anfangsgeschwindigkeit des Koagulationsprozesses zu.

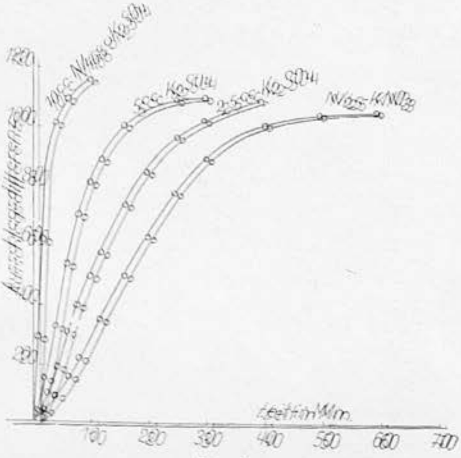

Fig. 3.

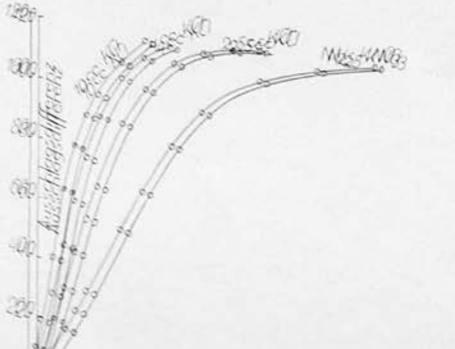

Fig. 4.

Das Bild ändert sich aber sofort, wenn das Ion, das die gleiche Ladung trägt wie das Kolloid, nicht in beiden Komponenten des Elektrolytgemisches das gleiche ist und im Vergleich zum koagulierenden Ion sich stärker adsorbieren läßt. Das läßt Fig. 2, 5 und 6 erkennen.

Wie aus Fig. 2 hervorgeht, nimmt mit steigender Zugabe von HCl die Koagulationsgeschwindigkeit ab, trotzdem die Gesamtmenge an koagulierendem Ion ansteigt. Diese Abweichungen von der Regel im Falle von $K_2SO_4 + HCl$ lassen sich nur damit erklären, daß das eine der beiden Ionen, die die gleiche Ladung tragen wie das Sol, in der Mischung eine starke peptisierende Wirkung ausübt. Dieser „Ionenantagonismus" rührt davon her, daß das H·-Ion größere Adsorptionsfähigkeit und größeres Stabilisierungsvermögen besitzt als das K·-Ion. Aus dem, was in Teil III über die Beziehung zwischen Peptisationsvermögen und Beweglichkeit gesagt worden ist, hätte man dieses Verhalten des H·-Ions erwarten können. Die gegenüber Alkali- und Erdalkaliionen größere Beweglichkeit des H·-Ions bedingt seine größere Peptisationswirkung. Dieser peptisierende Einfluß des H·-Ions wird nicht aufgewogen durch die Einführung einer äquivalenten Menge von Cl'-Ion und vermindert die Koagulationsgeschwindigkeit des mit K_2SO_4 koagulierten Sols.

Fig. 2 läßt weiter erkennen, daß die Differenz in der Koagulationsgeschwindigkeit zwischen K_2SO_4 und $K_2SO_4 + 0{,}2$ ccm $\frac{n}{20}$ HCl verhältnismäßig kleiner ist als zwischen K_2SO_4 und 0,5 ccm HCl. Dieser Anstieg des Ionenantagonismus bei größeren $H^{\cdot}$-Konzentrationen geht auf zwei Ursachen zurück. Erstens, da die Menge des Adsorbenten in der Lösung gleich blieb, wird der Betrag an adsorbiertem $H^{\cdot}$-Ion abhängen von seiner Konzentration in der Lösung; zweitens, da das Koagulationsvermögen des SO_4''-Ions sehr groß ist, sind kleinere Beträge an $H^{\cdot}$-Ion nicht imstande, die Stabilisierung des Sols zu bewirken. Nimmt dagegen die $H^{\cdot}$-Ionenkonzentration beträchtlich zu, so ist das SO_4''-Ion nicht mehr imstande, die stabilisierende Wirkung des $H^{\cdot}$-Ions völlig aufzuwiegen; es tritt „Ionenantagonismus" auf. Hieraus erklärt sich auch, warum das acht Tage dialysierte Biltz-Sol (Teil II) keine Abweichungen gegenüber der Verdünnungsregel bei der Koagulation mit K_2SO_4 aufwies.

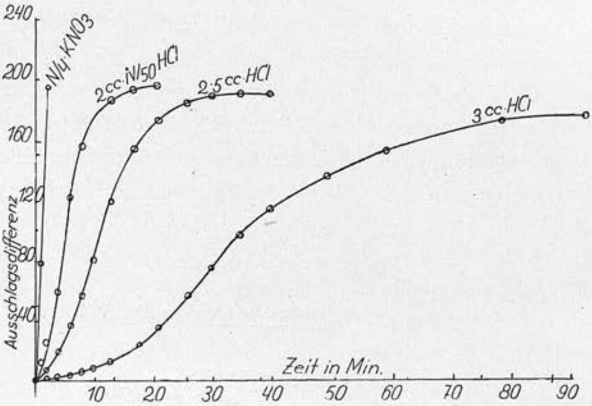

Fig. 5.

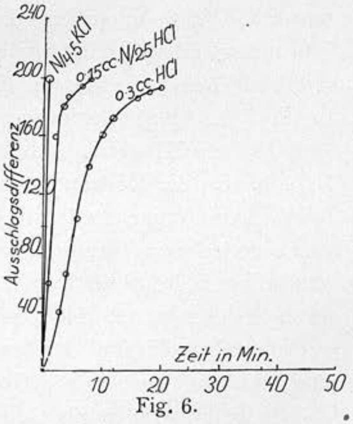

Fig. 6.

Fig. 5 und 6 bestätigen, was über Fig. 2 bereits gesagt wurde, nur tritt hier die stabilisierende Wirkung des $H^{\cdot}$-Ions noch augenfälliger in Erscheinung als bei HCl + K_2SO_4, und zwar deswegen, weil das Koagulationsvermögen des einwertigen NO_3'-Ions bedeutend geringer ist als eines zweiwertigen Ions. Mit steigender $H^{\cdot}$-Ionenkonzentration wird also die Koagulationsgeschwindigkeit herabgesetzt, der Bereich der langsamen Koagulation nimmt zu, die S-förmige Gestalt der Kurven wird ausgeprägter.

Aus Fig. 2 und 5 könnte geschlossen werden, daß der in diesen

Fällen auftretende Ionenantagonismus auf der Verschiedenheit der koagulierenden wie der stabilisierenden Ionen beruht. Das erstere ist nicht gut möglich, denn wie Fig. 6 lehrt, läßt sich die gleiche Erscheinung des Ionenantagonismus auf mit KCl + HCl beobachten, wo die koagulierenden Ionen gleich, und nur die stabilisierenden verschieden sind. Man kann also nur annehmen, daß das eine Ion, das die gleiche Ladung trägt wie das Kolloid, bevorzugt adsorbiert wird. Es sei aber darauf aufmerksam gemacht, daß natürlich die Zunahme des Ionenantagonismus mit steigender Menge Salzsäure nicht ins Unendliche gehen kann, denn die Menge des koagulierenden Ions wächst auch beständig, und so wird der Flockungswert des KCl, anstatt weiter abzunehmen, wenn eine gewisse Menge HCl zugesetzt ist, wieder ansteigen.¹)

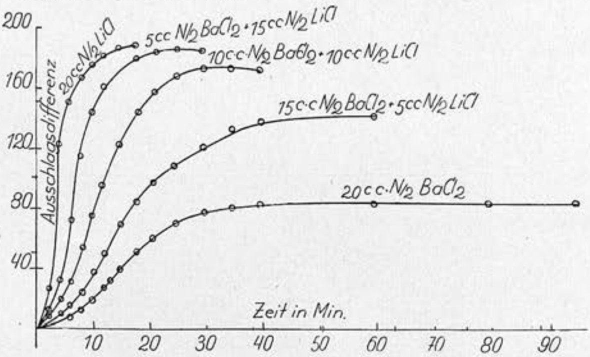

Fig. 7.

In Tabelle II und Fig. 7 sind die Versuchsergebnisse der Koagulation eines zwei Tage lang dialysierten Sols (Müller) eingetragen. Als Koagulator wurden verschiedene Gemische von $BaCl_2 + LiCl$ verwandt, wobei die Konzentration des koagulierenden Ions konstant gehalten und nur das Ion mit gleicher Ladung variiert wurde. Aus Fig. 7 sieht man, daß mit steigendem Gehalt an $Ba^{\cdot\cdot}$-Ion und gleichzeitiger Abnahme an $Li^{\cdot}$-Ion die Koagulationsgeschwindigkeit abnimmt. Es wurde in Teil II und III gezeigt, daß $Ba^{\cdot\cdot}$-Ion stärker stabilisierend wirkt als $Li^{\cdot}$-Ion. Da die Konzentration an koagulierendem Ion stets die gleiche blieb, hätte keine Änderung des Kurvenverlaufes der Koagulationsgeschwindigkeit eintreten dürfen, wenn das gleichgeladene Ion keinen Einfluß auf die Reaktion hätte. Der auch hier beobachtete Ionenantagonismus stützt den oben gezogenen Schluß, daß jener auf dem verschiedenen Einfluß des Ions mit gleicher Ladung wie das Sol beruht und nicht auf einer Adsorptionsverminderung des koagulierenden Ions.

N. R. Dhar²) ist gleichfalls der Meinung, daß der bei Verwendung von Elektrolytgemischen beobachtete „Ionenantagonismus" von einer

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¹) S. Ghosh u. N. R. Dhar, loc. cit.

²) N. R. Dhar, loc. cit.

Adsorption des gleichgeladenen Ions herrührt. Die vorliegenden Untersuchungen stehen also mit seinen Folgerungen in Einklang.

Die Ansicht H. Weisers[1]), daß der Ionenantagonismus in der verminderten Adsorption des koagulierenden Ions in Gegenwart eines anderen flockenden Ions begründet sei, findet in seinen eigenen Beobachtungen keine Stütze. Er fand[2]), daß bei der Koagulation von As_2S_3-Sol durch $LiCl + BaCl_2$, $NaCl + BaCl_2$ und $KCl + BaCl_2$ die antagonistische Wirkung sich in folgender Reihenfolge abstuft: $LiCl > NaCl > KCl$. Weiser[3]) stellte ferner fest, daß die Adsorption von $Ba^{\cdot\cdot}$-Ion in Gegenwart von $K^{\cdot}$-Ion geringer ist als in Gegenwart von $Li^{\cdot}$-Ion (Gemische von $LiCl + BaCl_2$ und $KCl + BaCl_2$ in äquivalenten Mengen auf die gleiche Solmenge). Sie betrug bei Zugabe von $K^{\cdot}$-Ion 0,009 und bei Anwesenheit von $Li^{\cdot\cdot}$ 0,019 mg-Äquivalente pro Liter. Neuerdings geben S. Ghosh und N. R. Dhar (loc. cit.) an, daß As_2S_3 ein gutes Adsorbens für negativ geladene Ionen darstellt. H. Freundlich und Zeh[4]) haben ebenfalls festgestellt, daß As_2S_3 eine große Affinität zu mehrwertigen Ionen mit gleicher Ladung besitzt bei Vorhandensein eines schwach koagulierenden Ions. Da das Koagulationsvermögen des $Li^{\cdot}$-Ions schwächer ist als das des $K^{\cdot}$-Ions, wird die schützende Wirkung des gleichgeladenen Cl'-Ions im ersteren Falle deutlicher in Erscheinung treten als bei letzterem. Die adsorbierte Cl'-Menge wird also im ersteren Falle größer sein, d. h. das Sol wird stärker aufgeladen als im letzteren. Infolge der größeren Ladung des Sols ist wiederum mehr $Ba^{\cdot\cdot}$-Ion notwendig, um — nach Adsorption — das Sol zu flocken. Die stärkere antagonistische Wirkung und höhere Adsorption von $Ba^{\cdot\cdot}$ in Gegenwart von $LiCl$ im Gegensatz zu KCl ist schon von Weiser beobachtet worden, ein Beweis, daß unsere Deutung den Erscheinungen im weitesten Umfange gerecht wird.

In gleicher Richtung liegen die Beobachtungen über As_2S_3-Sol und andere Elektrolytkombinationen.[5]) Die antagonistische Wirkung bei $LiCl + BeCl_2$, $LiCl + MgCl_2$, $LiCl + CaCl_2$, $LiCl + SrCl_2$, $LiCl + BaCl_2$ nimmt in folgender Reihenfolge ab: $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$. Das ist nach den oben entwickelten Darlegungen auch zu erwarten infolge der Tatsache, daß das Koagulationsvermögen der Erdalkalien in der Reihenfolge $Be < Mg < Ca < Sr < Ba$ zunimmt. Die stärker koagulierende Kraft des $Ba^{\cdot\cdot}$-Ions drängt den Einfluß des gleich-

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[1]) Weiser, loc. cit.

[2]) Weiser, Journ. of Physical Chem. **30**, 20 (1926).

[3]) Weiser, Journ. of Physical Chem. **29**, 955 (1925).

[4]) H. Freundlich u. Zeh, Zeitschr. f. phys. Chem. **114**, 65 (1924).

[5]) H. Freundlich, Colloid and Capillary Chemistry S. 461 (1926).

geladenen Cl'-Ions mehr zurück als Be¨-Ion; es muß im ersteren Falle also auch eine geringere antagonistische Wirkung beobachtet werden. Die Koagulationsversuche an Schwefelsol [S. Odén][1]) werden verständlich, wenn man sie unter dem gleichen Gesichtspunkt wie das As_2S_3-Sol betrachtet. S. Ghosh und N. R. Dhar (loc. cit.) fanden, daß sich dieses Sol abnorm gegenüber der Verdünnungsregel verhält und beträchtliche Mengen an Ionen gleicher Ladung adsorbiert. Demgemäß müßte es auch bei der Koagulation mit einem passenden Elektrolytenpaar Ionenantagonismus zeigen, was tatsächlich der Fall ist. Es ist nun aus den Resultaten zu ersehen, daß das Phänomen des Antagonismus mit $AlCl_3$ und $CeCl_3$ als Koagulatoren stärker in Erscheinung tritt als bei $MgCl_2$ oder $BaCl_2$. Das steht zu oben Gesagtem in Widerspruch, da Al˙˙˙ und Ce˙˙˙ stärker koagulierend wirken als Ba¨ oder Mg¨-Ionen. Die Tatsache indes, daß $AlCl_3$ und $CeCl_3$ in Lösung hydrolysiert sind, kompliziert den Vorgang, und hierin liegt auch die Erklärung für die Anomalie. Die Versuche mit $\frac{Li_2SO_4}{2} + MgCl_2$ im Vergleich zu den Ergebnissen mit Gemischen von $NaCl + MgCl_2$ oder $BaCl_2$ stützen die Regel. Die stabilisierende Wirkung ist um so stärker, je höher die Wertigkeit des Ions ist, das die gleiche Ladung trägt wie das Sol. Mit $\frac{Li_2SO_4}{2} + MgCl_2$ ist der Ionenantagonismus viel ausgeprägter als bei $NaCl + MgCl_2$, und das läßt sich nur auf die Zweiwertigkeit des SO_4''-Ions zurückführen. Der von Sen[2]), Sen und Mehrotra[3]) und Weiser[4]) bei der Koagulation von Kupferferrozyanidsol mit Elektrolytgemischen beobachtete Ionenantagonismus läßt sich gleichfalls mit einer Adsorption gleichgeladener Ionen erklären.

Die Tatsache, daß sich Mastixsol gegenüber der Verdünnungsregel[5]) anormal verhält, läßt erwarten, daß es bei der Koagulation mit Elektrolytgemischen auch Ionenantagonismus zeigen wird. Bender[6]) hat dagegen nichts derartiges mit Elektrolytgemischen festgestellt, wo die eine Komponente HCl war. Das negative Ergebnis darf nicht wundernehmen, wenn man sich vor Augen hält, daß das Koagulationsvermögen des H˙-Ions sehr groß ist und dadurch der Ionenantagonismus vollständig zurückgedrängt wird.

Zusammenfassend läßt sich also sagen, daß die Erscheinung des

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[1]) Ibid. S. 620.

[2]) Sen, Journ. of Physical Chem. **29**, 517, 539 (1925).

[3]) Sen u. Mehrotra, Zeitschr. f. anorg. Chem. **142**, 345 (1925).

[4]) Weiser, Journ. of Physical Chem. **30**, 1527 (1926).

[5]) S. Ghosh u. N. R. Dhar, loc. cit.

[6]) Bender, Koll.-Zeitschr. **14**, 255 (1914).

Ionenantagonismus am besten von der Adsorption gleichgeladener Ionen durch das Sol ausgehend erklärt wird. Es scheint irrig, den Ionenantagonismus mit dem hydrophilen Charakter des Sols in Beziehung zu bringen und den entscheidenden Einfluß des Ions mit gleicher Ladung zu leugnen. Dieser Ionenantagonismus ist im weitesten Ausmaß bei solchen Solen beobachtet worden, die sich gegenüber der Verdünnungsregel anormal verhalten, welche Erscheinung ihrerseits durch die Gegenwart eines peptisierenden Agens im Sol bedingt ist, wie in Teil II gezeigt wurde. Zu gleichem Ergebnis kommt N. R. Dhar. Alle Sole, die von S. Ghosh und N. R. Dhar (loc. cit.) als anormal befunden wurden, enthalten beträchtliche Mengen an peptisierenden Stoffen. Anderseits wies Verfasser in Teil II nach, daß in den Fällen, wo das Schulze-Hardy-Gesetz gültig ist und kein Einfluß gleichgeladener Ionen in Frage kommt, keine Anomalie gegenüber der Verdünnungsregel festzustellen ist.

Zusammenfassung und Schluß.

1. Es ist die Koagulation von $Th(OH)_4$-Sol (Müller) mit Elektrolytgemischen von $KCl + HCl$, $KCl + KNO_3$, $KCl + K_2SO_4$, $KNO_3 + K_2SO_4$, $KNO_3 + HCl$, $HCl + K_2SO_4$ und $LiCl + BaCl_2$ studiert worden und sind die Koagulationsgeschwindigkeitskurven für jedes Paar aufgenommen worden.

2. Ionenantagonismus wurde festgestellt bei: $KCl + HCl$, $KNO_3 + HCl$, $K_2SO_4 + HCl$, $LiCl + BaCl_2$.

3. Der Ionenantagonismus wurde mit der Adsorption von Ionen gleicher Ladung wie das Sol erklärt.

4. Es wurde nachgewiesen, daß Weisers Ansicht über Ionenantagonismus weder theoretisch noch experimentell haltbar ist.

5. Der Standpunkt H. Freundlichs, daß der Ionenantagonismus ein Charakteristikum hydrophiler Kolloide sei, ist unrichtig; denn so gut wie jedes Sol wird gleich dem $Th(OH)_4$-Sol unter geeigneten Bedingungen dieses Phänomen zeigen.

6. Anomalie gegenüber der Verdünnungsregel, Abweichungen vom Schulze-Hardy-Gesetz und Ionenantagonismus beruhen auf starker Adsorption des Ions, das die gleiche Ladung trägt wie das betreffende Sol.

Es sei mir gestattet, Herrn Professor Sir James Walker für sein dauerndes Interesse an dieser Arbeit und für die durch ihn veranlaßten Erleichterungen bei der Durchführung derselben meinen verbindlichen Dank auszusprechen. Gleichfalls danke ich Herrn T. R. Bolam für wertvolle Anregungen.

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Studien über Cerhydroxyd-Sol und -Gel.

Von B. N. Desai[1]).

(Mit 8 Figuren.)

(Eingegangen am 24. Oktober 1927.)

Einleitung.

Kieselsäure, Cerhydroxyd und Wolframsäure sind drei interessante Beispiele anorganischer Kolloide, die sich in vieler Hinsicht wie Emulsoide verhalten. Kieselsäure ist eingehend studiert worden von van Bemmelen[2]), R. Zsigmondy und Mitarbeitern[3]), W. Bachmann[4]), Anderson[5]) und Bütschli[6]). Obwohl Cerhydroxydsol bereits lange bekannt ist, scheint man sich wenig mit seiner Untersuchung beschäftigt zu haben. Wo. Pauli und Fernau[7]) haben den Einfluß von α- und β-Strahlen auf Cerhydroxydsol mittels Beobachtung der Viskositätsänderung studiert. Sie fanden, daß die Viskosität infolge Dehydrierung der Teilchen abnimmt. Nach Müller[8]) tritt bei Cerammoniumnitrat bei der Dialyse Hydrolyse ein, und es bildet sich kolloides Cerhydroxyd. Bei Elektrolytzusatz bildet sich ein Gel. Gibt man den Elektrolyten nach Erhitzen des Sols zu, so bleibt die Gelatinierung aus, und es bildet sich ein Niederschlag von Cerhydroxyd. Nach diesem Autor geht durch Erhitzen die Hydratation der Kolloidteilchen zurück; es kann sich deshalb bei Elektrolytzugabe zu einem erhitzten Sol kein Gel bilden.

Es scheint bisher der Beobachtung entgangen zu sein, daß bei lang ausgedehnter Dialyse von Cerammoniumnitratlösung im Dialysator

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[1]) Übersetzt von W. Rödiger (Leipzig).

[2]) van Bemmelen, Zeitschr. f. anorg. Chem. **13**, 233 (1897); **18**, 14, 98 (1898); **30**, 265 (1902); Rec. d. trav. d. Pays-Bas **7**, 37 (1888).

[3]) R. Zsigmondy, Zeitschr. f. anorg. Chem. **71**, 356 (1911).

[4]) W. Bachmann, Zeitschr. f. anorg. Chem. **73**, 163 (1911).

[5]) Anderson, Zeitschr. f. physikal. Chem. **88**, 191 (1914).

[6]) Bütschli, Verh. d. naturw. med. Ver z. Heidelberg N. F. **6**, 287 (1900).

[7]) Wo. Pauli u. Fernau, Koll.-Zeitschr. **20**, 20 (1917).

[8]) Müller, Allgemeine Chemie der Kolloide (1907).

Gelbildung eintritt. Verfasser hielt es deshalb für interessant, Bildung und Eigenschaften von Cerhydroxyd-Sol und -Gel zu untersuchen.

Experiment.

Gelbildung sowohl als Wasserbindung scheinen von der Temperatur abhängig zu sein, bei der die Cerammoniumnitratlösung dialysiert wird. In der Tabelle I sind die Eigenschaften eines Sols, das in Bombay hergestellt wurde (Sol A), mit denen eines Sols verglichen, das wir im hiesigen Laboratorium erhielten (Sol B).

Tabelle I.

Dialyse einer elfprozentigen Cerammoniumnitratlösung.

	Sol A	Sol B
1. Temperatur, bei welcher die Dialyse ausgeführt wurde	25—27° C	17—19° C
2. Zeit bis zur Gelbildung im Dialysator	3 Tage	15 Tage
3. In den Dialysator aufgenommene Wassermenge auf 100 ccm Sol	150 ccm	360 ccm
4. Mole Wasser auf 1 Mol CeO_2 im Gel	3848,8	2424,7
5. Aussehen des Gels	Weich, durchscheinend, homogen	Wie A, nur weniger deutlich
6. Einfluß der Hitze auf das Gel (100° C)	Verringerung der Hydratation der Teilchen und Bildung eines Niederschlags von Ceroxydhydrat	Viskoses Sol, das auch beim Abkühlen auf Zimmertemperatur keine Gelbildung zeigte. (Auch auf Elektrolytzusatz trat keine Gelbildung ein)
7. Verhalten des Sols bei Zugabe von Elektrolyt vor der Gelbildung	Wandelt sich in durchsichtiges, heterogenes Gel um	Wie A
8. Zugabe von Elektrolyt zum erhitzten (100°) Sol	Bildung eines Niederschlags von Ceroxydhydrat	Wie A
9. Verhalten des Gels beim Abkühlen durch eine Kältemischung	Wird fest und gelblichweiß. Läßt man es wieder Zimmertemperatur annehmen, so findet keine Rückbildung statt, sondern es bildet sich ein Cerhydroxydniederschlag	Wie A

Tabelle I (Fortsetzung).

	Sol A	Sol B
10. Alternlassen an der Luft	Allmähliches Auftreten von Synäresis	Wie A, aber langsamer
11. Verhalten des Gels im Exsikkator über konzentrierter Schwefelsäure	Schnelle Synärese	Gibt sehr langsam Wasser ab
12. Verhalten des Gels im Exsikkator über Wasser	Gibt langsam Wasser ab	Wie A
13. Verhalten des Gels beim Trocknen	Ständige Volumverminderung, bis fast alles Wasser abgegeben ist. Das Gel wird steifer und undurchsichtig. Die Farbe des getrockneten Gels ist rötlichbraun; es läßt sich zwischen den Fingern zerdrücken	Wie A
14. Verhalten des getrockneten Gels beim Auftropfenlassen eines Tropfens Wasser	Zerbricht mit knackendem Geräusch. Die Farbe wird gelb. Die Wasseraufnahme ist sehr gering, und der Ausgangszustand des Gels läßt sich nicht wieder erhalten	Wie A
15. Gel als Ultrafilter	Läßt kolloide Teilchen von $Th(OH)_4$ bis zu einer gewissen Größe durch	Wie A
16. Brechungsindex des Gels	Wie Wasser	Wie A
17. Gel unter dem Ultramikroskop a) starkes Okular	—	Kein Tyndallkegel; zwei oder drei Submikronen. Homogenes Aussehen
18. b) schwaches Okular	—	Schwacher Tyndalleffekt. Ein halbes Dutzend Submikronen in unregelmäßiger Anordnung; homogenes Aussehen

Dampfdruckmessungen.

van Bemmelen (loc. cit.) hat den Dampfdruck von Kieselsäuregel in verschiedenen Hydratationsgraden gemessen, wobei er es im Exsikkator über Schwefelsäurelösungen verschiedener Konzentration aufbewahrte, bis sich Gleichgewicht einstellte. Der Dampfdruck des Gels nach Erreichung des Gleichgewichts war gleich dem Dampfdruck der entsprechenden Schwefelsäurelösung. Es vergingen in einigen Fällen Monate, bis das Gleichgewicht erreicht war. R. Zsigmondy (loc. cit.) reduzierte die Zeit, indem er im Vakuum und in möglichst kleinen Gefäßen arbeitete. Durch eine Abänderung dieser Methode gelang es mir, die Zeit noch weiter zu begrenzen, so daß es möglich war, eine Serie von Messungen in weniger als einer Woche durchzuführen.

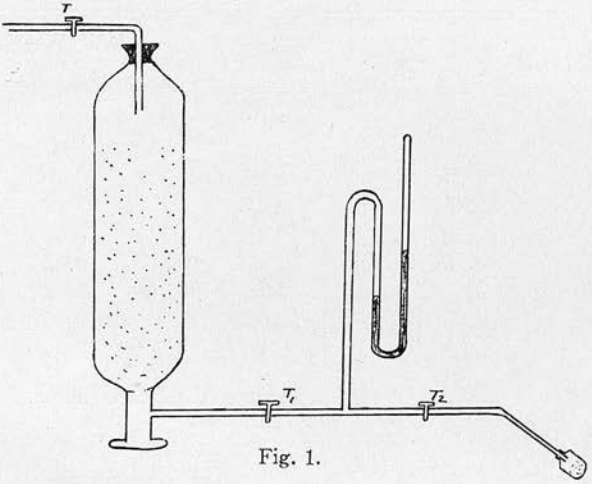

Fig. 1.

Das Gel wurde über konzentrierte Schwefelsäure in einem Exsikkator entwässert, der mit einer ständig laufenden Wasserstrahlpumpe verbunden war. Von Zeit zu Zeit wurde das das Gel enthaltende Gläschen herausgenommen und Gewicht und Dampfdruck bestimmt. Der Dampfdruck wurde durch eine Anordnung gemessen, wie sie Fig. 1 zeigt. Vor Öffnung des Hahnes T_2 wurde die Apparatur bis auf $^1/_{100}$ mm evakuiert. Dann wurde T geschlossen und T_2 langsam geöffnet. Nach Ausgleichung des Druckes wurde T_2 wieder geschlossen und nach Öffnung von T erneut evakuiert. Dieses Verfahren wurde drei- bis viermal wiederholt, bis bei Öffnung von T_2 keine Druckzunahme mehr erfolgte. Dann wurde T_1 geschlossen, so daß Manometer und das Gläschen mit dem Gel unter gleichem Druck standen. Der Dampfdruck wurde am Manometer abgelesen. Dabei stellte sich heraus, daß das Gel nicht vollständig entwässert werden kann. Tabelle II gibt die Mittelwerte zweier Versuchsreihen wieder.

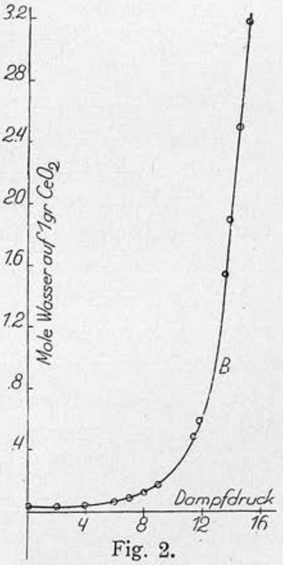

Fig. 2.

In Fig. 2 ist die Beziehung zwischen Wassergehalt und Dampfdruck des Gels graphisch dargestellt.

Tabelle II.
Temperatur = 21° C;
Druck des gesättigten Dampfes = 18,5 mm Hg.

Mole Wasser auf 1 g Ceroxyd	Dampfdruck des Gels	Mole Wasser auf 1 g Ceroxyd	Dampfdruck des Gels
14,000	18,3	3,300	15,1
10,050	18,3	1,970	13,9
8,570	18,3	0,600	11,8
7,800	18,3	0,170	8,1
7,100	18,3	0,031	3,9
5,700	17,3	0,027	1,7
5,300	16,9	0,022	0,8
4,200	16,2	0,019	0,5

Viskositätsmessungen.

Die Hydratation der Kolloidteilchen von Cerhydroxyd wurde mittels Viskositätsmessungen untersucht und zwar nach folgenden Gesichtspunkten:

1. Viskositätsänderung des Sols während der Dialyse.
2. Viskositätsänderung des Sols mit der Konzentration.
3. Viskositätsänderung nach Erhitzen auf verschiedene Temperaturen.
4. Viskositätsänderung des Sols nach 48stündiger Dialyse (d. h. vor der Gelbildung).

Alle Viskositätsmessungen wurden nach Hatschek[1]) bei konstantem Druck ausgeführt. Unter dieser Bedingung ist die Viskosität des Sols proportional der Durchflußzeit.

Da die Viskosität bei 1° Temperaturdifferenz bereits um 3—5 Proz. schwankte, mußten die Messungen bei konstanter Temperatur im Thermostaten ausgeführt werden. Die Temperatur wurde durch einen Gasthermoregulator reguliert, dessen Kugel mit 10prozentiger $CaCl_2$-Lösung gefüllt war. Der Regulator wurde auf 30° eingestellt und die Messungen bei dieser Temperatur ausgeführt. Die Temperaturschwankungen während des Versuchs betrugen höchstens $^1/_{10}$°. Vor jeder Messung wurde das Sol erst einige Zeit im Viskosimeter belassen, bis sich die richtige Temperatur eingestellt hatte (5—10 Min.). Die in den Tabellen enthaltenen Werte sind Mittelwerte aus vier Messungen. Die Durchlaufzeit für Leitfähigkeitswasser in dem benutzten Viskosimeter be-

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[1]) Hatschek, Laboratory manual 105 (1920).

trug 37,1 Sekunde. Auf diesen Vergleichswert beziehen sich alle übrigen Messungen.

Für die Versuchsreihe 1 (s. o.) wurde von Zeit zu Zeit — wie in der Tabelle angegeben — eine Probe aus dem Dialysator in das Viskosimeter gebracht, während die Dialyse ihren Fortgang nahm. Die Resultate sind in Tabelle III und Fig. 3 wiedergegeben. Die Kurve gibt ein Bild von dem Hydrationsgrad der Teilchen während der Dialyse.

Für die Versuchsreihe 2 wurde von einer 11prozentigen, 10 Stunden dialysierten Lösung ausgegangen; diese wurde als 100 angenommen und durch entsprechendes Verdünnen mit Wasser 80-, 60-, 40-, 20- und 0prozentige Sole hergestellt. Gleiche Messungen wurden mit einer 11prozentigen nicht dialysierten Lösung von Cerammoniumnitrat und mit je einer 40 Stunden dialysierten und auf 50 bzw. 100° erhitzten Lösung ausgeführt. Die Resultate sind aus Tabelle IV zu ersehen und in Fig. 4 und 5 graphisch dargestellt als Kurven A, B, C und D.

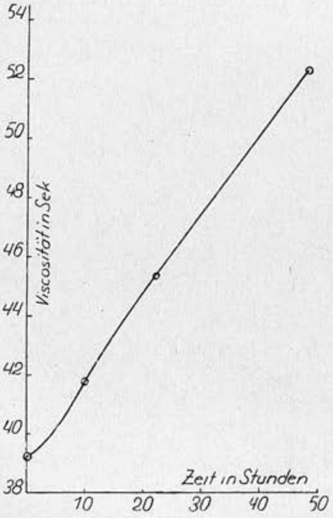

Fig. 3.

Die Tatsache, daß die hydratisierten Kolloidteilchen von Cerhydroxyd mit steigender Temperatur stufenweise ihr Wasser abgeben, erhellt aus Versuchsreihe 3. Dabei wurde ein 48 Stunden dialysiertes Sol in Portionen zu 50 ccm in einzelnen Flaschen auf verschiedene

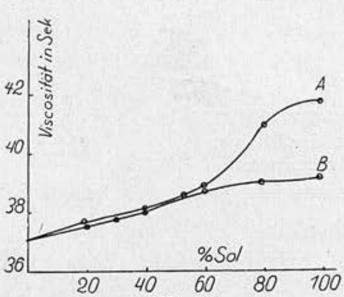

Fig. 4.

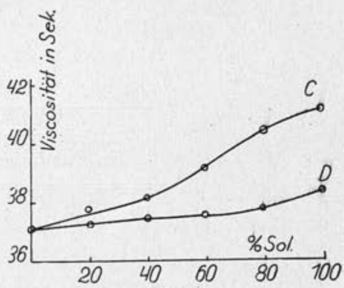

Fig. 5.

Temperaturen erhitzt und wieder auf Zimmertemperatur abgekühlt. Damit wurden dann Viskositätsmessungen angestellt. Tabelle V und Fig. 6 geben die Resultate wieder.

Der plötzliche Anstieg der Viskosität, wenn Gelbildung eintritt, wird deutlich aus Versuchsreihe 4. Die Viskosität eines 48 Stunden dialysierten Sols wurde von 5 zu 5 Minuten gemessen, bis zu dem Zeitpunkte, wo Gelbildung eintrat und weitere Messungen unmöglich waren. Fig. 7 und Tabelle VI enthält die Resultate.

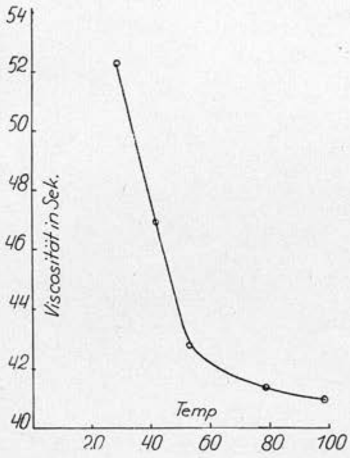

Fig. 6.

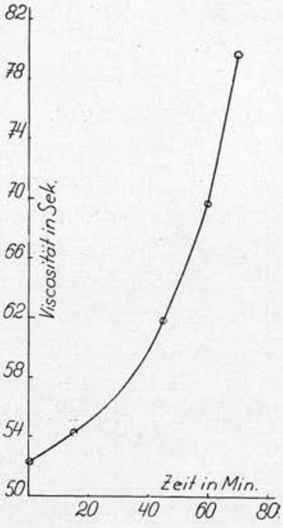

Fig. 7.

Tabelle III.

Viskosität in Sekunden	Zeit der Dialyse in Stunden
39,15	0 (11 prozentige undialysierte Lösung)
40,20	5
41,75	10
45,35	22
47,80	31
52,30	48

Tabelle IV.

a) 10 Stunden dialysiert		b) 11prozentige undialysierte Lösung	
Viskosität in Sekunden	Konzentration in Proz.	Viskosität in Sekunden	Konzentration in Proz.
37,10	0	37,10	0
37,70	20	37,60	20
38,10	40	38,00	40
38,90	60	38,75	60
41,00	80	39,00	80
41,75	100	39,15	100

c) 40 Stunden dialysiert und auf 50° erwärmt		d) 40 Stunden dialysiert und 5 Minuten zum Sieden erhitzt	
Viskosität in Sekunden	Konzentration in Proz.	Viskosität in Sekunden	Konzentration in Proz.
37,1	0 (reines H_2O)	37,10	0
37,7	20	37,25	20
38,1	40	37,40	40
39,1	60	37,50	60
40,4	80	37,70	80
41,1	100	38,30	100

Tabelle V.

Viskosität in Sekunden	Temperaturen, auf die das Sol erhitzt wurde
52,3	28,2° C
47,0	42,0° C
42,8	53,0° C
41,4	79,0° C
41,0	99,0° C

Tabelle VI.

Viskosität in Sekunden	Zeit in Minuten
52,3	0 (sofort nach Beendigung d. Dialyse)
54,3	15
56,8	30
61,8	45
69,8	60
79,8	70

Diskussion.

Aus Punkt 1 und 2 (Tabelle I) geht hervor, daß die Zeit, die nötig ist, bis das Gel sich bildet, von der Temperatur abhängig ist, bei der die Dialyse sich vollzieht. Die Diffusionsgeschwindigkeit bei 18° C ist geringer als bei 26° C, und deswegen ist natürlich die Zeit, die man zur Herstellung eines gut gereinigten Sols braucht, nicht in beiden

Fällen die gleiche. Die Bildungsgeschwindigkeit der Kolloidteilchen durch Hydrolyse wird bei niedrigerer Temperatur gleichfalls kleiner sein, woraus sich ergibt, daß sich ein Sol gleicher Beschaffenheit bei höherer Temperatur schneller bildet als bei niedrigerer. Es ließe sich also aus den Beobachtungen die Regel ableiten, daß die Zeit bis zur Gelbildung um so kürzer ist, je höher die Temperatur ist, bei der die Dialyse ausgeführt wird; bei einer Dialyse bei 50° C etwa wird die Gelbildung nach wenigen Stunden vollständig sein. Jedoch sollte man Vorsicht walten lassen. Es ist zwar richtig, daß die Diffusionsgeschwindigkeit mit steigender Temperatur bei der Dialyse zunimmt und dadurch die Zeit, die nötig ist, ein Sol von bestimmtem Reinheitsgrad zu erhalten, beträchtlich reduziert wird, aber man muß dabei bedenken, daß durch Erwärmung des Sols über eine gewisse Temperatur hinaus die Wasserhülle um die Teilchen zerstört wird, und zwar in um so größerem Ausmaße, je höher die Temperatur steigt. Tatsächlich tritt keine Gelbildung ein, wenn das Sol über 40° hinaus erwärmt wird. Auf den Temperatureinfluß bei der Gelbildung werden wir später noch einmal zurückkommen.

Durch Punkt 3 und 4 (Tabelle I) wird die starke Hydratation des Gels gekennzeichnet. Man sieht, daß bis zu einem gewissen Grad die Hydratation des Gels von den Herstellungsbedingungen abhängt. Es wurde beobachtet, daß die Wassermenge, die während eines bestimmten Zeitabschnittes zu Beginn der Dialyse in den Dialysator eintrat, kleiner war als die in einem gleichlangen späteren Abschnitt eintretende, trotzdem zu Beginn alles Cer in Ionenzustand vorhanden und deswegen der osmotische Druck sehr hoch war. Das zeigt deutlich, daß die Affinität gegen Wasser mit steigender Anzahl Kolloidteilchen wächst, die ihrerseits mit zunehmender Hydrolyse ansteigt. Kieselsäure-, Gelatine und andere Gele, die dahingehend untersucht worden sind, sind bei weitem nicht so hoch hydratisiert wie Ceroxydgel. Die Frage, wie eine so große Menge Wasser durch kolloides Ceroxyd gebunden sein kann, wird später unter Berücksichtigung aller in Tabelle I verzeichneten Beobachtungen diskutiert werden.

Aus der hohen Hydratation des Gels kann man schließen, daß die Eigenschaften des Gels, Durchsichtigkeit und Brechungsindex, nahezu wie beim Wasser sein müssen. Tatsächlich wird das durch die Beobachtungen in 5 und 16 (Tabelle I) bestätigt. Das Gel ist sehr weich, homogen und durchsichtig. Bei der Messung des Brechungsindex nach der Keilmethode zeigte es sich, daß bei gleicher Richtung des Einfallsstrahls der Ausfallsstrahl gegenüber Wasser keine Ablenkung zeigt, wenn er durch einen Gelblock hindurchgeht. Neben dem großen Überschuß an Dispersionsmittel kann der im Verhältnis dazu minimale disperse Anteil nicht zur Geltung kommen.

Der Temperatureinfluß bei der Gelbildung wird klar aus den Beobachtungen 6 und 8. Hitze zerstört die Wasserhülle der Kolloidteilchen, weshalb bei Elektrolytzusatz zum erhitzten Sol keine Gelbildung auftritt. Diese Beobachtung steht in Übereinstimmung mit der von Müller gemachten (loc. cit.). Auf den Temperaturkoeffizienten werde ich nochmals bei der Besprechung der Viskositätsmessungen zurückkommen.

Wie aus Punkt 5 und 7 in Tabelle I zu ersehen ist, ist die Struktur des Gels durch die Herstellungsart bedingt.

Über die Frage der Anzahl der Phasen im Gel sind die Meinungen geteilt. Katz¹) nimmt an, daß Gele einphasig sind. Die äußerlich homogene Natur des Cerxoydgels scheint diese Ansicht zu bestätigen. Es ist indes zu bedenken, daß das Gel hier nur deshalb homogen erscheint, weil der minimale disperse Anteil im Gel neben der großen Menge Wasser darin völlig verschwindet. R. Zsigmondy (loc. cit.) und andere sind ihrerseits der Meinung, daß Gele mehrphasig sind. Hinsichtlich des Ceroxydgels bestätigt sich diese Annahme durch Beobachtung 9. Wäre die Ansicht von Katz richtig, dann dürfte das Gel durch Gefrieren nicht so intensiv beeinflußt werden. Es wurde aber gefunden, daß die Gelstruktur zerstört und beim Wiedererwärmen auf Zimmertemperatur der ursprüngliche Zustand nicht wiederherzustellen war. Die Wassermoleküle sind im Ceroxydgel in einer bestimmten Art und Weise verteilt; ist nun die Gelstruktur einmal zerstört, so vermögen sie sich nicht in ihre ursprüngliche Lage zurückzufinden, es kann keine Rückbildung des Gels stattfinden, sondern es bildet sich ein Niederschlag von Ceroxydhydrat. R. Zsigmondys Erklärung wird der Natur der Gele eher gerecht.

Wird das Gel im Exsikkator über konzentrierter H_2SO_4 stehen gelassen, so gibt es sein Wasser rasch ab, und es tritt Synäresis auf (Beobachtung 11 bzw. 10). Sol A gab bereits in der ersten halben Stunde seines Verbleibens im Exsikkator über konzentrierter H_2SO_4 reichlich Wasser ab, da es stärker hydratisiert war als Sol B und deshalb das Wasser in Sol A weniger fest gebunden war als bei letzterem.

Beobachtung 12 ist ein Beispiel für die Erscheinung, die unter dem Namen „Schröders Paradoxon“ bekannt ist.²) Schröder beobachtete, wenn er ein hochhydratisiertes Gel in einen Exsikkator über Wasser brachte, daß das Gleichgewicht, das sich eingestellt hatte, als

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¹) Katz, Kolloidchem. Beih. **9**, 1 (1917).

²) Schröder, Zeitschr. f. physikal. Chem. **45**, 109 (1903).

sich das Gel im Wasser befand, nicht dasselbe war, wie wenn er das Gel über Wasser brachte. Zur Erklärung dieses Effektes besitzt die Deutung von Wolf und Buchner[1]), daß der Dampfdruck des Wassers in der Gassphäre über ihm nicht überall vollständig gleich wäre und deshalb das Gel Wasser abgäbe, um den Druck auszugleichen, wenig Wahrscheinlichkeit. Der Grund ist vielmehr darin zu suchen, daß das Gel so hoch hydratisiert ist.

Die ständige Volumverminderung des Gels bei der Dehydratation (Beobachtung **13**) zeigt hinsichtlich dieser Eigenschaft Analogien zum Verhalten des Gelatinegels. Das Auftreten einer Trübung im Gel beim Trocknen läßt es dem Kieselsäuregel ähnlich erscheinen, doch zeigt das Nichtverschwinden der Trübung im Ceroxydgel beim weiteren Fortschreiten des Trocknungsprozesses, daß beide Gele in bezug auf ihr Verhalten nicht identisch sind.

Das Zerspringen des Gels (Beobachtung **14**) läßt sich auf der Grundlage der Anschauungen von R. Zsigmondy über die Gelstruktur[2]) erklären. Wenn ein Tropfen Wasser auf das trockene Gel gebracht wird, wird die in den Kapillaren des Gels enthaltene Luft einem plötzlichen Druck unterworfen und in dem Bestreben sich auszudehnen, zersprengt sie die Kapillarstruktur des Gels. Die Wände der Kapillaren zerspringen unter dem gesteigerten Druck mit knackendem Geräusch, und das Gel zerfällt zu Pulver. Die Farbe des Gels wird nach der Zugabe von Wasser gelb. Der ursprüngliche Zustand des Gels läßt sich nicht wiederherstellen, selbst wenn dieses lange Zeit über Wasser bewahrt wird. Das zeigt, daß das Gel in weitem Ausmaße irreversibel ist.

Das Ergebnis der Verwendung des Gels als Ultrafilter (Beobachtung **15**) bestätigt die Annahme, daß das Gel Kapillarstruktur besitzt. Butschli (loc. cit.) kommt auf Grund seiner Beobachtungen an Kieselsäure zu dem Schluß, daß das Gel Honigwabenstruktur haben müsse und daß Wasser der disperse Anteil sei. Diese Ansicht konnte von R. Zsigmondy und Mitarbeitern (loc. cit.) bei der ultramikroskopischen Prüfung des Gels nicht bestätigt werden. Das Ceroxydgel scheint aus feinen Kapillaren zusammengesetzt zu sein; bei der Verwendung des Gels als Ultrafilter lassen diese nur Teilchen bis zu einem gewissen Durchmesser hindurch. Durch Filtration von verschiedenen kolloiden Lösungen mit bekannter Teilchengröße ließe sich der Durchmesser der Kapillaren im Gel annähernd bestimmen.

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[1]) Wolf u. Buchner, Zeitschr. f. physikal. Chem. **89**, 271 (1915); Koninkl. Akad. v. Wetense Amsterdam **17**, 92 (1915).

[2]) Bhatnagar u. Mathur, Koll.-Zeitschr. **33**, 368 (1922).

Beobachtung 17 gibt uns ein Bild von der Größe der Teilchen im Gel. Mit einem starken Okular konnte man nur 2 oder 3 Submikronen erkennen. Ein schwacher Tyndallkegel war indessen mit schwachem Okular zu sehen, die Zahl der im Kegel sichtbaren Submikronen betrug etwa das Doppelte. Das Auftreten eines schwachen Tyndallkegels beweist, daß das Gel größtenteils aus Amikronen besteht und daß das CeO_2 im Gel nicht in echter Lösung vorhanden ist.

Dieselbe Beobachtung (17) stützt weiter die Ansicht, die wir in einer anderen Arbeit[1]) ausgesprochen haben, daß nämlich die Wasserhülle um jedes einzelne Teilchen keinen bemerkenswerten Einfluß auf die Lichtzerstreuung der Kolloidteilchen haben könne. Andernfalls müßte das hochhydratisierte CeO_2-Gel einen starken Tyndalleffekt gezeigt haben infolge Zunahme der Teilchengröße durch Hydratation.

Im folgenden sei eine Schilderung der Art und Weise, in der eine so große Wassermenge durch das Ceroxydgel gebunden ist, gegeben, die viel Wahrscheinlichkeit für sich hat:

Die Kolloidteilchen können als Einheiten angesehen werden, von denen aus nach verschiedenen Richtungen Restvalenzen wirksam sind. Diese ermöglichen es dem Teilchen, irgendetwas in der Nähe Befindliches in einem Zustand leichter Bindung festzuhalten. Diese Bindung wird fester, wenn alle Valenzen nur durch eine geringe Menge einer anderen Substanz abgesättigt werden. Diese Restvalenzen spielen auch eine wesentliche Rolle im Kristallgitter, indem sich durch diese die Moleküleinheiten gegenseitig festhalten. Die Kristallstruktur ist nicht so locker wie die Gelstruktur, weil dort die Valenzen regulär orientiert und die Zwischenräume zwischen den Struktureinheiten sehr klein sind.[2]) In den Gelen haben die Restvalenzen zwei Funktionen. Einmal halten sie zwei Partikeln untereinander zusammen. (Da die Ceroxydteilchen im Gel durch relativ große Distanzen voneinander getrennt sind, dürfte die Anziehungskraft zwischen ihnen sehr gering sein. Die Möglichkeit besteht, daß sie untereinander nur durch gemeinsame Einwirkung auf die zwischenbefindliche Wasserschicht zusammengehalten werden.) Zweitens halten sie Wasserschicht und Kolloidteilchen zusammen. Man kann sich das Wasser rund um die Kolloidteilchen angeordnet denken, wie Fig. 8 zeigt und wie dies schon von J. M. van Bemmelen angenommen wurde. Die dem Teilchen zunächst befindliche Wasserhülle wird fester gebunden sein als die zweite und diese ihrerseits wieder fester als die dritte. In dem Maße, als die Entfernung der Wasserhülle vom

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[1]) B. N. Desai, „Die Kinetik der Koagulation."

[2]) Arsem, Journ. of Physical Chem. **30**, 306 (1926).

Kolloidteilchen wächst, vermindert sich die Kraft, die sie festhält. Wenn diese Ansicht über die Wasserbindung durch das Kolloidteilchen richtig ist, muß die Wasserabgabe bei einem höher hydratisierten Gel leichter erfolgen als bei einem weniger hydratisierten. Das ist, wie bei Ceroxydgel beobachtet wurde, in der Tat der Fall. Sol A, das sich — wie Beobachtung 4 lehrt — in einem Zustand höherer Hydratation befindet, gibt schneller Wasser ab als Sol B unter sonst gleichen Bedingungen (Beobachtung 10 und 11). Mit dem Fortschreiten der Dehydratation nimmt weiter in dem Maße, als der Abstand zwischen den Kolloidteilchen und der Radius der äußeren Wasserhülle kleiner wird, auch die Geschwindigkeit der Wasserabgabe ab. Das ist auch der Grund, weshalb Kieselsäuregel von R. Zsigmondy nicht vollständig getrocknet werden konnte (loc. cit.), obwohl er es beträchtlich lange über konzentrierter Schwefelsäure aufbewahrte. Wie Tabelle II angibt, bleibt im Ceroxydgel auch bei langem Trocknen im Vakuum etwas Wasser zurück, das sich nur durch Erhitzen entfernen läßt.

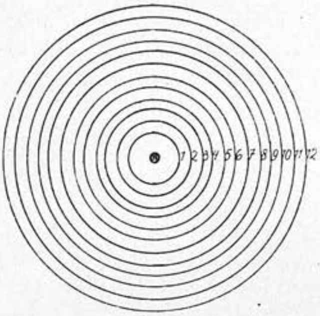

Fig. 8

Im Anschluß an obige Darlegungen läßt sich nun auch verstehen, daß das Volumen des Gels abnimmt und dieses immer steifer wird. Durch Entfernung der Wasserhülle um das Teilchen werden die Rest valenzen, die sie hielten, frei. Wenn man nun weiter annimmt, daß die Valenzkräfte in gerader Linie vom Ausgangspunkt aus wirksam sind, wird sich die freie Restvalenz mit anderen verbinden und demzufolge die vereinigte Energie stärker sein als die der einzelnen Valenzkräfte. Durch diese Kraftzunahme durch Verkleinerung der Wasserhülle und darauf folgende Volumreduktion werden die zurückbleibenden Wasserhüllen um so fester gebunden sein, und dadurch wird das Gel starrer erscheinen. Der bröcklige Zustand des fast trockenen Gels (Beobachtung 13) wäre auf den Umstand zurückzuführen, daß die Kapillaren — teilweise wenigstens — mit Luft gefüllt sind und deshalb die Wände der Kapillaren dem verstärkten Druck beim Zerreiben nachgeben, wodurch sich das Gel in Pulver verwandelt.

Ergebnisse der Dampfdruckmessungen.

Wie aus Tabelle II hervorgeht, bleibt der Dampfdruck des Gels konstant, bis nahezu die Hälfte allen Wassers abgegeben ist, und ist in diesem Punkte praktisch gleich dem Druck des gesättigten Wasser-dampfes bei dieser Temperatur, was die hohe Hydratation des Gels anzeigt. Fig. 2 zeigt, daß die Abnahme des Dampfdruckes bis zum Punkte B sehr klein ist (1 Mol H_2O pro Gramm CeO_2). Mit fortschreitender Entwässerung des Gels sinkt der Dampfdruck sehr rasch, obgleich die Entwässerungsgeschwindigkeit abnimmt. Bei den Versuchsbedingungen konnte das Gel nicht vollständig entwässert werden; die zurückbleibende Wassermenge, 19 Millimole Wasser pro Gramm CeO_2, kann nur durch Erhitzen entfernt werden. Ähnlich liegen die Verhältnisse bei SiO_2-Gel.

Die Dampfdruckisotherme (Fig. 2) ist analog der von van Bemmelen (loc. cit.) für SiO_2 erhaltenen mit einer Ausnahme, nämlich dem Fehlen eines Knickes in der Kurve, wo der Dampfdruck für einige Zeit konstant blieb, obwohl fortgesetzt Wasser abgegeben wurde. Das steht in Zusammenhang mit der Tatsache, daß bei CeO_2-Gel kein Auftreten und Verschwinden einer Trübung wie beim SiO_2-Gel zu beobachten ist. Das Gel wird zwar im Punkte B rötlich-braun und schwach trübe. Diese beiden Eigenschaften, Färbung und Trübung, treten mehr und mehr hervor. Aber in keinem Punkte zeigt das Gel bei weiterer Entwässerung die Tendenz, wie SiO_2-Gel wieder klarer zu werden.

Ergebnisse der Viskositätsmessungen.

Der Unterschied zwischen Ceroxydsol und -gel ist mehr einer des Grades als der Art. Im Sol wie im Gel sind die Teilchen hydratisiert, nur nicht in gleichem Maße. Der Verlauf der Hydratation von dem Zeitpunkt an, wo das Cerammoniumnitrat in den Dialysator gegeben wurde, bis dahin, wo die Dialysierzeit 48 Stunden betrug, ist in Fig. 3 graphisch dargestellt. Der Kurvenverlauf zeigt, daß der Hydratationsgrad der Teilchen in den ersten fünf Stunden ziemlich gering ist, mit fortschreitender Dialyse aber stark ansteigt.

W. Biltz[1]) erhielt bei einer analogen Arbeit über Benzopurpurinsol, dessen Teilchen sich beim Stehen bekanntlich immer mehr hydratisieren, eine ähnlich verlaufende Kurve.

Die Änderungen der Viskosität und dementsprechend des Hydratationsgrades, die man bei zunehmender Konzentration beobachtet, sind in Fig. 4 eingezeichnet. Und zwar zeigt Kurve A, daß die Hydratation bis zu einer Konzentration von 60 Proz. verhältnismäßig wenig zunimmt, daß aber zwischen 60 und 80 Proz. ein auffälliger Sprung auftritt. Über 80 Proz. ist der Anstieg nicht mehr beträchtlich; der Kurvenverlauf ist also S-förmig.

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[1]) W. Biltz, Zeitschr. f. physikal. Chem. **73**, 500 (1910).

Die in der gleichen Figur eingetragene Kurve B für eine 11prozentige nichtdialysierte Cerammoniumnitratlösung beleuchtet eine sehr wichtige Tatsache. Beim Vergleich der beiden Kurven A und B stellt sich heraus, daß ein zehn Stunden und ein nicht dialysiertes Sol hinsichtlich ihrer Viskosität bis zu einer Konzentration von 60 Proz. nur wenig voneinander abweichen. Bei diesem Punkte tritt ein plötzlicher und auffälliger Unterschied auf.

Wenn man gleicherweise die Viskositäten von Solen variierender Konzentration graphisch darstellt, die bis zu bestimmten Temperaturen erhitzt worden sind, so ergibt sich, daß die Teilchen dehydriert werden, und zwar bis zu einem Ausmaße, das von der Temperatur abhängig ist, auf welche die Sole erhitzt worden sind. C und D sind solche Kurventypen (Fig. 5), die für ein 40 Stunden dialysiertes und auf 50° bzw. 100° erwärmtes Sol aufgestellt worden sind. Die Gestalt der Kurve C ist die eines flachen S, woraus sich ergibt, daß das Sol noch schwach hydratisiert ist, jedenfalls aber nicht so ausgeprägt wie das bei Zimmertemperatur (28°) gehaltene und nur zehn Stunden dialysierte Sol (Kurve A, Fig. 4).

Bei der Kurve D ist die S-Form gänzlich verschwunden, was beweist, daß die Hydratation vollständig zurückgegangen ist. Der Kurvenverlauf ist charakteristisch für ein hydrophobes Sol und ähnelt den von Woudstra[1]) an Silberhydrosole erhaltenen, dessen Teilchen bekanntlich überhaupt nicht hydratisiert sind.

Ein Vergleich von Fig. 4 und 5 zeigt, daß die Teilchen durch Erhitzen dehydratisiert werden und daß die Viskositäts-Konzentrationskurve um so tiefer verläuft, je höher das Sol erhitzt worden ist. Zu demselben Schlusse sind W. Biltz und Steiner (loc. cit.) bei einer Arbeit über Nachtblausol gekommen. In Fig. 6 tritt der Temperatureffekt noch deutlicher in Erscheinung. Der scharfe Kurvenabfall bei der Temperatursteigerung von 28° auf 35° zeigt, daß die hochhydratisierten Teilchen ihr Wasser sehr leicht abgeben. Die Neigung der Kurve oberhalb 60° wird immer flacher, woraus hervorgeht, daß die Hydratation stufenweise zurückgeht.

Der Kurvenverlauf zeigt, daß die Kolloidteilchen den Hauptteil ihres gebundenen Wassers bis 60° verlieren, während das restliche Wasser mit steigender Temperatur immer langsamer abgegeben wird. Das wird sofort verständlich, wenn wir in Betracht ziehen, daß — wie oben schon gesagt — die Bindungen zwischen der zurückbleibenden Wasserhülle und den Kolloidteilchen bei allmählicher Dehydratation

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[1]) Woudstra, Zeitschr. f. physikal. Chem. **63**, 619 (1908).

immer fester werden, weil die Restvalenzen dann eine geringere Menge Wasser festzuhalten haben als bei hoch hydratisierten Solen.

Die letzte Fig. 7 zeigt, wie die Viskosität des Sols stark ansteigt, wenn es nach 48 Stunden aus dem Dialysator herausgenommen wird. Wie wir schon gesehen hatten, braucht das Sol, wenn es im Dialysator belassen wird, 72 Stunden, bis Gelbildung eintritt, während derselbe Effekt in etwa einer Stunde eintritt, wenn das Sol nach 48 Stunden dem Dialysator entnommen wird. Das dürfte auf einer Alterungswirkung beruhen, wie es ja bekannt ist, daß Sole, wenn man sie einige Zeit stehen läßt, empfindlicher werden infolge Abnahme der Ladung.[1] Mit der Abnahme der Ladung wächst die Hydratation der Teilchen und demzufolge die Viskosität der Sole[2]), bis sich schließlich eine Gallerte bildet. Die Gelbildung im Dialysator läßt sich analog erklären. Mit fortschreitender Dialyse diffundiert immer mehr von dem Peptisationsmittel hinaus, wodurch die Ladung der Teilchen abnimmt. Auch hier wächst mit der Abnahme der Ladung Hydratation und Viskosität des Sols, bis schließlich der Punkt erreicht wird, wo Gelbildung eintritt.

Zusammenfassung.

1. Es wurde gefunden, daß bei CeO_2-Sol der Zeitpunkt, bei dem Gelbildung eintritt, sowie der Hydratationsgrad des Gels von der Temperatur abhängig sind, bei der die Dialyse ausgeführt wird.

2. Ultramikroskopische Untersuchung des Gels ergibt, daß es nur Amikronen enthält. Der Brechungsindex des Gels ist gleich dem des Wassers, was aus der hohen Hydratation des Gels erklärt wird.

3. Die Benutzung des Gels als Ultrafilter wie das Zerspringen des trocknen Gels lassen die Richtigkeit von R. Zsigmondys Ansichten über die Gelstruktur vermuten. Das Verhalten des Gels bei der Behandlung mit einer Kältemischung lassen die Annahme berechtigt erscheinen, daß das Gel mehrphasig ist.

4. Die Art und Weise, in der durch die CeO_2-Teilchen Wasser gebunden wird, wird beschrieben auf Grund der Theorie der Restvalenzen. Unter diesem Gesichtspunkt läßt sich auch die Volumabnahme und die Verfestigung des Gels bei der Entwässerung erklären.

5. Die Dampfdruckisotherme des Gels wurde bestimmt und dabei gefunden, daß der allgemeine Charakter der Kurve derselbe ist wie beim SiO_2-Gel.

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[1]) Gann, Kolloidchem. Beih. **8**, 84 (1916).

[2]) N. R. Dhar u. Chakravarti, Journ. of Physical Chem. **30**, 1646 (1926).

6. Die Viskositätsmessungen am Sol ergeben, daß es sich wie ein hochhydratisiertes Kolloid verhält. Durch Erhitzen wird die Hydratation zerstört; die Viskosität-Konzentration-Kurve eines erhitzten Sols ist typisch für ein hydrophobes Sol.

7. Alterung des Sols und damit in Zusammenhang stehende Gelbildung wird mit der Annahme erklärt, daß das Sol empfindlicher wird infolge Abnahme der Ladung und dementsprechender Zunahme der Hydratation und Viskosität.

Dem Verfasser sei gestattet, an dieser Stelle Herrn Prof. Sir James Walker und Herrn T. R. Bolam für wertvolle Unterstützung zu danken.

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University of Edinburgh.

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THE KINETICS OF COAGULATION

THE KINETICS OF COAGULATION.

By A. M. Patel and B. N. Desai.

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It has been shown by one of us [1] that the rate of coagulation of a colloid in the sensitive range of electrolyte concentration is not a simple reaction as postulated by v. Smoluchowski,[2] but that the nature of the coagulation process is " auto-catalytic."

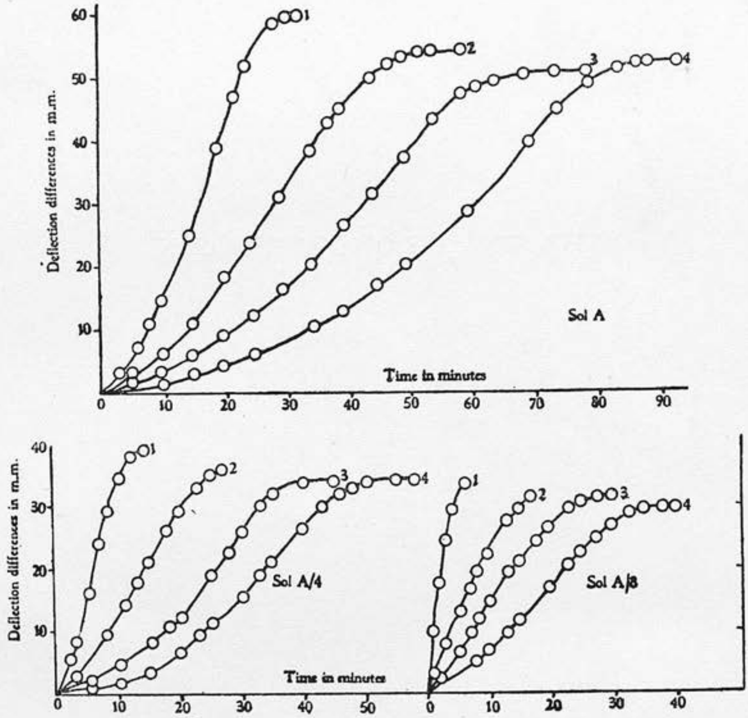

Fig. 1.—Sol dialysed for two days. Concentration of Sol A 4·88 gms./litre.
Curve 1 $N/2$ NaCl. Curve 2 $N/3$ NaCl.
Curve 3 $N/4$ NaCl. Curve 4 $N/5$ NaCl.

Desai [1] has discussed in detail the reasons why many investigators could not detect the " auto-catalytic " nature of the coagulation process, and the associated " S " shaped curves for the coagulation velocity. He showed that apart from the suitability of the method employed, the factors which should be kept under control in order to demonstrate the

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[1] Desai, *Trans. Faraday Soc.*, **24**, 181, 1928; *Kolloidchem. Beih.*, **26**, 357, 1928.
[2] *Physikal. Z.*, **17**, 557, 583, 1916; *Z. physik. Chem.*, **92**, 129, 1917.

auto-catalytic nature of coagulation are: (i) the concentration of the colloid; and (ii) its purity or charge. No experiments were, however, made to confirm these statements, and it was, therefore, decided to test their validity by suitable experiments.

The coagulation velocity was measured by the photo-electric cell method, which is described in detail in a previous paper.[1] Thorium hydroxide sol was prepared by Müller's method.[3] Sols of varying concentrations were prepared by diluting a concentrated sol to the requisite extent with conductivity water. Dialysis was employed to obtain sols containing different amounts of the peptising agent.

Experiments were carried out with different samples of the same sol dialysed for different times and also with sols of different concentrations, when coagulated by solutions of sodium chloride of varying concentrations. Each set of experiments with the same sample of sol was carried out the same day. The results are plotted in Figs. 1 to 4.

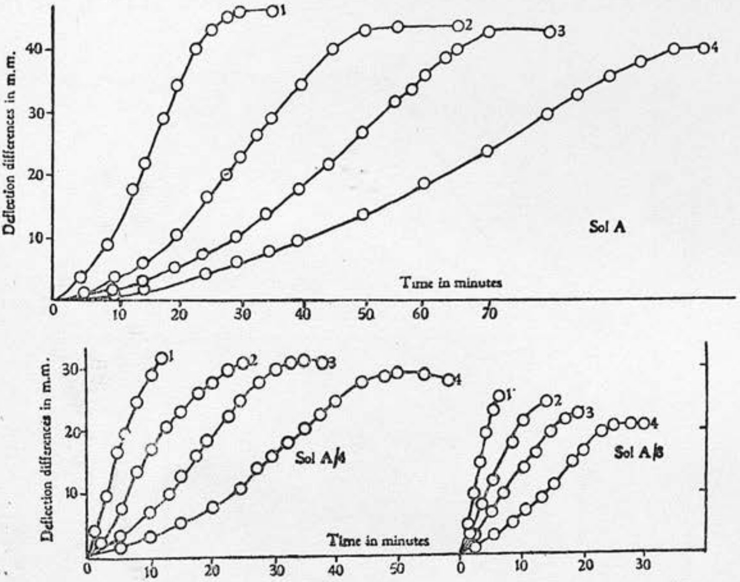

FIG. 2.—Sol dialysed for five days. Concentration of Sol A 4·88 gms./litre.
Curve 1 $N/20$ NaCl. Curve 2 $N/40$ NaCl.
Curve 3 $N/60$ NaCl. Curve 4 $N/80$ NaCl.

From Figs. 1, 2 and 3 for sols dialysed for two days, five days, and eight days respectively, it is seen that with an increase in the dilution of the colloid, the curves for the same electrolyte concentration show a definite tendency to become less and less "S" shaped. The tendency of the curves to lose the "S" shaped character becomes more and more pronounced as one passes from a sol dialysed for two days to a sol dialysed for five or eight days.

Although we get "S" shaped curves for a concentrated sol dialysed for eight days, the same is not found to be the case with the sol dialysed for fourteen days, as seen from Fig. 4. The most interesting

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[3] *Allgemeine Chem. Koll.*, 1907.

fact about these latter curves is that at no concentration of the electrolyte, even for a concentrated sol, are the curves "S" shaped.

On looking at Figs. 1 to 4 as a whole, the fact of the gradual disappearance of the "S" shaped curves with an increase in the dilution and the purity of the sol (i.e. on decrease of the charge on the colloid due to the removal of the stabilising ion) is seen to be definitely established.

It will not be out of place to mention here two criticisms which have been raised against the method, and which, according to the critics, might be responsible for the appearance of the "S" shaped curves. One of the criticisms is that as white light was used in the experiments, the fine colloid particles in the initial stages of coagulation would scatter more light in the blue portion of the visible spectrum than in the red, and this might give rise to the "S" shape of the coagulation velocity curves. In the first place, although the incident light was white, and hence composite, the complications due to inhomogeneity of the light are not in any way serious, because owing to the selective action of the photo-electric cell used (K in helium), the range of wave-lengths which are in the main operative is restricted, and lies between 3500 and 5000 Å.U. The "S" shaped nature of the curve would not be appreciably altered even if light of longer wave-lengths were used. For example, if yellow light were used, there would be less scattering and greater transmission in the initial stages of coagulation when the particles are small compared with the wave-length, and this, if anything, would accentuate the flatness of the initial portion of the curve. The second objection raised is that although in the earlier stages of coagulation, when the particles are small compared with the wave-length of the light

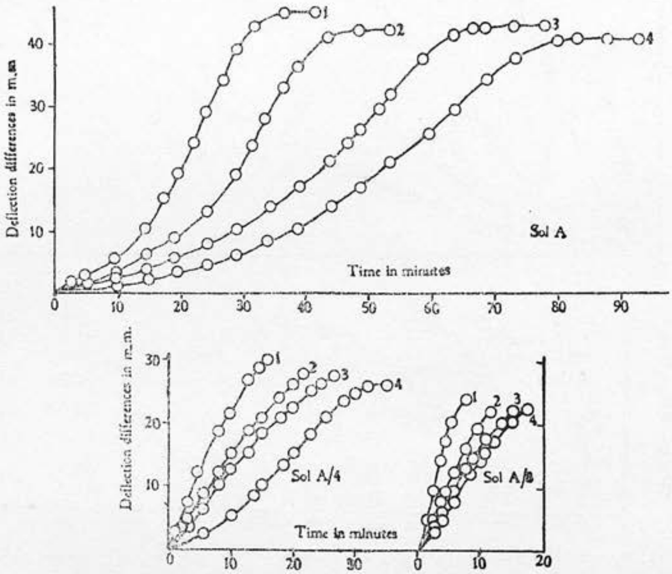

FIG. 3.—Sol dialysed for eight days. Concentration of Sol A 4·88 gms./litre.
Curve 1 $N/40$ NaCl. Curve 2 $N/60$ NaCl.
Curve 3 $N/80$ NaCl. Curve 4 $N/100$ NaCl.

used, the amount of the scattered light may be proportional to the size of the particles; this would no longer be the case when the particles have reached sizes comparable with the wave-length, and this might change the nature of the curve in the later stages of coagulation. However, if this effect did not come into play, the scattering would be greater than what it actually was, and hence the transmitted light or the photo-electric current would be smaller. This would make the deflection difference greater, and thus increase the steepness of the curve in the later stages of coagulation. The "S" shaped nature of the curve thus does not become less marked, due to this effect.

There is yet another point which is worth considering in this connection. As the photo-electric cell was placed within a short distance of the colloid cell, the light affecting the former would not only be the transmitted light, but also the portion of the light scattered in the forward direction by the particles and collected by the cell. This effect is more pronounced when the particles are large in comparison with the wave-length. If the scattered light could be prevented from entering the photo-electric cell, or reduced considerably by placing it at a great distance from the colloid cell, the amount of light received by the photo-electric cell would be relatively smaller in the later stages of coagulation or the deflection differences would be larger. In other words, the latter portion of the coagulation velocity curve would be made steeper than what it was in the present case.

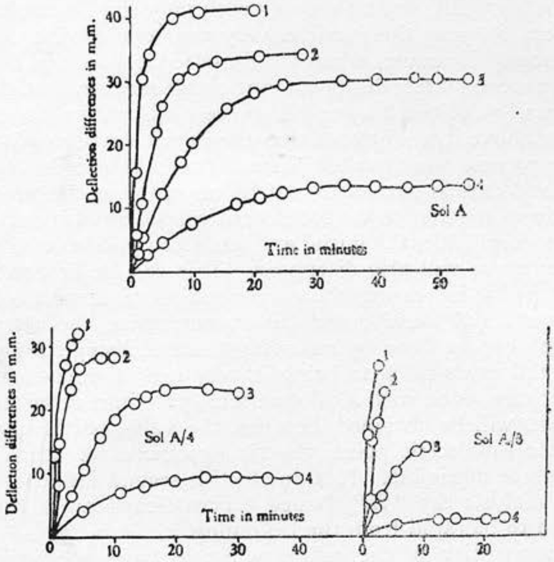

FIG. 4.—Sol dialysed for fourteen days. Concentration of Sol A 4·88 gms./litre.
Curve 1 $N/80$ NaCl. Curve 2 $N/100$ NaCl.
Curve 3 $N/150$ NaCl. Curve 4 $N/200$ NaCl.

It is well known that coagulation begins before the iso-electric point is reached (Freundlich's second critical potential). When an electrolyte is added to a sol, the charge on the colloid decreases, and at the same time the repulsive forces between the particles also decrease. Till the value of the charge is brought down to that corresponding to the first critical potential (Freundlich's first critical potential), no collisions will be successful in bringing about coalescence, because the repulsive forces between the particles will be sufficiently strong to oppose the tendency to coalescence. Matters will, however, become different when the value of the charge corresponding to the first critical potential is reached, for then, owing to a decrease in the repulsive forces between the particles, there will be a greater tendency for the collisions to be successful in bringing about the coalescence. The tendency for all the collisions to be successful in bringing about coalescence will increase with a further decrease in the charge on the particles, until the charge corresponding to the second critical potential is reached, when all the collisions become successful. Between the values of the first critical charge and the iso-electric point, the collisions are not all successful, because some particles may be moving with only small velocities, which are insufficient to bring the particles very near one another against the repulsive forces. However, when the iso-electric point is reached the repulsive forces completely disappear, and therefore even particles moving with very small velocities may collide successfully with coalescence.

From the above it will be seen that the initial slow coagulation refers only to the process which takes place between the region of the first and the second critical potentials. If by any process the time required for passing from the first to the second critical potential is made appreciably small or negligible, the initial and less steep portion of the coagulation velocity curve will also disappear. This can be brought about in two ways: (i) by increasing the concentration of the coagulator to a sufficient extent, (*cf.* Desai); and (ii) by decreasing the charge on the colloid (which can be done by removing the stabilising ion by dialysis) to a very small value so as to bring it very near the iso-electric point. In the latter case, even with a dilute electrolyte concentration, no "S" shaped curves will be obtained, because, the value of the charge being very near the iso-electric point, the time required for coagulation will be very small or negligible. It is due to this second influence that with progress of dialysis the "S" shaped curves disappear or the coagulation is found to be rapid from the beginning.

The concentration of the colloid will affect the appearance of the "S" shaped curves in the following manner:—

It is seen from Figs. 1, 2 and 3 that when a sol is coagulated by an electrolyte of the same concentration throughout the tendency of coagulation velocity curves to be "S" shaped becomes less and less with an increase in the dilution of the sol. These changes in the nature of the curves are similar to those produced when to the sol of the same concentration an electrolyte of increasing concentration is added, as shown by the curves in Figs. 1 to 3. The effect in the case of a dilute sol will thus be to bring down the charge on the particles more nearly to that corresponding to the first or the second critical potentials than will happen in the case of a concentrated sol. This will mean that the time required to reach the iso-electric point after adding the electrolyte to the sol will be less with a dilute sol than with a concentrated one. With the progress of dialysis, as the charge on the colloid particles is brought nearer and nearer to that corresponding to the second critical potential the time required to reach the iso-electric point will be so small with the dilute sol, when compared with the concentrated one, that it may pass unnoticed. Thus the effect will be more pronounced in the case of a sol dialysed for a longer period (and consequently having a smaller charge on the particles) than in the case of one dialysed for a shorter period and having a greater charge on the particles.

In fine, one can say that the appearance of the " S " shaped curves or demonstration of the " auto-catalytic " nature of the coagulation reaction depends on (i) the concentration of coagulator ; (ii) the charge ; and (iii) the concentration of the colloid. The " S " shape of the coagulation velocity curves depends on the control of the first two factors, while the third factor only helps to make the " S " shape more conspicuous.

Summary.

1. The effects of (*a*) the purity, and (*b*) the concentration of colloidal thorium hydroxide on its coagulation velocity in the presence of an electrolyte has been studied.

2. It is observed that (*a*) with the progress of dialysis, and (*b*) with an increase in the dilution of the colloid, the " S " shape of the coagulation velocity curve gradually disappears.

3. It is shown that a proper control of the purity and the concentration of the colloid is necessary to demonstrate the " auto-catalytic " nature of the coagulation process.

We should like to express our thanks to Professors A. R. Normand and D. B. Naik for their interest in this work. We also wish to thank Dr. K. R. Ramanathan of the Indian Meteorological Department for some valuable suggestions.

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Effect of Non-Electrolytes on the Precipitation of Thorium Hydroxide from its Salt Solution in Presence of Alkali.

BY

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Effect of Non-Electrolytes on the Precipitation of Thorium Hydroxide from its Salt Solution in Presence of Alkali.

By A. M. Patel and B. N. Desai.

Dhar (*Kolloid Z.*, 1923, **33**, 193), Mehrotra (*J. Indian Chem. Soc.*, 1927, **4**, 117) and Sen (*ibid.*, 1927, **4**, 131) have studied the peptisation of various metallic hydroxides in presence of sugars in a semi-quantitative way. Kuhn and Pirsch (*Kolloid Z.*, 1925, **36**, 310) have made a detailed study of the peptisation of bismuth hydroxide in presence of several sugars. The inhibition of the precipitation of thorium hydroxide in presence of non-electrolytes when caustic soda solution is added to a salt solution of thorium has not yet been studied. It was, therefore, decided to try the effect of non-electrolytes on the precipitation of thorium hydroxide.

An approximately $N/20$ solution of thorium nitrate was prepared and the amount of thorium per 100 c.c. of the solution was then estimated by precipitating as hydroxide and weighing as thorium oxide. A stock solution of caustic soda was also prepared and standardised against oxalic acid. Glycerol and other non-electrolytes, except urea and cane sugar, used in these experiments were purified by redistillation.

The minimum amount of the non-electrolyte necessary to prevent the appearance of the hydroxide of the metal was determined as follows :—

A known volume of the salt solution was taken in a number of test tubes and mixed with varying amounts of the non-electrolyte. In a number of other sets of test tubes a definite amount of alkali was diluted with the calculated amount of water in order to make the total volume (salt solution + non-electrolyte + alkali + water) 25 c.c. The contents of the two sets of test tubes were mixed throughout in a uniform manner. The amounts of the non-electrolyte necessary to prevent the instantaneous appearance of the precipitate of thorium hydroxide were very carefully determined. Experiments were repeated twice and the mean value was taken in all the cases. The amount of alkali added was greater than what would have been required for the complete precipitation of the hydroxide. The non-electrolytes tried were cane sugar, glycerol acetone, methyl, ethyl and *iso*propyl alcohols and urea. It was found that only cane sugar and glycerol prevented the appearance of the hydroxide.

Effect of the Concentration of the Salt Solution.

Table I contains the results which show the effect of the addition of different amounts of the salt on the inhibition of the precipitation of its hydroxide in presence of cane sugar and glycerol.

TABLE I.

Total volume=25 c.c. NaOH=0·6 millimole.

Thorium nitrate (in millimoles).	Cane sugar sufficient to prevent precipitation. (in millimoles).	Glycerol sufficient to prevent precipitation. (in millimoles).
0·00768	1·24	13·7
0·01536	1·64	28·77
0·02304	3·25	71·36
0·03072	5·84	120·83
0·03840	9·62	173·62
0·04608	13·75	—

It is seen from the table that cane sugar is a better inhibiting agent than glycerol. The inhibition of the precipitation of the metallic hydroxide is due to the adsorption of the non-electrolyte and the greater the adsorption of a non-electrolyte, the greater should be its inhibitive power. The fact that the alcohols do not inhibit the precipitation of the hydroxide even when added in large amounts leads one to postulate that the number of hydroxyl groups in the non-electrolyte has something to do with the inhibition of the precipitation of the hydroxide. This view is supported by the results because cane sugar acts is a better inhibiting agent than glycerol due to its having eight OH-groups. The effect of alcohols was negligible because they contain only one OH-group. Urea and acetone have no OH-groups and, therefore, they could not act as inhibiting agents.

According to Graham, the solutions which are formed by the addition of caustic soda to a salt solution of copper or iron in presence of sugar, contain the sucrates of copper and iron. If a definite chemical compound is formed the ratio C_m/C_n should be constant (C_m and C_n are the concentrations in millimoles of the metallic hydroxide and the non-electrolyte respectively). Table II gives the values of the above ratio.

TABLE II.

Amount of salt (in millimole).	Sugar. C_m/C_n.	Glycerol. C_m/C_n.
0·00768	0·00620	0·00056
0·01536	0·00936	0·00530
0·02304	0·00709	0·00032
0·03072	0·00526	0·00025
0·03840	0·00400	0·00022
0·04608	0·00335	—

The value of the ratio C_m/C_n does not remain constant. It first increases and then decreases throughout with an increase in the concentration of the salt solution. The fact that the value of the ratio C_m/C_n is not constant is distinctly in favour of the non-existence of any definite compound of thorium and the non-electrolytes.

Effect of Volume.

Tables III and IV give an idea about the effect of volume change on the amounts of sugar required to prevent precipitation of thorium hydroxide when caustic soda solution is added to a solution of thorium nitrate of different concentrations.

TABLE III.

NaOH=0·6 millimole.

Amount of salt (in millimoles).	Vols. of cane-sugar soln. necessary to prevent precipitation.	
	15 c.c.	25 c.c.
0·00768	1·25	1·24
0·01536	3·15	1·64
0·02304	4·33	3·25
0·03072	7·45	5·84
0·03840	10·73	9·62

TABLE IV.

NaOH = 0·6 millimole.

Amount of salt (in millimoles).	Cane sugar necessary to prevent precipitation (in millimoles).					
	12	15	20	25	30	35 c.c.
0·01536	2·20	2·15	1·84	1·64	1·48	1·10

From Table III it is seen that the amount of sugar required to inhibit the precipitation of hydroxide from the salt solution of a definite concentration in presence of a fixed amount of caustic soda varies with a change in the total volume of the system. Table IV shows that although the amounts of the metal ion and the alkali remain the same, the amount of sugar decreases with an increase in dilution of the system. This volume-effect can be explained in the following manner:—

At a smaller dilution the distances between the individual particles will be smaller than what they will be at a greater dilution and therefore the chances of collisions between the particles will be greater in the former than in the latter. Hence a greater amount of sugar will be required to inhibit the precipitation of the hydroxide at smaller dilutions. Moreover, water itself will act as a peptising agent at greater dilutions and, therefore, the particles will be disintegrated into finer ones thus making the whole system clearer than what it will be at smaller dilutions. This effect will also partly explain why smaller amounts of sugar are required to inhibit the precipitation of a particular amount of the hydroxide at higher dilutions.

The above results can also be explained on the basis of the fact that adsorption is greater from a dilute solution than from a concentrated one. The adsorption of the non-electrolyte being greater from a dilute solution than from the concentrated one less of the non-electrolyte will be required to inhibit the precipitation of the hydroxide in the former case than in the latter.

Amount of Alkali.

It was observed in the preliminary experiments that the amount of sugar or glycerol necessary to prevent the appearance of the hydroxide depended upon the amount of the alkali present in the system although the amount of the metal ion was kept constant. Some experiments were, therefore, tried to investigate this effect. The results of these experiments are given in Table V.

TABLE V.

Total volume = 25 c.c.

Amount of salt (in millimoles).	Cane sugar required to prevent the precipitation of hydroxide (in millimoles). Amount of NaOH in millimoles.					
	0·1	0·2	0·3	0·4	0·5	0·6
0·00768	15·1	1·52	1·24	1·24	1·24	1·24
0·01536	—	5·52	4·25	3·15	2·65	1·65
0·02304	—	15·10	9·82	7·21	5·70	4·20
0·03702	—	19·00	15·31	10·82	8·30	5·85

	Glycerol required to prevent the precipitation of hydroxide (in millimoles). Amount of NaOH in millimoles.					
	0·1	0·2	0·3	0·4	0·5	0·6
0·00768	3·10	2·12	1·41	1·0	1·0	1·0
0·01536	—	5·51	3·82	2·52	1·91	1·71
0·02304	—	20·10	15·12	11·60	8·88	6·31

It will be seen from Table V that when the amount of the metal ion is small the decrease in the amount of alkali is not continuous but soon reaches a minimum value which does not decrease further with any more increase in the amount of the alkali (as far as the maximum amount of the alkali tried in this experiment is concerned). This, however, is not found to be the case with higher concentrations of the metal ion. Although the precipitation of thorium hydroxide from a solution containing 0·03072 millimole of thorium nitrate could be prevented by the addition of 15·1 millimoles of cane sugar in the presence of 0·3 millimole of caustic soda, 19 millimoles of cane sugar were found to be insufficient for the purpose in the presence of 0·2 millimole of alkali. These results are in line with those obtained by Mehrotra (*loc. cit.*) and may be explained on the basis of the view that the non-electrolyte inhibits the precipitation of metallic hydroxide from its salt solution only in the presence of an excess of the alkali. It will thus be seen that neither cane sugar nor glycerol can inhibit the precipitation of the metallic hydroxide by itself in the absence of an excess of the alkali. The fact that alcohols could not inhibit the precipitation of the hydroxide from its salt solution and that even sugar and glycerol could do so only in the presence of an excess of the alkali supports the conclusion arrived at in another paper ("Relation between purity of thorium hydroxide and its sensitisation by electrolytes," in course of publication) in that as these non-electrolytes coagulate the thorium hydroxide sol they should not be able to peptise it.

The fact that in the presence of increasing amounts of the alkali less and less amounts of the non-electrolyte are required to prevent the precipitation of a colloid can be explained on the ground that a greater amount of the alkali will exert a greater stabilising influence on the colloid and hence the amount of a non-electrolyte required to inhibit the precipitation of the metallic hydroxide will be less.

Summary.

1. The inhibition of the precipitation of thorium hydroxide from the solution of thorium nitrate in the presence of sugar, glycerol, urea, acetone, and methyl ethyl, and *iso*propyl alcohols when sodium hydroxide is added to it has been studied.

2. It is observed that of the above non-electrolytes only cane sugar and glycerol can inhibit the precipitation of the hydroxide and that the former is more effective in its action than the latter.

3. The amount of sugar or glycerol necessary to prevent the precipitation of the hydroxide, other conditions being same, is found to (*a*) increase with an increase in the amount of metal ion, (*b*) decrease with an increase in the dilution of the system—colloid + alkali + non-electrolyte + water, and (*c*) decrease with an increase in the amount of sodium hydroxide.

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Ueber die Wirkung von Nichtelektrolyten auf kolloides Thoriumhydroxyd bei fortschreitender Dialyse des letzteren in Gegenwart und Abwesenheit von Elektrolyten

Von

A. M. Patel und B. N. Desai (Bombay)

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VERLAG VON THEODOR STEINKOPFF, DRESDEN UND LEIPZIG

Ueber die Wirkung von Nichtelektrolyten auf kolloides Thoriumhydroxyd bei fortschreitender Dialyse des letzteren in Gegenwart und Abwesenheit von Elektrolyten.

Von A. M. Patel und B. N. Desai[1]. (Eingegangen am 17. November 1929.)

(Aus dem Chemistry Dpt. Wilson College Bombay, India.)

Von verschiedenen Autoren[2]) wurde gezeigt, daß Alkohol die Neigung hat, negativ geladene Sole zu flocken, und daß der sensibilisierende Einfluß von Nichtelektrolyten um so mehr hervortritt, wenn das Sol durch Elektrolytzusatz relativ instabil gemacht wurde[3]). Mukherjee und seine Mitarbeiter[4]) haben beobachtet, daß die Wanderungsgeschwindigkeit von kolloidem Arsensulfid mit der Zunahme des Alkoholgehaltes abnahm. H. Freundlich[5]) konnte indessen keine sensibilisierende Wirkung des Alkohols auf Arsensulfid feststellen, selbst wenn er die Mischung eine Reihe von Tagen stehen ließ. Van Bemmelen[6]) zeigte, daß Alkohol positiv geladene Sole peptisiert. Anderseits wird von H. Kruyt und van der Made[7]) berichtet, daß Alkohol auch ein positiv geladenes Sol sensibilisiert. Aus oben Gesagtem geht hervor, daß Nichtelektrolyte bei ihrer Einwirkung auf Kolloide eine sehr verwickelte Rolle spielen, und daß es angebracht wäre, unter einem neuen Gesichtspunkt Versuche auszuführen, um die Sachlage zufriedenstellend klarzustellen.

Der eine von uns [Desai[8])] hat gezeigt, daß der Unterschied im Verhalten der Elektrolyte gegenüber Kolloiden mit zunehmender Reinheit der letzteren verschwindet. Deshalb entschieden wir uns, Versuche mit Nichtelektrolyten in gleicher Weise auszuführen und nachzusehen, ob die Reinheit des Kolloids auch für die offenbar komplizierten Erscheinungen bei der Einwirkung von Nichtelektrolyten verantwortlich zu machen war.

Vorläufige Versuche mit positiv geladenem, kolloiden Al_2O_3, Fe_2O_3 und ThO_2 zeigten, daß ungereinigte Sole dieser Stoffe selbst durch beträchtliche Zusätze von Nichtelektrolyten (aliph. Alkohole) nicht sensibilisiert werden konnten. Mit fortschreitender Dialyse stellte sich indessen heraus, daß sie nach und nach gegen Nichtelektrolyten immer sensibler wurden, und daß annähernd reine Sole schon durch ganz geringe Zusätze koaguliert werden konnten.

Im Nachstehenden wird die Wirkung von Nichtelektrolyten auf kolloides Thoriumhydroxyd bei fortschreitender Dialyse des Sols untersucht. Und zwar wurde sie studiert in Gegenwart und Abwesenheit von Elektrolyten ($NaCl$).

Das Thoriumhydroxydsol wurde hergestellt nach der Methode von Müller[9]), da hier ThO_2 von Anfang an in kolloider Form vorliegt und

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[1]) Uebersetzt von W. Rödiger (Leopoldshall).

[2]) Siehe ältere Literatur bei Wo. Ostwald, Grundriß, 1. Aufl. (1909), 26, 460, 471 ff.; Arbeiten von O. Lehmann, J. Billitzer, G. Quincke, K. Spiro u. a., ferner W. D. Bancroft, Rec. trav. chim. **4**, 733 (1923).

[3]) Burton, Phil. Mag. **12**, 472 (1906); **17**, 583 (1909).

[4]) Mukherjee und Mitarb., Journ. Ind. Chem. Soc. **4**, 493 (1927); **5**, 697 (1928).

[5]) H. Freundlich, Zeitschr. f. physik. Chem. **44**, 136 (1903).

[6]) Ehrenberg, Die Bodenkolloide (1915), 57.

[7]) H. Kruyt und van der Made, Rec. trav. chim. **4**, 294 (1923).

[8]) B. N. Desai, Kolloidchem. Beih. **26**, 384 (1928).

[9]) Müller, Allgemeine Chemie der Kolloide (1907).

daher während der Dialyse nicht herausdiffundieren kann. Nach der Herstellung wurde das Sol in einem Pergamentsack gefüllt, der am Rande eines 2-Liter-Becherglases befestigt war. Das Wasser wurde dreimal täglich in bestimmten Abständen gewechselt.

Die für diese Untersuchung verwandten Elektrolyte und Nichtelektrolyte wurden von B. D. H. (A. R.) bezogen. Sie wurden weiter durch Destillation und Kristallisation gereinigt. Die Alkohole wurden über K_2CO_3 getrocknet und destilliert, die mittlere konstant siedende Fraktion wurde dann für die Koagulationsversuche verwandt. Die Nichtelektrolyte waren mit Wasser in jedem Verhältnis unsichtbar.

Die Koagulationsgeschwindigkeiten wurden mittels photoelektrischer Zelle gemessen. Die entsprechende Methode wurde im einzelnen in einer früheren Arbeit beschrieben[10]. Die Abstände zwischen den verschiedenen Apparatteilen wurden so justiert, daß mit Wasser allein auf der Galvanometerskala ein Ausschlag von 176 mm erfolgte. Mit 5 ccm Kolloid und 15 ccm Wasser betrug der Ausschlag 165 mm. Dies wurde als Nullwert des Galvanometers genommen. Durch vorläufige Versuche war festgestellt, daß die Lösungen der bei diesen Versuchen zu verwendenden Nichtelektrolyte und Elektrolyte den Galvanometerausschlag nicht beeinflußten, d. h. der Galvanometerausschlag blieb der gleiche, wenn das Wasser in der Kolloidzelle durch sie ersetzt wurde. Durch einen Blindversuch wurde festgestellt, daß das Licht bei der Koagulation des Thoriumhydroxydsols keine Wirkung zeigte.

In ein Reagenzglas wurden 5 ccm des Kolloids gegeben und in ein anderes 1 ccm NaCl (von einer Konzentration, die ausreichte, um das Sol ohne Nichtelektrolytzusatz in 30—40 Min. zu flocken), 5—10 ccm eines Nichtelektrolyten zugesetzt und die Mischung auf 20 ccm mit Leitfähigkeitswasser aufgefüllt. Die Mischung wurde zu dem Kolloid in der Form zugegeben, daß man jene an der Glaswand herablaufen ließ. Das Ganze wurde dann, bei allen Versuchen, gleichmäßig gemischt. Das Gesamtgemisch (Kolloid + Elektrolyt + Nichtelektrolyt + Wasser) wurde in die Kolloidzelle gefüllt und die Photozelle dem Lichte in Abständen von einigen Minuten ausgesetzt durch Einschieben eines Asbestschirmes zwischen Lichtquelle und photoelektrischer Zelle.

Nach verschieden langer Dialysierdauer wurden dem Sol Proben entnommen und damit die beschriebenen Versuche ausgeführt. Es wurde darauf geachtet, daß jede Versuchsreihe mit der gleichen Solprobe am gleichen Tage ausgeführt wurde, um Irrtümer infolge Alterungserscheinungen zu vermeiden. Jeder Versuch wurde doppelt gemacht und dabei festgestellt, daß die Ergebnisse der Parallelversuche stets übereinstimmten.

Die bei Anwesenheit von Elektrolyten (NaCl) oder Nichtelektrolyten (Methyl-, Aethyl-, Isopropylalkohol, Harnstoff, Rohrzucker und Azeton) oder beider zusammen erhaltenen Resultate für die Flockungsgeschwindigkeit des verschieden lange dialysierten Soles zeigen Fig. 1—8. (Koagulationsgeschwindigkeitskurven für 3, 6, 8 und 11 Tage dialysierte Sole bei Koagulation durch 7 ccm Nichtelektrolyt und NaCl, und 8 und 11 Tage dialysierte Sole bei Koagulation mit 10 ccm Nichtelektrolyt allein, sind nicht gegeben).

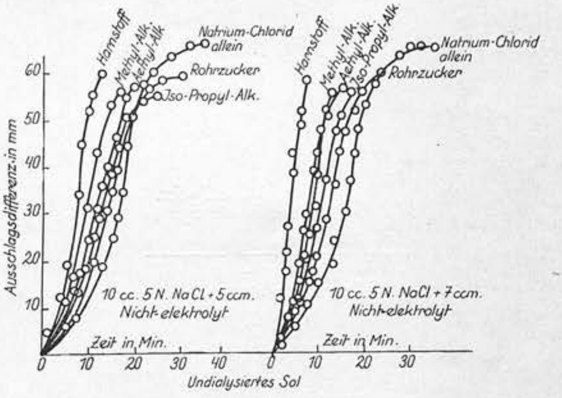

Fig. 1

Man erkennt aus Fig. 1, daß bei einem undialysierten Sol die Kurven für Natriumchlorid + Nichtelektrolyt mehr gegen die Ordinate zu gekrümmt sind, als die für Natriumchlorid allein, was besagt, daß der Zusatz von Nichtelektrolyten zum Natriumchlorid bis zu gewissem Grade in allen Fällen die Koagulationsgeschwindigkeit erhöht. Die Koagulationsgeschwindigkeit steigt ferner mit zunehmender Menge Nichtelektrolyt. Azeton scheint die Koagulationsgeschwindigkeit nicht zu erhöhen, weder in kleinen noch in großen Mengen.

Zugabe von Azeton oder 5 ccm Zuckerlösung zum NaCl erhöht die Koagulationsgeschwindigkeit bei einem 3 Tage dialysierten Sol, wie Fig. 2 zeigt.

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[10] B. N. Desai, Kolloidchem. Beih. 26, 357 (1928).

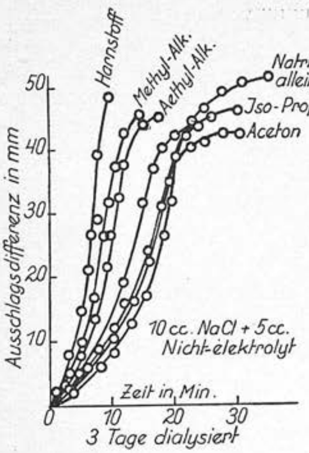

Fig. 2

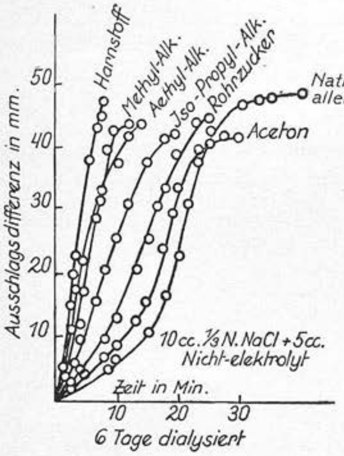

Fig. 3

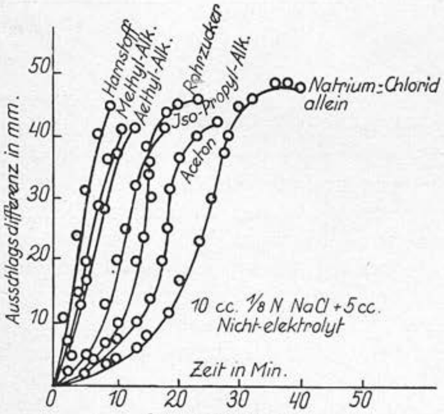

Fig. 4

Fig. 3, 4 und 5 für 6, 8 und 11 Tage dialysierte Sole lassen erkennen, daß mit fortschreitender Dialyse die Nichtelektrolyten hinsichtlich der Erhöhung der Koagulationsgeschwindigkeit immer wirksamer werden.

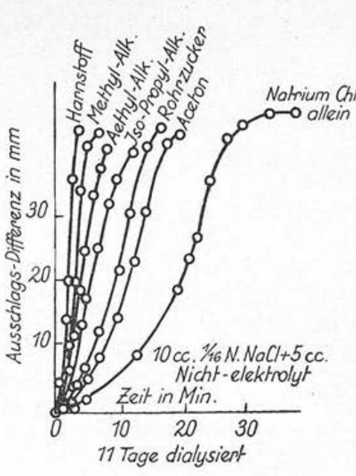

Fig. 5

Die Wirkung von Nichtelektrolyten in Abwesenheit von Elektrolyten zeigen Fig. 6, 7 und 8 für 6, 8 resp. 11 Tage dialysierte Sole. Messungen mit Nichtelektrolyten allein an einem undialysierten und einem 3 Tage dialysierten Sol wurden nicht vorgenommen, weil durch qualitative Versuche festgestellt war, daß von den Nichtelektrolyten, die bei unseren Versuchen angewendet wurden, einzig und allein Harnstoff diese Sole koagulieren könnte. Aus diesen Versuchen tritt sehr klar hervor, daß das Koagulationsvermögen der Nichtelektrolyte mit steigender Reinheit des Sols zunimmt. Bei sechstägiger Dialyse kann durch 5 ccm Azeton und 5 ccm Zucker das Sol nicht koaguliert werden, selbst nicht bei 3 Stunden Stehen, wohingegen es bei 8 und 11 Tage dialysierten Solen der Fall ist.

Man erkennt, daß in allen Fällen die Reihenfolge der Wirksamkeit der verschiedenen Nichtelektrolyten in den in vorliegender Untersuchung verwandten Einzelmengen hinsichtlich der Koagulation von verschieden lange dialysierten Solen stets die gleiche ist, nämlich Harnstoff > Methylalkohol > Aethylalkohol > Isopropylalkohol > Rohrzucker > Azeton.

Tabelle I enthält die Werte für das Produkt aus der Konzentration der Nichtelektrolyten (Kolloid + Nichtelektrolyt + Wasser = 25 ccm) in Molen und dem Flockungsgrad nach 5, 10 und 15 Minuten vom Augenblick der Durchmischung, ausgedrückt durch die Aenderungen des Galvanometerausschlags nach Ablauf der einzelnen Fristen. Nimmt man die Werte in der Tabelle

Tabelle I.

Zeit in Minuten		Menge Nichtelektrolyt in Molen											
		Harnstoff		CH_3OH		C_2H_5OH		C_8H_7OH (Iso)		Rohrzucker		Azeton	
		0,0625	0,135	6,45	12,9	4,38	8,76	3,29	6,57	0,25	0,50	4,26	8,52
A	5	0,44	2,70	12,90	64,50	4,38	35,04	3,29	13,14	—	1,50	—	8,52
	10	1,06	4,86	38,70	154,80	17,52	78,84	6,57	32,85	—	4,00	—	25,56
	15	1,94	—	64,50	233,20	26,28	131,40	13,14	52,56	—	6,50	—	42,46
B	5	1,44	4,99	26,80	166,41	8,76	87,60	3,29	32,85	0,25	2,00	4,26	—
	10	2,19	—	70,95	309,60	21,90	166,40	9,86	78,84	0,75	5,50	8,52	54,08
	15	—	—	116,10	374,10	35,04	227,80	19,71	131,40	1,75	10,00	17,04	559,64
C	5	2,50	—	90,30	309,60	26,28	157,68	13,14	72,27	0,50	6,00	4,26	34,08
	10	—	—	161,25	—	65,70	254,04	32,85	151,10	1,50	12,50	17,04	102,24
	15	—	—	193,50	—	105,12	—	55,84	190,50	2,75	16,50	29,80	170,40

A = Werte für ein 6 Tage dialysiertes Sol
B = „ „ „ 8 „ „ „
C = „ „ „ 11 „ „ „

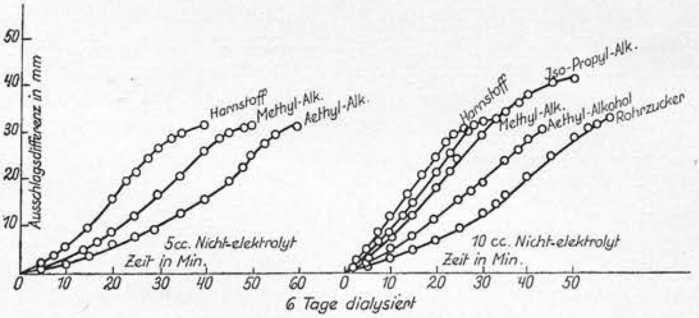

Fig. 6

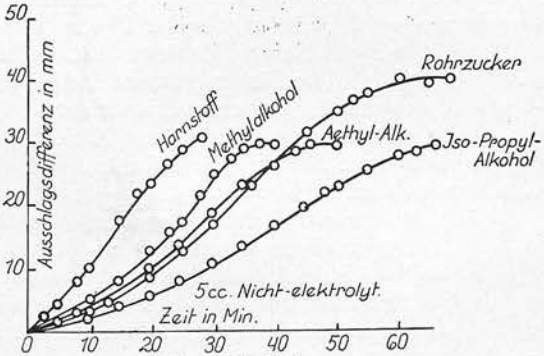

Fig. 7

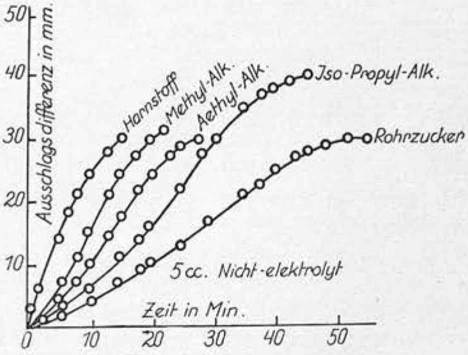

Fig. 8

als Ausdruck für die Wirksamkeit der Nichtelektrolyte bei der Koagulation der Sole, dann erhält man für Alkohole die Reihenfolge Methylalkohol > Aethylalkohol > Isopropylalkohol, oder die Wirksamkeit sinkt mit steigender Anzahl von CH_2-Gruppen. Das haben auch Mukherrjee und Mitarbeiter[11]) gefunden, für As_2S_3-Sol. Die Werte für Harnstoff und Zucker zeigen, daß die gleiche Reihenfolge nicht für Nichtelektrolyte verschiedener spezifischer Eigenschaften aufrecht erhalten bleibt. Die Werte in der Tabelle scheinen darauf hinzudeuten, daß verschiedene zur selben Serie gehörige Nichtelektrolyte bei Sensibilisierung des Sols einen Effekt zei-

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[11]) Mukherjee und Mitarb., Journ. Ind. Chem, Soc. **5**, 697 (1928).

gen, der von ihrer Stellung in der homologen Reihe abhängt.

Als Resultate dieser Versuche stellen sich folgende Punkte heraus:

1. Die sensibilisierende Wirkung der Nichtelektrolyte steigt mit zunehmender Reinheit des Sols (im Verlauf der Dialyse).
2. Eine praktisch reine Probe des Sols (lange dialysiert) kann schon durch kleine Nichtelektrolytmengen koaguliert werden, und das sogar in Abwesenheit von Elektrolyten.
3. Die sensibilisierende Wirkung steigt für den gleichen Nichtelektrolyten mit seiner Menge.

Die logische Folge dieser drei Punkte ist, daß bei zwei Untersuchungsreihen über das gleiche Sol mit den gleichen Nichtelektrolyten keine vergleichbaren Resultate zu erwarten sind, wenn nicht die verwendeten Sole den gleichen Grad der Reinheit besitzen. Wenn insbesondere auf der einen Seite eine reine Solprobe untersucht wird, während anderseits ein ungereinigtes mit beträchtlichen Mengen peptisierend wirkender Stoffe vorliegt, vermag die Menge an Nichtelektrolyt, die im ersteren Falle sensibilisierend oder sogar koagulierend wirkt, im letzteren Falle das Sol nicht nennenswert zu beeinflussen.

Die Sensibilisierung des Sols im vorliegenden Falle läßt sich nicht von der Annahme ausgehend erklären, daß die Adsorption des fällenden Ions durch den Nichtelektrolyten unterbunden wurde[12]), denn wir finden stets eine Zunahme der Koagulationsgeschwindigkeit bei Zugabe der Nichtelektrolyten. Man könnte ja nun sagen, das wäre kein ausreichender Beweis gegen die Ansicht Weiser's (loc. cit.), da Adsorptionsfähigkeit und Koagulationsvermögen nicht Hand in Hand zu gehen brauchen[13]). Die Tatsache indessen, daß ein sehr reines Sol durch geringe Mengen von Nichtelektrolyten geflockt werden kann, selbst wenn kein Elektrolyt zugegen ist, zeigt doch, daß das Argument einer Unterbindung der Adsorption des fällenden Ions bei Zusatz von Nichtelektrolyten nicht wesentlich zur Deutung der Ergebnisse der vorliegenden Untersuchung beitragen kann.

Weiser[14]) hat noch eine andere Ansicht zur Erklärung des Sensibilierungsphänomens entwickelt, nämlich die Verdrängung des stabilisierenden Ions durch den Nichtelektrolyten. Die Verdrängung des stabilisierenden Ions durch den Nichtelektrolyten würde das Sol instabiler machen und damit würden, falls man die Stabilität durch die Höhe der Koagulationskonzentration definiert, geringere Mengen von Elektrolyt ausreichen, um das Sol zu koagulieren. Die Resultate aus vorliegender Untersuchung scheinen diese zweite Ansicht Weiser's zu bestätigen insofern, als das Sol in Gegenwart von Nichtelektrolyten sensibilisiert wird.

H. Freundlich[15]) entwickelte weiter einen von Wo. Ostwald vor 20 Jahren geäußerten Gedanken[16]), indem er das Sensibilisierungsphänomen mit der Aenderung der Dielektrizitätskonstante in Zusammenhang brachte, die die Ladung der Kolloidteilchen beeinflußt. Nach Wo. Ostwald und H. Freundlich wird, falls anzunehmen ist, daß der Nichtelektrolyt an der Grenzfläche adsorbiert wird, die Dielektrizitätskonstante wesentlich erniedrigt, da alle Nichtelektrolyten eine viel geringere Dielektrizitätskonstante als Wasser haben. Durch diese Erniedrigung der Dielektrizitätskonstanten wird auch die Ladung verringert nach der Gleichung

$$e = \frac{V \varepsilon \varrho (\varrho + d)}{d},$$

wo e die Ladung des Teilchens ist, ϱ der Radius, d die Dicke der Doppelschicht, V die konstante Potentialdifferenz zwischen den beiden Seiten der Doppelschicht und ε die Dielektrizitätskonstante des Mediums. Wenn die Ladung des Teilchens bei Zusatz von Nichtelektrolyten geringer wird, dann ist weniger Elektrolyt notwendig, um das Sol zu flocken. Mit anderen Worten, bleibt die Elektrolytkonzentration dieselbe, so wird die Koagulationsgeschwindigkeit größer sein in Gegenwart eines Nichtelektrolyten als ohne diesen. Diese Ansicht von Wo. Ostwald und H. Freundlich findet eine Stütze in den Ergebnissen der Messungen der Wanderungsgeschwindigkeiten von Fe_2O_3-[17]) und As_2S_3[18])-Solen bei Anwesenheit von Nichtelektrolyten. Es wurde beobachtet, daß die Wanderungsgeschwindigkeit der Kolloidteilchen bei Zusatz eines Nichtelektrolyten, der das Sol sensibilisiert, abnimmt. Nach der oben angeführten Ansicht müßte ein Nichtelektrolyt mit kleinerer Dielektrizitätskonstante eine stärkere sensibilisierende Wirkung haben als ein Nichtelektrolyt mit größere DK. Es läßt sich jedoch keine ausgesprochene Parallelität zwischen sensibilisieren-

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[12]) H. B. Weiser, Journ. Phys. Chem. **28**, 1253 (1924).

[13]) H. B. Weiser, ibid. **32**, 1481 (1928).

[14]) H. B. Weiser, loc. cit.

[15]) H. Freundlich, Kapillarchemie (1922), 638.

[16]) Wo. Ostwald, Grundriß, 1. Aufl. (1909), 471.

[17]) H. Freundlich, Kapillarchemie (1922), 638.

[18]) Mukherjee, loc. cit.

der Wirkung der Stoffe und ihrer Dielektrizitätskonstante feststellen. Es ist auch schwer zu verstehen, warum V und d als konstant angenommen werden sollen, selbst wenn sich in Nachbarschaft des Teilchens Moleküle anderer Art befinden.

Mukherjee[19]) hat die Ansicht geäußert, daß die Sensibilisierung der Sole durch Nichtelektrolyten sich besser erklären läßt unter der Annahme einer Aenderung der Ladungsdichte der Teilchen wie einer Aenderung der Dicke der Doppelschicht. Aber das Fehlen jeglicher experimenteller Daten, die die Annahme einer Aenderung der Dicke der Doppelschicht stützen könnten, läßt die Brauchbarkeit der Hypothese zweifelhaft erscheinen.

Wie schon gesagt, sensibilisieren die Nichtelektrolyten des Sols nicht nur, sondern sie können — auch in Abwesenheit von Elektrolyten — auch koagulierend wirken, wenn das Sol keine größeren Mengen von peptisierenden Stoffen enthält. Von Mukherjee[20]) wurde beobachtet, daß die Wanderungsgeschwindigkeit des kolloiden As_2S_3 schon abnimmt, wenn dem Sol nur ein Nichtelektrolyt zugesetzt wird. Seine Messungen treffen sich also mit unseren Resultaten. Sicher ist, daß der Mechanismus der Koagulation eines Kolloids durch diese Nichtelektrolyten nicht der gleiche ist wie bei der Elektrolytkoagulation. Es läßt sich kein Beweis dafür erbringen, daß etwa diese Nichtelektrolyten ionisiert würden, was sie befähigen würde, die Ladung des Kolloids zu neutralisieren, wie Elektrolyte das tun. Die Koagulation des kolloiden ThO_2 durch einen Nichtelektrolyten läßt sich aber bis zu einem gewissen Grade folgendermaßen deuten:

Bei der Dialyse wird der Peptisator (HCl) entfernt, und wenn wir annehmen, daß die Entfernung des Peptisators bei fortschreitender Dialyse die Ladung vermindert oder die Stabilität herabsetzt, dann nähert sich die Größe der Ladung und damit das Potential des Kolloids mehr und mehr dem ersten kritischen Potentialwert (Frendlich's erstes kritisches Potential), bei welchem die langsame Koagulation beginnt. Bei einem Sol, das eine größere Peptisatormenge enthält, ist die Ladung viel größer als der dem ersten kritischen Potential entsprechende Wert, deshalb reicht die Menge des adsorbierenden Nichtelektrolyten nicht aus, um das stabilisierende Ion soweit zu verdrängen, daß die Ladung bis auf den dem ersten kritischen Potential entsprechenden Wert herabgesetzt wird. Die geringe wirklich erfolgte Verdrängung und die dadurch bedingte Potentialerniedrigung hat aber eine Erhöhung des Koagulationsvermögens des Elektrolyten zur Folge. Die Lage wird indessen eine andere, wenn die Menge des Peptisationsmittels nicht sehr groß ist, denn dann ist auch die Menge des stabilisierenden Ions sehr klein oder die Ladung des Kolloids nicht viel höher als der dem ersten kritischen Potential entsprechende Wert. Dann genügt auch die Menge des adsorbierten Nichtelektrolyten völlig, das Potential bis auf den ersten kritischen Wert oder sogar bis nahe an den zweiten kritischen Wert (Freundlich's zweites kritisches Potential) herabzusetzen, so daß je nachdem langsame oder rasche Koagulation erfolgt. Somit vermögen Nichtelektrolyten allein schon das Sol zu koagulieren, wenn dieses keine größeren Peptisatormengen enthält. Jedenfalls spricht die Tatsache, daß ein gereinigtes Sol durch Nichtelektrolyten geflockt werden kann, in unserem Sinne.

Es ist anzunehmen, daß, wenn man alle Kolloide in gleicher Richtung wie in vorliegender Arbeit untersucht, d. h. also sorgfältig dialysierte Sole benutzt, man über die Rolle der Nichtelektrolyten bei der Sensibilisierung wie auch der Koagulation von Kolloiden zu hinreichender Klarheit kommt.

Zusammenfassung.

1. Die Wirkung von Nichtelektrolyten auf kolloides Thoriumhydroxyd in verschiedenen Stadien der Dialyse wird in Gegenwart und Abwesenheit von Elektrolyten durch Messung der Koagulationsgeschwindigkeit studiert.

2. Es wurde festgestellt, a) daß mit zunehmender Reinheit des Sols (bei fortschreitender Dialyse) die sensibilisierende Wirkung der Nichtelektrolyten auch zunimmt, und b) daß ein annähernd reines Sol (nach genügend langer Dialyse) durch Nichtelektrolyte allein schon leicht koaguliert werden kann.

3. Die Resultate werden vom Standpunkt der verschiedenen Theorien über Sensibilisierung und Koagulation aus diskutiert.

* * *

Es ist uns eine angenehme Pflicht, den Herren Professoren A. R. Normand und D. B. Naik zu danken für das Interesse an unsrer Arbeit. Unser Dank gilt auch Herrn Dr. K. R. Ramanathan vom „The Indian Meteorological Department“ für seine wertvollen Ratschläge.

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[19]) Mukherjee, loc. cit.
[20]) Mukherjee, loc. cit.

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Adolf, Mona: Physikalische Chemie der Globuline. VII. Ueber das Verhalten von Säure- und Laugenglobulin bei Salzzusatz XXI, H. 7—12
Krausse, W.: Einige Beiträge zur Kenntnis des optischen Verhaltens der Tonerdefasern (mit 1 Abb.) XXI, H. 7—12
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— und H. **Jores:** Ueber die Viskosität und Elastizität von Seifenlösungen XXII, H. 1—2
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Hauser, E. A., und H. **Mark:** Zur Kenntnis der Struktur gedehnter Kautschukproben (mit 12 Abb.) XXII, H. 3—5
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VERLAG VON THEODOR STEINKOPFF, DRESDEN UND LEIPZIG

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THE INFLUENCE OF HYDROLYSED GELATINE ON THE PRECIPITATION OF SILVER CHROMATE.

By B. N. Desai and G. M. Nabar.

Received 11th January, 1932.

It has been shown by various workers[1, 2, 3] that unhydrolysed gelatin has to a very marked degree the power of retarding the appearance of a red colour in a mixture of aqueous solutions of silver nitrate and potassium chromate. Electromotive force and conductivity data [2] indicate that prior to the change from yellow to red the silver chromate is in solution and not in the colloidal state.[4] Apparently a portion of the silver ion forms a supersaturated solution of silver chromate, while the remainder enters into combination with the gelatin.[2]

Bolam and Desai [5] found that under comparable conditions the time which elapses before the separation of solid silver chromate decreases when the gelatin is hydrolysed by heating. Since an increase in the concentration of free silver ion would favour precipitation, the following electrometric investigation was carried out to test whether the hydrolysis decreases the combination between the gelatin and the silver.

Experimental.

The gelatin used in these experiments was a specially purified sample supplied by Messrs. Cox of Edinburgh. The moisture content was 16·35 per cent., and the ash, mainly calcium sulphate, 1·18 per cent. Since it has been shown [2] that calcium has no effect on the precipitation, no attempt was made to render the gelatine ash-free.

The gelatin was hydrolysed by heating a 3 per cent. solution in a fused silica flask (with a water-cooled reflux condenser) on a water bath at 100°. The flask and its contents were weighed before and after each period of heating and any loss (which was always small) was made good by the addition of conductivity water.

The activity of the silver ion in the chromate mixtures was determined by means of a cell of the type

$$\text{Hg, Hg}_2\text{Cl}_2 + \text{N . KCl, Saturated NH}_4\text{NO}_3\text{, X, Ag,}$$

where X denotes the solution of silver chromate with or without other electrolytes or gelatin. The cell was kept at a temperature of 30° ± 0·1° C. Before each experiment the silver gauze electrode was carefully cleaned and electroplated. Its constancy was tested by

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[1] Williams and Mackenzie, *J. Chem. Soc.*, **117**, 844, 1920.

[2] Bolam and Mackenzie, *Trans. Far. Soc.*, **22**, 151, 162, 1926.

[3] Hedges and Henley, *J. Chem. Soc.*, 2714, 1928.

[4] Chatterjee and Dhar, *Trans. Far. Soc.*, **23**, 23, 1927; *J. Indian Chem. Soc.*, **5**, 175, 1928.

[5] Bolam and Desai, *Trans. Far. Soc.*, **24**, 50, 1928.

measurements in a pure solution of silver nitrate, and it was found that the potential did not vary with time. The potential of the silver electrode in a saturated solution of silver chromate was determined and the observed value agreed quite satisfactorily with the calculated value.

In the precipitation experiments 5 c.c. of (say) $N/100$ $AgNO_3$ + 3·7 c.c. of 3 per cent. gelatin and 5 c.c. of $N/100$ K_2CrO_4 + 3·7 c.c. of 3 per cent. gelatin were mixed, after allowing the separate solutions to attain a temperature of 30° C. The mixture was immediately transferred to the electrode vessel, which was kept in the thermostat, and the potential developed by the silver electrode measured from time to time.

The activity of the silver ion was calculated from the equation

$$E = E_0 - \frac{RT}{nF} \ln a_{Ag+},$$

where E_0 was calculated from data given by Lewis and Randall.[6] E, the observed *e.m.f.*, for $Ag/AgNO_3$ was found to be within 0·16 per cent. of the calculated value.

Results and Discussion.

Table I. contains the initial and final values, as well as the differences between them, of the activity of the silver ion in the reacting mixtures containing different concentrations of the reactants in gelatin hydrolysed to different extents. The values of the activity of the silver ion at different times after mixing the solutions in the case of 0·01 N $AgNO_3$ + 0·01 N K_2CrO_4 + gelatin have been plotted in Fig. 1. Similar curves were obtained for the other systems.

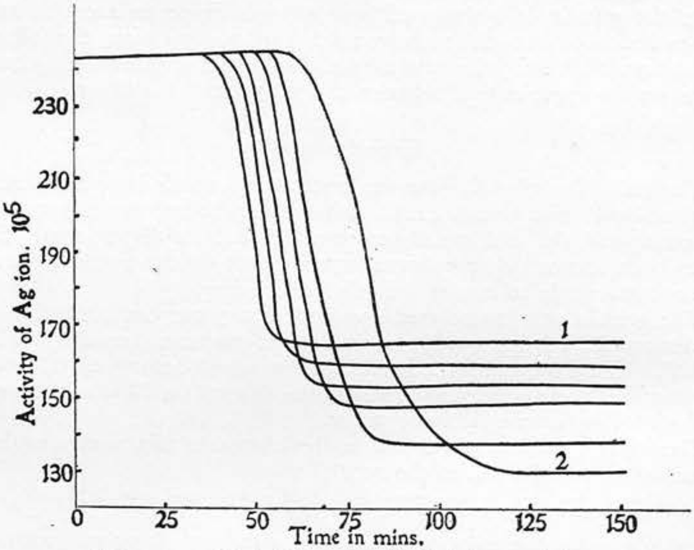

FIG. 1.—0·01 N . $AgNO_3$ + 0·01 N . $K_2C_2O_4$ + gelatine.
1 = 10 hours hydrolysis. 2 = No hydrolysis.

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[6] Lewis and Randall, *Thermodynamics*, 1923.

It will be seen that the activity remained constant for some minutes, then rapidly decreased and finally became constant. It was noted that there was no further change even after six hours. The point at which the activity commenced to fall corresponded in every case with the first appearance of a red colour. Until this point was reached the mixture remained clear yellow. It is evident that our experiments support the conclusion of Bolam and Mackenzie [2] that the red colour is due to the precipitation of the silver chromate from true solution, and is not the result of the coagulation of a sol of silver chromate.

If the time required for the appearance of the precipitate is taken as a measure of the inhibitive power of the gelatine, it appears that the efficiency of the gelatine in this respect is the lower the longer the gelatin is hydrolysed. This is in agreement with the observations of Bolam and Desai.[5]

Table I. and the curves show that the initial value * of the activity was unaffected by the hydrolysis of the gelatin. The greater tendency to precipitation brought about by heating the gelatine cannot, therefore, be ascribed to an increase in the concentration of the free silver ions.

TABLE I.

Gelatin Dispersed at 35° C. and Hydrolysed for	Concentration of Reactant.									
	0·01 *N* $AgNO_3$, 0·01 *N* K_2CrO_4.		0·01 *N* $AgNO_3$, 0·011 *N* K_2CrO_4.		0·01 *N* $AgNO_3$, 0·012 *N* K_2CrO_4.		0·011 *N* $AgNO_3$, 0·01 *N* K_2CrO_4.		0·012 *N* $AgNO_3$, 0·01 *N* K_2CrO_4.	
	Initial Activity of Ag ion × 10^5. 243.						Initial Activity of Ag ion × 10^5. 280.		Initial Activity of Ag ion × 10^5. 317.	
Hrs.	Final Activity of Ag ion × 10^5.	Difference × 10^5.	Final Activity of Ag ion × 10^5.	Difference × 10^5.	Final Activity of Ag ion × 10^5.	Difference × 10^5.	Final Activity of Ag ion × 10^5.	Difference × 10^5.	Final Activity of Ag ion × 10^5.	Difference × 10^5.
0	130	113	120	123	105	138	128	152	133	184
2	139	104	125	118	116	127	145	135	150	167
4	149	94	137	106	123	120	157	123	160	157
6	154	89	143	100	128	115	165	115	167	150
8	160	83	149	94	135	108	174	106	177	140
10	166	77	154	89	139	104	179	101	183	134

A striking feature of the results is that the final value of the activity increases with increase in the hydrolysis, although precipitation takes place more readily. At present it is difficult to suggest an explanation of this effect and the matter requires further investigation.

The p_H of the gelatin at various stages of hydrolysis was determined colorimetrically and the values are given in Table II.

While increase in the p_H would, on the one hand, tend to favour precipitation, on the other it might be expected to promote combination

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* The initial value was the same as the value of the activity obtained when the silver nitrate alone was present in the gelatin solution. In agreement with previous experience it was found that the gelatin produced an appreciable decrease in the activity of the silver ion.

TABLE II.

Treatment of Gelatin.	p_H.
Dispersed at 35° C.	5·15
Heated for—	
6 hours	5·25
8 ,,	5·30
12 ,,	5·40

between the gelatin and the silver ion (see Bolam and Mackenzie).[2] It is thus all the more surprising that the final value of the activity increases with the hydrolysis.

The authors wish to thank Prof. A. R. Normand for his constant interest and some valuable suggestions, and Dr. T. R. Bolam (*Edinburgh*) for helpful criticism.

Note by Referee.—It should be mentioned that Liesegang quite clearly realised an effect of gelatose (hydrolysed gelatin) on the precipitation of silver chromate and more particularly on the formation of rings.[7]

[7] R. E. Liesegang, *Z. physik. Chem.*, **88**, 1, 1914.

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Studien über den Einfluß von Nichtelektrolyten, die eine verschiedene Anzahl von Hydroxylgruppen enthalten, auf die Fällung von Thoriumhydroxyd aus einer Thoriumnitratlösung durch NaOH.

(Eingegangen am 31. Juli 1931.)

Von G. M. Nabar, A. M. Patel und B. N. Desai.[1]
(Physical Chemistry Laboratory, Wilson College, Bombay, Indien.)

Von Patel und Desai[2, 3] wurde darauf hingewiesen, daß der Wirkungsgrad eines Nichtelektrolyten im Verhindern der Fällung von Thoriumhydroxyd aus einer Thoriumnitratlösung durch NaOH bis zu einem gewissen Grade von der An-

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[1] Übersetzt von E. Lottermoser (Dresden).

[2] Patel und Desai, Journ. Ind. Chem. Soc. 7, 162 (1930).

[3] Im Zusammenhang mit dieser Arbeit sei ergänzend auf folgende ältere Veröffentlichungen hingewiesen: Th. Graham, Phil. Trans. **151**, 183 (1861), erkannte, daß Cupri-, Ferri- und Uranylsalze bei Gegenwart von Zucker mit Kalilauge keinen Nieder-

zahl der Hydroxylgruppen des Nichtelektrolyten abhängt. Bei den daraufhin von ihnen untersuchten Nichtelektrolyten zeigte es sich, daß nur Rohrzucker und Glyzerin als fällungshemmende Verbindungen wirken, und zwar ist der erstere wirksamer als das letztere; Azeton, Methyl-, Äthyl- und Isopropylalkohol konnten selbst bei Zusatz von großen Mengen die Fällung des Thoriumhydroxyds nicht verhindern. In der vorliegenden Arbeit wurde der hemmende Einfluß von Nichtelektrolyten, die eine verschiedene Anzahl von Hydroxylgruppen enthalten, auf die Fällung von Thoriumhydroxyd aus einer Thoriumnitratlösung durch NaOH untersucht mit dem Ziel, die Gültigkeit dieses oben erwähnten Hinweises zu prüfen.

Der geringste Betrag des zur Verhinderung der Thoriumhydroxydfällung notwendigen Nichtelektrolyten wurde in genau der gleichen Weise bestimmt wie Patel und Desai angeben (loc. cit.).

Die erhaltenen Resultate sind in der folgenden Tabelle angegeben und auch in Fig. 1 dargestellt.

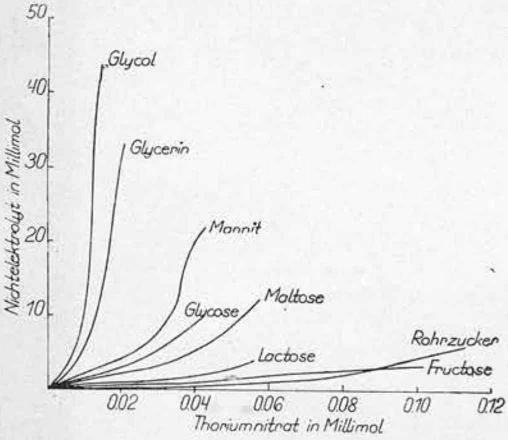

Fig. 1

Aus den Kurven der Fig. 1 ergibt sich, daß, nach der hemmenden Wirkung geordnet, die Reihenfolge der hier untersuchten Nichtelektrolyte Fruktose > Rohrzucker > Laktose > Maltose > Glukose > Mannit > Glyzerin > Glykol ist. Fruktose enthält 5 Hydroxylgruppen, Rohrzucker, Maltose und Laktose je 8, Glukose 5, Mannit 6, Glyzerin 3 und Glykol 2. Die Ergebnisse zeigen, daß Fruktose und Glukose sich anomal verhalten. Der Unterschied im Verhalten von Rohrzucker, Maltose und Laktose kann durch die Verschiedenheit ihrer Konfiguration erklärt werden.

Tabelle.

Gesamtvolumen (Salzlösung + Nichtelektrolyt + NaOH + Wasser) = 30 ccm.

Menge der Natronlauge = 0,5 Millimole	
Millimole des Thoriumnitrat	Millimole des Nichtelektrolyten
Glykol	
0,0057	4,00
0,0086	10,00
0,0114	20,00
0,0143	44,00
Glyzerin	
0,0086	4,00
0,0114	9,60
0,0143	14,90
0,0171	21,00
0,0214	33,00
Mannit	
0,0143	3,00
0,0200	4,20
0,0286	7,00
0,0371	18,00
0,0428	22,00
Fruktose	
0,0286	0,85
0,0428	1,27
0,0571	2,03
0,0714	2,35
0,0857	3,00
0,1000	4,14
Maltose	
0,0114	0,80
0,0143	2,50
0,0429	6,25
0,0571	12,00
Glukose	
0,0200	3,00
0,0286	4,75
0,0371	7,50
0,0429	10,00
Laktose	
0,0286	1,00
0,0371	1,56
0,0429	2,13
0,0571	4,86
Rohrzucker	
0,0571	1,25
0,0857	3,00
0,0971	4,25
0,1143	6,25

Es wurde gefunden, daß die nach Zusatz des Nichtelektrolyten und eines Überschußes von NaOH zu einer Thoriumnitratlösung erhaltene klare Flüssigkeit eine kolloide Lösung von negativ geladenem Thoriumhydroxyd war. Sie war sehr stabil und konnte tagelang klar erhalten

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schlag geben. H. W. Fischer, Biochem. Ztschr. **27**, 223 und 311 (1910) stellte mit Hilfe organischer hydroxylhaltiger Verbindungen ein negativ geladenes Ferrioxydsol her. Endlich haben sich Dumanski und Mitarbeiter [Koll.-Ztschr. **38**, 208; **41**, 108; **44**, 273; **47**, 121; **48**, 49; 155) eingehend mit der Wirkung der Weinsäure bei der Kolloidbildung befaßt und sie durch Komplexbildung erklärt. A. Lottermoser.

werden. Fügte man äquivalente Mengen von $MgCl_2$ und NaCl zu derselben Menge des Sols, das genügend dialysiert war, so daß es nur noch Spuren von Alkali enthielt, so wurde festgestellt, daß das erstere Salz viel besser koagulierend wirkte als das letztere.

Die für die Fällungshinderung des Metallhydroxydes notwendigen Bedingungen sind:

1. Der Nichtelektrolyt muß der Metallsalzlösung vor dem Alkalizusatz zugefügt werden.
2. Ein gewisser Überschuß des Alkalis ist nötig, ehe irgendeine Menge des Nichtelektrolyten die Bildung eines sichtbaren Niederschlages verhindern kann.

Ein Zusatz des Nichtelektrolyten allein zur Metallsalzlösung führte ebensowenig zur Bildung eines negativ geladenen Metallhydroxydsoles wie ein Alkalizusatz bei Abwesenheit des Nichtelektrolyten.

Die oben angeführten Tatsachen lassen annehmen, daß die Verhinderung der Fällung des Metallhydroxydes und die Bildung einer negativ geladenen kolloiden Lösung der vereinten Einwirkung sowohl des Alkalis als auch des Nichtelektrolyten zuzuschreiben ist. Die Verhinderung der Fällung des Metallhydroxydes und die Bildung des negativ geladenen Sols kann auf folgende Weise erklärt werden:

Auf Grund der chemischen Reaktion wird Alkalizusatz das Metallhydroxyd fällen. Das so gebildete Hydroxyd wird den Nichtelektrolyten adsorbieren. Die Adsorption des Nichtelektrolyten wird die Adsorbierbarkeit der sowieso im Überschuß anwesenden OH-Ionen vermehren, und das Ergebnis der OH-Ionenadsorption wird eine negativ geladene kolloide Lösung sein. Da der Nichtelektrolyt, dessen Adsorption eine stärkere Adsorption der OH-Ionen begünstigt, von vornherein anwesend ist, so wird nicht ein solcher Thoriumhydroxydniederschlag erhalten, wie er gewöhnlich bei Abwesenheit des Nichtelektrolyten entsteht, wenn NaOH einer Thoriumnitratlösung zugefügt wird.

Direkte Messungen, die Aufschluß darüber geben könnten, bis zu welchem Grad die OH-Ionenadsorption infolge der Gegenwart eines Nichtelektrolyten bei einem Vorgang der Art, wie er in dieser Arbeit beschrieben wird, ansteigt, sind nicht möglich. Zur Erforschung dieser Frage wurden Versuche zur Messung der Ladung der bei Gegenwart verschiedener Mengen Alkali und des Nichtelektrolyten entstehenden kolloiden Lösung angestellt. Diese Ergebnisse sollten auch dazu dienen, den Mechanismus der Kolloidflockung durch Nichtelektrolyte zu erklären.

Ist die in dieser Arbeit gegebene Erklärung richtig, so dürfte es zweifelhaft erscheinen, ob der Nichtelektrolyt die Rolle einer schützenden Verbindung spielt oder ob er als peptisierende Verbindung im wahren Sinne des Wortes wirkt.

Zusammenfassung.

1. Es wurde die Verhinderung der Fällung von Thoriumhydroxyd bei Zusatz von NaOH zu einer Thoriumnitratlösung in Gegenwart verschiedener Mengen von Nichtelektrolyten, die eine verschiedene Anzahl von Hydroxylgruppen enthalten, studiert.
2. Es wurde gefunden, daß im allgemeinen der Wirkungsgrad der Nichtelektrolyte in der Fällungshinderung des Hydroxydes mit steigender Zahl der Hydroxylgruppen wächst.
3. Die entstehende kolloide Lösung enthält negativ geladenes Thoriumhydroxyd.
4. Eine wahrscheinliche Erklärung des Mechanismus der Fällungshinderung des Hydroxydes, die sowohl die Rolle des Alkalis als auch des Nichtelektrolyten berücksichtigt, wurde gegeben.

* * *

Wir möchten nicht versäumen, Herrn Prof. A. R. Normand unsern Dank für sein Interesse an dieser Arbeit auszusprechen.

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A Note on the Liesegang Rings of Silver Chromate in Gelatine.

BY

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CALCUTTA UNIVERSITY PRESS
1932

A Note on the Liesegang Rings of Silver Chromate in Gelatine.

By B. N. Desai and G. M. Nabar.

It is well-known that sometimes it is not possible to get Liesegang rings of silver chromate in different samples of gelatine. The explanation of this particular behaviour lies in the observation of Liesegang (*Z. Phys. Chem.*, 1914, **88**, 3) himself who has stated that the best rings are obtained if the gelatine is not too pure and contains suitable amounts of acid and gelatose. The purpose of this note is to give some results which indicate the probable role of the p_H of gelatine on the nature of Liesegang rings of silver chromate.

A 20 per cent. solution of silver nitrate was allowed to diffuse into a 15 per cent. gelatine gel impregnated with 0·1 per cent. of potassium dichromate. The experiments were carried out at a temperature of 28°. The results (mean of three independent experiments) are given in the table at the end of the paper.

The results show that an increase in the acidity of gelatine is accompanied by a decrease (*i*) in the time after which the first ring appears, (*ii*) in the distances between the same successive rings and (*iii*) in the number of rings which can be obtained. The statement that addition of suitable proportions of acid increases the width of the chromate rings until, with excessive amounts, the whole precipitate forms a continuous band (E. Hatschek, " A Laboratory Manual of Elementary Colloid Chemistry " 1920 Ed., p. 125) is not supported by these experiments and it is difficult to understand the reasons of differences in the results in the two cases. A decrease in the distances between successive rings with an increase in the acidity of gelatine might be due to the following effect.

We have shown (paper by Desai and Nabar which is in course of publication in the *Trans. Faraday Soc.*) that the inhibitive power of gelatine increases with a decrease of its p_H (addition of acetic acid) due to an increase in the opposition to the growth of crystallisation centres and that a sample of gelatine with lower p_H can keep a greater amount of silver chromate in ionic condition than another sample with higher p_H. The degree of supersaturation having increased with an increase in the acidity of gelatine, once a crystallisation centre is formed, both its rate of growth and the ultimate size of the particle of the precipitate will be great. Now an increase in the size of the particles of the precipitate will decrease the adsorption of the substances present in the neighbourhood due to a decrease in the specific surface and hence silver nitrate will not have to travel a great distance before the metastable limit for the appearance of the next ring is reached. It would thus appear that the distances between successive rings will decrease with an increase in the acidity of gelatine due to an increase in its inhibitive power.

With an increase in the acidity of the gel the rings are found to be spiral shaped, broken at places, or are not obtained at all because of the fact that there is a tendency for the particles of the precipitate to become bigger as shown by these results. As pointed out by Bradford (*J. Soc. Chem. Ind.*, 1929, **48**, 79) if the precipitate can be obtained in a fine condition good rings can always be obtained. He achieved this purpose by working with dilute solutions of the reactants or by decreasing the solubility of the precipitate in the gel by adding alcohol to it. One would thus expect that perfectly good rings of silver chromate should be obtained in gelatine having a higher p_H, because the number of crystallisation centres being increased the precipitate will be obtained in a finer condition. But this process cannot probably go on indefinitely. For, as we have shown (Desai and Nabar, *loc. cit.*) increase of p_H causes a decrease in the maximum possible saturation and, therefore, we may expect that ultimately the supersaturation value will coincide with that corresponding to the saturation solubility product. The consequence of this will be that although the precipitate may be in a fine condition it will be deposited more or less in a continuous manner throughout the medium without the formation of rings. The rate of diffusion may also change with a change in the p_H of gelatine and might probably be connected with this. The question, however, requires further investigation. It is possible that there might be definite limits to the p_H value of gelatine within which good rings of silver chromate can be obtained.

We are at present investigating in detail the influence of the inhibitive power of different gels on the formation of banded precipitates of various sparingly soluble substances.

TABLE

p_H of the gel.	Approximate time after which first ring appears.	Distance from the top at which first ring appears.	Distances between the successive rings.					
			† 1−2	2−3	3−4	4−5	5−6	6−7
5·15	48 hr.	32 mm.	1·2 mm.	2·0 mm.	2·8 mm.	4·2 mm.	6·0 mm.	7·3 mm.
5·10	28	23	*	1·5	2·0	3·0	4·8	...
5·00	13	19	*	*	1·5	2·0	3·0	...
4·00	...	...	...	...	...	...	...	...

Remarks : In the case of the gel having p_H 5·15 the rings were well-defined. In the gel having p_H 5·10 the rings had a tendency to become spiral shaped and after the appearance of the sixth ring no further rings formed but reddish black spherical and thread-like crystals appeared here and there. With gel having p_H 5·00 the rings were not complete but broken at places; after the fifth ring there appeared reddish black spherical and threadlike crystals here and there. Gel having p_H 4·00 did not give any rings but contained reddish black spherical crystals spread here and there. The size of the particles in the rings becomes bigger and bigger as the acidity ofthe gel increases.

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† First ring in each case corresponds to the first band which appears after the initial continuous precipitate as examined under the microscope.

* The rings were not quite well-defined and so it was difficult to measure the distances.

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Relation between Charge and Stability of Colloidal Solutions of Gold and Ferric Hydroxide Dialysed to Different Extents.

BY

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CALCUTTA UNIVERSITY PRESS
1932

Relation between Charge and Stability of Colloidal Solutions of Gold and Ferric Hydroxide Dialysed to Different Extents.

By B. N. Desai, G. M. Nabar and P. M. Barve.

It is believed by most colloid chemists that the stability of a colloid, as determined by the coagulating concentration of an electrolyte, depends on the charge on its particles and that the greater the charge the greater will be the stability. The results of coagulation of colloids by electrolytes as well as the effect of dialysis on the stability of colloids have been explained on the basis of this view. Mukherjee, Choudhury and Rai Choudhury (*J. Indian Chem. Soc.*, 1927, **4**, 493) working on colloidal arsenious sulphide found that the stability is not directly related to the charge as is generally believed to be; in some of the results they found a greater stability in spite of smaller charge on the colloid. Their conclusion is however based on the results obtained with mixtures of electrolytes as well as with single electrolytes containing organic anions. It was therefore considered necessary to investigate if the same behaviour is also shown by other sols under much more simple conditions.

It is well known, that although in most cases, the stability of the sol decreases with the progress of dialysis, colloidal gold prepared by the formaldehyde method becomes more stable towards electrolytes with progress of dialysis up to a certain stage, after which stability towards electrolytes decreases (Freundlich, "Colloid and Capillary Chemistry," 1926, English Translation, p. 506). It has also been shown by Galecki (*Z. anorg. Chem.*, 1912, **74**, 196 *et seq*) that the cataphoretic speed of gold sol increases with the progress of dialysis along with an increase in the flocculation value. In what follows results of simultaneous measurements of charge and flocculation value with potassium chloride of colloidal solutions of gold and ferric hydroxide dialysed to different extents have been given.

EXPERIMENTAL.

Preparation of colloidal solutions.—Gold sol was prepared by Zsigmondy's nucleus method in batches of 100 c.c. Ferric hydroxide sol was prepared in instalments of 500 c.c. by adding 30 c.c. of a 45% solution of ferric chloride drop by drop to 500 c.c. of boiling distilled water ; the mixture was stirred all the time and the resulting brown red sol was boiled for ½ hour.

The sols were transferred to parchment paper bags for dialysis. The bags were previously treated with distilled water to remove soluble matter. The outer water was changed twice a day. Suitable amounts of colloids were withdrawn every time for experiments by means of a pipette.

Method of measuring the charge.—The charge was measured according to Mukherjee's improved **U**-tube method (*Proc. Roy. Soc.*, 1923, **A**, **103**, 102 ; also Mukherjee, Choudhury and Rai Choudhury, *loc. cit.*). The electrodes were put in the side bulbs and not in the limbs of the **U**-tube in order to avoid the disturbing effect of electrolysis on the sharpness of the boundary.

Mukherjee, Raichoudhury and Bhattacharyya (*J. Indian Chem. Soc.*, 1928, **5**, 735) have shown that unless the upper liquid has got the same ionic composition as the intermicellary liquid the results of charge measurements are sure to be erroneous. Mukherjee, Raichoudhury and Biswas (*J. Indian Chem. Soc.*, 1931, **8**, 373) have also shown that the use of ultrafiltrate as the upper liquid does not give reliable results. The upper liquid in our measurements of gold sol consisted of solution of potassium chloride having the same conductivity as the colloid ; it gave quite satisfactory results. In the case of ferric hydroxide the upper liquid was prepared in the same manner as given by S. N. Mukherjee (*Kolloid Z.*, 1930, **52**, 63).

We also performed some experiments in case of ferric hydroxide sol to see if the dialysate could be used as an upper liquid (*cf.* "Colloid and Capillary Chemistry", Eng. Trans., p. 372). It was found that in the initial stages in the case of sols dialysed for short periods and containing still appreciable amounts of HCl and $FeCl_3$, the dialysate obtained by keeping distilled water in contact with the colloid in the parchment bag for about 36 hours could be used as a satisfactory upper liquid. The results obtained by using the dialysate as the upper liquid for the sol dialysed for 2 days are given below, the cataphoretic speed corrected for viscosity is expressed in centimetres per second per volt per centimetre × 10^5.

TABLE I.

Resistance of the dialysate = 66 Ohms.

,, ,, ,, colloid = 65 ,,

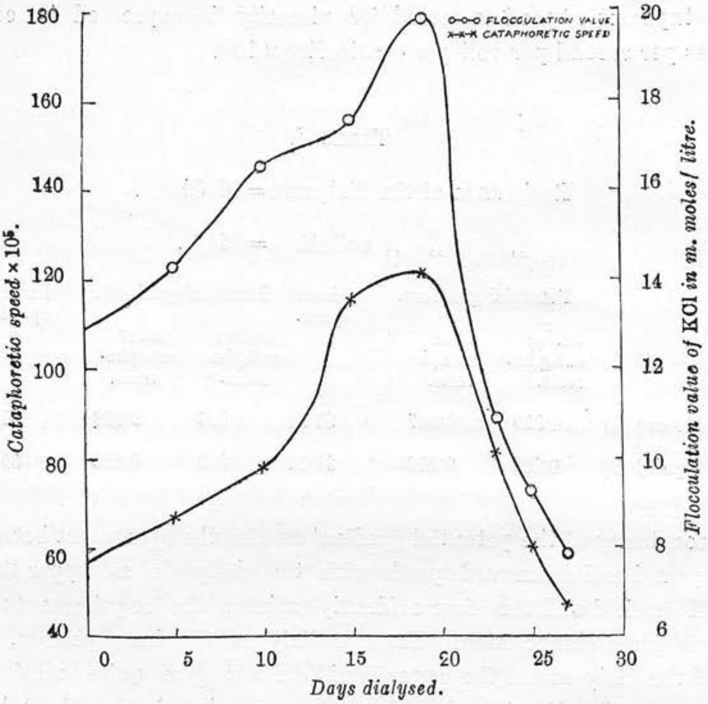
		Potential gradient.		Direct speed.	Potential gradient.		Reverse. speed
		before cataphoresis.	after cataphoresis.		before cataphoresis.	after cataphoresis.	
Dialysate as upper liquid	(1)	0·810	0·807	35·64	0·805	0·808	36·45
	(2)	0·802	0·813	35·64	0·809	0·803	35·64

The constancy of the potential gradient as also the agreement between the upward and downward speeds with the dialysate as upper liquid is well marked and therefore evidently satisfies the requirements for uniform ionic composition. For sols dialysed for long periods, the use of the dialysate as the upper liquid did not give quite consistent values for the direct and reverse movements of the boundary, probably due to the effect of the Donnan equilibrium coming into operation. It was however found that in all cases, even for sols dialysed for long periods, the dialysate forms a very convenient liquid to start with for preparing the necessary upper liquid by adding suitable amounts of electrolytes for getting the same ionic composition as the intermicellary liquid. Further experiments to investigate fully the possibilities of the use of the dialysate as the upper liquid are in progress.

The flocculation values were determined by finding out the amount of KCl necessary for giving a definite blue colour after 5 minutes in case of gold sol and for the instantaneous precipitation of the colloid in case of colloidal ferric hydroxide, the volume of the mixture colloid + electrolyte being kept constant throughout.

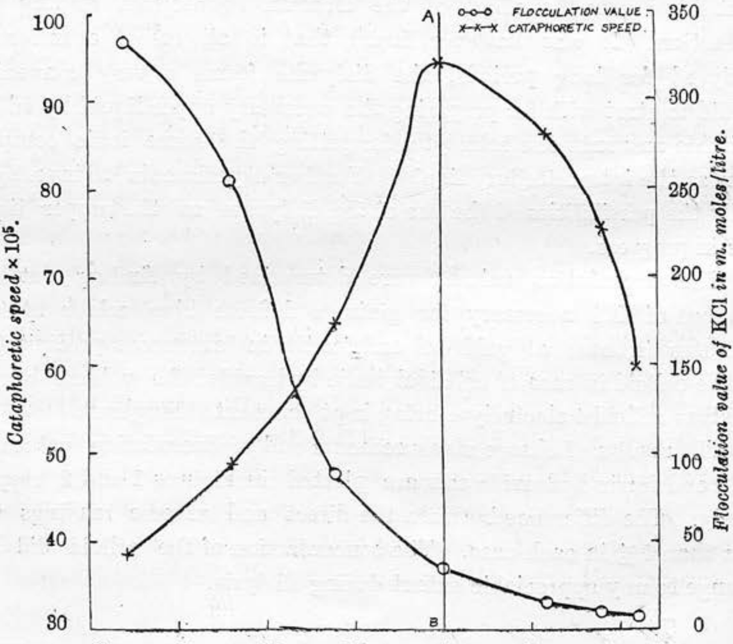
The results of charge measurements and of flocculation values of gold and ferric hydroxide sols are plotted in Figures 1 and 2 respectively. The difference between the direct and reverse readings was less than 5% in each case. The concentration of the colloid did not change to any appreciable extent during dialysis.

FIG. 1



O-O-O FLOCCULATION VALUE
X-X-X CATAPHORETIC SPEED
Cataphoretic speed × 10⁵.
180
160
140
120
100
80
60
40
Flocculation value of KCl in m. moles/ litre.
20
18
16
14
12
10
8
6
0
5
10
15
20
25
30
Days dialysed.

FIG. 2.



A
B
O-O-O FLOCCULATION VALUE
X-X-X CATAPHORETIC SPEED.
Cataphoretic speed × 10⁵.
100
90
80
70
60
50
40
30
Flocculation value of KCl in m. moles/litre.
350
300
250
200
150
100
50
0
0
5
10
15
20
25
30
32
Days dialysed.

Discussion.

From Fig. 1 it is seen that in the case of gold sol both charge (assuming that the rate of migration represents the density of the charge) and flocculation value behave similarly on subjecting the colloid to dialysis; they first increase with the progress of dialysis, reach a maximum and then beign to decrease simultaneously. In the case of ferric hydroxide sol (Fig. 2) although with the progress of dialysis the charge first increases and then decreases, the flocculation value continuously decreases.

The initial increase in charge with the progress of dialysis might be due to the following effect.

We have observed that the cataphoretic speed of colloidal gold and of ferric hydroxide first increases and then decreases on addition of small increasing amounts of KOH and of HCl and $FeCl_3$ respectively (unpublished results). This is due to " preferential " adsorption of the similarly charged ions in the beginning, the word " preferential " indicating that the ions are adsorbed in the inner sheet of the double layer. The amounts of stabilising ions (OH ion in case of gold sol and H and Fe ions in case of ferric hydoxide sol) in the sol continuously decreases with the progress of dialysis. The process of dialysis can be taken as the reverse of the above process, the amounts of the stabilising agent initially present in the sol being appreciably more than what will correspond to the maximum in the cataphoretic speed-concentration curve of the colloid with the particular electrolyte and therefore with the progress of dialysis the charge on the colloid will first increase and then decrease (*cf.* Freundlich, *loc. cit.*). On extreme dialysis the colloid will coagulate due to the removal of the stabilising ions from the double layer. It is therefore likely that various colloidal solutions when subjected to dialysis might show a first increase and then a decrease or a continuous decrease in the cataphoretic speed according to whether the amount of stabilising agent is more or equal to or less than what will correspond to the maximum in the cataphoretic speed-concentration curve of the sols with particular electrolytes.

The continuous decrease in the flocculation value in the case of ferric hydroxide sol, instead of an increase first and decrease thereafter as in the case of the cataphoretic speed, can be due to either or both the following effects:

(1) Rona and Michaelis (*Biochem. Z.*, 1919, **97**, 85) have found that the amount of H ion adsorbed by charcoal was greater in the presence of potassium chloride than without it and that it reached a maximum with increasing amounts of potassium chloride (*cf.* Parks and Bartlett, *J. Amer. Chem. Soc.*, 1927, **49**, 1698). Mukherjee, Choudhury and Rai Choudhury (*loc. cit.*) have found that the charge on colloidal arsenious sulphide in the presence of small amounts of an electrolyte increased on the addition of another electrolyte having a common coagulating ion but a different similarly charged ion. On the addition of KCl the colloid can be said to be under the influence of a mixture of electrolytes ($KCl+HCl+FeCl_3$) and therefore if we presume that on its addition more H and Fe ions are adsorbed in the inner sheet of the double layer, the charge on the colloid will also increase and a larger amount of potassium chloride will be required to coagulate the sol. With the progress of dialysis, the concentration of intermicellary HCl and $FeCl_3$ decreases and the charge on the particles increases. If KCl is now added the increase in the adsorption of H and Fe ions may not be so much as to raise the final charge on the particles to the value which would obtain in the case of a sol dialysed for a shorter period. (Measurements of cataphoretic speed of colloidal solution of ferric hydroxide, dialysed to different extents, in the presence of varying amounts of HCl and KCl as well as HCl+KCl indicate that the adsorption of H ions does increase under certain circumstances in the presence of KCl—unpublished results.) If this be the case a smaller amount of the electrolyte will be required to coagulate the dialysed sol inspite of the higher initial charge on its particles. This mechanism will go on till the maximum in the cataphoretic speed-dialysis curve is reached. After the maximum (the portion of the curve to the right of line AB in Fig. 2) as the charge on the colloid continuously decreases with further progress of dialysis progressively smaller amounts of KCl will be required to coagulate the sol.

In the case of the gold sol the stability and charge showed a similar behaviour even during the period when the charge increased because the amount of electrolytes initially present in the intermicellary liquid (KOH and KCl) being very small, addition of KCl to the colloid may not have increased the adsorption of either or both OH and Cl ions in the inner sheet of the double layer as in the case of ferric hydroxide which contains appreciable amounts of HCl and $FeCl_3$ in the beginning. In fact we have observed that charge on colloidal gold does not increase in the presence of small amounts of KCl as it does in the case of ferric hydroxide (unpublished results).

(2) As the charge on ferric hydroxide first increases on the addition of KCl, a greater amount of electrolyte will be required to coagulate the sol even when the charge on the colloid is initially small. We have observed that this effect becomes less marked as the purity of the colloid increases (unpublished results).

Conclusions.

From the foregoing considerations it would appear that there is nothing to warrant the view that charge and stability are not related with each other. The abnormal behaviour shown in any case can be traced to the part played by the similarly charged ions. It must, however, be pointed out at the same time that it is not safe to draw conclusions about the charge on colloidal particles from the results of stability as determined by flocculation values although in some cases flocculation values may serve a useful criterion for the same.

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The Importance of Dialysis in Colloid Chemistry. Behaviour of Colloids towards Electrolytes and Non-electrolytes with Progress of Dialysis.

BY

B. N. DESAI.

CALCUTTA UNIVERSITY PRESS
1933

The Importance of Dialysis in Colloid Chemistry. Behaviour of Colloids towards Electrolytes and Non-electrolytes with Progress of Dialysis.

By B. N. Desai.

On going through the rapidly increasing literature of colloid chemistry one comes across cases where different investigators trying the same experiments on the same colloid and with the same electrolytes have not been able to get similar results. No serious attempts seem to have been made till recently to find out the causes of this peculiar behaviour of colloids. It has been recognised that generally a colloid becomes more sensitive to electrolytes on subjecting it to dialysis. Dialysis has been utilised since the time of Graham for freeing a colloidal solution from the "impurities" necessarily introduced into it at the time of preparation, *viz.*, the peptising agent and the other electrolytes formed as a result of double decomposition. The purpose of this article is to summarise some recent work on the behaviour of colloids with the progress of dialysis towards electrolytes and non-electrolytes.

Dhar and collaborators (*J. Phys. Chem.*, 1922, **26**, 70; 1924, **28**, 313; 1925, **29**, 453, 659; *Kolloid Z.*, 1924, **34**, 262; 1925, **36**, 129), from their extensive work with different colloids came to the conclusion that the dilution rule, *viz.*, that the greater the concentration of a colloid the greater is the amount of an electrolyte necessary for coagulating it, is valid only for those colloids which are not capable of adsorbing appreciably from the coagulating electrolytes the ion carrying the same charge as the colloid. On the other hand, those colloids which appreciably adsorb the ion carrying the same charge as the colloid do not follow the general dilution rule when coagulated by *monovalent* coagulating ions. They have thus divided sols into two water-tight compartments. Dhar and Ghosh (*J. Phys. Chem.*, 1927, **31**, 187), have shown that a fairly pure sample of prussian blue sol is abnormal to the dilution rule when coagulated by KCl and that the abnormality is increased by adding $K_4Fe(CN)_6$ to the sol before coagulation. Weiser and Nicholas (*J. Phys. Chem.*, 1921, **25**, 742), have, however, observed that the prussian blue sol behaved normally when coagulated by KCl. These results of Dhar and Ghosh and Weiser and Nicholas on the prussian blue sol, if considered critically indicate that the initial presence of different amounts of $K_4Fe(CN)_6$ in their sols might be responsible for the different behaviour of the sol with KCl in the two cases. Desai (*Koll. Chem. Beih.*, 1928, **26**, 384), has shown that colloidal solution of thorium hydroxide can be made to show normal or abnormal behaviour to the dilution rule when it is coagulated by electroytes containing monovalent coagulating ion by subjecting the colloid to dialysis for different periods. These observations do show that it is erroneous to classify colloids into two divisions according to their behaviour towards the dilution rule, for a suitable adjustment of the amount of the peptising agent (by subjecting it to dialysis) seems to make a colloid behave normally or abnormally as in the case of colloidal thorium hydroxide.

According to the Schulze-Hardy law, equivalent amounts of different electrolytes with the same oppositely charged ion should coagulate a given sample of the colloid in the same time. Desai (*loc. cit.*) has observed that in the case of colloidal thorium hydroxide an impure sample of the sol (dialysed only for a small period and hence containing appreciable amounts of peptising agent) does not obey the Schulze-Hardy law. This abnormality, however, decreases with the progress of dialysis and a fairly pure sample of the sol (dialysed for a long period) does not show any deviation from the law. It is thus evident that colloidal thorium hydroxide can be made to behave either normally or abnormally to the Schulze-Hardy law by subjecting it to dialysis for different periods.

It has been shown (Desai, *Trans. Faraday Soc.*, 1928, **24**, 181), that the rate of coagulation of colloidal thorium hydroxide in the sensitive range of electrolyte concentration is not a simple reaction as postulated by Smoluchowski (*Physikal. Z.*, 1916, **17**, 557, 583; *Z. Phys. Chem.*, 1917, **92**, 129), but that the nature of the coagulation process is auto-catalytic. The demonstration of the auto-catalytic nature of the coagulation reaction and the appearance of the S-shaped curves, however, depends on various factors, and of these the purity of the colloid is an important factor to be reckoned with. Patel and Desai (*Trans. Faraday Soc.*, 1930, **26**, 128) have shown that the coagulation velocity curves which are obtained with colloidal solution of thorium hydroxide dialysed for a sufficiently long period (and therefore containing only a very small amount of the peptising agent) are not S-shaped at any concentration of an electrolyte even for a concentrated sol.

It is a common belief that the stability of a colloid depends on the charge on its particles and that the greater the charge the greater is the stability. In the case of the gold sol prepared by Zsigmondy's nucleus method, it has been found that both charge and stability as determined by the flocculation value of KCl behave in a similar fashion on subjecting the colloid to dialysis (Freundlich, "*Colloid and Capillary Chemistry*," English Translation, 1926, p. 506; Nabar and Desai, *Nature*, 1931, **127**, 666). With colloidal arsenious sulphide Mukherjee and collaborators (*J. Indian Chem. Soc.*, 1927, **4**, 493),, have observed that the stability is not so directly related to the charge as is generally believed to be. Measurements with colloidal ferric hydroxide have shown that although with the progress of dialysis the charge first increases and then decreases, the flocculation value with KCl shows a continuous decrease (Desai and Barve, *Nature*, 1931, **128**, 907). These results would also seem to show that there is no direct relation between charge and stability.

In a paper which will be published in due course, it is however shown that if proper consideration is given to changes in the adsorption of the similarly charged ions with the progress of dialysis when KCl is added, the initial decrease in the stability of colloidal ferric hydroxide in spite of an increase in the charge can be accounted for satisfactorily.

The results of viscosity measurements of colloids in presence of electrolytes are generally explained on the assumption that the viscosity is related to the charge on the colloid and that the smaller the charge on the colloid the greater will be its viscosity. The results of the viscosity measurements of colloids with the progress of dialysis are also explained on the basis of the same view. No simultaneous measurements of charge and viscosity have however been carried out to test the validity of the above view. Our preliminary results (unpublished) of the measurement of charge and viscosity of colloidal ferric hydroxide have shown that with the progress of dialysis, although the charge first increases and then decreases, the viscosity increases continuously. The explanation of this behaviour will be given in a subsequent paper.

Patel and Desai (*Kolloid Z.*, 1930, **51**, 318), have studied the behaviour of colloidal thorium hydroxide with the progress of dialysis towards non-electrolytes in the presence and absence of electrolytes. They have observed that with the progress of dialysis the sol is more and more easily sensitised by non-electrolytes and that a fairly pure sample of the sol (dialysed for a very long time) can be coagulated by non-electrolytes alone.

From the foregoing it would appear that a colloidal solution of any substance can probably show different behaviours towards electrolytes and non-electrolytes by subjecting it to dialysis for different periods. Dialysis removes along with other substances also the peptising agent and the initial presence of the latter in varying amounts can probably make a colloid show either a simple or complicated behaviour. It is, therefore, necessary that results of coagulation should always be accompanied with a statement about the purity of the sample of the colloid which has been investigated.

Summary.

Several cases of apparent abnormality of colloids in their behaviour towards electrolytes and non-electrolytes are considered. Experiments on colloids dialysed for different periods show that the apparent inconsistencies can be explained as being due to the initial presence in the colloids of varying amounts of the peptising electrolytes.

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19p

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A NOTE ON THE EXISTENCE OF CRITICAL POTENTIAL CHARACTERISTIC OF COAGULATION OF A COLLOID BY AN ELECTROLYTE

By

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The widespread opinion, first put forward by Hardy (*Proc. Roy. Soc.* Vol. 66,110,1900), that coagulation begins only when colloid particles are completely discharged and the iso-electric point is reached, has been found to be erroneous by Powis (*Zeitschr. f. physik. Chemie,* Vol. 89,186,1915). He determined, by means of cataphoretic experiments, the charge upon oil drops at various concentrations of the coagulator and found that coagulation begins as soon as the electro-kinetic potential or the electric charge falls below a certain absolute value. This value of the electro-kinetic potential, at which coagulation first begins, has been termed by Freundlich the "first critical potential" and is said to have the same characteristic value for any particular sol when coagulated with salts having coagulating ions of different valencies. Burton's cataphoretic experiments (*Phil. Mag.,* Vol. 17, 583, 1909) with positively charged copper oxide sol showed a similar behaviour. The results of Kruyt, Roodvoets and van der Willigen (*Fourth Colloid Symposium,* 1926, pp. 304-310) and of Kruyt and van der Willigen (*Z. physikal Chem.,* Vol. 130,170, 1927) have shown that their results also support Powis' theory of critical potential.

Freundlich has utilised the existence of the first critical potential to explain the phenomenon of "slow coagulation". According to him slow coagulation begins after the first critical potential value is reached. The slow coagulation passes into rapid coagulation when the value of the potential difference becomes zero or the iso-electric point is reached (Freundlich's second critical potential). In the region of slow coagulation all collisions between the particles do not bring about coalescence. Only those collisions are successful in which the velocity of the particles exceeds a certain value. With the lowering of the value of the potential difference below the critical value, the repulsive forces between the particles become less and less and ultimately disappear at the iso-electric point. Therefore at the iso-electric point all collisions will be successful in spite of the fact that the velocity with which the particles move might be very small in some cases. Between the value of the critical potential and the iso-electric point when the charge has not been completely neutralised, the velocity of the particles must reach a certain value in order to overcome the repulsive forces between them. Desai (*Trans. Faraday Soc.*, Vol. 24,181,1928) has discussed the reasons of the non-observance of the slow coagulation region by many investigators and shown that besides the suitability of the methods employed to measure the rate of coagulation, the purity and the concentration of the colloid, the concentration of the electrolyte and the valency of the coagulating ion are important factors to be reckoned with which govern the appearance of the 'S' shaped curves of the coagulation velocity and the auto-catalytic nature of the coagulation process (Patel and Desai, *Trans. Faraday Soc.*,Vol. 26,128,1930).

The existence of the critical potential has been recently called into question by Mukherjee and co-workers. On the basis of some of their investigations Mukherjee, Roy Chaudhari and Rao (*Journ. Indian Chem. Soc.*, Vol. 5, 697, 1928; also cf. Mukherjee and Chaudhari, ibid. Vol. 2, 296, 1925 and Mukherjee, Chaudhari and Rai Chaudhari, ibid. Vol. 4, 493, 1927) have concluded that there is no definite critical potential characteristic of the coagulation of a colloid by an electrolyte as has been suggested by Powis (loc. cit.). Experiments of Powis (*Journ. Chem. Soc.*, Vol. 109, 734, 1916) upon As_2S_3 sols showed that although the value of the critical potential with $BaCl_2$,$AlCl_3$ and $Th(No_3)_4$ was almost the same, the same was not found to be the case with salts having univalent cations—HCl and KCl. Powis ascribed this behaviour in the case of univalent cations to the higher concentration of the sol employed and to the salting out effect of the potassium salt at a higher potential. According to Freundlich (*Colloid and Capillary Chemistry*, Eng. Translation, 1926, p. 419) the abnormality observed by Powis might be connected with hydration and that markedly electrocratic sols will show a uniform behaviour not only with multivalent coagulating ions but also with univalent coagulating ions.

It is considered that it is not only the electrocratic nature of the sol which will decide strict adherence to the idea of critical potential but also the nature of the stabilising ion and the valency of the coagulating ion of the electrolyte employed in bringing about coagulation. It is generally observed that with electrolytes having a univalent coagulating ion the cataphoretic speed first increases and reaches a maximum value on the addition of small amounts of an electrolyte, and then decreases on the addition of further larger amounts of the electrolyte. The initial increase in the cataphoretic speed on the addition of an electrolyte is due to the "preferential" adsorption of the similarly charged ion (the word "preferential" is used to show that the ion goes to the inner side—nearest to the particle—of the double layer). The value of the maxima in the cataphoretic speed—concentration curve with different electrolytes with the same univalent coagulating ion but different similarly charged ions will not be the same due to a difference in the adsorbability of those ions. With electrolytes containing polyvalent coagulating ions the initial increase in the cataphoretic speed will not be noticed at all because of their very marked coagulating power, the preferential adsorption of the similarly charged ions being not allowed to take place. The value of the maxima being different with different similarly charged ions and being obtained at different equivalent concentrations of the electrolytes, it is possible that the sol may not begin to coagulate at the same value of the potential. For this will be equivalent to starting with sols having different initial charges and with intermicellary liquids of different compositions. The changes in the intermicellary liquid will considerably modify the behaviour of the sols with regard to the value of the critical potential at which they may begin to coagulate and will not allow them to coagulate with the same equivalent amounts of different electrolytes.

Some results of cataphoretic speed measurements which are being carried on in our laboratory have shown that the adsorption of the similarly charged ions being negligible in the case of a fairly pure sample of the colloid (dialysed for a long period and hence containing only traces of the peptising agent), the value of the critical potential at which the coagulation begins may be the same even in the case of electrolytes with univalent coagulating ions but with different similarly charged ions.

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INFLUENCE OF ACIDITY OF GELATINE SOLUTION ON ITS INHIBITIVE POWER AND ON THE SOLUBILITY OF SILVER CHROMATE

By

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It has been shown by various workers (Williams and Mackenzie, *J. Chem. Soc.*, Vol. 117, 844, 1920 ; Bolam and Mackenzie, *Trans. Faraday Soc.*, Vol. 22, 151, 162, 1926 ; Hedges and Henley, *J. Chem. Soc.*, 2714, 1928) that unhydrolysed gelatine has to a very marked degree the power of retarding the appearance of red colour in a mixture of aqueous solutions of silver nitrate and potassium chromate. Electromotive force and conductivity data (Bolam and Mackenzie, loc. cit.; also see Desai and Nabar, *Trans. Faraday Soc.*, Vol. 28, 449, 1932) indicate that prior to the change from yellow to red the silver chromate is in solution and not in the colloidal state (Chatterjee and Dhar, *Trans. Faraday Soc.*, Vol. 23, 23, 1927 ; *J. Indian Chem. Soc.*, Vol. 5, 175, 1928). Desai and Nabar (*J. Indian Chem. Soc.*, Vol. 9, 141, 1932) have studied the effect of addition of acetic acid to gelatine solution on the Liesegang rings of silver chromate and found that an increase in the acidity of gelatine is accompanied by a decrease (i) in the time after which the first ring appears, (ii) in the distances between the same successive rings and (iii) in the number of rings which can be obtained. In what follows the results obtained on the influence of acidity of gelatine solution (addition of acetic acid) on its inhibitive power and on the solubility of silver chromate have been presented.

The amount of silver ion in the chromate mixtures was determined electrometrically as before (Desai and Nabar, *Trans. Faraday Soc.*, Vol. 28, 449, 1932). In Table I (on p. 29) are given the results obtained with a saturated solution of silver chromate under different conditions.

From this Table we find that the concentration of *Ag* ion in a saturated solution of silver chromate is not increased by a slight increase in the acidity of water or of gelatine (by the addition of acetic acid) as shown by the constancy of the e. m. f.

e. m. f. measurements of the mixture N/100 silver chromate + N/100 potassium chromate + gelatine (to which varying amounts of

TABLE I

Saturated solution of silver chromate (Temp. 30°C) in	Observed e. m. f. volts.
Conductivity water	0·8575
3 per cent gelatine solution. $p_H = 5{\cdot}15$	0·8582
Water $p_H = 5{\cdot}15$ (addition of acetic acid)	0·8569
3 per cent gelatine pH = 5·00 (Addition of acetic acid)	0·8566

acetic acid were added) were carried out and the results of these experiments are given in Table II.

TABLE II

Gelatine having p_H.	Initial e. m. f. of the system volts	Calculated e. m. f. volts	Remarks
5·15	0·9185	0·9234	Precipitate appears after 98 minutes.
5·10	0·9187		Precipitate does not appear even after 8 days; the mixture remains clear yellow.
5·00	0·9181		Do

The results indicate that addition of acetic acid to gelatine markedly increases its inhibitive power.

If we consider together the results given in Tables I and II, we find that although slight changes in p_H of gelatine do not affect the silver ion concentration in a saturated solution of silver chromate in gelatine, they markedly affect its inhibitive power and that the smaller the p_H of gelatine, the greater is its inhibitive power.

In Table III are given the amounts of silver chromate which can remain in ionic condition (clear yellow mixture of 3 per cent unhydrolysed gelatine and equivalent amounts of silver nitrate and potassium chromate before the appearance of the red precipitate) for 98 minutes in gelatine having different p_H.

TABLE III

p_H of gelatine	Amount of silver chromate which can remain in ionic condition for 98 minutes
5·15 (gelatine as such)	$2{\cdot}87 \times 10^{-3}$N
5·10 (gelatine and acetic acid)	$4{\cdot}10 \times 10^{-3}$N
5·00 (gelatine and more acetic acid)	$5{\cdot}92 \times 10^{-3}$N

It will be seen from the results that the amount of silver chromate which can be kept in ionic condition or the degree of supersaturation increases with a decrease in the p_H of gelatine or with an increase in its inhibitive power (Table II).

The results given in Tables I and III would appear to be inconsistent. It is, however, not so, for the effect due to the initial presence of the acid before the solutions are mixed and the precipitate of silver chromate comes out will not be the same as the effect produced when acid is added after the precipitate has already appeared.

These results show that (i) the concentration of silver ion in a saturated solution of silver chromate does not increase due to slight changes in the acidity of water or of gelatine (addition of acetic acid), (ii) the inhibitive power of gelatine increases with a decrease of its p_H and (iii) a sample of gelatine with lower p_H can keep a greater amount of silver chromate in ionic condition than another sample with higher p_H.

22 P

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS. PART I. COLLOIDAL FERRIC HYDROXIDE.

By B. N. Desai and S. K. Borkar.

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Dialysis has been utilised since the time of Graham for freeing a colloidal solution from the impurities necessarily introduced into it at the time of its preparation, *viz.*, the peptising agent and the other electrolytes formed as a result of double decomposition. The importance of the influence of dialysis on the various properties of colloidal solutions has, however, not been generally realised by colloid chemists. No systematic investigations seem to have been made to determine simultaneously the relation between the charge on the particles and the stability, viscosity and other related properties of colloidal solutions dialysed and diluted to different extents. The present investigation was undertaken with a view to study extensively several properties of colloidal ferric hydroxide with reference to the changes in charge on the colloidal particles.

Experimental.

Preparation of Ferric Hydroxide Sol.—100 gm. of hydrous ferric chloride were dissolved in 300 c.c. of water. The sol was prepared in instalments of 500 c.c. About 50 c.c. of ferric chloride solution were added to 500 c.c. of boiling distilled water drop by drop, the mixture being stirred all the time. The resulting brown red sol was further boiled for half an hour.

Dialysis of the Sol.—The sol was dialysed in a parchment paper bag which was previously kept soaked in distilled water for 3 to 4 days. The outer water was changed twice a day. The amount of ferric chloride in the dialysate decreased with progress of dialysis. The amount of colloidal ferric hydroxide was estimated from time to time by adding potassium sulphate in excess to the sol, the resulting coagulum being filtered, washed, dried and weighed as Fe_2O_3. The concentration of the colloid is expressed in gms. of Fe_2O_3 per litre. Samples of sol were withdrawn after different periods of dialysis for experiments on the variation of its properties with progress of dialysis.

Measurements of Cataphoretic Speed.—The cataphoretic speed was measured by Mukherjee's improved U-tube method.[1] In order to get reliable results, it is necessary, as pointed out by Mukherjee,[1] to have the upper liquid such that the direct and reverse boundary movement as well as the potential gradient before and after the experiment will be the same. Desai, Nabar and Barve [2] have shown that dialysate can be used as a satisfactory upper liquid under certain circumstances in the case of colloidal ferric hydroxide. In the present investigation the upper liquid was prepared by making the dialysate equiconducting with the sol by the addition of a suitable amount of concentrated ferric chloride solution. In all the cases the upper liquid so prepared was found to satisfy the requirements of the constancy of potential gradient both before and after the experiment as well as a close agreement between the direct and reverse movements. The electrodes were put in the side bulbs and not in the limbs of the U-tube in order to avoid the disturbing effect of electrolysis on the sharpness of the boundary. In the results given in this paper, the difference between the direct and reverse movements was never found to exceed 5 per cent., it being about 3 per cent. in most of the cases.

40 c.c. of the colloid required in each experiment were made up by adding 30 c.c. of the colloid and 10 c.c. of water (distilled) or water + electrolyte together. In the experiments for studying the effect of electrolytes on the colloid, the electrolytes were also added to the upper liquid so as to get the same ionic environment. In dilution experiments, sols of different concentrations were prepared by adding requisite amounts of distilled water to the colloid.

As considerable time was required to complete various kinds of measurements with a sample of the sol dialysed for a particular period, the effect of ageing on the cataphoretic speed was also studied in some cases. On repeating some of the experiments after a period of more than eight weeks, it was found possible to reproduce the results within the limits of experimental error. In all the tables of results, the cataphoretic speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre $\times 10^5$. The concentration of the electrolytes added is expressed in millimoles per litre.

Determination of Stability.—The stability was determined by finding out the amount of KCl necessary to give instantaneous precipitation

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[1] Mukherjee, *Proc. Roy. Soc.*, **103A**, 102, 1923; Mukherjee, Choudhury and Rai Choudhury, *J. Indian Chem. Soc.*, **4**, 493, 1927; Mukherjee, Rai Choudhury and Bhattacharya, *ibid.*, **5**, 735, 1928; Mukherjee, Rai Choudhury and Biswas, *ibid.*, **8**, 373, 1931; Mukherjee, *J. Physic. Chem.*, **36**, 593, 1932.

[2] Desai, Nabar and Barve, *J. Indian Chem. Soc.*, **9**, 463, 1932.

of the colloid (flocculation values), the volume of the mixture colloid + electrolyte being kept constant throughout (total volume 20 c.c. = 10 c.c. colloid + electrolyte + water). The flocculation values are expressed in millimoles per litre.

Viscosity Measurements.—Viscosity was determined by using an Ostwald viscometer. The same volume (10 c.c.) of the colloid or the mixture colloid + electrolyte was taken in all the experiments. The time of flow was measured by means of a stop watch reading to one-tenth of a second. The results have been expressed in terms of the viscosity of distilled water at the temperature of the experiment as unity.

Temperature of Experiments.—All the measurements of cataphoretic speed and viscosity were made at a temperature of 30° C. For this purpose, an electrically controlled thermostat with two opposite glass sides was used. The temperature could be maintained correct to within ± 0·1° C.

Results and Discussion.

(*a*) Cataphoretic Speed and Stability Determinations of Ferric Hydroxide with the Progress of Dialysis.

The results of cataphoretic speed and stability with the progress of dialysis are given in Table I.

For facility of discussion, the following results have been plotted in Fig. 1.* It will be seen that the charge on the particles, assuming that it is represented by the rate of migration, in colloidal ferric hydroxide when it is subjected to dialysis first increases and reaches a maximum after which it gradually decreases. The flocculation value or the stability of the sol, on the other hand, continuously decreases with the progress of dialysis. These results are similar to those obtained by Desai, Nabar and Barve.[2] The values of cataphoretic speed and stability for sols dialysed for different periods given here are not the same as those obtained by Desai [2] with ferric hydroxide sol dialysed for the same periods probably because of the different rates of dialysis in the two cases. The nature of the curves is, however, the same.

TABLE I.

Period of Dialysis.	Concentration of Colloid.	Cataphoretic Speed.	Flocculation Value.
3 days	3·0	27·24	550
6 ,,	2·9	43·80	375
9 ,,	2·9	55·65	250
12 ,,	2·9	71·85	100
15 ,,	2·9	68·69	25
18 ,,	2·9	63·84	15
21 ,,	2·9	51·17	11

Desai [2] has explained the initial increase in charge with the progress of dialysis as due to " preferential adsorption " (the word preferential indicating that the ions are adsorbed in the inner sheet of the double layer) of the similarly charged ions and the subsequent decrease in charge as due to a continuous decrease of the amount of the peptising agent. The continuous decrease in the flocculation value with the progress of dialysis has been explained on the assumption of certain changes in the preferential adsorption of H and Fe ions in the presence of KCl. No

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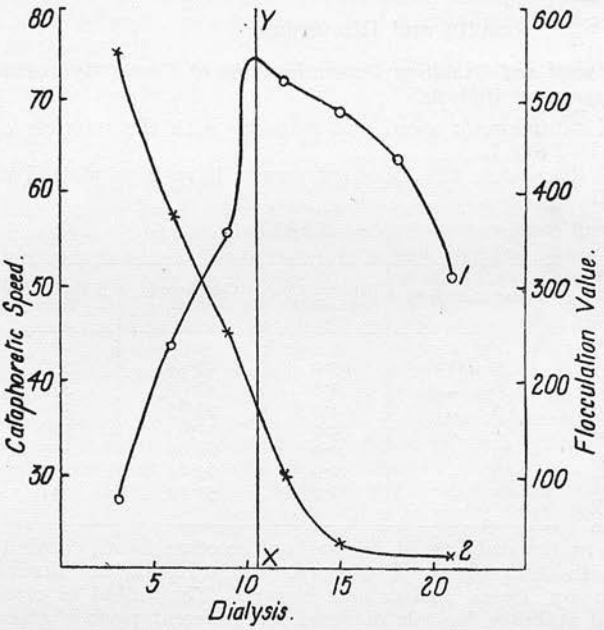
* As shown in section (*c*) the maximum value of cataphoretic speed with the progress of dialysis must have occurred after a dialysis of nine days and before twelve days, the value of the maximum cataphoretic speed being greater than 71·85. It is because of this reasoning that in Fig. 1 the maximum value of cataphoretic speed is shown to have occurred on the tenth to eleventh day of dialysis.

experiments have, however, been performed to test the validity of the above assumptions. In the following tables are given the measurements of cataphoretic speed in the presence of HCl, KCl and HCl + KCl of colloidal ferric hydroxide dialysed to different extents.

It will be seen from Table II. that the charge on colloidal particles continuously increases up to a certain stage on adding small increasing amounts of HCl and KCl. On the addition of larger amounts of electrolytes, however, the charge begins to decrease. The initial increase in the cataphoretic speed on the addition of an electrolyte is due to preferential adsorption of the similarly charged ion, while the subsequent decrease is due to the preferential adsorption of the oppositely charged ion. Also in all the cases the initial increase in charge is greater with HCl than with KCl. This is probably due to greater adsorption of H ion than K ion in conformity with the strong peptising action of the former ion. Again in all the cases the concentration of the electrolyte at which the maximum value of charge is reached is greater in the case of HCl than of KCl. This is what one should expect in view of greater adsorbability of H ion than K ion which will not allow the preferential adsorption of the oppositely charged ion to be noticeable even when larger amounts of HCl than KCl are added.



1. Cataphoretic speed—dialysis curve.
2. Flocculation value—dialysis curve.

FIG. 1.

With the progress of dialysis, the amounts of stabilising ions, H and Fe, in the sol continuously decrease as both HCl and $FeCl_3$ pass out in the dialysate. From Table I. it will also be seen that the concentration of the colloid does not change to any appreciable extent with the progress of dialysis. Hence the process of dialysis might be taken roughly as the reverse of the process of adding small increasing amounts of electrolytes to the colloid. If this analogy is correct, one would expect that with the progress of dialysis, the charge on the colloid will first increase and then decrease. On extreme dialysis, the colloid will coagulate due to the removal of the stabilising agent from the double layer. Thus a colloid solution of ferric hydroxide when subjected to dialysis will show first an increase and then a decrease or a continuous decrease in the cataphoretic speed according as whether the amount of HCl and $FeCl_3$ initially present is more, equal to or less than what would correspond to the maximum in the cataphoretic speed-concentration curve of the sol with those electro-

TABLE II.—Sol B. Concentration 2·98 gms./litre Fe_2O_3 on the Fourth Day of Dialysis.

Period of Dialysis of Sol.	Concentration of Electrolyte.		Cataphoretic Speed.
(1) 4 days	HCl †	0·000	40·92
		0·013	41·88
		0·025	44·86
		0·037	50·42
		0·050	54·49*
		0·063	48·82
		0·075	47·96
		0·125	44·23
		0·250	41·67
	KCl	0·000	40·92
		0·013	44·13
		0·019	47·54
		0·025	50·75*
		0·037	48·18
		0·050	46·69
		0·125	44·66
		0·250	37·12
	Initial HCl=0·025;		
	KCl	0·000	44·86
		0·025	45·61
		0·037	46·47*
		0·050	46·26
		0·075	43·25
	Initial HCl=0·125;		
	KCl	0·000	44·23
		0·013	46·79
		0·025	47·01
		0·037	47·64*
		0·050	44·66
(2) 8 days	HCl	0·000	62·82
		0·013	65·06
		0·019	67·30*
		0·025	67·10
		0·037	64·21
		0·050	63·66
		0·125	56·72
	KCl	0·000	62·82
		0·009	65·49*
		0·013	64·10
		0·025	61·32
		0·050	53·95
		0·125	52·77
	Initial HCl=0·013;		
	KCl	0·000	65·06
		0·013	65·82
		0·019	66·13
		0·025	66·56*
		0·037	64·10
		0·050	62·92
	Initial HCl=0·050;		
	KCl	0·000	63·66
		0·006	64·21
		0·013	65·60
		0·019	66·56*
		0·025	64·85
		0·050	58·87
(3) 18 days	HCl	0·000	52·35
		0·013	54·38
		00·19	58·01
		0·025	58·76
		·0037	61·51*
		0·050	57·27
		0·075	55·12
		0·123	51·92
	KCl	0·000	52·35
		0·013	55·24
		0·019	55·98
		0·025	56·52*
		0·037	54·17
		0·050	49·15
	Initial HCl=0·013;		
	KCl	0·000	54·38
		0·006	55·88
		0·013	59·82
		0·025	64·10
		0·037	64·95*
		0·050	60·15
		0·075	56·62
	Initial HCl=0·050;		
	KCl	0·000	57·27
		0·025	57·90
		0·037	58·43*
		0·050	53·20
(4) 25 days	HCl	0·000	49·57
		0·013	52·88
		0·025	54·49
		0·050	56·62
		0·063	57·58*
		0·075	53·31
		0·130	51·48
	KCl	0·000	49·57
		0·013	53·10
		0·025	54·70
		0·037	55·55*
		0·050	53·63
		0·125	52·46
	Initial HCl=0·013;		
	KCl	0·000	52·88
		0·013	54·49
		0·025	58·22*
		0·037	56·10
		0·050	53·50
	Initial HCl=0·075;		
	KCl	0·000	53·31
		0·013	59·19
		0·019	65·27*
		0·025	63·66
		0·037	59·07
		0·050	55·01

* Indicates the highest value of cataphoretic speed obtained in each case.

† On the addition of small increasing amounts of $FeCl_3$ to colloidal ferric hydroxide, it was also found that in all the cases the cataphoretic speed first increases, reaches a maximum and begins to decrease thereafter.

lytes. These results thus fully support the assumption made by Desai[2] in explaining changes in charge on dialysis.

It should, however, be pointed out that the process of dialysis is not exactly the reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid. For if it were so one would expect that with the samples of the sol dialysed for periods shorter than what correspond to the maximum in the cataphoretic speed-dialysis curve and containing amounts of the peptising electrolyte more than what correspond to the maximum in the cataphoretic speed-concentration curve, the cataphoretic speed should continuously decrease on adding small increasing amounts of the peptising electrolyte. It will, however, be seen from Table II. that with such samples of the sol also the cataphoretic speed has increased at first on the addition of small increasing amounts of the peptising electrolyte. As shown later in this section the cataphoretic speed also increases on the addition of small increasing amounts of KCl to the sol even when an amount of HCl more than what corresponds to the maximum in the cataphoretic speed concentration curve with it (HCl) has been added to the sol in the beginning. The initial increase in the cataphoretic speed observed in the above cases is apparently due to an increase in the preferential adsorption of the similarly charged ions in the presence of the peptising or other electrolyte which has been added subsequently.

In Table III. (this table is constructed from data given in Table II.) are given the values of the maximum cataphoretic speed obtained in presence of HCl, KCl and HCl + KCl in case of sols dialysed to different extents.

TABLE III.

Period of Dialysis.	Electrolyte.	Concentration at which Maximum Value of Cataphoretic Speed is Obtained.	Initial Amount of HCl Added.	Maximum Value of Cataphoretic Speed.
4 days	HCl	0·050	—	54·49
	KCl	0·025	—	50·75
	HCl + KCl	—	0·025	46·47
	HCl + KCl	—	0·125	47·64
8 days	HCl	0·019	—	67·30
	KCl	0·009	—	65·49
	HCl + KCl	—	0·013	66·56
	HCl + KCl	—	0·050	66·56
18 days	HCl	0·037	—	61·51
	KCl	0·025	—	56·52
	HCl KCl	—	0·013	64·95
	HCl KCl	—	0·050	58·43
25 days	HCl	0·063	—	57·58
	KCl	0·037	—	55·55
	HCl + KCl	—	0·013	58·22
	HCl + KCl	—	0·075	65·27

The following conclusions can be drawn from the above table :—

(1) In all the cases except for the sol dialysed for four days, the maximum value of the cataphoretic speed is higher in the presence of HCl + KCl than with KCl alone.

(2) For sol dialysed for twenty-five days, the maximum value of the cataphoretic speed obtained in the presence of HCl + KCl is higher than with either HCl or KCl alone.

(3) (*a*) When an amount of HCl more than what corresponds to the maximum value of cataphoretic speed with it is initially added to the sol, the cataphoretic speed increases in the beginning on adding KCl to the mixture although one would ordinarily expect that in such cases the speed should continuously decrease on the addition of more and more of the same or other electrolyte. (*b*) The difference between the maximum value of cataphoretic speed in the presence of HCl + KCl and of KCl alone seems to be increasing with the progress of dialysis of the sol in all the cases—the initial amount of HCl added being more than what corresponds to the maximum in the cataphoretic speed-concentration curve of the colloid with HCl. There does not appear any regular behaviour in cases when the initial amount of HCl added is less than what corresponds to the maximum in the cataphoretic speed-concentration curve.

These results support the assumption made by Desai,[2] *viz.*, that on the addition of KCl the preferential adsorption of the similarly charged ions will increase, in explaining the continuous decrease in the flocculation value with the progress of dialysis in spite of a first increase and then a decrease in the cataphoretic speed. Thus we find from 3 (*a*) that the preferential adsorption of H ion increases in the presence of KCl. From 3 (*b*) above, it will further appear that the preferential adsorption of the similarly charged ion is increased in the presence of KCl when the colloid initially contains the amount of HCl more than what corresponds to the maximum in the cataphoretic speed-concentration curve. As stated before, since electrolytes are removed by dialysis, this process can be considered roughly as the reverse of the process of adding small increasing amounts of electrolyte to the colloid. Therefore the other assumption of Desai,[2] *viz.*, that as with the progress of dialysis the concentration of the intermicellary HCl and $FeCl_3$ decreases the preferential adsorption of H and Fe ions in the presence of KCl will also decrease, is supported to a certain extent by these results.

As mentioned by Desai, Nabar and Barve [2] on p. 469 of their paper, it was observed in some preliminary experiments that the initial preferential adsorption of the similarly charged ion decreases with the progress of dialysis. Subsequent experiments did not confirm the previous results. It will also be seen from results given in Table II. that there is no regular decrease in the preferential adsorption of the similarly charged ion with the progress of dialysis.

There are probably other factors besides those mentioned above which should also be considered to explain the abnormal behaviour for the portion of the curves to the left of the line XY in Fig. 1. In the case of gold sol, it has been observed by Desai [2] that with the progress of dialysis both charge and stability, as determined by the flocculation value with KCl, first increase, reach a maximum after which both begin to decrease simultaneously. In the case of colloidal ferric hydroxide, the influence of hydration—colloidal ferric hydroxide is undoubtedly highly hydrated when compared with colloidal gold—is also partly responsible for its abnormal behaviour. It is well known that the hydrophilic sols require very large amounts of electrolytes for their coagulation. It will be seen from section (*d*) that with the progress of dialysis viscosity of colloidal ferric hydroxide first decreases and then increases. Now if viscosity is taken to indicate the effect of hydration (greater viscosity greater hydration and smaller viscosity smaller hydration), the hydration of colloidal ferric hydroxide can be said to be decreasing in the initial stage of dialysis. If this be the case, then in spite of the charge increasing with the progress of dialysis smaller amounts of electrolytes may be necessary for coagulation. It should, however, be stated that the relation between charge and viscosity is not so simple as will be shown in section (*d*).

Also with the progress of dialysis the size of the particles will to a certain extent continuously increase. It is therefore quite likely that for the portion of the curves to the left of the line XY in Fig. 1, in spite of higher initial charge smaller amounts of electrolytes may be necessary for coagulation. For what is observed in determining flocculation values is the appearance of turbidity and a smaller amount of electrolyte will be required to produce a given degree of turbidity in a given time in the case of a sol which initially contains particles of bigger size than the sol which contains particles of smaller size. In what way the charge will be affected during dialysis due to a change in the size of particles when the concentration of the intermicellary HCl and $FeCl_3$ also continuously changes is difficult to say. This point requires a further investigation.

For the portion of the curves to the right of the line XY in Fig. 1, both charge and flocculation value decrease with further progress of dialysis. If stability is considered as directly related to charge, one would expect that the smaller the charge the smaller will be the amount of an electrolyte necessary for the coagulation of the sol.

It will be clear from the foregoing considerations that in the case of colloidal ferric hydroxide it is not safe to draw conclusions about the charge on colloidal particles from the measurements of stability, as determined from the flocculation values, although in some cases they may afford a correct criterion for the same.

(*b*) Measurements of Cataphoretic Speed from the Point of View of Critical Potential.

The changes in the cataphoretic speed till the coagulation point of the colloid was reached with HCl, KCl, $MgCl_2$, H_2SO_4, K_2SO_4 and $MgSO_4$ at two stages of dialysis—one before the maximum value of charge is reached and the other after it—are given on Table IV.

It will be seen that for both the samples of the sol the initial increase in the cataphoretic speed is greater and occurs at a higher concentration in the case of HCl than with KCl. This is due to greater preferential adsorption of H ion than K ion as stated in section (*a*). It will also be seen that the initial increase in speed is greater in the case of $MgCl_2$ than in the case of KCl. This is probably due to greater adsorption of Mg ion than K ion. One can possibly ascribe the greater adsorption of Mg ion than of K ion to a difference in their valency.[3]

The initial increase in the cataphoretic speed is not obtained in the case of H_2SO_4, K_2SO_4 and $MgSO_4$ when small increasing amounts of these electrolytes are added to the colloid. This is not surprising in view of the fact that SO_4 ion has a very large coagulating power. In these cases the preferential adsorption of the similarly charged ion is not allowed to be noticed at all as in the case of electrolytes containing univalent coagulating ion—SO_4 ion is preferentially adsorbed from the beginning due to its large coagulating power. These results therefore support the view that the preferential adsorption of the similarly charged ion is noticeable only in those cases when the electrolyte contains univalent coagulating ion.[4]

From Table IV. it will be seen that except in the case of HCl, the value of cataphoretic speed at which coagulation begins is almost the same in case of both the samples of the sol although they had different initial cataphoretic speeds—38·16 in the case of sol dialysed for eight days and 53·42 in the case of sol dialysed for twenty-five days. The difference in the stage of dialysis, *i.e.*, whether the sample of the sol refers to the stage before or after the maximum value of charge on dialysis is reached does not appear to affect the value of the critical charge in the case of colloidal ferric hydroxide. It is also interesting to note that although the colloid begins to coagulate at almost the same value of the charge, the amounts of electrolyte necessary to lower the charge to critical value are not the same.

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[3] Desai, *Koll. Chem. Beih.*, **26**, 409, 1928.

[4] *Ibid.*, 384, 1928.

TABLE IV.—SOL C. CONCENTRATION 3·00 GMS./LITRE Fe_2O_3 ON THE EIGHTH DAY OF DIALYSIS

	Sol Dialysed for 8 Days.		Sol Dialysed for 25 Days.	
	Concentration of Electrolyte.	Cataphoretic Speed.	Concentration of Electrolyte.	Cataphoretic Speed.
HCl	0·000	38·16	0·000	53·42
	0·063	43·59	0·013	56·83
	0·094	45·72*	0·019	59·82*
	0·125	44·01	0·037	55·34
	0·250	39·42	0·075	53·84
	0·750	36·11	0·125	47·64
	1·250	35·46	0·250	46·81
	25·000	33·97	1·250	46·15
	150·000	33·12*	2·500	45·72
			25·000	43·48
			50·000	42·20
			100·000	34·82
			125·000	32·58*
KCl	0·000	38·16	0·000	53·42
	0·025	40·60	0·013	57·16*
	0·075	43·55*	0·019	56·40
	0·125	43·45	0·125	45·19
	0·190	41·67	0·250	42·31
	0·250	33·97	1·250	38·57
	0·500	32·48	5·000	28·74
	1·250	32·16	15·000	26·71
	5·000	31·84	25·000	26·50*
	50·000	31·52		
	125·000	28·42*		
$MgCl_2$	0·000	38·16	0·000	53·42
	0·031	39·85	0·019	57·90*
	0·063	42·52	0·025	56·10
	0·125	44·44*	0·125	53·95
	0·250	39·14	0·250	41·13
	0·370	34·72	0·370	34·82
	1·250	31·62	0·500	32·37
	2·500	30·98	0·750	30·12
	25·000	26·93	1·250	25·31*
	50·000	26·50*		
H_2SO_4	0·0000	38·16	0·0000	53·42
	0·0007	37·92	0·0025	50·86
	0·0025	30·45	0·0125	40·60
	0·0250	27·24*	0·0250	32·91
			0·0500	28·31*
K_2SO_4	0·0000	38·16	0·0000	53·42
	0·0007	36·76	0·0025	51·59
	0·0025	35·26	0·0125	38·46
	0·0125	29·59	0·0200	30·98
	0·0250	26·17*	0·0250	27·35*
$MgSO_4$	0·0000	38·16	0·0000	53·42
	0·0007	35·15	0·0025	50·54
	0·0025	32·58	0·0125	38·03
	0·0250	30·98	0·0250	29·06*
	0·0500	28·70*		

* In the case of HCl, KCl and $MgCl_2$ the first asterisk indicates the maximum value of cataphoretic speed obtained and the second asterisk the cataphoretic speed at which the sol begins to coagulate. In the case of H_2SO_4, K_2SO_4 and $MgSO_4$ the asterisk indicates the value of charge at which the sol begins to coagulate.

The higher value of critical charge with HCl than with other electrolytes tried in these investigations is probably due to marked preferential adsorption of H ions. It is, however, to be noted that even in this case the value of the cataphoretic speed at which the coagulation begins is almost the same for the sol dialysed for eight days and twenty-five days and having different initial cataphoretic speed.

Powis [5] working on arsenious sulphide sol found that although there was good agreement in the value of critical potential with electrolyte having multivalent coagulating ions, the same was not found to be the case with electrolytes having univalent coagulating ions. Freundlich [6] has ascribed this anomaly in the case of univalent coagulating ions to the influence of hydration of the colloid particles and has further stated that markedly electrocratic sols will show a uniform behaviour with univalent as well as multivalent coagulating ions. It will be agreed that ferric hydroxide is distinctly more like hydrophilic sols as far as hydration is concerned. However the value at which the coagulation begins is almost the sample with all the electrolytes tried except HCl. The influence of hydration thus does not appear to be playing an important part in the case of colloidal ferric hydroxide. On the other hand, the suggestion of Desai [7] that the value of the critical charge may be different for the same sol when it is coagulated by electrolytes containing same univalent coagulating ion but similarly charged ions of markedly different peptising action seems to be supported by these observations. The doubts expressed by Mukherjee and co-workers [8] about the existence of critical potential characteristic of coagulation of colloid by electrolytes do not seem to be justified in the case of colloidal ferric hydroxide.

(*c*) Cataphoretic Speed Measurements of Ferric Hydroxide Sol Dialysed and Diluted to Different Extents.

The results of these experiments are given in Table V.

TABLE V.*—Sol A.

Period of Dialysis.	3 Days.		6 Days.		9 Days.		12 Days.		15 Days.		18 Days.		21 Days.	
Dilution.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.
0	27·24	—	43·80	—	55·65	250·0	71·85	100·0	68·69	25·0	63·84	15·5	51·17	11·0
2	43·27	—	46·79	—	58·55	170·0	69·55	60·0	65·10	17·5	60·57	—	48·61	9·0
4	45·40	—	53·89	—	64·10	147·5	68·58	45·0	57·00	12·5	54·17	—	42·94	6·5
6	41·43	—	62·61	—	57·69	115·0	66·88	30·0	56·03	11·0	49·95	—	38·99	5·0
10	42·09	—	51·81	—	44·86	85·0	54·17	25·0	49·68	7·0	44·01	—	37·80	4·5
15	—	—	52·72	—	48·07	75·0	54·45	22·0	48·18	6·3	39·69	—	37·00	4·0
20	40·70	—	52·13	—	45·94	60·0	54·98	17·5	45·13	5·0	36·64	—	36·96	3·3

For facility of discussion the results of dilution experiments have been divided into two types according as whether the charge on dilution first increases and then decreases and remains almost constant thereafter or first decreases and remains almost constant thereafter. These are plotted

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* In column 1 are given the values of cataphoretic speed, while in column 2 are given the flocculation values with KCl.

[5] Powis, *J.C.S.*, **109**, 734, 1916.

[6] Freundlich, *Colloid and Capillary Chemistry*, 1926 Edition, p. 419.

[7] Desai, *J. Bombay Univ.*, **1**, (*Z*), 25, 1932.

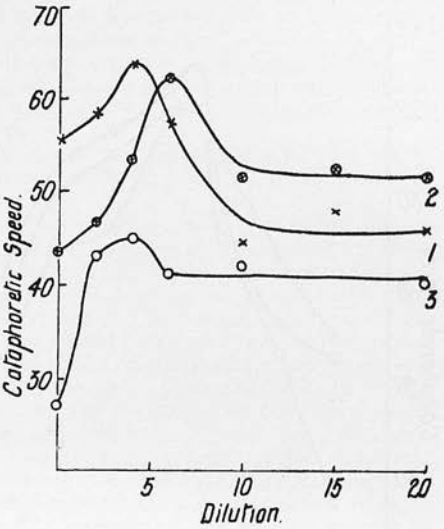
[8] Mukherjee, Rai Choudhury and Rao, *J. Indian Chem. Soc.*, **5**, 697, 1928; Mukherjee, Choudhury and Rai Choudhury, *ibid.*, **4**, 493, 1927; Mukherjee and Rai Choudhury, *Nature*, **122**, 960, 1928.

in Figs. 2 and 3. Cataphoretic speed has also been plotted for the different samples of the sol (different dilutions) against dialysis in Figs. 4 and 5.

The flocculation values with KCl for sols diluted to different extents and dialysed for different periods continuously decrease with an increase in dilution. Colloidal ferric hydroxide when coagulated with KCl thus behaves normally to the dilution rule, *viz.*, that the greater the concentration of the colloid the greater the amount of electrolyte necessary to coagulate it.

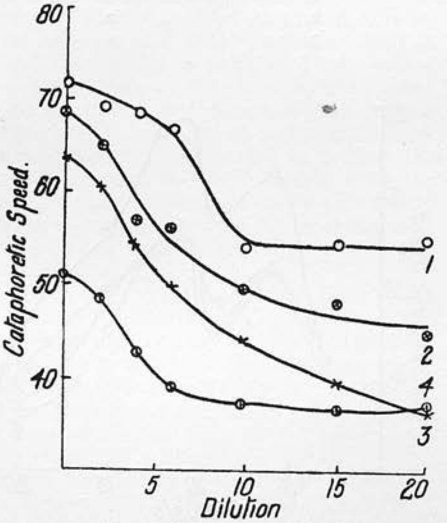
It will be seen that in the case of sols dialysed for three, six and nine days on diluting the sol the cataphoretic speed first increases, reaches a maximum value, then decreases and tends to become constant there after (Fig. 2). The maximum value of cataphoretic speed on dilution occurs between dilution 4 and 6 inthese cases. On the other hand, in the case of sols dialysed for twelve, fifteen, eighteen and twenty-one days (Fig. 3) the charge decreases in the beginning and shows a tendency to become constant thereafter on further dilution.

The maximum value of cataphoretic speed is seen to occur at the stage of twelve days dialysis (Table V.). It is likely that it might have occurred either before or after twelve days dialysis. However, in view of the act that the sol dialysed for twelve days behaves on dilution similar to the samples dialysed for fifteen, eighteen and twenty-one days, one may be inclined to the view that the maximum value of cataphoretic speed might have occurred after a dialysis of nine days and before the twelfth day, the value of the cataphoretic speed corresponding to the dialysis of twelve days actually lying on the part of the cataphoretic speed dialysis curve after the maximum. It thus appears



1. Curve for 3 days dialysis.
2. ,, ,, 6 ,, ,,
3. ,, ,, 9 ,, ,,

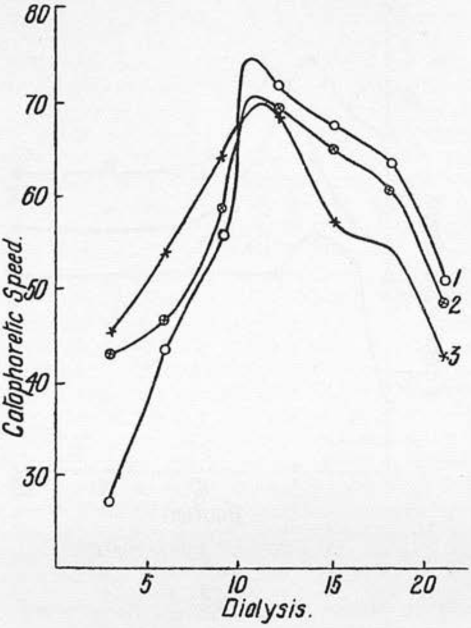
FIG. 2.



1. Curve for 12 days dialysis.
2. ,, ,, 15 ,, ,,
3. ,, ,, 18 ,, ,,
4. ,, ,, 21 ,, ,,

FIG. 3.

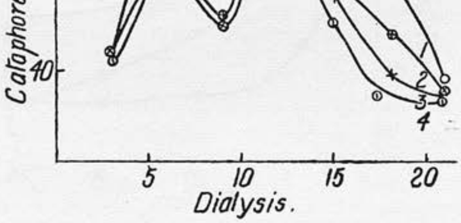
that in the case of ferric hydroxide at least the manner in which changes will take place in the cataphoretic speed on dilution can indicate whether any particular sample of this sol has been dialysed for a period more or less than the period corresponding to the maximum value of cataphoretic speed on dialysis. As shown in section (*a*) this sol shows an abnormal behaviour as far as the relation between charge and stability is concerned till the period of the maximum value of charge on dialysis is reached. It will be interesting to know if the behaviour of cataphoretic speed on dilution of any one sample of a sol can enable us to know whether the sample falls on one or the other side of maximum of the cataphoretic speed-dialysis curve. Further investigation of different sols from this point of view is necessary to see if this particular behaviour is a general property of colloids.



1. Curve for dilution 0.
2. ,, ,, ,, 2.
3. ,, ,, ,, 4.

FIG. 4.

From Table V. it will be seen that the nature of curves obtained by plotting cataphoretic speed against dialysis of sols having same dilution is not the same in all the cases. It is observed that in the case of sols having dilution 0, 2 and 4 the charge first increases, reaches a maximum value and then de creases (Fig. 4). On the other hand, in the case of sols having dilution 6, 10, 15 and 20 (Fig. 5) there is also a second maximum point in the cataphoretic speed dialysis curve for a period corresponding to six days dialysis. It is, however, to be noted that for all dilutions almost a regular behaviour is shown by a sol dialysed for twelve days or more. The causes of the second maximum point in the case of sols having dilutions 6, 10, 15 and 20 are not quite clear. Dilution



1. Curve for dilution 6.
2. ,, ,, ,, 10.
3. ,, ,, ,, 15.
4. ,, ,, ,, 20.

FIG 5.

of the colloid may give rise to many complications. For example dilution with the dispersion medium may actually give rise to a peptising action and this effect is specially marked with hydroxide sols as observed by Linder and Picton.[9] Also the concentration of the " active electrolyte " will change with dilution and this may ultimately affect the distribution in the double layer. But why these factors should affect only dilutions greater than 4 and that too for a period of dialysis of six days only is difficult to understand from the present results.

The flocculation values (Table V.) show a regular behaviour in all the cases, there being a gradual decrease with an increase in the period of dialysis.

The nature of charge-dilution curves (Fig. 2) is somewhat similar to the charge dialysis curve (Figs. 1 and 4), and one may be inclined to think that the processes of dilution and dialysis are similar. It is seen that the initial increase in the cataphoretic speed on dilution is noticeable only in the case of sols dialysed for three, six and nine days. The maximum value of cataphoretic speed having occurred at a period of about ten days dialysis, it is certain that the samples of the sol dialysed for shorter periods will contain an amount of the stabilising agent (HCl and $FeCl_3$) which is more than what would correspond to the maximum in the cataphoretic speed-concentration curve of the colloid with these electrolytes. As stated in section (*a*) if a colloid initially contains an amount of the stabilising agent which is more than the maximum in the cataphoretic speed-concentration curve, on dialysing, the charge on the colloid will first increase and then decrease. Just as with the progress of dialysis the amount of the " active electrolyte " continuously decreases, dilution also brings about a decrease in the concentration of the active electrolyte. It is therefore likely that if a sample of the sol initially contains an amount of the stabilising agent which is more than what corresponds to the maximum in the cataphoretic speed-concentration curve (this is certainly the case in the sols dialysed for three, six and nine days as stated above), on diluting it the charge will first increase and then decrease. This is what is observed in Fig. 2. In the case of the sols dialysed for twelve, fifteen, eighteen and twenty-one days (Fig. 3) the cataphoretic speed does not show an initial increase on dilution. In these cases the amount of the " active electrolyte " is less than what corresponds to the maximum in the cataphoretic speed-concentration curve. As stated in section (*a*) under the circumstances the cataphoretic speed will regularly decrease on dialysis. Now dialysis and dilution being similar specially as regards the changes in the concentration of the active electrolyte, the sols dialysed for twelve, fifteen, eighteen and twenty-one days should show a decrease in the cataphoretic speed on dilution (Fig. 3).

If the analogy between the processes of dilution and dialysis given in the preceding paragraph is correct, one should also expect that the maximum value of cataphoretic speed should occur at smaller and smaller dilutions with the progress of dialysis. A tendency to this effect is noticeable in the case of sols dialysed for six and nine days ; in the former case the maximum cataphoretic speed occurs at a dilution of 6 while in the latter at a dilution of 4. In the case of the sol dialysed for three days the maximum value, however, also occurs at a dilution of 4.

How far dialysis and dilution can be strictly compared is, however, difficult to say. For although the concentration of the " active electrolyte " changes in both the cases, the concentration of the disperse phase does not change during dialysis while on dilution it changes to the same extent as the active electrolyte. Moreover, as stated before, dilution may give rise to peptisation as well as a decrease in the size of the particles due to the action of the dispersion medium while dialysis may give rise to aggregation of particles and a consequent increase in their size.

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[9] Linder and Picton, *J. C.S.*, **87**, 1926 *et seq.*, 1905 ; also see Freundlich and Leonhardt, *Koll. Chem. Beih.*, **7**, 172, 1915.

From Table V. (also see Figs. 2 and 3) it will be seen that there is a tendency for the cataphoretic speed to become constant at higher dilutions. It has been shown above that dialysis and dilution are similar as regards changes in the concentration of the " active electrolyte." In section (*a*) it has also been stated that on carrying the dialysis to extreme the stabilising electrolyte is removed from the double layer and therefore the charge decreases to such a low value as to coagulate the sol. On extreme dilution, however, a similar process of removing stabilising agent from the double layer possibly does not take place and therefore the cataphoretic speed remains constant at large dilutions. Also the point where the charge does not further decrease on dilution possibly corresponds to the stage when the amount of the " active electrolyte " still remaining becomes negligible. Further for dialysis for a period longer than twenty-one days (say twenty-five to thirty days) the amount of " active electrolyte " still remaining in the sol will be negligible and stabilising agent would have begun being removed from the double layer ; for such samples of the sol the charge may not decrease at all on dilution but remain practically the same at all dilutions. A tendency for this type of effect is noticeable in the results given in Table V., for the cataphoretic speed becomes constant at smaller dilutions in the case of sols dialysed for twenty-one days than with sols dialysed for twelve, fifteen and eighteen days. The stage of dialysis at which the cataphoretic speed does not decrease but remains practically the same on dilution may be termed the " critical point of dilution." As stated in section (*b*) the cataphoretic speed at which the coagulation begins in the case of ferric hydroxide (stage corresponding to the first critical potential of Freundlich) is about 28 and it is likely that the value of the cataphoretic speed corresponding to the " critical point of dilution " will in most cases be larger than the above value (*i.e.*, 28 in the present case). It will be interesting to investigate different sols on dilution from this point of view.

Finally it may be stated that in the case of ferric hydroxide sol the behaviour to the dilution rule as determined by flocculation values with electrolytes should not be explained by assuming changes in charge produced on dilution, thinking that the stability results always indicate changes in charge.[10] For it has been shown in these measurements that for ferric hydroxide although on dilution stability continuously decreases in all the cases the changes in charge on dilution are not regular.

(*d*) Measurements of Viscosity and Cataphoretic Speed of Ferric Hydroxide Sol with the Progress of Dialysis and in the Presence of HCl and KCl with Samples of the Sol Dialysed to Different Extents.

The results of these experiments are given in Tables VI. and VII.

It will be seen from Table VI. that with the progress of dialysis the cataphoretic speed first increases, reaches a maximum and then begins to decrease. The viscosity, on the other hand, first decreases, reaches a minimum and then increases. It must, however, be noted that the maximum value of cataphoretic speed and the minimum value of viscosity do not occur simultaneously at the same stage of dialysis of the sol. With highly concentrated sols of $Fe(OH)_3$, which show a great tendency to gelation, the viscosity continuously increases with the progress of dialysis. (Desai, Special Number of the Indian Chemical Society, 1933, p. 37.)

From Table VII. it will appear that in the case of sol dialysed for six days the maximum value of cataphoretic speed and the minimum value of viscosity occur simultaneously when small increasing amounts of HCl are added to the colloid. In the other three cases, the minimum value

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[10] Dhar and co-workers, *J. Physic. Chem.*, **31**, 187, 666, 1927, and earlier papers. Also see in this connection Desai, *Current Science*, **1**, 125, 1932, in which article Dhar's view has been criticised.

of viscosity and the maximum value of cataphoretic speed do not occur simultaneously.

There are two different views at present about the relation between charge and viscosity. According to v. Smoluchowski [11] the movement of electrically-charged particles of a sol causes the development of an electric field, which hinders the flow of the sol resulting in an increase of its viscosity. He also observed that a sol with greater electric charge shows greater viscosity than a sol containing particles of feeble electric charge. On the other hand, Dhar and co-workers [12] have tried to show from experimental results with a number of sols that the view of v. Smoluchowski is untenable. They conclude that other things being identical, a decrease in the electric charge on colloid particles causes an increase in hydration and necessarily in the viscosity of the sol.

TABLE VI.—SOL D. CONCENTRATION 2·80 GMS./LITRE Fe_2O_3 ON THE SECOND DAY OF DIALYSIS.

Period of Dialysis.	Viscosity.	Cataphoretic Speed.
2 days	1·042	39·53
4 ,,	1·034	46·15
6 ,,	1·031	49·57
8 ,,	1·023	50·31
10 ,,	1·013*	51·48
12 ,,	1·025	52·24*
15 ,,	1·030	51·81
18 ,,	1·035	49·25
21 ,,	1·042	48·51
24 ,,	1·045	47·75

TABLE VII.—SOL. E. CONCENTRATION 2·90 GMS./LITRE Fe_2O_3 ON THE SIXTH DAY OF DIALYSIS.

	6 Days Dialysis.			21 Days Dialysis.		
	Concentration of Electrolyte.	Viscosity.	Cataphoretic Speed.	Concentration of Electrolyte.	Viscosity.	Cataphoretic Speed.
HCl	0·000	1·035	37·39	0·000	1·053	40·70
	0·025	1·034	38·46	0·025	1·047*	45·72
	0·050	1·024*	39·85*	0·050	1·052	49·78
	0·075	1·037	36·71	0·075	1·055	54·49*
	0·125	1·042	32·91	0·125	1·056	53·50
KCl	0·000	1·035	37·39	0·000	1·053	40·70
	0·013	1·030	38·24	0·025	1·040	44·86
	0·025	1·020*	38·46	0·050	1·036*	47·11
	0·050	1·024	39·10*	0·075	1·043	50·20*
	0·075	1·031	35·04	0·125	1·048	47·00

From the results presented in this section, it will appear that the view of Dhar is not completely supported. The theory of v. Smoluchowski is also not supported by these results.

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* Indicates minimum value of viscosity and maximum value of cataphoretic speed.

[11] v. Smoluchowski, *Koll. Z.*, **18**, 194, 1916; Kruyt, *Koll. Chem. Beih.*, **28**, 1, 1929; *ibid.*, **29**, 413, 1929; also see Wo. Ostwald, *Handbook of Colloid Chemistry*, 1919 Edition, p. 180.

[12] Dhar and co-workers, *J. Physic. Chem.*, **30**, 1646, 1926; *Z. anorg. Chem.*, **152**, 393, 1926; *Koll. Z.*, **42**, 124, 1927; *ibid.*, **48**, 43, 1929; *J. Indian Chem. Soc.*, **6**, 641, 1929; *ibid.*, **9**, 315, 441, 455, 1932.

In a recent note in *Current Science*, Desai[10] has reported that although with the progress of dialysis of colloidal thorium hydroxide viscosity continuously increases, the cataphoretic speed first increases, reaches a maximum and then decreases. Discussing these results from the point of view of various factors, *viz.*, (1) Electro-viscous effect, (2) Hydration, (3) Structure and shape of particles, and (4) Electrolyte content, Desai has concluded that neither the view of v. Smoluchowski nor of Dhar can individually explain the changes in charge and viscosity with the progress of dialysis in the case of thorium hydroxide sol.

It must be stated that Dhar has drawn conclusions about changes in charge from the viscosity and flocculation value determinations; he has not determined the cataphoretic speed of colloidal solutions under different conditions, although those measurements alone can give an idea about changes in charge. As shown here it is unsafe to draw conclusions about changes in charge on colloidal particles from viscosity measurements just as in the case of flocculation values, for although in some cases they may afford a correct criterion they are likely to lead to erroneous conclusions in other cases.

Summary.

Colloidal ferric hydroxide has been studied from different points of view. The following results have been obtained :—

(*a*) With the progress of dialysis the cataphoretic speed first increases, reaches a maximum value and decreases thereafter, while stability as determined by flocculation values with KCl continuously decreases. The results have been explained on the basis of changes in the " preferential adsorption " of similarly charged ions. The influence of hydration and changes in the size of particles with the progress of dialysis has also been considered.

(*b*) Sols having different initial cataphoretic speeds are found to begin to coagulate at the same value of the cataphoretic speed. Departures in certain cases have been explained on the view of " preferential adsorption " of similarly charged ions.

(*c*) Stability determinations with KCl show that the sol is normal to dilution rule. Changes in cataphoretic speed are not found to be regular. In the sols dialysed for periods shorter than what correspond to the maximum in the cataphoretic speed-dialysis curve, the charge on dilution first increases, then decreases and tends to become constant thereafter; for sols dialysed for longer periods the charge first decreases and tends to become constant thereafter. These changes in cataphoretic speed on dilution are explained by assuming similarity between processes of dilution and dialysis.

(*d*) Viscosity and cataphoretic speed determinations show that neither the view of v. Smoluchowski nor of Dhar can individually explain the results.

Conclusion.

It is erroneous to draw conclusions about changes in charge on the colloidal particles from the results of stability and viscosity determinations in the case of ferric hydroxide sol. For although in some cases they afford a correct criterion, in others they do not support the same relation between charge, stability and viscosity. Also as far as this sol is concerned, the idea of critical potential is supported.

The authors wish to thank Professor A. R. Normand for interest in the work and some valuable suggestions, Dr. T. R. Bolam (Edinburgh) for helpful criticism of the paper, and Mr. G. M. Nabar for the useful help in the preliminary stage of the work.

Note.—In section (*a*) it has been stated that in so far as the removal of the peptising electrolyte is concerned, the process of dialysis can be taken as a reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid. It should, however, be stated that during dialysis both hydration and the size of the colloidal particles also change besides the amount of the peptising electrolyte. It is therefore likely that on adding small increasing amounts of the peptising electrolyte to the sols, the hydration and the size of the particles may not be brought back to the same stage as in the undialysed sol. If this be the case, the adsorption of the ions will also be affected and with it the cataphoretic speed. Under the circumstances, it may not be possible in practice to obtain the actual reverse of dialysis on adding small increasing amounts of the peptising electrolyte to the colloid although the analogy may be quite correct in so far as the question of removal of the peptising electrolyte during dialysis is concerned.

According to Pauli and Walter,[13] on diluting a sol the aggregates are broken down giving greater number of colloidal ions; and this effect might be responsible for abnormal rise in colloidal ion mobility on dilution. It should be stated that the present results on dilution cannot be explained on the basis of their view; our results can be explained easily as shown in section (*c*) by assuming similarity between the processes of dilution and dialysis.

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[13] *Knoll. Chem. Beih.*, **17**, 256, 1923.

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Vol. XXX., Part 2, February, 1934.

IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS. PART II. COLLOIDAL THORIUM HYDROXIDE.

By B. N. Desai and A. K. Desai.

Received 16th October, 1933.

In a previous paper[1] we have given the results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric hydroxide dialysed and diluted to different extents. In the present paper similar results obtained with colloidal thorium hydroxide have been presented. It will be seen from the results that the behaviour of this sol as regards dialysis, dilution and critical potential is similar to that of ferric hydroxide; the viscosity changes on dialysis and in the presence of electrolytes are, however, found to be different.

Experimental.

The sol was prepared in the same manner as done by Desai[2] and the dialysis was carried exactly in the same way as with ferric hydroxide. The concentration of the colloid did not change to any appreciable extent during dialysis. For cataphoretic speed measurements, the upper liquid prepared by making the dialysate equiconducting with the sol by adding suitable amounts of HCl, was found to be quite satisfactory.

Thorium hydroxide, being a colourless sol, the movement of the boundary was followed with the help of the Tyndall phenomenon. A

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[1] Desai and Borkar, *Trans. Faraday Soc.*, **29**, 1269, 1933.

[2] *Kolloidchem. Bei.*, **26**, 384, 1928.

beam of light was allowed to pass vertically down through a hole in the top cover of the thermostat. Just below this hole was placed the limb of the U-tube in which the movement of the boundary was to be observed. In every case a well-defined boundary was observed between the colloid and the upper liquid. As difficulty was experienced in following the movement of the boundary in the case of very dilute sols, 0·5 c.c. of 0·1 per cent. solution of Neutral Red (amino-dimethylamino-toluphenazonium chloride, p_H 6·8-8·0) was added to 100 c.c. of the upper liquid in all dilution experiments for the sake of uniformity. Cataphoretic speed was determined both in the presence and absence of the Neutral Red in the case of concentrated sols, and it was found that the mean cataphoretic speed obtained in the two cases agreed within 2 per cent. Also the boundary obtained between the colloid and the coloured upper liquid was always very sharp, there being practically no diffusion of the dye into the colloid. The effect of ageing on the cataphoretic speed was found to be quite inappreciable. The other details of the experiments were exactly as before.

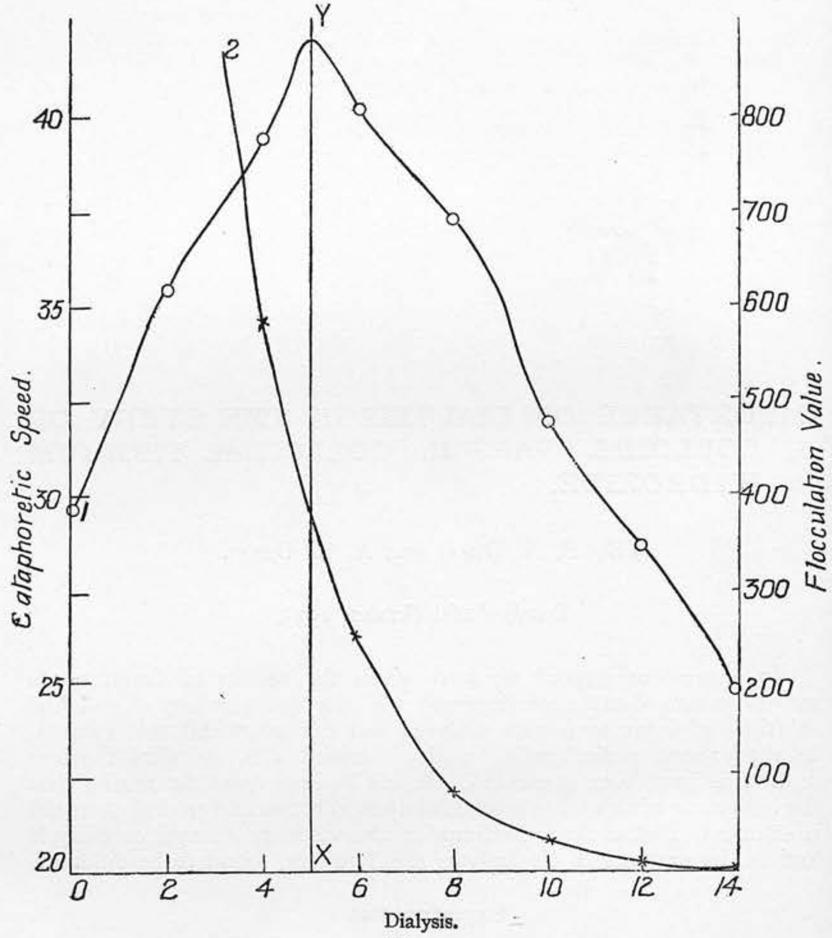

FIG. 1.

1. Cataphoretic speed—dialysis curve. 2. Flocculation value—dialysis curve.

Results and Discussion.

(*a*) Cataphoretic Speed and Stability Changes with the Progress of Dialysis.

The results of these experiments have been plotted in Fig. 1.* It will be seen that when the colloidal solution is subjected to dialysis the cataphoretic speed first increases and reaches a maximum after which it gradually decreases. The stability, on the other hand, continuously decreases with the progress of dialysis. Measurements of cataphoretic speed in the presence of HCl, KCl, $ThCl_4$ and HCl + KCl were made with samples of sol dialysed to different extents and the same type of preferential adsorption of the similarly charged ions as in the case of ferric hydroxide sol was also noticed in this case. The behaviour of colloidal thorium hydroxide is thus similar to the behaviour of ferric hydroxide.

(*b*) Measurements of Cataphoretic Speed from the point of view of Critical Potential.

Measurements of cataphoretic speed were made with HCl, KCl, $MgCl_2$, H_2SO_4 and $MgSO_4$ at two stages of dialysis, one before the maximum value of charge is reached and the other after it. A typical set of results obtained with HCl and H_2SO_4 is given in Table I.; the table also contains results of viscosity measurements which will be discussed in section (*d*).

TABLE I.—CONCENTRATION OF THE SOL 12·82 GMS. ThO_2/LITRE ON FOURTH DAY. CONCENTRATION OF THE SOL 12·76 GMS. ThO_2/LITRE ON FOURTEENTH DAY.

Sol Dialysed for 4 Days.			Sol Dialysed for 14 Days.		
Concentration of Electrolytes. Millimoles/litre.	Cataphoretic Speed × 10^5.	Relative Viscosity.	Concentration of Electrolytes. Millimoles/litre.	Cataphoretic Speed × 10^5.	Relative Viscosity.
HCl					
0·000	33·41	1·0254	0·000	24·78	1·0467
0·063	36·73	1·0255	0·013	28·07	1·0464
0·125	38·62	1·0259	0·019	29·81	1·0460
0·188	32·51	1·0261	0·025	31·16	1·0452
0·250	29·10	1·0263	0·050	29·59	1·0442
0·500	26·95	1·0265	0·100	25·50	1·0457
1·000	25·06	1·0268	0·125	22·90	1·0464
1·250	24·07	1·0269	0·188	20·83	1·0474
2·500	22·00	1·0275	0·250	17·96	1·0483
12·500	20·30	1·0293	0·375	16·95†	1·0500
25·000	19·63	1·0310	—	—	—
125·000	18·60†	1·0333	—	—	—
H_2SO_4					
0·000	33·41	1·0254	0·000	24·78	1·0467
0·025	30·49	1·0254	0·005	23·80	1·0465
0·050	28·96	1·0256	0·013	22·19	1·0461
0·075	27·25	1·0258	0·025	19·09	1·0466
0·100	26·49	1·0260	0·050	17·96	1·0467
0·125	25·15	1·0264	0·100	16·48	1·0475
0·188	22·80	1·0271	0·125	15·86†	1·0484
0·250	21·51	1·0277	0·150	14·41	1·0490
0·375	20·52†	1·0349	—	—	—

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* As shown in section (*c*), where the same sample of the sol was used for experiments (13·5 gms. ThO_2 per litre in original sol), the maximum value of cataphoretic speed with the progress of dialysis must have occurred in this case after a dialysis of four days and before six days, the value of the maximum cataphoretic speed being greater than 41·04. It is because of this reasoning that in Fig. 1, the maximum value of the cataphoretic speed is shown to have occurred on about the fifth day of dialysis.

† Sol begins to coagulate.

It will be seen that the initial increase in cataphoretic speed is noticed only with electrolyte having univalent coagulating ion as in the case of colloidal ferric hydroxide. The value of the cataphoretic speed at which coagulation begins is about 19 to 21 in case of sol dialysed for four days and having an initial cataphoretic speed of 33·41 and about 16 to 17 in case of sol dialysed for fourteen days and having an initial cataphoretic speed of 24·78. It will thus appear that although the two samples of the sol had different initial cataphoretic speeds they begin to coagulate at about the same value of the cataphoretic speed. The idea of critical potential thus seems to be supported by these measurements. It is also interesting to note that although the colloid begins to coagulate at almost the same value of the charge with HCl and H_2SO_4 in case of both the sols, the amounts of respective electrolytes necessary to lower the charge to critical value are not the same.

(c) Cataphoretic Speed and Stability Changes of Sols Dialysed and Diluted to Different Extents.

The results of these experiments have been plotted in Figs. 2 and 3. The flocculation values with KCl for sols diluted to different extents and dialysed for different periods were found to decrease continuously with increase in dilution, thus indicating that the sol behaves normally to the dilution rule.

It will be seen from Fig. 2 that on diluting the sol, the cataphoretic speed first increases, reaches a maximum and then decreases in the case of sol dialysed for nothing, two and four days. The maximum value of cataphoretic speed on dilution occurs at a dilution of 4 in the case of undialysed sol and at dilutions 3 and 2 for sol dialysed for two and four days respectively. It is interesting to note that the maximum value of the cataphoretic speed on dilution lies between 39 and 41 and this is not far different from the maximum value of about 44 of cataphoretic speed obtained on dialysis of the sol (Fig. 1). On the other hand in the case of sols dialysed for six, eight, ten, twelve and fourteen days (Fig. 3) the cataphoretic speed continuously decreases on dilution of the sol. These results of dilution can be explained as in the case of colloidal ferric hydroxide by assuming similarity between processes of dilution and dialysis.

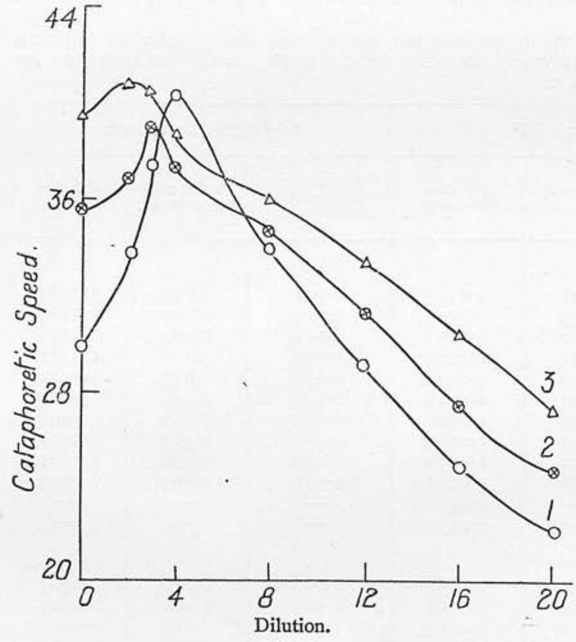

FIG. 2.

1. Curve for 0 day dialysis. 2. Curve for 2 days dialysis. 3. Curve for 4 days dialysis.

The maximum value of the cataphoretic speed is seen to occur at the stage of six days dialysis in the case of this sol (0 dilution). From the behaviour on dilution of the sol dialysed for six days (it behaves similarly to samples dialysed for eight, ten, twelve and fourteen days), it can be inferred that the maximum value of cataphoretic speed on dialysis might have occurred after a dialysis of four days and before the sixth day, the value of the cataphoretic speed corresponding to the dialysis of six days actually lying on the part of the cataphoretic speed-dialysis curve after the maximum. For this reason the maximum speed is shown to have occurred on about the fifth day in Fig. 1 in section (*a*). It thus appears that in this case also as in the case of colloidal ferric hydroxide, the changes in charge on dilution can enable one to know whether the particular sample of the sol has been dialysed for a period shorter or longer than that corresponding to the maximum in the cataphoretic speed dialysis curve.

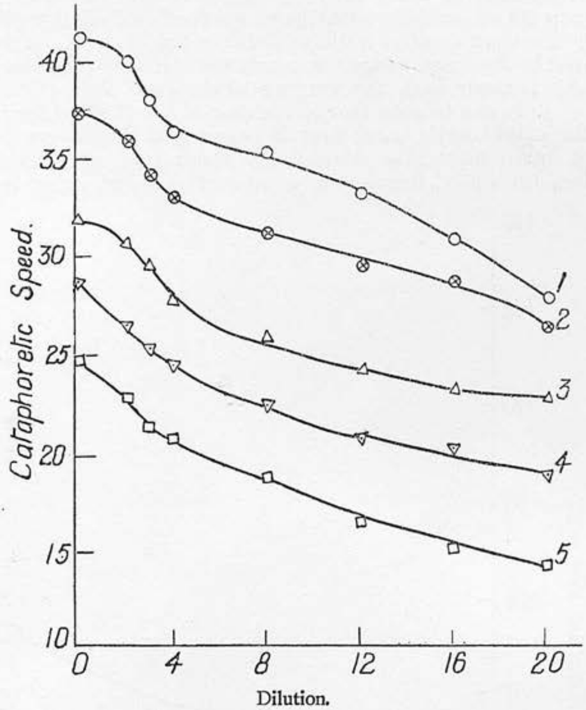

FIG. 3.

1. Curve for 6 days dialysis. 2. Curve for 8 days dialysis.
3. Curve for 10 days dialysis. 4. Curve for 12 days dialysis.
5. Curve for 14 days dialysis.

(*d*) Measurements of Viscosity and Cataphoretic Speed under Different Conditions.

1. The results of viscosity with the progress of dialysis are plotted in Fig. 4. It appears that in the initial stages of dialysis (sol having dilution 0) the viscosity increases only very slowly while in the latter stages the viscosity rises very rapidly. On the other hand, as shown in section (*a*), the cataphoretic speed first increases and then decreases with the progress of dialysis.

2. It has been observed by us that for all samples of the sol the viscosity increases regularly with an increase in concentration. As stated in section (*c*), on diluting the sol the cataphoretic speed first increases and then decreases for samples of sol dialysed for none, two and four days and continuously decreases for samples dialysed for longer periods. Thus it is apparent that the relation between charge and viscosity is not very simple.

In Fig. 4 is also plotted viscosity against dialysis for sol having dilution 20. It appears from the figure that in this case the increase in viscosity with the progress of dialysis is very small and that the viscosity increases at almost the same rate throughout. On the other hand, the rate of increase of viscosity with the progress of dialysis for sol having dilution 0 is considerable after a dialysis of about eight days. It may thus so happen that in the case of very dilute sols the viscosity may not show any appreciable increase with the progress of dialysis.

3. It will be seen that in the case of sol dialysed for four days (Table I.) the cataphoretic speed first increases and then decreases on the addition of small increasing amounts of electrolyte with univalent coagulating ion, the initial increase in cataphoretic speed being not noticeable with electrolytes having bivalent coagulating ion. Viscosity, on the other hand, increases continuously in all the cases. This sample of sol, as stated before, was dialysed for a period shorter than what corresponds to the maximum in the cataphoretic speed-dialysis curve. For sols dialysed for longer periods the behaviour is somewhat different. Thus for sample of sol dialysed for fourteen days (Table I.), the viscosity seems to be decreasing continuously in the beginning when small increasing amounts of electrolyte are added, although later on it increases continuously as in the former case. The cataphoretic speed changes in this case are exactly similar to those in the former case.

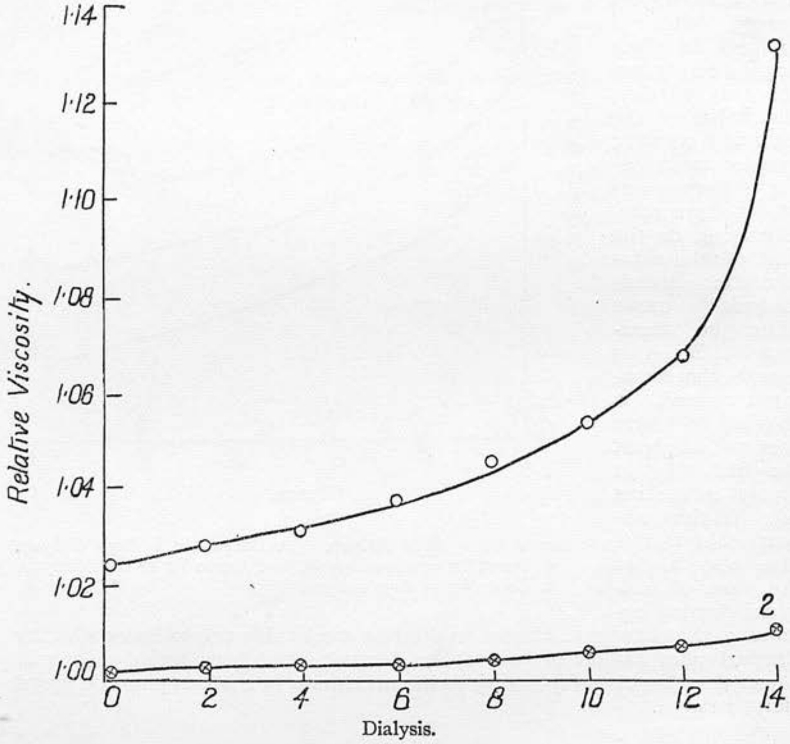

FIG. 4.

1. Curve for 0-dilution. 2. Curve for 20-dilution.

It would appear from the foregoing results that neither the view of v. Smoluchowski (smaller charge smaller viscosity and greater charge greater viscosity) nor of Dhar (smaller viscosity smaller hydration and greater charge and greater viscosity greater hydration and smaller charge) can individually explain the changes in charge and viscosity under different conditions. One should consider the effect of changes in the concentration of the sol and of the factors mentioned in our previous paper [1] if the results of changes in charge and viscosity are to be explained satisfactorily.

The authors wish to thank Professor A. R. Normand for interest in the work, and Mr. A. M. Patel for assistance in the preliminary stage of the work.

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Condition of Silver Chromote, Silver Iodide and Lead Iodide in Gelatine.

By

B. M. Naik, H. N. Desai and B. N. Desai.

CALCUTTA UNIVERSITY PRESS.
1934

Condition of Silver Chromate, Silver Iodide and Lead Iodide in Gelatine.

By B. M. Naik, H. N. Desai and B. N. Desai.

When one considers the various theories that have been put forward by different investigators to explain the formation of Liesegang rings, it becomes quite clear that a knowledge about the condition—ionic, colloidal, etc., of the substances deposited in the bands will be of great help in understanding the process of periodic precipitation.

Williams and Mackenzie (*J. Chem. Soc.*, 1920, **117**, 844), Bolam and Mackenzie (*Trans. Faraday Soc.*, 1926, **22**, 162; 1928, **24**, 50) and Bolam and Donaldson (*ibid.*, 1933, **29**, 864) have shown by *e. m. f.* and conductivity measurements that prior to the appearance of the red colour, the activity of the silver ion in the yellow mixture is very much higher than in a pure saturated solution of silver chromate at the same temperature, and that when the red colour appears the activity of the silver ion simultaneously decreases to a marked extent. Desai and Nabar (*Trans. Faraday Soc.*, 1932, **28**, 449) have shown from electrometric measurements that the activity of silver ion in a mixture of silver nitrate and potassium chromate in gelatine remains constant for some minutes, then rapidly decreases and finally becomes constant, and that the point at which the activity commences to fall corresponds in every case with the first appearance of red colour. These experiments lead to the conclusion that the yellow mixture contains silver chromate in supersaturated solution and that the red colour is due to the actual formation of the solid phase, and not to the coagulation of a solid phase which is already present in the form of colloidal particles.

Dhar and collaborators (*J. Phys. Chem.*, 1924, **28**, 41; *Kolloid Z.*, 1924, **34**, 270; *J. Indian Chem. Soc.*, 1928, **5**, 175; *Trans. Faraday Soc.*, 1927, **23**, 23) have, on the other hand, shown from their electrometric and conductivity measurements that silver chromate is produced in the form of a colloidal solution. According to them, the yellow mixture contains particles which are negatively charged through adsorption of chromate ions, while the red substance is a less stable sol containing particles which are positively charged through adsorption of silver ions. They have shown that a greater part of silver chromate in gelatine is present in colloidal condition, only about one-third being present in ionic condition. It is difficult to understand why the results of various investigators on the condition of silver chromate in gelatine are so conflicting.

Chatterji and Dhar (*J. Indian Chem. Soc.*, 1930, **7**, 177) have shown from *e.m.f.* and conductivity measurements that more than 97% of silver iodide in gelatine exists in condition other than ionic; they believe that it is present in colloidal condition.

Desai and Naik (Paper on " Inhibitive power of Gelatine " which will be published in the September issue of the Journal of the Bombay University, 1933) have shown that the inhibitive power with reference to Ag_2CrO_4 is minimum for gelatine of p_H 5·75 and is greater for higher or lower values of p_H. In the case of AgI the inhibitive power continuously decreases with a decrease of p_H of gelatine. The inhibitive power with reference to PbI_2 is maximum for gelatine of p_H 5·0 and is smaller for higher or lower values of p_H.

Condition of Silver Chromate in Gelatine.

If yellow solution contains silver chromate in supersaturated solution and not in colloidal condition, one would expect that the conductivity of the yellow mixture should remain the same as that calculated on the basis that all silver chromate exists in ionic condition as long as the colour does not change and that it should gradually decrease with the appearance of the red coloured precipitate. To test this point, a series of conductivity experiments were also undertaken.

The gelatine used in these experiments was the same as used by Desai and Naik (*loc. cit.*) and the p_H of gelatine solution was varied in the same manner as done by them. The conductivity was measured by the usual method using an amplifying circuit similar to the one used by Lorenz and Klauer (*Z. anorg. Chem.*, 1924, **136**, 121) (for details please see paper by H. N. Desai, D. B. Naik and B. N. Desai on conductivity measurements in course of publication in *Indian J. Phys.*). The conductivity of the mixture was determined

from time to time. A typical result of conductivity experiments is given in Table I. In Table II is given a summary of all such results obtained with silver chromate.

TABLE I.

Total volume of mixture with conductivity water = 20 c.c. Conc. of gelatine soln. = 3%. pH of gelatine soln. = 5·52. A. Conductivity of 5·5 c.c. gelatine + water = $1·355 \times 10^{-4}$. B. Conductivity of 5·5 c.c. gelatine + 5 c.c. $N/100$-$AgNO_3$ + water = $4·547 \times 10^{-4}$. C. Conductivity of 5·5 c.c. gelatine + 5 c.c. $N/100$-K_2CrO_4 + water = $4·579 \times 10^{-4}$. D. Conductivity of 5·5 c.c. gelatine + 5 c.c. $N/100$-KNO_3 + water = $4·926 \times 10^{-4}$ Temp. = 30°.

Colour of mixture.	Time.	Obs. conductivity (mhos) of mixture 5·5 c.c. gelatine + 5 c.c. $N/100$-$AgNO_3$ + 5 c.c. $N/100$-K_2CrO_4 + water. E.	Obs. conductivity (mhos) of Ag_2CrO_4 alone. E—D.	Calc. conductivity (mhos) if whole of Ag_2CrO_4 in ionic condition. B + C—D—A.	% of Ag_2CrO_4 in ionic condition.
Yellow	1 min.	$6·842 \times 10^{-4}$	$1·916 \times 10^{-4}$	$2·845 \times 10$	67
,,	6	6·842	1·916		67
,,	10	6·798	1·872		66
,,	15	6·842	1·916		67
,,	20	6·821	1·895		67
,,	25	6·798	1·872		66
,,	30	6·821	1·895		67
,,	35	6·842	1·916		67
,,	40	6·842	1·916		67
,,	45	6·798	1·872		66
,,	50	6·821	1·895		67
,,	55	6·842	1·916		67
First appearance of red colour.	59	6·842	1·916		67
Red	65	6·798	1·872		66
,,	70	6·842	1·916		67
,,	75	6·821	1·895		67

TABLE II.

Temp. = 30°. Total volume = 20 c.c.

p_H of gelatine.	Vol. of gelatine.	$N/100$-$AgNO_3$ and $N/100$-K_2CrO_4.	Obs. conductivity (mhos) of Ag_2CrO_4 alone in mixture.	Calc. conductivity (mhos) if whole of Ag_2CrO_4 in ionic condition.	% of Ag_2CrO_4 in ionic condition.
			E − D.	B + C − D − A.	
5·52	5·5 c.c.	5 c.c.	1·895 × 10^{-4}.	2·845 × 10^{-4}	67
5·52	2·8	4	1·239	1·978	62
5·52	5·0	5	1·260	2·268	56
5·52	6·0	6	1·126	2·576	44
5·52	7·0	6	1·130	2·592	44
4·50	1·25	6	1·889	3·685	51
4·50	1·3	5	1·670	2·561	65
6·00	7·2	6	1·210	2·850	43

It will appear from Table I that when equivalent amounts of $AgNO_3$ and K_2CrO_4 are added to the same amount of gelatine, the conductivity is slightly less in the former case than in the latter. This is probably due to the fact that more of Ag ions than CrO_4 ions combine with gelatine (*cf.* Bolam and Mackenzie, *loc. cit.*). It will also be seen that the conductivity is reduced more in the presence of K_2CrO_4 than in the presence of an equivalent amount of KNO_3. This will mean that there is greater combination between gelatine and CrO_4 ions than between gelatine and NO_3 ions. An exactly similar behaviour is noticed in all the cases whether p_H of gelatine is made smaller or larger than 5·52.

The other and most significant fact noticeable from Table I is that no sooner the solutions are mixed, the conductivity is immediately reduced and thereafter its value does not change even when the red coloured precipitate makes its appearance. Also there is no gradual decrease in the conductivity with the appearance of more and more red coloured precipitate. Whatever changes are to take place in the conductivity occur immediately on mixing the solutions. The same behaviour is noticed when the p_H of gelatine solution is made smaller or larger than 5·52 or when the amount of gelatine is varied keeping the amount of the reactants the same. These results therefore show that (*i*) the yellow coloured mixture contains some insoluble precipitate of silver chromate and (*ii*) that the change from the yellow coloured mixture to the red coloured one is not due to release of supersaturation. From the cataphoretic experiments, it is seen that neither the yellow nor red coloured mixture contains any charged particles. It thus appears that the change from the yellow coloured to red coloured mixture is not due to a change in the charge on the particles of the insoluble precipitate formed in the beginning, but simply due to a change in the size of the particles. One can actually see that the particles are invisible in the yellow mixture, while they are sufficiently large to be visible in red coloured mixture. It was also observed that when the reaction is allowed to take place in test tubes and specially when the mixture sets to a gel, the precipitate is first localised at certain points and the mixture ultimately becomes turbid red. A change in the colour due to a change in the size of particles is a very common phenomenon, for example gold sol containing fine particles is ruby red while the one containing larger particles is blue ; one can quote many such instances. It appears that the yellow mixture contains some insoluble precipitate of silver chromate whose particles are in a highly dispersed form, probably even in molecular condition. If the precipitation is molecularly dispersed, it is quite likely that this portion will diffuse at an appreciable rate. This process of diffusion may give rise to union of groups of molecules which may form centres of crystallisation. More of the molecularly dispersed material will, as a result of diffusion, allow the nuclei already formed to grow and thus larger particles, which may be quite visible will, appear. Growth of larger particles at the expense of smaller particles is thus not at all impossible or precluded. The transition from the yellow to red colour will thus be gradual, but in actual practice is noticed only when red coloured fine particles appear.

It will also be seen from Table I that in this particular case about 67% of silver chromate remains in ionic condition and the remaining 33% in a finely dispersed condition in the yellow mixture. As stated before, the colour change from yellow to red does not seem to be due to a sudden release of supersaturation or due to a change in the nature of charge on the colloidal particles.

In all the cases given in Table II, it was also noticed that whatever changes in the conductivity are to take place, occur immediately on mixing the solutions and that the change from the yellow to the red colour is not accompanied by any changes in conductivity. These results, therefore, apparently support the observations of Chatterji (*Proc. Indian Science Congress*, 1932, p. 10) that the *e. m. f.* does not decrease with time with either yellow or red mixtures. It is surprising that the present results do not support either our previous results (Desai and Nabar, *loc. cit.*) or those of Bolam and co-workers (*loc. cit.*). It is, however, a fact that both types of results are based on accurate experiments. Therefore some more work is necessary to find out the conditions favourable for the occurrence of the different behaviours noticed so far.

It will also appear from Table II that by varying the p_H and the concentration of gelatine and of the reactants, the amount of silver chromate which can remain in ionic condition can also be varied ; in the present case it has varied from 43 to 67%. In view of this, it is not impossible that under certain circumstances the amount of silver chromate which can remain in ionic condition can be as much as 95% (Nabar and Desai, *Nature*, 1931, **127**, 628). It is quite likely that the same causes which are operative in this case might also be responsible for the conflicting results discussed in the previous paragraph. We are of the opinion that if the p_H of gelatine and the concentration of gelatine and of the reactants are such that on mixing the solutions more than 95% of silver chromate can remain in ionic condition, on allowing the mixture to stand the *e. m. f.* or conductivity may not change at all till the colour remains yellow (as observed by Bolam and co-workers, *loc. cit.*, and by Desai and Nabar, *loc. cit.*) and that with the appearance of red colour, the *e. m. f.* and conductivity may change gradually ; in such a case the colour change will be due to release of supersaturation. This point is being investigated.

Condition of Silver Iodide in Gelatine.

A typical result of conductivity measurements of silver iodide is given in Table III and a summary of all such results in Table IV.

TABLE III.

Temp. = 30°. Total volume with conductivity water = 20 c.c. Conc. of gelatine soln. used = 3%. p_H of gelatine soln. = 5·52. A. Conductivity of 12 c.c. gelatine + water $= 2{\cdot}746 \times 10^{-4}$ mhos. B. Conductivity of 12 c.c. gelatine + 3 c.c. $N/10\text{-}AgNO_3$ + water $= 1{\cdot}981 \times 10^{-3}$ mhos. C. Conductivity of 12 c.c. gelatine + 3 c.c. $N/10$-KI + water $= 2{\cdot}201 \times 10^{-3}$ mhos. D. Conductivity of 12 c.c. gelatine + 3 c.c. $N/10\text{-}KNO_3$ + water $= 2{\cdot}245 \times 10^{-3}$ mhos.

Colour of mixtures.	Time.	Obs. conductivity (mhos) of mixture 12 c.c. gelatine + 3 c.c. $N/10$-$AgNO_3$ + 3 c.c. $N/10$-KI + water. E.	Obs. conductivity (mhos) of AgI alone. E − D.	Calc. conductivity (mhos) if whole of AgI in ionic condition. B + C − D − A.	% of AgI in ionic condition.
Greenish	1 min.	$2{\cdot}259 \times 10^{-3}$	$0{\cdot}014 \times 10^{-3}$	$1{\cdot}662 \times 10^{-3}$	N
	5	2·259	0·014		
	10	2·252	0·007		
	15	2·259	0·014		
	20	2·259	0·014		
Gradual	25	2·245	...		
change	30	2·252	0·007		
	35	2·259	0·014		
	40	2·259	0·014		
	45	2·252	0·007		
Appearance of	50	2·252	0·007		
whitish yellow colour	55	2·252	0·014		

TABLE IV.

Temp. = 30°. Total volume = 20 c.c.

p_H of gelatine.	Vol. of gelatine.	$N/100$-$AgNO_3$ and $N/10$-KI.	Obs. conductivity (mhos) of AgI alone in mixture. E − D.	Calc. conductivity (mhos) if whole of AgI in ionic condition. B + C − D − A.	% of AgI in ionic condition.
5·52	2·6 c.c.	1 c.c.	$0{\cdot}010 \times 10^{-3}$	$0{\cdot}469 \times 10^{-3}$	2
5·52	5·2	2	0·017	1·030	2
5·52	8·1	3	0·031	1·706	1
5·52	12·0	3	0·014	1·662	nil
4·50	10·0	3	0·018	1·531	1
4·50	12·0	3	0·022	1·774	nil
6·00	7·2	3	0·012	0·947	1

It will appear from Table III that the conductivity of silver nitrate in gelatine is somewhat smaller than that of an equivalent amount of potassium iodide in gelatine. This again indicates as in the previous case that Ag ions combine more readily with gelatine than CrO_4 ions. Also the conductivity is smaller with potassium iodide in gelatine than with an equivalent amount of potassium nitrate in gelatine. Here there is evidence to show that iodide ions combine more readily with gelatine than nitrate ions. A similar tendency is noticeable in all the experiments whose results are summarised in Table IV.

The colour of the mixture becomes greenish on mixing the solutions of $AgNO_3$ in gelatine and KI in gelatine. The mixture, however, does not contain any visible particles. On allowing the mixture to stand, the colour gradually changes and with it the mixture also begins to develop turbidity. With the progress of time, the turbidity continuously increases. It will, however, appear from the table that the conductivity changes immediately on mixing the solutions and that it does not change at all thereafter although the colour of the mixture continuously changes and the particles of silver iodide become visible and gradually increase in size. These results therefore show that colour changes are not due to any release of supersaturation.

It will be seen from Tables III and IV that about 98% of silver iodide exists in condition other than ionic. Our results therefore support the results of Chatterji and Dhar (*loc. cit.*) in this respect. They, however, believe that silver iodide in gelatine exists in colloidal condition. To test this point, a series of cataphoretic experiments were undertaken. In no case the presence of charged particles could be detected. We are therefore inclined to the view that silver iodide in gelatine exists in the beginning in a very highly dispersed form probably in molecular condition. As pointed out before, this portion in molecularly dispersed form will, as a result of diffusion, give rise to large particles and the colour changes are due to changes in the size of the particles. As is well known there is always a tendency for larger particles to grow further at the expense of relatively smaller particles.

A change in the p_H or in the concentrations of gelatine and the reactants does not very appreciably alter the amount of silver iodide in ionic condition. In this respect silver iodide in gelatine is quite distinct from silver chromate in gelatine. In so far as can be judged from the present results, the fact that the inhibitive power of gelatine decreases with a decrease of its p_H, does not seem to be of any significance in explaining the results about condition of silver iodide in gelatine.

Condition of Lead Iodide in Gelatine.

A typical result .of changes in the conductivity with time in the case of lead iodide in gelatine is given in Table V. A summary of all such experiments is also given in Table VI.

TABLE V.

Temp. = 30°. Total volume with conductivity water = 20 c.c. Conc. of gelatine soln. = 3%. p_H of gelatine = 5·52. A. Conductivity of 9 c.c. gelatine + water = $2\cdot096 \times 10^{-4}$ mhos. B. Conductivity of 9 c.c. gelatine + 2 c.c. $N/10$-Pb $(NO_3)_2$ + water = $1\cdot022 \times 10^{-3}$ mhos. C. Conductivity of 9 c.c. gelatine + 2 c.c. $N/10$-KI + water = $1\cdot479 \times 10^{-3}$ mhos. D. Conductivity of 9 c.c. gelatine + 2 c.c. $N/10$-KNO_3 + water = $1\cdot683 \times 10^{-3}$ mhos.

Colour of mixture.	Time (hrs. min.).	Observed conductivity (mhos) of mixture 9 c c. gelatine + 2 c.c. $N/10$-Pb $(NO_3)_2$ + 2 c.c. $N/10$-KI + warer. E.	Observed conductivity (mhos) of PbI_2 alone. E−D.	Calculated conductivity (mhos) if whole of PbI_2 in ionic condition. B+C−D−A.	% of PbI_2in ionic condition.
Colourless	0·01 hr.	$2\cdot187 \times 10^{-3}$	$0\cdot504 \times 10^{-3}$	$0\cdot608 \times 10^{-3}$	83
	0·30	2·179	0·496		82
	0·45	2·187	0 504		83
	1·00	2·179	0·496		82
	1·15	2·184	0·501		82
	1·30	2·173	0·490		81
↓	1·45	2·187	0·504		83
Gradual change	2·00	2·179	0·496		82
	2·30	2·187	0·504		83
	3·00	2·179	0·496		82
	3·30	2·184	0·501		82
	4·00	2·173	0·490		81
↓	4·30	2·187	0·504		83
Apparance of greenish colour	4·50	2·179	0·496		82
	5·00	2·179	0 496		82
↓ Gradual change	5·45	2·187	0·504		83
	6·30	2·179	0·496		82
↓ Appearance of yellow colour	8·30	2·184	0 501		82

TABLE VI.

Temp. = 30°. Total volume = 20 c.c.

p_H of gelatine.	vol of $N/10$-Pb(NO$_3$)$_2$ gelatine.	and $N/10$-KI	Observed conductivity (mhos) of PbI$_2$ alone in mixture.	Calculated conductivity (mhos) if whole of PbI$_2$ in ionic condition.	% of PbI$_2$ in ionic condition.
			E−D	B+C−D−A	
5·52	5·6c.c.	2·0 c.c.	$0·586 \times 10^{-3}$	$0·761 \times 10^{-3}$	76
5·52	12·6	2·5	0·630	0·960	65
5·52	9·0	2·0	0·501	0·608	82
4·50	13·2	2·5	0·554	0·819	68
4·50	10·0	2·0	0·511	0·616	83

A well marked tendency for the combination of lead ions with gelatine is noticeable from the results given in Table V, for it is observed that the conductivity with lead nitrate is less than that with an equivalent amount of potassium iodide. These results also support the conclusion arrived at in the case of silver iodide in gelatine, namely that iodide ions combine more readily with gelatine than nitrate ions.

When lead nitrate in gelatine is mixed with potassium iodide in gelatine, the mixture is colourless. On allowing the mixture to stand, however, a colour develops which gradually changes from greenish to yellow. Simultaneously with these colour changes the mixture which is quite clear in the beginning develops turbidity and gradually the size of the particles also increases. However as in the case of silver chromate and silver iodide in gelatine, the colour changes are not due to any release of supersaturation, for whatever changes are to take place in the conductivity of the mixture occur immediately on mixing the solutions of lead nitrate and potassium iodide in gelatine. The conductivity also does not change at all with time. The cataphoretic experiments showed that at no stage the particles of lead iodide in gelatine are charged and it therefore appears to us that the insoluble portion of lead iodide in gelatine exists in a very highly dispersed condition as in the case of insoluble portion of silver chromate and of silver iodide in gelatine. In this case also the colour changes might be due to changes in the size of the particles.

It will appear from Table V that in this particular case about 40% of lead iodide exists in a finely dispersed condition and the remaining 60% in ionic condition. It is also noticed from Table VI that the amount of lead iodide which can remain in ionic condition in gelatine varies from (65% to 83%) with its p_H as well as with a change in the concentration of gelatine and of the reactants. Lead iodide thus behaves exactly as silver chromate in these respects. The present results however do not show if the fact that the inhibitive power of gelatine with reference to lead iodide is maximum for p_H value 5·00 has any significance in explaining the results about condition of lead iodide in gelatine.

Bolam (*Trans. Faraday Soc.*, 1928, **24**, 463; 1930, **26**, 133) has come to the conclusion on the basis of conductivity and *e. m. f.* measurements that lead iodide is maintained in a highly supersaturated solution in agar gel. Chatterji and Dhar (*loc. cit.*) have discussed these results of Bolam and shown that the percentage of lead iodide in the ionic state decreases (from 99·3 to 52) as the concentration of lead iodide increases. We are of the opinion that this case is similar to the case of silver chromate and lead iodide in gelatine and the influence discussed under silver chromate (last para, under condition of Ag_2CrO_4) might also be responsible for these conflicting results. It thus seems necessary to investigate further these cases in a greater detail in order to get a correct idea about the condition of these substances in gel.

It will not be out of place to discuss here the meaning of the term " inhibition " as used by various investigators.

We (Desai and Naik, *loc. cit.*) have observed that gelatine of p_H 5·75 has the smallest inhibitive power with reference to Ag_2CrO_4. According to Bolam and Donaldson (*loc. cit.*), the degree of supersaturation and therefore the inhibitive action of gelatine, probably, has an optimum value at p_H 5·0.

This conclusion of theirs is, however, difficult to reconcile with the inferences that can be drawn from Fig. 1 of their paper (*cf.* Bolam and Mackenzie, *loc. cit.*) as well as with our results namely that gelatine of p_H 5·75 has the smallest inhibitive power. If inhibition gives rise to supersaturation, one would have expected least supersaturation for gelatine of p_H 5·75 and greater for gelatine solutions of higher or lower p_H than 5·75. The results of Bolam and Donaldson however do not support this view. It thus appears that the inhibition experiments (inhibition in the sense of power to prevent precipitation) cannot always be utilised to give an idea of the degree of supersaturation although they may do so in some cases and under certain circumstances. A highly supersaturated solution can only be produced if by some means the formation or the growth of crystallisation centres is prevented. If inhibition gives rise to a colloidal solution (Dhar and co-workers, *loc. cit.*), one would expect that the stability of the yellow sol containing negatively charged particles of Ag_2CrO_4 should regularly decrease with an increase of acidity of gelatine and therefore more and more of gelatine should be required for inhibition with a decrease of p_H; our results however do not completely support the view for the inhibitive power of gelatine of p_H 5·75 to be minimum. Gelatine as an agent preventing precipitation of sparingly soluble substances generally (as in the case of Ag_2CrO_4, AgI and PbI_2), can possibly function as producing either supersaturation or a colloidal solution by preventing aggregation of small particles to larger masses or particles in a very highly dispersed form or two of these three forms or even all the three forms simultaneously. Hedges ("Liesegang rings and other periodic structures" 1932, p. 62) has pointed out "it seems, on the whole, that sparingly soluble substances readily form relatively stable, highly supersaturated solutions in gels......... The formation of colloidal solutions is not ruled out, however, for such a system would probably be produced by a sudden release of supersaturation through some cause or other, just as relatively large crystals would be formed as a result of very slow release of supersaturation". To this one may also add a third possibilty namely that gels may help in producing the sparingly soluble substances in a very highly dispersed form probably in molecular condition and that the union of these very fine particles by diffusion may ultimately give rise to larger visible particles. It thus appears necessary to investigate this problem further in order to understand clearly the difference in the rôle of gelatine in producing supersaturation and in preventing the precipitation of sparingly soluble substances and giving rise to colloidal solutions or in producing particles in a very highly dispersed form. In view of the conflicting results about the condition of silver chromate in gelatine, it is necessary to use the term "inhibition" in all cases of prevention of precipitation of sparingly soluble substances whether due to production of either supersaturation or a colloidal solution or particles having a very high degree of dispersion or any two of the three or even all the three forms simultaneously instead of using that term to indicate only supersaturation as done by Bolam and Mackenzie (*loc. cit.*), Bolam and Desai (*Trans. Faraday Soc.*, 1928, **24**, 50), Bolam and Donaldson (*loc. cit.*) and Desai and Nabar (*loc. cit.*, *cf.* also *J. Indian Chem. Soc.*, 1932, **9**, 141; *J. University of Bombay*, 1932, **1**, Part II, 28).

SUMMARY.

1. Experiments have been carried out to determine the condition of silver chromate, silver iodide and lead iodide in gelatine.

2. The conductivity results show that whatever changes in the conductivity are to take place occur immediately on mixing the solutions and that there is no gradual decrease of conductivity with changes in colour of the mixtures. The cataphoretic experiments do not show the presence of any charged colloidal particles in any of the cases. These results suggest that immediately the solutions are mixed some insoluble precipitate is produced, the particles of which are in a very highly dispersed condition—probably in molecular condition—and that changes in the colour of the mixtures are due to growth of these very fine particles into larger ones. A suggestion is made as to the likely causes of the conflicting results about the condition of silver chromate in gelatine.

3. The amount of silver chromate and lead iodide in ionic and highly dispersed condition varies to a large extent, depending on the p_H of gelatine and the concentration of gelatine and of the reactants, silver iodide does not show such a behaviour.

4. There is evidence to show that the tendency for the combination of various ions with gelatine is in the order

$$\left\{\begin{array}{l} Ag > CrO_4 > NO_3 \\ Ag > I > NO_3 \\ Pb > I > NO_3. \end{array}\right.$$

5. It is pointed out that the term "inhibition" should be used to indicate power to prevent precipitation generally whether it may be due to production of supersaturated solution or of colloidal solution or of particles in a very highly dispersed condition.

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Influence of Acidity of Gelatine on the Liesegang Rings of Silver Chromate and Silver Iodide.

By
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Influence of Acidity of Gelatine on the Liesegang Rings of Silver Chromate and Silver Iodide.

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Desai and Nabar (*J. Indian Chem. Soc.*, 1932, **9**, 141) have studied the changes in the nature of rings of silver chromate in gelatine when the acidity of the latter is increased. They have observed that an increase in the acidity of gelatine is accompanied by a decrease (*i*) in the time after which the first ring appears, (*ii*) in the distance between the same successive rings, and (*iii*) in the number of rings that can be obtained. While discussing their results they have suggested that there might be definite limits to the p_H value of gelatine within which good rings of silver chromate can be obtained. The present work was undertaken with a view to test this suggestion by obtaining rings of silver chromate in gelatine whose p_H is varied over a wide range and also to see if the variation of p_H has any influence on the nature of rings of silver iodide in gelatine. The sample of gelatine used in these experiments was the same as used by Desai and Naik (Paper on "Inhibitive power of gelatine" which will be published in the September issue of the Journal of the Bombay University, 1933) and the p_H of gelatine solution was varied in the same manner as done by them.

Rings of Silver Chromate in Gelatine.

1·5 C.c. of a normal solution of silver nitrate were allowed to diffuse into 20 c. c. of a 20 % gelatine gel impregnated with 0·9 c.c. of a normal solution of potassium chromate. The test tubes used in these experiments were all of the same diameter. The experiments were carried out in a room whose temperature (30°) did not appreciably fluctuate during the day. The distances between successive rings were measured by means of a cathetometer. The results are summarised below.

(1) Maximum number of rings are obtained with samples of gelatine having p_H 5·25 and 5·00 and their number decreases in gels of higher or lower p_H than this range.

(2) The distances between successive rings increase with all samples of gelatine. The distances between the same successive rings are greatest for gelatine of p_H 5·75 and smaller for samples of gelatine of p_H higher or lower than 5·75.

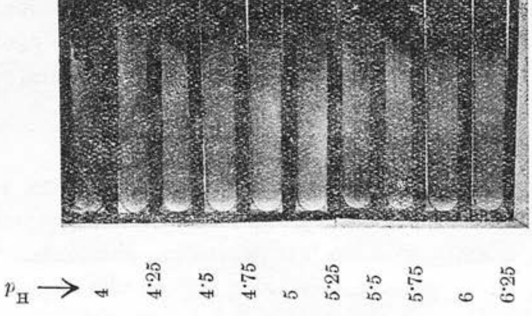
(3) Rings appear early in acidified gelatine while their appearance is delayed in samples whose acidity has been decreased. In conformity with this, the distance of the first ring from the top increases with an inrease of p_H.

The following observations were also made during this work.

(4) There is a tendency to get spiral shaped or broken rings in samples of acidified gelatine and larger and larger crystals are obtained with an increase of acidity. In samples of gelatine whose p_H is high, no rings are obtained and the precipitate is found to be more or less uniformly distributed.

(5) The size of the particles in the rings generally increases from the first to the last ring.

FIG. 1



In Fig. 1 is given a photograph of rings of silver chromate in samples of gelatine of different p_H. This photograph was taken with transmitted light. It corroborates what has been stated above. In test tube No. 1, one can easily see the presence of big crystals. The following additional conclusions can be drawn from the photograph.

(6) With an increase in the acidity of gelatine the thickness of the rings decreases.

(7) In any particular sample of gelatine, the thickness of the rings increases from the first ring to the last ring, but its compactness decreases at the same time.

These results support largely the observations of Desai and Nabar (*loc. cit.*). The slight differences in the results are due to changes in the concentration of gelatine and the reactants used in their experiments and in the present investigation. The influence of these factors is being further studied in greater detail.

The present results, however, completely support the suggestion of Desai and Nabar (*loc. cit.*) that there might be a definite range of p_H of gelatine within which good rings of silver chromate can be obtained.

It has been shown by us (Naik, Desai and Desai, *J. Indian Chem. Soc.*, 1934, **11**, 45) that the results about condition of silver chromate in gelatine in the yellow mixture are rather conflicting. It might exist either in supersaturated condition, colloidal condition or in a highly dispersed condition—particles being even of molecular size (*cf.* Naik, Desai and Desai, *loc. cit.*), in any two of the three or even simultaneously in all the three conditions. It is therefore considered advisable not to explain these results of ring experiments until we are able to find out the causes of the conflicting nature of the results of different investigators as well as our own different sets of experiments about the condition of silver chromate in the yellow mixture. It should, however, be stated that these experiments clearly show that samples of gelatine which are slightly acidic give good rings of silver chromate while those which may be relatively more alkaline may not give any rings at all. Also there is a definite range of p_H of gelatine in which good rings of silver chromate can be obtained ; the fact that gelatine with p_H 5·75 (Desai and Naik, *loc. cit.*) shows a minimum inhibitive power seems to have a bearing on the distances *between the same successive rings* (*cf. section* 2 above). Bolam and Donaldson *Trans. Faraday Soc.*, 1933, **29,** 864) have pointed out that the degree of supersaturatian of silver chromate in gelatine increases slightly as the p_H decreases from 5·7 to 5·0, and then falls off more rapidly as the p_H is further decreased. They have concluded that the degree of supersaturation probably has an optimum value at p_H 5·0. This fact seems to have some bearing on the nature of rings of silver chromate in gelatine, for as shown above best rings are obtained in samples of gelatine of p_H range, 5·0 to 5·25.

Rings of Silver Iodide in Gelatine.

1·5 C.c. of a 20% silver nitrate solution were allowed to diffuse into 20 c.c. of a 20% gelatine gel impregnated with 1 c.c. of a normal solution of potassium iodide. The test tubes were kept in a dark box during the period of formation of rings in order to prevent the effect of light as far as possible. The results of these experiments are summarised below.

(1) All samples of gelatine are equally effective in giving rings of silver iodide. Thirty three rings were obtained in each case.

(2) In all the cases the distances between successive rings first decrease regularly and then increase. The closest rings are those which occur between the eighteenth and the twentythird ring.

(3) The distances between the same successive rings decrease more or less regularly with an increase of the p_H of gelatine.

(4) The first ring appears after about 23 hours in all the cases.

From observation (3) it would appear that for values of p_H much higher than 6·0, only a continuous band of precipitate might be obtained instead of a number of rings. This is rather interesting in view of the fact as shown by Desai and Naik (*loc. cit.*) that the inhibitive power of gelatine with reference to AgI continuously increases with an increase in the p_H of gelatine. It is, however, necessary to carry out more experiments before this fact can be utilised to explain the nature of rings of silver iodide in gelatine.

Silver iodide being relatively very much sensitive to light when compared with silver chromate, it was not found possible to get a good photograph of rings either with transmitted or reflected light. We would however like to record the following visual observations here.

(1) The thickness of the rings is generally much greater than the distance of the clear interspace between the rings.

(2) The thickness of the rings almost regularly decreases from the first ring upto the eighteenth to twentythird ring after which it again begins to increase regularly.

(3) All the rings have got almost the same compactness.

(4) The size of the particles in almost all the rings remains almost the same.

(5) The clear interspace between the first and the eighteenth to twentythird ring became somewhat darkish on exposure to light, while that between the eighteenth to twentythird and the thirtythird ring became deep brown.

According to the various theories that have been put forward to explain the Liesegang phenomena, there should be a gradual increase in the spacing between the successive rings. The fact that the distance between the successive rings of AgI in gelatine decreases up to about the twentieth ring cannot therefore be explained on the basis of any of the existing theories. The other noteworthy instances of this type, *i.e.*, where the distance between the successive rings decreases, are those reported by Davis (*J. Amer. Chem. Soc.*, 1917, **39**, 1312) about bands of mercury obtained by allowing mercurous nitrate to diffuse in agar gel impregnated with sodium formate, by Hedges and Henley (*J. Chem. Soc.*, 1928, 2714) about bands of arsenious sulphide obtained by allowing solutions of ferric chloride or aluminium sulphate to diffuse into agar gel containing sols of arsenious sulphide, and by Mukherjee and Chatterji (*Kolloid Z.*, 1930, **50**, 147) about bands of zinc and nickel ferricyanide and cobalt ferrocyanide. The rings of AgI in gelatine obtained by us are, however, peculiar in this respect that although the distance between successive rings first decreases, it increases in case of the later rings (twentieth to twentythird ring). More detailed work is necessary before these anomalies can be explained.

It has been shown by us (Naik, Desai and Desai, *loc. cit,*) that about, 90% of AgI in gelatine exists in the mixture in condition other than ionic or colloidal. The particles of silver iodide which form on the meeting of $AgNO_3$ and KI are first probably in molecular condition and they grow further due to diffusion . The particles being in a very highly dispersed form, might absorb to a certain extent the substances that may be present in the neighbourhood. However in view of the fact that the space between the rings becomes coloured when exposed to light, it appears that the adsorption may not be very marked.

SUMMARY.

1. Liesegang rings of silver chromate and silver iodide have been obtained in samples of gelatine of different p_H.

2. In the case of silver chromate rings, the results in general support the preliminary results of Desai and Nabar. The suggestion of these authors that there might be a definite range of p_H of gelatine within which good rings of silver chromate can be obtained is also supported by the present results.

3. All samples of gelatine appear to be equally effective in giving rings of silver iodide. The distance between successive rings first decreases and then increases. Also the distances between the same successive rings decrease more or less regularly with an increase of the p_H of gelatine.

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INHIBITIVE POWER OF GELATINE

By

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Bolam and Desai (Trans. Faraday Soc., 24, 50, 1928) have observed that the time required for the appearance of red coloured precipitate from a yellow mixture of $AgNO_3$ and K_2CrO_4 in gelatine decreases and its p_H increases on subjecting it to hydrolysis. This property of preventing the precipitation of insoluble salt has been termed " inhibitive power ". Desai and Nabar (Journ. University of Bombay 1, Part II, 28, 1932) have shown that the inhibitive power of gelatine with reference to Ag_2CrO_4 increases on decreasing the p_H of gelatine. Desai and Nabar (Trans. Faraday Soc. 28, 449, 1932; also see Bolam and Mackenzie, ibid., 22, 151, 162, 1926) have further shown that in the yellow coloured mixture Ag_2CrO_4 exists in ionic condition. In the present paper are given the results of the study of precipitation of Ag_2CrO_4, AgI and PbI_2 in gelatine under different conditions.

(*a*) *Preparation of Ag_2CrO_4 in samples of gelatine of different p_H.*

The gelatine used in these experiments contained 1.177% ash and 18% moisture. The inhibitive power was determined in exactly the same manner as before. The p_H of gelatine was determined colourometrically. Samples of gelatine having different p_H were prepared by adding suitable amounts of acetic acid or sodium acetate. Experiments were carried out by using different equivalent amounts of the reactants. The results of these experiments are given in Tables I to VII.

TABLE I.

Total Volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

p_H of gelatine = 4·5.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

5 c. c. $\frac{N}{100}$ $AgNO_3$+ 5 c. c. $\frac{N}{100}$ K_2CrO_4		6 c. c. of $\frac{N}{100}$ $AgNO_3$+ 6 c. c. $\frac{N}{100}$ K_2CrO_4		7 c. c. $\frac{N}{100}$ $AgNO_3$+ 7 c. c. $\frac{N}{100}$ K_2CrO_4		8 c. c. $\frac{N}{100}$ $AgNO_3$+ 8 c. c. $\frac{N}{100}$ K_2CrO_4		9 c. c. $\frac{N}{100}$ $AgNO_3$+ 9 c. c. $\frac{N}{100}$ K_2CrO_4	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
0·6	1	1·0	2	1·4	2	1·9	2	2·4	2
0·7	2	1·1	6	1·5	4	2·0	4	2·6	5
0·8	7	1·2	16	1·6	9	2·1	7	2·8	11
0·9	19	1·3	45	1·7	24	2·2	13	3·0	21
1·0	43	1·4	120	1·8	49 to 50	2·3	23	3·2	40
						2·4	44		

TABLE II.

Total volume of mixture = 20 c. c.
Concentration of gelatine = 3%.
p_H of gelatine = 4·75.
Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{10}$ $AgNO_3$ + 4 c. c. $\frac{N}{100}$ K_2CrO_4		5 c. c. $\frac{N}{100}$ $AgNO_3$ + 5 c. c. $\frac{N}{100}$ K_2CrO_4		6 c. c. $\frac{N}{100}$ $AgNO_3$ + 6 c. c. $\frac{N}{100}$ K_2CrO_4		7 c. c. $\frac{N}{100}$ $AgNO_3$ + 7 c. c. $\frac{N}{100}$ K_2CrO_4	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1·0	1	1·8	1	2·8	1	4·0	2
1·2	3	1·9	2	3·0	3	4·2	3
1·4	10	2.0	3	3·2	6	4·4	5
1·6	24	2·1	6	3·4	13	4·6	9
1·8	50 to 51	2·2	9	3·6	26	4·8	15
		2·3	13	3·8	53	5·0	25
		2·4	21			5·2	39
		2·5	30				

TABLE III.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

p_H of gelatine = 5·00.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ $AgNO_3$+ 4 c. c. $\frac{N}{100}$ K_2CrO_4		5 c. c. $\frac{N}{100}$ $AgNO_3$+ 5 c. c. $\frac{N}{100}$ K_2CrO_4		6 c. c. $\frac{N}{100}$ $AgNO_3$+ 6 c. c. $\frac{N}{100}$ K_2CrO_4		7 c. c. $\frac{N}{100}$ $AgNO_3$+ 7 c. c. $\frac{N}{100}$ K_2CrO_4	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1·6	2	2·8	1	4·2	1	5·8	1
1·8	4	3·0	2	4·4	2	6·1	2
2·0	8	3·2	4	4·6	3	6·4	4
2·2	13	3·4	6	4·8	5	6·7	6
2·4	23	3·6	11	5·0	7	7·0	10
2·6	35	3·8	17	5·2	10	7·3	16
		4·0	27	5·4	15	7·6	25
		4·2	42	5·6	21	7·9	39
				5·8	27		

TABLE IV.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

p_H of gelatine = 5·25.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ $AgNO_3$+ 4 c. c. $\frac{N}{100}$ K_2CrO_4		5 c. c. $\frac{N}{100}$ $AgNO_3$+ 5 c. c. $\frac{N}{100}$ K_2CrO_4		6 c. c. $\frac{N}{100}$ $AgNO_3$+ 6 c. c. $\frac{N}{100}$ K_2CrO_4		7 c. c. $\frac{N}{100}$ $AgNO_3$+ 7 c. c. $\frac{N}{100}$ K_2CrO_4	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1·7	1	3·7	4	5·2	3	7·0	2
2·0	4	4·0	8	5·6	6	7·4	4
2·3	10	4·3	14	6·0	10	7·8	7
2·6	20	4·6	23	6·4	19	8·2	10
2·9	37	4·9	40	6·8	33	8·6	17
3·1	53	5·2	63	7·2	54	9·0	27
				7·6	85 to 87	9·4	43

TABLE V.

Total volume of mixture = 20 c. c.
Concentration of gelatine = 3%.
p_H of gelatine = 5·52 (gelatine as such).
Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ AgNO$_3$+ 4 c. c. $\frac{N}{100}$ K$_2$CrO$_4$		5 c. c. $\frac{N}{100}$ AgNO$_3$+ 5 c. c. $\frac{N}{100}$ K$_2$CrO$_4$		6 c. c. $\frac{N}{100}$ AgNO$_3$+ 6 c. c. $\frac{N}{100}$ K$_2$CrO$_4$		7 c. c. $\frac{N}{100}$ AgNO$_3$+ 7 c. c. $\frac{N}{100}$ K$_2$CrO$_4$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1·6	1	3·4	1	5·4	2	7·4	2
1·9	3	3·7	3	5·7	3	7·7	3
2·2	6	4·0	5	6·0	6	8·0	5
2·5	12	4·3	8	6·3	9	8·3	8
2·8	23	4·6	15	6·6	13	8·6	11
3·1	41	4·9	25	6·9	20	8·9	17
		5·2	39	7·2	27	9·3	26
						9·7	42

TABLE VI.

Total Volume of mixture = 20 c. c.
Concentration of gelatine = 3%.
p_H of gelatine = 5·75.
Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ $AgNO_3$+ 4 c. c. $\frac{N}{100}$ K_2CrO_4		5 c. c. $\frac{N}{100}$ $AgNO_3$+ 5 c. c. $\frac{N}{100}$ K_2CrO_4		6 c. c. $\frac{N}{100}$ $AgNO_3$+ 6 c. c. $\frac{N}{100}$ K_2CrO_4		7 c. c. $\frac{N}{100}$ $AgNO_3$+ 7 c. c. $\frac{N}{100}$ K_2CrO_4	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
2·4	3	4·4	2	6·5	2	9·4	2
2·7	5	4·7	3	6·8	3	9·8	3
3·0	10	5·0	5	7·1	3	10·2	3
3·3	17	5·3	7	7·4	4	10·6	4
3·6	31	5·6	10	7·7	5	11·0	6
3·9	48	5·9	15	8·0	6	11·4	8
		6·2	21	8·3	8	11·8	10
		6·5	29	9·0	15	12·2	13
						12·6	17
						13·0	21

TABLE VII.

Total volume of mixture = 20 c. c.

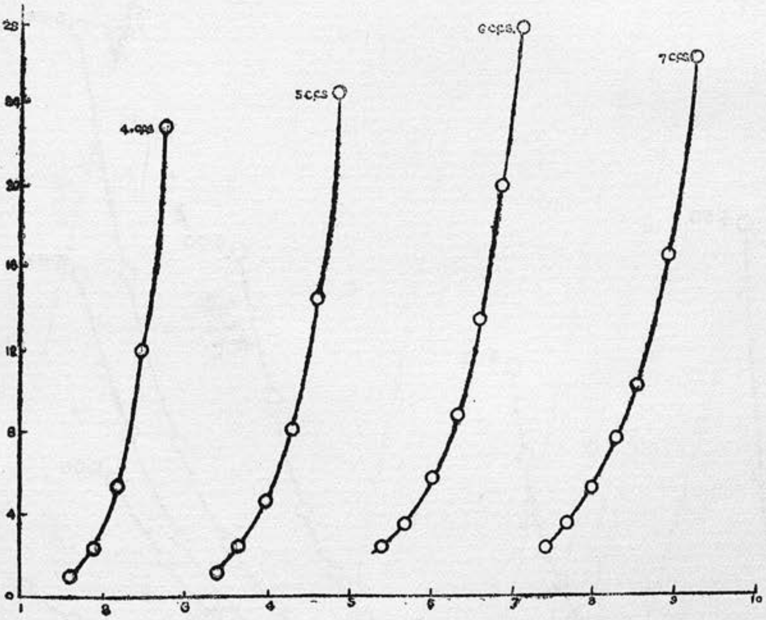
Concentration of gelatine = 3%.

p_H of gelatine = 6·00.

5 c. c. of $\frac{N}{100}$ $AgNO_3$ + 5 c. c. of $\frac{N}{100}$ K_2CrO_4	
c. c. of gelatine.	Time of Inhibition in minutes.
3·8	2
4·1	4
4·4	7
4·7	13
5·0	20

It will appear from the tables that in every case the time of inhibition or the inhibitive power of gelatine increases with an increase n the amount of gelatine added. In Fig. 1 is plotted the amount of

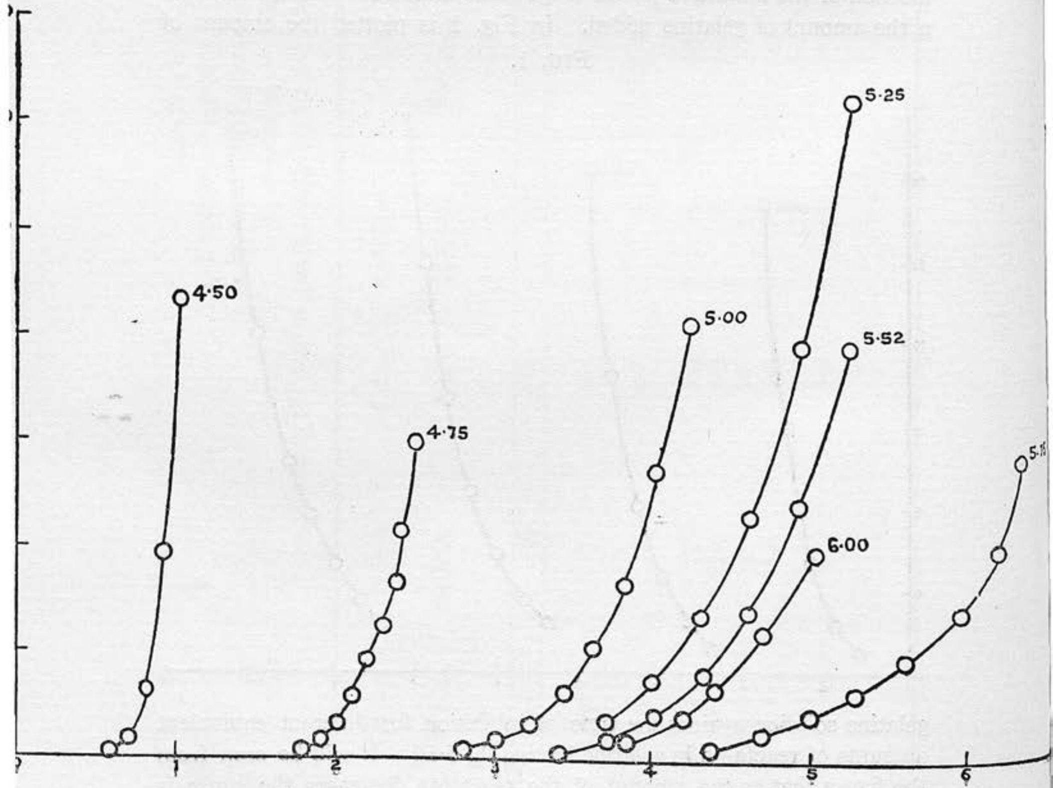
FIG. 1.



gelatine solution against the time of inhibition for different equivalent amounts of reactants in gelatine having P_H 5·52. It will be seen from the figure that as the amount of the reactants decreases the curve is displaced more and more towards the Y-axis and that the curves are displaced by almost the same distance for a change in the amount of the reactants by 1 c. c. It would thus appear as if the amount of the reactants whose curve corresponds to the ordinate will approximately give an idea about the solubility of Ag_2CrO_4 in that particular sample of gelatine. The curves for other samples of gelatine are also exactly of the same nature as those given in Fig. 1. The solubility of Ag_2CrO_4 in gelatine of p_H 5.75 calculated on the basis of above ideas comes to about 10 times more than that in water. The solubility of Ag_2CrO_4 in samples of p_H 4·5 and 6·0 comes to about 10% more than that in gelatine of p_H 5·75. It would thus appear that although with slight changes in the p_H of gelatine the inhibitive power changes considerably, the solubility of Ag_2CrO_4 in gelatine is not affected to any appreciable extent by those changes. These results are therefore in line with those obtained by Desai and Nabar (Journ. University of Bombay, loc. cit.).

In Fig. 2 is plotted the amount of gelatine (C) against the time of

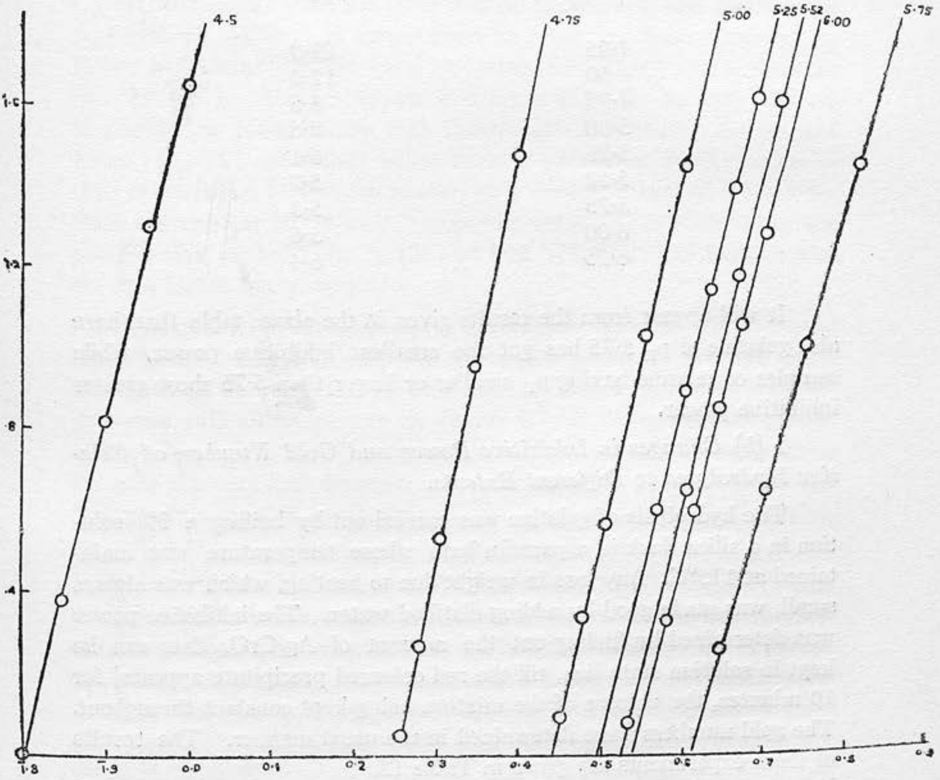
FIG. 2.



inhibition (T) for samples of different p_H in the case of 5 c. c. of $\frac{N}{100}AgNO_3$ + 5 c. c. of $\frac{N}{100}K_2CrO_4$. It will appear from the figure that the curves for samples of gelatine of p_H either smaller or larger than 5·75 are displaced towards the left of the curve for p_H 5·75. Also as the p_H increases or decreases more and more than 5·75 the curves are displaced more and more towards the ordinate. The curves obtained with different amounts of the reactants show exactly the same behaviour. These results thus show that the inhibitive power of gelatine of p_H 5·75 is minimum and that the inhibitive power of other samples of gelatine of p_H smaller or larger than 5·75 is greater than that of sample of p_H 5·75. These results have a very important bearing on the nature of rings of Ag_2CrO_4 in gelatine for as argued by Desai and Nabar (Journ. Indian Chem. Soc., 9, 141, 1932) there might be a definite range of p_H of gelatine within which good rings can be obtained. This point will however be dealt with in another paper.

In Fig. 3 is given the plot of log C and log T for the same values

FIG. 3



which have been used in Fig. 2. It will appear from this figure that the plot is a straight line and the relation between C and T can be expressed by an equation of the form

$$T = K\ (C)^m$$

where K and m are constants. The time of inhibition thus varies exponentially with the amount of gelatine.

In Table VIII are given the results of inhibitive power of gelatine with reference to Ag_2CrO_4 obtained in another manner. In these experiments the amount of Ag_2CrO_4 that can be kept in the mixture for 10 minutes before the appearance of the red colour when 6 c. c. of 3% gelatine solution are added, has been determined.

TABLE VIII.

Total volume of the mixture = 20 c. c.
Concentration of gelatine = 3%.
Amount of gelatine = 6 c. c. in 20 c. c. of mixture.
Time of inhibition (fixed) = 10 minutes.

p_H of gelatine	c. c. of $\frac{N}{100}$ Ag_2CrO_4
4·25	22·0
4·50	12·0
4·75	8·6
5·00	6·8
5·25	6·1
5·52	5·7
5·75	5·3
6·00	5·6
6·25	6·4

It will appear from the results given in the above table that here also gelatine of p_H 5·75 has got the smallest inhibitive power, while samples of gelatine having p_H smaller or larger than 5·75 show greater inhibitive power.

I (*b*) *Changes in Inhibitive Power and Gold Number of Gelatine Hydrolysed to Different Extents.*

The hydrolysis of gelatine was carried out by boiling a 3% solution in a silica flask in a paraffin bath whose temperature was maintained at 115°C. Any loss in weight due to heating, which was always small, was made good by adding distilled water. The inhibitive power was determined by finding out the amount of Ag_2CrO_4 that can be kept in solution state (i.e., till the red coloured precipitate appears) for 10 minutes, the volume of the mixture being kept constant throughout. The gold numbers were determined in the usual manner. The results of these experiments are given in Table IX.

TABLE IX.

Total volume of mixture (for inhibitive power) = 20 c. c.
Conc. of gelatine = 3%.
Conc. of gelatine (for protective power) = 0·001%.
Time of inhibition = 10 minutes.

Gelatine hydrolysed for hours.	Resulting p_H.	c. c. of $\frac{N}{100}$ Ag_2CrO_4.	Gold Numbers.
0 (dispersed at 40°C.)	5·52	5·67	·0125
1	5·54	5·60	·0139
2	5·57	5·55	·0149
4	5·62	5·50	·0160
7	5·69	5·40	·0168
10	5·72	5·35	·0172

It will appear from the table that on hydrolysing the gelatine its p_H increases. This is in agreement with what has been observed by Bolam and Desai (loc. cit.) and by Desai and Nabar (Trans. Faraday Soc., loc. cit.). Also hydrolysed gelatine is found to be less effective in preventing precipitation than unhydrolysed gelatine. Bolam and Desai (loc. cit.) got a clear indication of a maximum in the value of time of inhibition (inhibitive power) at a certain stage of hydrolysis. Such a maximum in the inhibitive power has not been observed in the present case, probably due to the fact that hydrolysis has been carried out at a higher temperature.

The gold numbers increase on hydrolysing gelatine. If the gold numbers are taken to indicate the protective power of gelatine as is usually done, the results show that the protective power of gelatine decreases with an increase in the degree of hydrolysis. Ganguly (Journ. Indian Chem. Soc., 3,177, 1926) observed that on hydrolysing gelatine the gold numbers first decrease and then increase. In view of the fact that gelatine solution has been boiled freely in silica flask in Ganguly's as well as our experiments it is not understood why a minimum in the value of gold numbers has not been observed in the present case.

In order to see how far the changes in the inhibitive and protective power of gelatine on hydrolysis are brought about by a change in the acidity of gelatine, some experiments were also carried out by bringing back the p_H of hydrolysed gelatine to original value and then determine its inhibitive power and gold numbers. These results are given in Table X.

TABLE X.

Inhibitive and protective power on restoring p_H to original value.

Gelatine hydrolysed for hours.	p_H of hydrolysed gelatine brought back to the value.	c. c. of $\frac{N}{100}$ Ag_2CrO_4.	Gold Numbers.
1	5·52	5·66	·0126
2	5·51	5·67	·0128
4	5·50	5·66	·0128
7	5·52	5·67	·0128
10	5·50	5·67	·0130

It will appear from the above table that on restoring the p_H of hydrolysed gelatine to its original value (i. e., to the value of p_H of unhydrolysed gelatine) both the inhibitive power as well as gold numbers become the same as for unhydrolysed gelatine. These results thus show that changes in inhibitive and protective power brought about by hydrolysis are mainly due to a change in acidity of gelatine.

Bolam and Desai (loc. cit.) have stated that obviously inhibition and protection do not go hand in hand for there is a difference in the function of gelatine in the two cases. In the former rôle gelatine opposes the formation or growth of crystallisation centres and thus gives rise to a highly supersaturated solution; in the latter rôle gelatine prevents aggregation of small particles to larger masses and thus gives rise to a colloidal solution. On comparing the results of inhibition and gold numbers on hydrolysis it will appear that if gold numbers are taken to indicate the protective power, both inhibitive and protective power of gelatine decrease on hydrolysis. This is apparently not in agreement with the view of Bolam and Desai. Hydrolysis increases the degree of dispersion of the precipitate as has been observed by Bolam and Desai (loc. cit.) as well as in these experiments. This is due to the fact that there is less resistance to the growth of crystallisation centres in the former case (less inhibitive power) and therefore if the number of crystallisation centres is large, one would naturally expect that, other things remaining same, the particles of the precipitate will be smaller in hydrolysed than in unhydrolysed gelatine. The changes in the gold numbers on hydrolysis can be due to either changes in the protective power as seen from finer precipitate or changes in the acidity of gelatine which affect coagulation of gold sol. The original gold number having been obtained on restoring the original p_H, it appears that the gold number changes on hydrolysis are mostly due to the effect of changes of acidity on the coagulation of gold sol.

In Table XI are given the values of gold numbers for samples of unhydrolysed gelatine of different p_H.

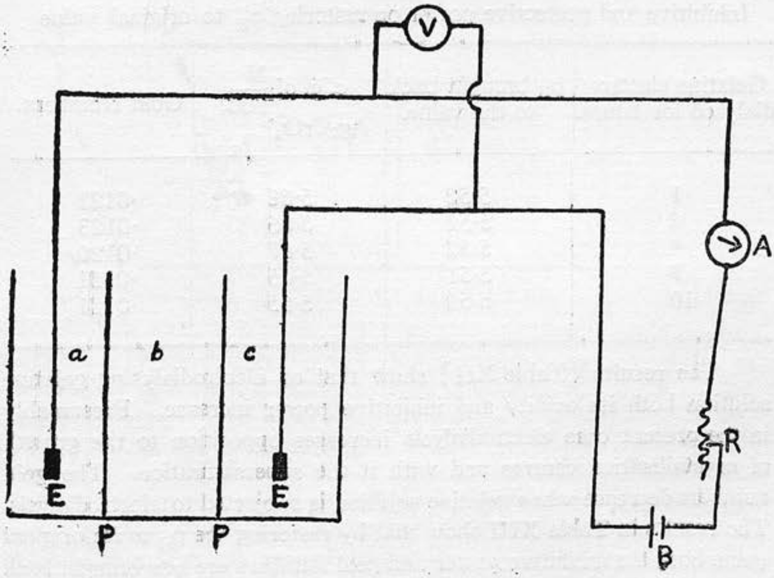
TABLE XI.

p_H of gelatine made equal to that of hydrolysed gelatine.	Gold Numbers.
5·57	·0139
5·62	·0160
5·69	·0165
5·72	·0172

It will appear from the results that with a decrease in the acidity of gelatine the gold number increases. Also whether the changes in p_H are brought about by hydrolysis (Table IX) or by adding sodium acetate (Table XI) the gold numbers change in the same fashion and almost to the same extent for same changes in p_H.

The changes in the inhibitive power of gelatine on hydrolysis would also seem to be wholly due to changes in its acidity as shown by results given in Tables VIII, IX and X. These results thus show that changes in the inhibitive power and gold numbers on hydrolysis are due to changes in its p_H.

DIA. A.



I (c) *Changes in the inhibitive power and gold number of gelatine electrodialysed to different extents.*

The arrangement for electrodialysis is shown in Diagram A. The gelatine solution was kept in the middle compartment of the electrodialyser ; the two side compartments were filled to the same level as the middle compartment with conductivity water. A direct current was passed using platinum plates as electrodes. Some soluble substances came out in the dialysate. Both inhibitive and protective power of gelatine electrodialysed for different periods as well as when the p_H was restored to original value were determined as before. The results are given in Tables XII and XIII.

TABLE XII.

Gelatine electro-dialysed for hours.	Resulting p_H.	c. c. of $\frac{N}{100}$ Ag_2CrO_4.	Gold Numbers.
0	5·52	5·67	·0125
1	5·48	5·75	·0119
2	5·42	5·88	·0108
4	5·35	6·05	·0098
7	5·28	6·18	·0090
10	5·20	6·30	·0084

TABLE XIII.

Inhibitive and protective power on restoring p_H to original value.

Gelatine electro-dialysed for hours.	p_H brought back to the value.	c. c. of $\frac{N}{100}$ Ag_2CrO_4.	Gold Numbers.
1	5·52	5·68	·0121
2	5·52	5·66	·0123
4	5·52	5·67	·0120
7	5·51	5·65	·0121
10	5·52	5·65	·0121

The results (Table XII) show that on electrodialysing gelatine solution both its acidity and inhibitive power increase. Presumably in the present case electrodialysis increases opposition to the growth of crystallisation centres and with it the supersaturation. The gold numbers decrease when gelatine solution is subjected to electrodialysis. The results in Table XIII show that by restoring the p_H to its original value both the inhibitive power and gold numbers are also brought back to their original values as in the case of hydrolysed gelatine. Thus in this case also the changes in the inhibitive power and gold numbers on electrodialysing gelatine solution seem to be mainly brought about by changes in the p_H of gelatine.

It should be noted that on hydrolysing gelatine the gold number increases but on electrodialysing it the gold number decreases. In the former case the amount of 0·001% gelatine solution necessary for protecting 10 c. c. of Zisgmondy gold sol when 1 c. c. of 10% solution of NaCl is added increases while in the latter case it decreases. It will thus appear that hydrolysed gelatine prevents the coagulation of gold sol much less effectively than the electrodialysed gelatine. The present results distinctly show that the nature of products of hydrolysis and electrodialysis is very different and that the products of electrodialysis have greater protective power than products of hydrolysis.

In Table XIV are given the results of gold number determinations of gelatine solution which has not been electrodialysed but whose p_H has been reduced to the same value as obtained during electrodialysis by adding to the gelatine solution suitable amounts of acetic acid. The results show that whether changes in p_H are brought about by electrodialysing gelatine solution (Table XII) or by adding acetic acid to it (Table XIV) the gold number changes in the same manner and almost to the same extent for same changes in p_H.

TABLE XIV.

p_H of gelatine made equal to that of electrodialysed gelatine.	Gold Numbers.
5·23	·0088
5·28	·0093
5·35	·0099
5·42	·0108
5·48	·0120

The results given in Tables XI and XIV show that on adding either sodium acetate or acetic acid to gelatine solution the gold number increases. This is due to the fact that the added electrolytes try to coagulate the gold sol and therefore more of gelatine solution is required for protection. Also there does not appear any influence of the similarly charged ion in either case.

II. *Precipitation of AgI in samples of Gelatine of different p_H.*

These experiments were performed in the same manner as done with Ag_2CrO_4. The influence of light was minimised by working in subduced light. On mixing solutions of $AgNO_3$ in gelatine, and KI in gelatine, the mixture attained somewhat greenish colour although no precipitation was visible. When precipitate of AgI began to separate from the mixture the colour changed to whitish yellow. The time required to get the whitish yellow colour of the same intensity as the standard was taken as a measure of inhibitive power in each case. The results of these experiments are given in Table XV.

TABLE XV.

Total volume of mixture = 20 c. c.
Concentration of gelatine = 3%.

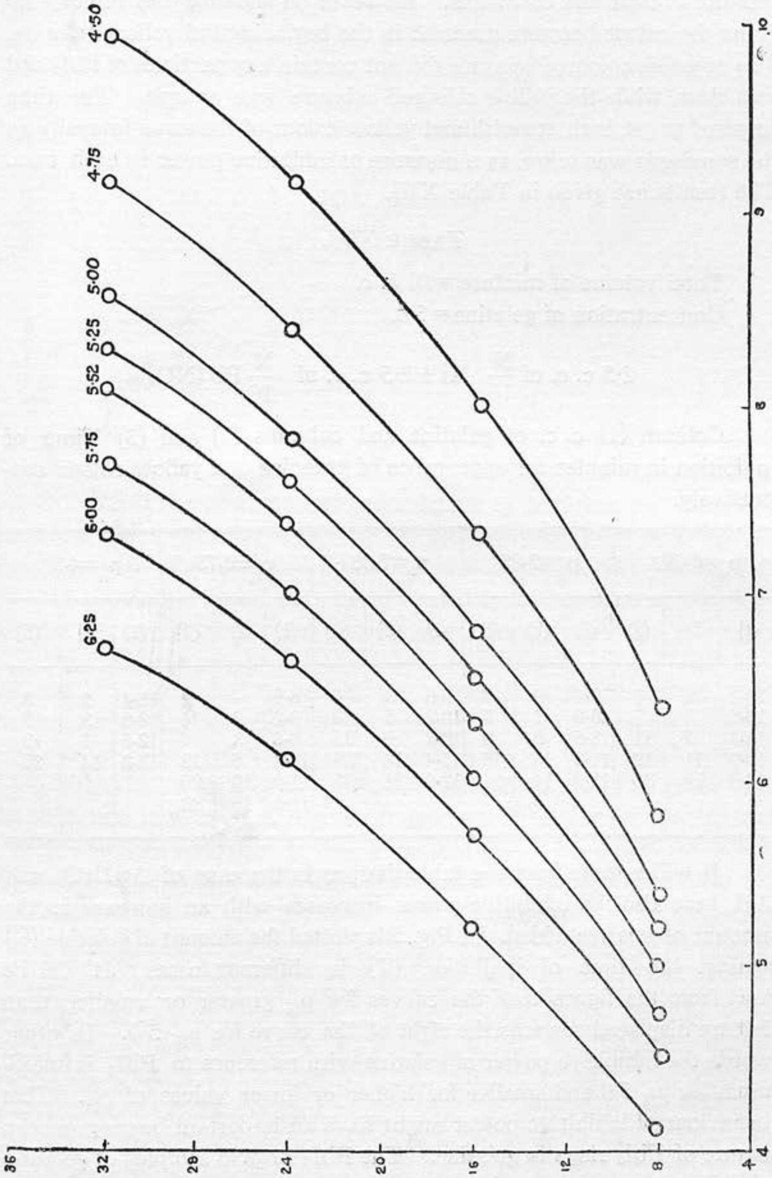
$$3 \text{ c. c. of } \frac{N}{10} \text{ KI} + 3 \text{ c. c. of } \frac{N}{10} \text{ AgNO}_3$$

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

$p_H=4\cdot5$		$p_H=4\cdot75$		$p_H=5\cdot00$		$p_H=5\cdot25$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
6·4	8	5·8	8	5·4	8	5·2	8
8·0	16	7·3	16	6·8	16	6·6	16
9·2	24	8·4	24	7·8	24	7·6	24
10·0	32	9·2	32	8·6	32	8·3	32
$_H=5\cdot52$		$p_H=5\cdot75$		$p_H=6\cdot00$		$p_H=6\cdot25$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
5·0	8	4·7	8	4·5	8	4·1	8
6·3	16	6·0	16	5·7	16	5·2	16
7·4	24	7·0	24	6·6	24	6·1	24
8·1	32	7·7	32	7·3	32	6·7	32

It will be seen from the above table that for all samples of gelatine the inhibitive power increases with an increase in amount of gelatine. This has also been observed in the case of Ag_2CrO_4. In Fig. 4 is given the plot of the amount of gelatine added (C) and the time of inhibition (T) for different samples of gelatine. It will appear from the figure that as the p_H of gelatine decreases the curves are displaced more and more away from the ordinate. In other words the inhibitive power decreases with a decrease of p_H of gelatine solution. This behaviour is therefore quite different from that with Ag_2CrO_4. This difference in the inhibitive power in the two cases probably influences the nature of rings of AgI and Ag_2CrO_4 in gelatine. We have observed that the nature of AgI and Ag_2CrO_4 rings in gelatine is not similar. This point will be dealt with separately elsewhere.

FIG. 4



In this case also as with Ag_2CrO_4 the plot of log C and log T is a straight line. The inhibitive power thus varies exponentially with the amount of gelatine.

III. *Precipitation of PbI_2 in samples of Gelatine of different p_H.*

When Pb $(NO_3)_2$ in gelatine and KI in gelatine are mixed, the mixture is clear and colourless. However on allowing the mixture to stand the colour becomes greenish in the beginning and yellow later on. The greenish coloured mixture did not contain any particles of PbI_2 and was clear, while the yellow coloured mixture was opaque. The time required to get both greenish and yellow colour of the same intensity as the standards was taken as a measure of inhibitive power in each case. The results are given in Table XVI.

TABLE XVI.

Total volume of mixture = 20 c. c.
Concentration of gelatine = 3%.

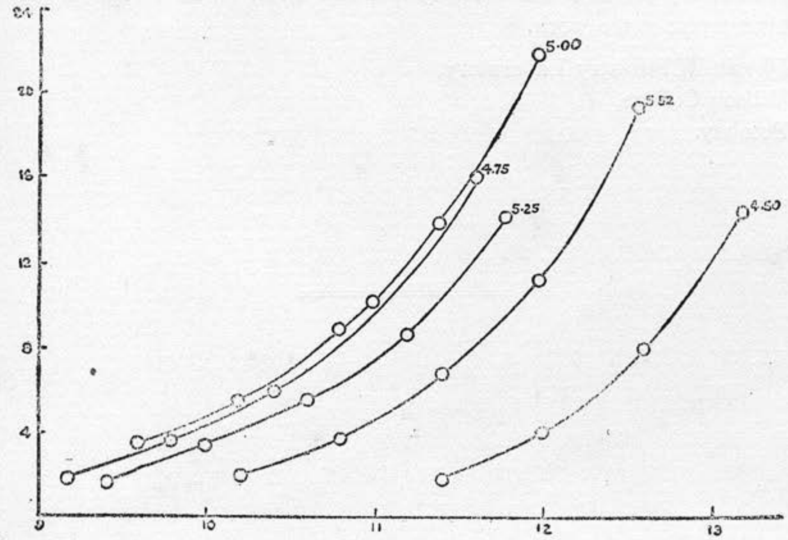
$$2{\cdot}5 \text{ c. c. of } \frac{N}{10} \text{ KI} + 2{\cdot}5 \text{ c. c. of } \frac{N}{10} \text{Pb} (NO_3)_2.$$

Column (1) c. c. of gelatine and columns (2) and (3) Time of inhibition in minutes for appearance of greenish and yellow colour respectively.

p_H=5·52			p_H=5·25			p_H=5·00			p_H=4·75			p_H=4·5		
(1)	2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
10·2	2	3	9·4	2	3	9·6	3	6	8·6	–	2	11·4	2	3
10·8	3	7	10·0	3	6	10·2	5	10	9·2	2	4	12·0	3	7
11·4	7	11	10·6	5	9	10·8	9	15	9·8	3	7	12·6	7	13
12·0	11	19	11·2	8	15	11·4	13	25	10·4	6	12	13·2	14	25
12·6	19	35	11·8	14	24	12·0	21	37	11·0	10	20			
									11·6	16	33			

It will appear from the table that, as in the case of Ag_2CrO_4 and AgI, here also the inhibitive power increases with an increase in the amount of gelatine added. In Fig. 5 is plotted the amount of gelatine (C) against the time of inhibition (T) in different cases. It will be seen from the figure that the curves for p_H greater or smaller than 5·0 are displaced towards the right of the curve for p_H 5·0. In other words the inhibitive power of gelatine with reference to PbI_2 is maximum for p_H 5·0 and smaller for higher or lower values of p_H. This behaviour of inhibitive power might have an important bearing on the nature of PbI_2 rings in gelatine. The PbI_2 rings in samples of gelatine of different p_H are under investigation.

FIG. 5.



SUMMARY.

Inhibitive power of samples of gelatine of different p_H with reference to precipitation of Ag_2CrO_4, AgI and PbI_2 has been determined. In all the cases the inhibitive power increases with an increase in the amount of gelatine added and the plot of log C (amount of gelatine added) and log T (time of inhibition) is a straight line. It is found that the inhibitive power with reference to Ag_2CrO_4 is minimum for gelatine of p_H 5·75 and is greater for higher or lower values of p_H. In the case of AgI the inhibitive power continuously decreases with a decrease of p_H of gelatine. The inhibitive power with reference to PbI_2 is maximum for gelatine of p_H 5·0 and is smaller for higher or lower values of p_H. It is suggested that the difference in the inhibitive power with reference to Ag_2CrO_4, AgI and PbI_2 might have an important bearing on the nature of rings of these substances in gelatine.

On hydrolysing gelatine, its p_H and gold number increase while inhibitive power with reference to Ag_2CrO_4 decreases. When gelatine solution is electrodialysed, its p_H and gold number decrease while inhibitive power with reference to Ag_2CrO_4 increases. On bringing back the p_H of gelatine to its original value both the original inhibitive power and gold numbers are restored, thus showing that the changes are mainly due to changes in p_H of gelatine. It is observed that the products of hydrolysis have less protective power than products of electrodialysis.

The authors wish to thank Mr. G. M. Nabar for some help in the preliminary stages of this investigation and Prof. A. R. Normand for his interest in the work.

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Note:—Since the present paper was submitted for publication there has appeared a paper by Bolam and Donaldson (Trans. Faraday Soc., 29 864, 1933) on the influence of gelatine on precipitation of silver chromate. From Fig. 1 of their paper it is clear that the inhibitive power (property of preventing the precipitation of insoluble salt) of gelatine steadily increases with an increase of acidity of gelatine (p_H range tried by them is 5·7 to 4·3). Our results (Fig. 2 of our paper) also point to the same conclusion for the same range of p_H and their results thus completely support our results. On p. 876 of their paper Bolam and Donaldson have calculated the degree of supersaturation according to the theory of Von Weimarn (Kolloid—Z., 2, 1'99, 1908, etc.; 3, 3, 1908, etc.; 4, 27, 1909 ; Grundzuge der Dispersoidchemie, 1911 ; Zum Lehre von dem Zustanden der Materie, 1914) and found that the degree of supersaturation increases slightly as the p_H decreases from 5·7 to 5·0, and then falls off more rapidly as the p_H is further decreased. They conclude that the degree of supersaturation, and therefore the inhibitive action of the gelatine, probably has an optimum value at P_H=5·0. It is difficult to reconcile this latter conclusion with the inferences that can be drawn from Fig. 1 of their paper as well as with our present results. It may however be pointed out that the optimum value of supersaturation for gelatine of p_H=5·0 seems to influence considerably the nature and number of Ag_2CrO_4 rings in gelatine, for as our results have shown (will be published in due course) best rings are obtained in samples of gelatine of p_H range 5·0 to 5·25.

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS

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Dialysis has been utilised since the time of Graham for freeing a colloidal solution from the impurities necessarily introduced into it at the time of its preparation, *viz.*, the peptising agent and the other electrolytes formed as a result of double decomposition. The importance of the influence of dialysis on the various properties of colloidal solutions has, however, not been generally realised by colloid chemists. In what follows (1) a summary of the results obtained in our laboratory on the variation of the different properties of some colloidal solutions on dialysing them to different extents is presented and (2) the views expressed in previous papers are considered from the point of view of changes in charge as observed by measuring the cataphoretic speed of colloidal solutions under varying conditions.

(a) Kinetics of coagulation.

2. According to Smoluchowski the rate of coagulation of a colloid in the sensitive range of electrolyte concentration is a simple reaction and the equation for rapid coagulation has the form

$$\theta = \frac{1}{\mathrm{K}v_0} = \frac{1}{4\pi \mathrm{D}rv_0}$$

where θ is the specific coagulation time, K the velocity constant, v_0 the number of particles at the beginning, r the radius of the sphere of attraction round each discharged particle and D the diffusion coefficient. He has distinguished slow coagulation from the rapid by the fact that in the former case all the encounters between the miscellae are not effective, but only a proportion which depends upon electrolyte concentration. Thus the expression for slow coagulation according to him will be

$$\theta_1 = \frac{1}{\mathrm{K}_1 v_0} = \frac{1}{8\pi\ Drv_0x}$$

where x is the fraction by which K, the velocity constant for rapid coagulation, must be multiplied. If this theory is correct, one should be able to pass from a coagulation velocity curve of rapid coagulation to one of slow coagulation at a lower electrolyte concentration by multiplying the time t by a certain numerical factor, *i. e.*, the curves of coagulation velocity must be related to one another. Several workers have found that the view of v. Smoluchowski is correct (for references see Desai, Trans. Faraday Soc., 24, 181, 1928; Patel and Desai, *ibid.*, 26, 128, 1930; Desai, Kolloidchem. Beih., 26, 357, 1928).

3. It has however been shown by other investigators (for references see papers of Desai quoted in Para. 2) that the rate of coagulation of a colloid over the sensitive range of electrolyte concentration is not a simple reaction as postulated by v. Smoluchowski and that the rate of slow coagulation has an auto-catalytic character and the reaction velocity can be represented by an equation of the form

$$\frac{dx}{dt} = \mathrm{K}\ (1+bx)\ (1-x)$$

where K and b are constants and x the amount of change in time t.

4. The widespread opinion, first put forward by Hardy (Proc. Roy. Soc., 66, 110, 1900) that coagulation begins only when colloidal particles are completely discharged and the iso-electric point is reached, has been found to be erroneous by Powis (Zeit. f. physik. Chemie, 89, 186, 1915). According to him coagulation begins as soon as the electro-kinetic potential or the electric charge falls below a certain absolute value. This value of the electro-kinetic potential, at which coagulation first begins, has been termed by Freundlich the "first critical potential" and is said to have the same characteristic value for any particular sol when coagulated with salts having coagulating ions of different valencies. The experiments of Burton (Phil. Mag., 17, 583, 1909), Kruyt Roodvoets and van der Willigen (Fourth Colloid Symposium, 1926, pp. 304-310) and Kruyt and van der Willigen (Z. physikal Chem., 130, 170, 1927) have shown that their results also support Powis' theory of critical potential.

5. Freundlich (Colloid and Capillary Chemistry Eng. Translation—1926, pp. 431-447) has utilised the existence of the first critical potential to explain the phenomenon of slow coagulation. According to him slow coagulation begins when the first critical potential value is reached. The slow coagulation passes into rapid coagulation when the value of the potential difference becomes zero or the iso-electric point is reached (Freundlich's second critical potential). In the region of slow coagulation as the particles are still charged, only those collisions are successful in bringing about coalescence in which the velocity of the particles exceeds a certain value. After the iso-electric point is reached all the collisions will be successful although the velocity with which the particles move might be very small in some cases, because there will be no repulsive forces between the particles.

6. Recently Mukherjee and co-workers (J. Indian Chem. Soc., 4 493, 1927; 5,697, 1928; Nature, 122, 960, 1928; Special Number of the Journal of the Indian Chemical Soc., 1933, p. 201) have expressed

doubts about the existence of critical potential characteristic of coagulation of a colloid by electrolytes. It should be stated that their conclusion is based on results most of which have been taken with mixtures of electrolytes and non-electrolytes as well as with electrolytes containing organic anions and much credence cannot be given to their conclusions. The charge on colloidal particles of a sol can be varied by changing the amount of the peptising agent in the sol. In our laboratory we have prepared colloidal solutions of ferric hydroxide and thorium hydroxide having different initial charge on the particles by dialysing the sols to different extents and studied coagulation in the presence of HCl, H_2SO_4, KCl, K_2SO_4, $MgCl_2$ and $MgSO_4$. Details of these measurements will be published in due course (B. N. Desai and S. K. Borkar on Ferric Hydroxide and B. N. Desai and A. K. Desai on Thorium Hydroxide). In the case of colloidal ferric hydroxide, the sol begins to coagulate in all the cases when the cataphoretic speed of colloidal particles is reduced to 25–29 although the two samples of the sol tried had different initial cataphoretic speeds—38 and 54. Similarly the two samples of thorium hydroxide sol having initial cataphoretic speed of 33 and 25 begin to coagulate when the cataphoretic speed of the particles is reduced to 19–21 in the former and 16–17 in the latter case. Differences in the value of the critical charge in individual cases can be easily understood if the preferential adsorption (the word preferential indicating that the ion is adsorbed in the inner sheet of the double layer) of similarly charged ions is considered as suggested by Desai (J. Bombay University, 1, Part II, 25, 1932). The idea of critical potential is thus completely supported by our measurements.

It should be pointed out here that generally it is observed that the value of the cataphoretic speed at which coagulation begins is somewhat higher in those cases where there is a marked preferential adsorption of the similarly charged ions. Why this is so is not quite clear. Some experiments are being undertaken for getting a clear idea of this point.

7. In our papers referred to in para. 2 it has been shown that in the case of colloidal thorium hydroxide the appearance of the S-shaped coagulation velocity (C. V.) curves or demonstration of the autocatalytic nature of the coagulation process depends on

(i) the suitability of the method employed in following the course coagulation,

(ii) the concentration of the coagulator,

(iii) the purity of the sol (this can be changed by dialysing the sol), and

(iv) the concentration of the disperse phase. The causes which might be responsible for the non-observance of auto-catalysis due to factor (i) (suitability of method) have been discussed in detail in our papers.

(ii) Concentration of the coagulator.—As stated in para. 5 slow coagulation begins when the charge is lowered to the critical value (first critical potential) and the slow coagulation passes into rapid coagulation when the iso-electric point (second critical potential) is reached. In the case of concentrated electrolytes the time required to pass from the first critical potential to the second will be very small (in seconds) and therefore with the limitations of the present methods of following the course of coagulation, it will be very difficult to get the S-shape of the C. V. curves. This however will not be the case with dilute electrolytes where the potential difference decreases slowly and the region of slow coagulation extends over some minutes (cf. Powis, loc. cit.), and hence the appearance of the S-shaped C. V. curves. It should however be stated that the C. V. curves are not found to be S-shaped even with dilute electrolytes having multivalent coagulating ions. We have observed that the amount of bivalent coagulating ion required to lower the charge to the critical value is much less than that of univalent coagulating ion. This is due to greater preferential adsorption of the former ions. As a result even with dilute electrolytes containing multivalent coagulating ions if the potential of the double layer is lowered at all, the rate of its lowering will be great in the beginning and hence the rate of coalescence also will be large. At very great dilutions, the coagulation will not proceed far as there is not sufficient electroyte left to lower the potential difference any further. The coagulation will therefore be partial in these cases. In fact cataphoretic experiments showed that in such cases a greater amount of uncoagulated sol was still left in the mixture. In those cases where there is complete coagulation *i. e.*, with somewhat concentrated electrolytes having multivalent coagulating ions, the time required to pass from the critical value to the iso-electric point will be very small (in seconds) and therefore it will be impossible to observe the slow coagulation phenomenon as in the case of concentrated electrolytes having univalent coagulating ions.

(iii) Purity of the sol.—In explaining the effect of this factor it was assumed by us (Patel and Desai, loc. cit.) as done by other workers that the charge on the colloidal particles in the case of thorium hydroxide also decreases continuously with the progress of dialysis. It was argued that as the initial slow coagulation refers only to the process which takes place between the region of the first and second critical potentials, if by any means the time required to pass from the first to the second critical potential is made appreciably small or negligible, the initial and less steep portion of the C. V. curves will also disappear. Continuous lowering of charge with the progress of dialysis will help to achieve this purpose and hence for very pure sols the C.V. curves will not be S-shaped. Even with a dilute electrolyte concentration in the case of very pure sols, the C. V. curves will not be S-shaped because the value of the charge being very near the iso-electric point, the time required for coagulation will be very small. Actual measurements of charge in the case of this sol have however shown that with the progress of dialysis the cataphoretic speed first increases, reaches a maximum value and then decreases continuously (Desai, Current Science, 1, 38. 1932 ; 1, 125, 1932 ; also paper by B. N. Desai and A. K. Desai, loc. cit.). The above line of argument therefore cannot be applied to the period of dialysis when the cataphoretic speed continuously increases with the progress of dialysis, as the charge on the colloidal particles will be removed further and further away from the first or the second critical charge. The C. V. curves were found to be S-shaped in the case of sols dialysed for about eight days while for sols dialysed for longer periods (about 14 days) no S-shaped C. V. curves could be obtained (Patel and Desai, loc. cit.). As found in the later investigation (B. N. Desai and A. K. Desai, loc. cit.) the cataphoretic speed increases with the progress of dialysis up to a period of only about 5 days (the rate of dialysis being almost the same in the two cases) and therefore the cataphoretic speed being regularly decreasing with progress of dialysis after eight days, the previous arguments used for explaining the non-observance of S-shaped C. V. curves for sols dialysed for long periods (very pure sols) still hold good.

(iv) Concentration of the disperse phase.—It was observed by us (Patel and Desai, loc. cit.) that when thorium hydroxide sol is coagulated by an electrolyte of the same concentration throughout, the tendency of the C. V. curves to be S-shaped becomes less and less with an increase in the dilution of the sol. This was explained by assuming that in the case of a dilute sol a particular amount of electrolyte will bring down the charge on the particles more nearly to the critical point or the iso-electric point than in the case of a concentrated sol. This will mean that the time required to reach the iso-electric point after adding the electrolyte to the sol will be less with a dilute sol than with a concentrated sol. With the progress of dialysis as the charge on the particles is brought nearer and nearer to the iso-electric point, the time required for coagulation will be so small with the dilute sol when compared with the concentrated one—the same amount of electrolyte having been added in both the cases—that the C. V. curves may not be S-shaped at all. This effect will be more marked in the case of a sol dialysed for longer periods than one dialysed for shorter periods. Now as stated before the charge on colloidal particles of thorium hydroxide increases in the initial stages of dialysis and therefore the ideas modified under factor (iii) in the preceding sub-para. should only be applied. Also our later measurements (B. N. Deasi and A. K. Desai, loc. cit.) have shown that for samples of this sol dialysed for periods shorter than what corresponds to the maximum in the cataphoretic speed dialysis curve on diluting the sol, the cataphoretic speed first increases, reaches a maximum value and then decreases ; on the other hand, for sols dialysed for longer periods, on diluting the sol, the cataphoretic speed continuously decreases. In view of the evidence of the charge measurements, the previous explanations do not hold good only for those cases in which the cataphoretic speed increases upto a certain dilution. There is however one additional factor which has not been hitherto considered in explaining this influence, namely, the effect of concentration of the disperse phase on the size of the particles. Desai (in paper referred to in para. 2) has shown that the auto-catalytic nature of the coagulation process and the S-shaped C. V. curves may not be observed at all with dilute sols. These can best be observed in fairly concentrated sols which contain a considerably larger number of particles because sufficiently large multiple particles can be formed in them. It is considered that this factor will have a considerable effect on the nature of the C. V. curves.

8. In a recent paper S. S. Joshi and V. L. Narayan (Special Number of the Journal of the Indian Chemical Soc., 1933, p. 41) have studied in detail the influence of wall area in the coagulation of colloidal solutions of MnO_2, Sb_2S_3 and positively charged Fe_2O_3. They have observed that the rate of coagulation is markedly increased in all cases when the wall area of the coagulating system is increased by introducing glass beads. They also find that when the same number of beads and the containing walls are paraffined the coagulation is sensibly retarded in all cases. In the light of their results they consider unlikely that the increase in the rate of coagulation, under wall effect alone, can convert a 'slow' into a 'rapid' coagulation. They conclude that autocatalysis cannot be considered as a general characteristic of coagulation as has been supposed by some workers, but that it is a secondary process which adds to the main course of coagulation under certain conditions.

Now as shown by electrosmotic, cataphoretic and stream-potentials measurements, the wall-layer of glass in contact with water becomes negatively charged. The nature of this charge will be modified considerably in the presence of electrolytes as well as when the glass surface is paraffined. It is therefore certain that the glass surface will help or retard the coagulation according to the nature of charge on it and on the colloidal particles. Moreover glass walls themselves, whether paraffined or not and whether charged or uncharged, will act as centres for coalescence. In view of these considerations it is not justifiable to say that the results of Joshi and Narayan (loc. cit.) support the conclusion that the nature of coagulation process is not intrinsically auto-catalytic.

On the other hand, their results can well be utilised to show that the nature of coagulation process is auto-catalytic. For as shown by them the walls of the containing vessel (unparaffined) make the S-shape of the C. V. curves less marked and it is quite likely that the non-observance of auto-catalysis by some workers might be to a certain extent due to this effect.

9. In the light of the foregoing evidence it can be stated that as yet no investigator has succeeded in showing that the nature of the coagulation process is not intrinsically auto-catalytic. Failure to observe the S-shape of the C. V. curves and the auto-catalytic nature of the coagulation process can be due to several factors which have been considered in this section and which as shown will considerably modify the nature of the C. V. curves and of coagulation. Also as shown in this section the idea of critical potential is completely supported ; if any deviations occur they can be explained by taking the influence of the similarly charged ions into consideration.

(*b*) *Applicability of Schulze-Hardy law.*

10. It has been shown by Desai (Kolloidchem. Beihefte, 26, 384, 1928) that in the case of colloidal thorium hydroxide containing appreciable amounts of HCl, the C. V. curves for equivalent concentrations of different electrolytes having the same coagulating ion (univalent) are not identical and that the C. V. is not the same in different cases. This is in contradiction to the requirements of the Schulze-Hardy law according to which the time required for the coagulation of a sol by electrolytes having the same oppositely charged ion is independent of the nature of that ion of the coagulator which carries the same charge as the colloidal particles. It has been expressed by several investigators (references are given in the above paper of Desai on p. 394) that unless and until the influence of the similarly charged ion is taken into consideration, no theory will be adequate enough to explain the results of coagulation of sols by electrolytes. In the case of multivalent coagulating ions the influence of the similarly charged ion being negligible, the Schulze-Hardy law is obeyed. It has also been shown by Desai (loc. cit.) that the applicability of the Schulze-Hardy law increases with the progress of dialysis. This has been explained by assuming that with the progress of dialysis the preferential adsorption of the similarly charged ions decreases.

11. The measurements of cataphoretic speed of colloidal solutions of ferric hydroxide (Desai and Borkar, loc. cit.) and of thorium hydroxide (B. N. Desai, and A. K. Desai, loc. cit.) in the presence

of varying amounts of electrolytes have shown that preferential adsorption of similarly charged ions takes place in the presence of small amounts of electrolytes containing monovalent coagulating ion, while with bivalent coagulating ion no preferential adsorption of similarly charged ions is allowed to take place. It has also been observed that the amounts of different electrolytes necessary to lower the value of the charge to the critical value are not the same. The earlier conclusions are thus supported by the evidence of charge measurements in these respects. The charge measurements, however, show that the preferential adsorption of similarly charged ions does not appreciably decrease with the progress of dialysis *i. e.*, with an increase in the purity of the sol. Therefore the explanation advanced in the previous paragraph about applicability of the Schulze-Hardy law with the progress of dialysis requires modification. In the case of thorium hydroxide the deviations from the Schulze-Hardy law only disappear after a period of dialysis of 10 days or so. During this period of dialysis the charge on the colloidal particles will be brought nearer and nearer to the iso-electric point (the maximum cataphoretic speed having occurred at a period of dialysis of 5 days or so) and thus as shown in section (a), coagulation tends to be rapid in all the cases (disappearance of S-shaped nature of the C. V. curves). Under the circumstances it is quite likely that although different similarly charged ions may be preferentially adsorbed to different extents in the beginning, this may not affect the nature of the C. V. curves to any appreciable extent.

12. In view of the evidence of charge measurements it is also considered that the mechanism of coagulation as pictured by Weiser (J. Phys. Chem., 28, 232. 1924; 29, 955, 1925) and Dhar (ibid., 28, 457, 1924) for explaining the preferential adsorption of similarly charged ions is difficult to understand. For, the preferential adsorption of the similarly charged ions is noticed only in the presence of small amounts of electrolytes and at these concentrations the colloidal solutions do not show at all any tendency for coagulation.

(c) Relation between charge and stability.

13. Numerous papers have been published by investigators in Colloid Chemistry on the stability of various colloidal solutions in the presence of electrolytes—greater floculation value (F. V.) greater stability and smaller F. V. smaller stability. These investigations have been made with colloidal solutions which have been purified to certain extent by dialysis. The decrease in the F. V. with the progress of dialysis has been explained generally by assuming that with the progress of dialysis, the charge on the colloidal particles continuously decreases. We have measured cataphoretic speed and stability simultaneously of colloidal solutions of gold, ferric hydroxide and thorium

hydroxide with the progress of dialysis. The following results have been obtained (for details refer to papers by Desai, Nabar and Barve, J. Indian Chem. Soc., 9, 463, 1932; Desai and Borkar, loc. cit., B. N. Desai, loc. cit.) :—

(*i*) In the case of colloidal gold, with the progress of dialysis both cataphoretic speed and stability as determined by F. V. increase in the beginning, reach a maximum value and begin to decrease simultaneously thereafter.

(*ii*) The cataphoretic speed of colloidal particles of ferric and thorium hydroxide, first increases, reaches a maximum value and then decreases on subjecting the sols to dialysis; the F. V., on the other hand, continuously decreases with the progress of dialysis in both the cases.

14. The above results show that although there is a direct relation between charge and stability in the case of colloidal gold, the same is not found to be the case with colloidal ferric and thorium hydroxide. In the latter case such relation is only found to exist for the period of dialysis when both cataphoretic speed and F. V. decrease regularly. The reasons for a regular decrease in the F. V. with the progress of dialysis, in spite of first an increase and then a decrease in the cataphoretic speed, have also been advanced by us. In both the cases—ferric as well as thorium hydroxide—an increase in the preferential adsorption of the stabilising ions in the presence of KCl (electrolyte added for F. V. determinations) as well as a change in the size of the particles during dialysis have been found to be very significant from the point of view of stability. In the case of ferric hydroxide the changes in the hydration of colloidal particles in the initial stage of dialysis are also partly responsible for the abnormal behaviour.

15. It has been observed by us that on adding small increasing amounts of KOH in the case of gold sol, of HCl and $FeCl_3$ in the case of ferric hydroxide sol and of HCl in the case of thorium hydroxide sol, the cataphoretic speed first increases and then decreases or that there is a maximum in the cataphoretic speed (C. S.)—concentration (C) curve. The initial increase in the cataphoretic speed is due to a preferential adsorption of the similarly charged ions. All these sols initially contain an amount of the stabilising electrolyte which is appreciably more than what corresponds to the maximum in the C.S.—C curve for that electrolyte. With the progress of dialysis, the amount of the stabilising agent continuously decreases. The process of dialysis can therefore be considered as a reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid in so far as the removal of the peptising electrolyte is concerned; one should thus expect that with the progress of dialysis the cataphoretic speed will first increase and then decrease. Thus a col-

loidal solution when subjected to dialysis will show (*a*) first an increase and then a decrease or (*b*) a continuous decrease of the cataphoretic speed according as it initially contains an amount of the peptising agent (*a*) more than or (*b*) equal to or less than what corresponds to the maximum in the C.S.—C curve with that electrolyte. Other sols are being investigated from this point of view.

16. From the foregoing it will appear that it is not safe to draw conclusions about changes in charge from the stability determinations as has hitherto been the practice, for although this may serve a useful criterion in some cases it may not do so in others.

(*d*) *Changes in cataphoretic speed and stability of colloidal solutions of ferric and thorium hydroxide dialysed and diluted to different extents.*

17. We have observed (Desai and Borkar, loc. cit.; B. N. Desai and A. K. Desai, loc. cit.) that (i) for samples of sol dialysed for periods shorter than what corresponds to the maximum in the C. S.—D (dialysis) curve, on diluting the sol, the cataphoretic speed of colloidal particles first increases, reaches a maximum value and then decreases and (ii) for samples of sol dialysed for longer periods, the cataphoretic speed regularly decreases on dilution of both the sols.

18. Both on diluting and dialysing the sol the amount of the peptising electrolyte decreases. The processes of dilution and dialysis can therefore be considered similar in this respect. Now as shown in section (c), if a colloidal solution initially contains an amount of the peptising electrolyte more than what corresponds to the maximum in the C. S.—C curve the cataphoretic speed first increases and then decreases on dialysis. The samples of the sol dialysed for periods shorter than what correspond to maximum in the C. S.—D curve do contain an amount of the peptising electrolyte which will be more than what corresponds to the maximum in the C. S.—C curve and therefore the processes of dilution and dialysis being similar, the cataphoretic speed should first increase and then decrease on dilution of the sol. Sols dialysed for longer periods than what corresponds to the maximum in the C. S. —D curve should show on diluting, a continuous decrease in the cataphoretic speed as they contain an amount of the peptising electrolyte less than what corresponds to the maximum in the C. S.—C curve; for such samples the cataphoretic speed also regularly decreases on dialysis.

19. If the analogy between processes of dialysis and dilution given in the preceding paragraph is correct, one should expect that the maximum in the C.S.—Dil. (dilution) curve should occur at lower dilutions in the case of sols dialysed for longer periods than those dialysed for shorter periods. This has actually been found to be the

case (Desai and Borkar, loc. cit. and B. N. Desai and A. K. Desai loc. cit.). In what respects dialysis and dilution cannot be considered similar has also been discussed by Desai in the above papers. It is however considered that changes in cataphoretic speed on dialysis and dilution are mostly due to changes in the concentration of the peptising electrolyte. Different sols are being investigated to see how far observations (i) and (ii) given in para. 17 are also noticed in them in order to find out if this behaviour is a general property of colloidal solutions.

20. On diluting the sol the stability as determined by the F.V. with KCl decreases regularly for both ferric and thorium hydroxide sols. As shown in para. 16 there does not appear a direct relation between charge and stability in all the cases ; for, as stated above, the changes in the cataphoretic speed on dilution are not the same for sols dialysed for different periods.

21. Dhar (for references see Desai, Kolloidchem. Beihefte, 26, 385, 1928) has divided colloidal solutions into two divisions according as they show normal or abnormal behaviour to the dilution rule, *viz.*, the greater the concentration of a colloid the greater the amount of an electrolyte necessary for coagulation. According to Dhar, only those sols show an abnormal behaviour to dilution rule which show appreciable preferential absorption of similarly charged ions from the solution. Desai (above quoted paper) has however shown that colloidal thorium hydroxide can be made to show either normal or abnormal behaviour to dilution rule by varying the purity of the sol (by subjecting the sol to dialysis), and that it is erroneous to divide the colloidal solutions into two classes as done by Dhar. We have also observed that both colloidal ferric and thorium hydroxide show appreciable preferential adsorption of K ion in the presence of KCl (Desai and Borkar, loc. cit ; B. N. Desai, and A. K. Desai, loc. cit.), and that both these sols show normal behaviour to dilution rule when they are coagulated with KCl. Thus Dhar's explanation about abnormal behaviour to dilution rule also does not seem to be correct.

22. In explaining the abnormal behaviour to the dilution rule, it has also been stated that a dilute sol adsorbs proportionally more of the similarly charged ion than the concentrated one. Our preliminary results (Desai and Barve, Nature, 128, 907, 1931) have shown that on the addition of small increasing amounts of KCl and $MgCl_2$, the cataphoretic speed first increases and then decreases, the initial increase being greater with the concentrated sol than with the dilute sol. It was also observed that the maximum value of cataphoretic speed occurs at a lower concentration of the electrolyte in the case of dilute sol than the concentrated one. These results thus do not support the conclusion that there being greater adsorption of the similarly charged ion in a dilute sol than a concentrated one, the charge will be greater in the

former case and hence a greater amount of electrolyte will be required for coagulation. Also the explanation for disappearance of abnormality to the dilution rule, as in the case of the Schulze-Hardy law, with the progress of dialysis should be modified as indicated in para. 11. It appears that increase in distance between colloidal particles on dilution, might have considerable influence on the coagulation and make the sol show an abnormal behaviour as regards stability (cf. Desai, Kolloidchem. Beihefte, 26, pp. 400–401, 1928).

(e) *Relation between charge and viscosity.*

23. There are two different views at present about relation between charge and viscosity. According to v. Smoluchowski (for references on this subject see papers by Desai and Borkar, loc. cit.; B.N. Desai and A.K. Desai, loc. cit.) the movement of electrically charged particles of a sol causes the development of an electric field, which hinders the flow of the sol resulting in an increase of its viscosity. This conclusion was found to be supported by Smoluchowski's measurements which showed that a sol containing particles of greater electric charge was more viscous than a sample containing particles of feeble electric charge. On the other hand, Dhar and co-workers from their measurements with a number of sols have tried to show that the view of Smoluchowski is untenable. According to them, other things being identical, a decrease in the electric charge on colloidal particles causes an increase in hydration and necessarily in the viscosity of the sol. It should however be stated that Dhar's conclusions about changes in charge are based on F.V. determinations and this is certainly not correct in view of what has been said in the foregoing sections about relation between charge and stability as determined by F.V.

24. We have made simultaneous measurements of charge and viscosity of colloidal solutions of ferric and thorium hydroxide dialysed to different extents and of different concentrations and in the presence of varying amounts of electrolytes. In the case of colloidal ferric hydroxide we have observed (Desai and Borkar, loc. cit.) that

(i) With the progress of dialysis, cataphoretic speed first increases and then decreases, while viscosity first decreases and then increases. The maximum in the C.S.—D curve and the minimum in the V (viscosity)—D curve however do not occur at the same stage of dialysis.

(ii) On adding small increasing amounts of electrolytes with univalent coagulating ion, cataphoretic speed first increases and then decreases, while viscosity first decreases and then increases. The maximum in the C.S.—C curve and the minimum in the V—C curve do not however occur at the same concentration of the electrolyte.

(iii) With highly concentrated sols of Fe_2O_3 the initial decrease in viscosity with the progress of dialysis is not noticed at all (Desai, Special Number of the Journ. Indian Chem. Soc. p. 37, 1933).

In the case of colloidal thorium hydroxide we have observed (B.N. Desai and A.K. Desai, loc. cit.) that

(i) With the progress of dialysis, cataphoretic speed first increases and then decreases, while viscosity continuously increases—the increase being more marked in the later stages of dialysis.

(ii) On diluting the sol cataphoretic speed first increases and then decreases for samples which have been dialysed for periods shorter than what corresponds to the maximum in the C.S.—D curve and it continuously decreases on dilution for samples which have been dialysed for longer periods. Viscosity, on the other hand, continuously decreases on dilution in all the cases although the samples of sol were dialysed to different extents. Also the percentage increase of viscosity on dialysis is greater in the case of concentrated sols than dilute sols.

(iii) For all the samples of the sol, whether dialysed for short or long periods, cataphoretic speed first increases and then decreases on the addition of small increasing amounts of electrolytes having univalent coagulating ion, the initial increase in cataphoretic speed being not noticeable with electrolytes having bivalent coagulating ion. Viscosity, on the other hand, increases continuously with all the electrolytes for samples of the sol which have been dialysed for periods shorter than what corresponds to the maximum in the C.S.—D curve, while for samples dialysed for longer periods the viscosity first decreases and then increases on adding small increasing amounts of electrolytes to the sol.

25. It will appear from the above results that neither the view of Dhar nor of v. Smoluchowski can alone explain the changes in charge and viscosity of colloidal ferric and thorium hydroxide under different conditions—with the progress of dialysis, with a change in dilution and when small increasing amounts of different electrolytes are added. As pointed out in our papers one has to consider the effect of various factors, which are given below, in explaining these changes in charge and viscosity.

(i) Changes in the concentration of disperse phase.—The viscosity of the sol will generally decrease with a decrease in the concentration of the disperse phase.

(ii) Electro-viscous effect.—The viscosity of the sol will increase with an increase in the cataphoretic speed of colloidal particles and decrease when the cataphoretic speed decreases.

(iii) Changes in hydration of colloidal particles.—With an increase in hydration of the colloidal particles (this tendency is most pronounced with the progress of dialysis when the sol shows a tendency to set to gel) the viscosity will also increase, there being an increase in the effective volume of the particles. On diluting the sol, the hydration of colloidal particles may increase and the viscosity may also increase due to an increase in the effective volume of the particles.

(iv) Variation in the shape and structure of particles.—As for the variation of the shape of the particles little is known. However the structure of the particles is sure to vary both during dialysis and dilution. During dialysis, there is a tendency for the particles to aggregate as during coalescence and thus increase their effective volume and the viscosity. On the other hand, on dilution the larger aggregates may break up into smaller ones and thus decrease the effective volume of the particles as well as viscosity.

(v) Changes in the concentration of the electrolyte.—The viscosity will increase regularly with an increase in the concentration of the electrolyte present in the sol except with those electrolytes which show a negative viscosity within a particular range of concentration.

26. In a previous paper Desai (Kolloidchem. Beihefte, 26, 422, 1928) has explained changes in viscosity on dialysis and ageing by assuming that as with the progress of dialysis and on ageing, the sol becomes unstable, the charge decreases and therefore viscosity increases. In view of what has been said in previous sections it is not right to draw conclusions about changes in charge from stability determinations and therefore the above explanation may have to be considerably modified. The influence of all the factors mentioned in the previous para. should be taken into account. As the ceric hydroxide sol initially contains quite a large amount of the peptising electrolyte it is likely that on dialysing, the charge on colloidal particles may first increase and then decrease as in the case of ferric hydroxide and thorium hydroxide sols. The changes in the various properties of colloidal particles of ceric hydroxide under different conditions are being investigated.

27. In a recent paper Ghosh and Banerji, (Bul. Acad. Sci. U. P., 2, 135, 1933) have given some measurements of viscosity of colloidal ferric phosphate dialysed and diluted to different extents, the flow of the liquid being caused under varying pressure. They have stated that if measurements of rates of flow of a colloid be undertaken at fairly high pressures, the change in the viscosity of colloids with the progress of dialysis will be either nil or insignificant. According to them hydration has to be assumed to be very labile. Our results of study (Desai, loc. cit.) of the ceric hydroxide sol and gel also seem to support the conclusion about labile nature of hydration. Ghosh and Banerji however believe that colloidal solutions show a high viscosity due to an orientation of the particles rather than due to high hydration of the disperse phase. According to them the tendency to orientation increases as the electric charge on the colloid particles is decreased and

as, during dialysis, the electric charge on colloidal particles continuously decreases the viscosity will increase. It should be pointed out here that their conclusion about changes in charge during dialysis is based on coagulation experiments as they themselves state. This is not justified in view of what has been stated in previous sections about changes in charge during dialysis. In fact the ferric phosphate sol which they have used initially contained a considerable amount of the peptising agent and therefore the charge on colloidal particles during dialysis will first increase and then decrease instead of continuously decreasing as shown by stability determinations. Our examination of ceric hydroxide gel under ultra-microscope (Desai, loc. cit.) has revealed no tendency for a definite orientation of the particles in that gel. Our gel contained more than 2000 mols. of water per one mol. of CeO_2 (the amount of water depending on temperature of gel formation) and it is considered that a considerable increase in viscosity during dialysis is due to an increase in hydration of the particles. Also the decrease in viscosity under high pressures noticed by Ghosh and Banerji (loc. cit.) is not due to a destruction of the orientation of colloidal particles under high pressures as supposed by them, but definitely due to a decrease in the hydration of the particles on account of some water molecules wrapping the particles having been torn off and the effective volume of the particles having thus been decreased. It is not necessary to consider that increase in hydration is as a result of adsorption of water by colloidal particles, for large amount of water held by the gel will demand adsorption several molecules deep and this is incompatible with Langmuir's theory (J. Amer. Chem. Soc., 38, 2221, 1916; 40. 1361, 1918), according to which the adsorbed layer cannot be several molecules deep. The picture of hydration suggested by Desai (Kolloidchem. Beihefte, 26. 434, 1928) will easily allow some water molecules being torn off under high pressures and thus explain the decrease in viscosity with an increase in the shearing force. There is also no evidence to suppose that orientation of colloidal particles in a sol changes during dialysis.

28. In view of what has been stated in this section it will be clear that it is erroneous to draw conclusion about changes in charge from changes in viscosity as in the case of stability (para. 16), and that there is a necessity to study simultaneously changes in charge and viscosity of colloidal solutions under different conditions. This is being done in our laboratory.

(*f*) *Sensitisation of colloidal solutions by non-electrolytes.*

29. We (Patel and Desai, Kolloid Zeit., 51, 318, 1930) have studied the influence of non-electrolytes—methyl, ethyl and iso-propyl alcohols, acetone, urea and cane-sugar on the rate of coagulation of

colloidal thorium hydroxide of different degrees of purity in the presence of NaCl ; the coagulation of the sol in the presence of non-electrolytes alone has also been studied. The following results have been obtained :—

(i) With the progress of dialysis the sol is more and more sensitised by non-electrolytes.

(ii) A fairly pure sample of the sol (sol dialysed for 6, 8 and 11 days) could be coagulated by non-electrolytes alone, the coagulating power of non-electrolytes increasing with an increase in the purity of the sol.

(iii) The C. V. curves for lower concentrations of electrolytes and non-electrolytes or non-electrolytes alone are found to be S-shaped The S-shape of the C. V. curves becomes less marked with an increase in the purity of the sol.

(iv) The order of effectiveness in sensitisation or coagulation of the sol by the non-electrolytes tried in these experiments is

Urea>methyl alcohol>ethyl alcohol>iso-propyl alcohol>cane-sugar >acetone.

30. The view of Weiser (J. Phys. Chem., 28, 1253, 1924) that sensitisation is caused due to the cutting down of the adsorption of the coagulating ion in the presence of non-electrolytes is not applicable in the present case because the C. V. increases in the presence of non-eloctrolytes. Also the fact that fairly pure samples of the sol could be coagulated with non-electrolytes alone shows that the above view is not of much help in explaining our results.

31. The other view of Weiser (loc. cit.) that the' non-electroytes displace the stabilising ion is supported by our results. For, such a displacement of the stabilising ion will make the sol unstable and if stability is defined in terms of coagulation concentration, smaller amounts of eletcrolytes will be required to coagulate the sol in the presence of non-electrolytes. This view will also explain the coagulation of the sol by non-electrolytes alone, for if the non-electrolytes are able to displace so much amount of the stabilising ion from the inner sheet of the double layer that the value of the charge on the particles is lowered to the critical value, the sol will begin to coagulate—slow coagulation phenomenon. If the amount of the stabilising ion displaced is quite considerable the value of the charge on the colloidal particles may be brought down to the iso-electric point and the coagulation may become rapid from the beginning. It should however be stated that it is not possible to say how far the displacement of the stabilising ion by the non-electrolytes will be shown by actual adsorption experiments.

32. The suggestion of Wo. Ostwald (Grundriss der Kolloid Chemie, 1 Aufl. 1909. p. 441) and of Freundlich (Colloid and Capillary

Chemistry. Eng. Translation, 1926, pp. 462-65) that changes in the dielectric constant decide the influence of non-electrolytes is found to be supported by these experiments. All the non-electrolytes tried in our measurements had dielectric constant lower than that of water and therefore if the non-electrolytes are adsorbed in the double layer the dielectric constant will be lowered and with it the electric charge on the colloidal particles. Whether there will be slow or rapid coagulation in the beginning will depend upon the extent of the lowering of the charge.

We have observed that with the progress of dialysis the charge on colloidal particles of thorium hydroxide first increases and then decreases. If the coagulation by non-electrolytes is due to a lowering of the dielectric constant and hence of the electric charge, one would expect that the samples of the sol having the same cataphoretic speed *i. e.*, on the one or the other side of the maximum in the C. S.–D curve should show the same behaviour when non-electrolytes are added. It will however be seen from our results that the sol could be coagulated with non-electrolytes alone only when it was dialysed for long periods (6, 8 and 11 days); sols dialysed for shorter periods *i. e.*, less than what corresponds to the maximum in the C. S.–D curve (sols dialysed for 0 day and 3 days) could be only sensitised but not coagulated by non-electrolytes alone. It thus appears that the non-electrolytes are not able to lower the dielectric constant as much in the presence of appreciable amounts of electrolyte (sols dialysed for 0 day and 3 days certainly contain quite appreciable amounts of the stabilising electrolyte when compared with samples dialysed for 6, 8 and 11 days) as they can do in their absence, or that the adsorption of the non-electrolytes in the presence of electrolytes is not quite appreciable. A tendency to this effect is noticeable somewhat in the results of Mukherjee, Rai Choudhuri and Rao (J. Indian Chem. Soc., 5, 697, 1928). This point however requires further investigation.

The results of Mukherjee and co-workers (loc. cit.) show that the cataphoretic speed of colloidal particles of arsenious sulphide is lowered more and more on adding larger and larger amounts of non-electrolytes which also sensitise the sol. It is therefore quite likely that even in the case of thorium hydroxide addition of non-electrolytes which sensitise the sol will lower the cataphoretic speed. This work is in progress.

33. Mukherjee and co-workers (loc. cit.; J. Indian Chem. Soc., 2, 307, 1925; 3, 349, 1926) consider that the diminution in the dielectric constant brings about two effects :—

(i) The electrical work, resulting from the displacement of the ions constituting the mobile sheet of the double layer and surrounding the colloidal particles, when two particles approach sufficiently near each other, will increase with a diminution of the dielectric constant. This effect will decrease the rate of coalescence and tend to stabilise the sol.

(ii) From Mukherjee's theory of the electrical adsorption of the precipitating ions it follows that the adsorbability will increase in a medium of low dielectric constant. This effect will give sensitisation. The net effect will depend on the relative magnitudes of factors (i) and (ii).

In our case the effect of factor (i) has been either absent or less predominant than the effect of factor (ii) because stabilisation of the sol did not take place in any experiment. Factor (ii) can be utilised to explain both sensitisation and coagulation of the sol by non-electrolytes.

Mukherjee and co-workers (loc. cit. ; also Choudhury, J. Phys. Chem., 32, 1481, 1928 ; Special Number of J. Indian Chem. Soc., 201, 1933) have also suggested that variation in the thickness of the double layer, changes in the interfacial tension of the medium etc., take place in the presence of non-electrolytes. It should however be stated that in the absence of any definite knowledge of variation of the above properties of the double layer it is not quite correct to use these factors in explaining the results of sensitisation by non-electrolytes (cf. Weiser. J. Phys. Chem., 44, 101, 1930). It appears that the role of dielectric constant in the sense proposed by Wo. Ostwald and Freundlich may, to a very large extent, explain the results of sensitisation, although in some cases some other influences may have also to be taken into account.

34. In a recent paper Prasad and Nabar (J. Indian Chem. Soc., 10, 53, 1933) have studied the influence of non-electrolytes on the coagulation of colloidal ceric hydroxide by the thermopile method. They find that alcohols affect the stability with the progress of dialysis of the sol in the same manner as observed by Patel and Desai (loc. cit.) in the case of thorium hydroxide sol; sugars are however found to stabilise the ceric hydroxide sol and this effect increases with the progress of dialysis. The stabilising effect of sugars in this case may be due to the effect of factor (i) discussed in para. 33 as well as due to the cutting down of the preferential adsorption of the coagulating ion by the sugars. Regarding Prasad and Nabar's results it must be stated that in explaining their results they have assumed that the charge decreases regularly with the progress of dialysis. This is not justified in view of the fact that their sol contained initially appreciable amount of the peptising agent and therefore during dialysis the charge may first increase and then decrease.

CONCLUSION

35. From the foregoing considerations it is apparent that changes which will be produced in the charge on colloidal particles during

dialysis are not so simple as many colloid chemists seem to imagine. It will also be clear that the results of viscosity and stability (towards electrolytes and non-electrolytes) cannot always be utilised for getting an idea about charge on colloidal particles. Under the circumstances it is difficult to understand how far one should consider as satisfactory the interpretations of the results of coagulation of colloids or of viscosity determinations whenever inferences have been drawn from them about changes in charge on the particles. There is thus a clear necessity of investigating simultaneously different properties of various colloidal solutions—cataphoretic speed, stability, viscosity etc.,—which have been dialysed to different extents in order to get a clear idea about relation between various properties.

Note—Paper by Desai and Borkar on Ferric Hydroxide referred to in para 6 has appeared in the December 1933 number of the *Transactions of the Faraday Society*, London.

30 P

Conductivity Measurements of some Chlorides, Iodides, and Nitrates of Alkalies & Alkaline Earths in Water and Methyl, Ethyl and *n*-Propyl Alcohols.

By

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Conductivity Measurements of Some Chlorides, Iodides and Nitrates of Alkalis and Alkaline Earths in Water and Methyl, Ethyl and n-Propyl Alcohols

By

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Abstract.

Measurements of conductivity of chlorides, nitrates and iodides of some of alkali metals and alkaline earths over a large range of concentration have been made using water and methyl, ethyl and *n*-propyl alcohols as solvents.

Λ_c. $\sqrt{C}$ curves in different solvents are not found to be straight lines showing that the Debye-Hückel-Onsager theory is not applicable for the concentrations tried in this investigation. For some salts in different solvents the value of Λ_c has also been calculated according to the interionic attraction theory. It is found that deviations of the calculated from the observed values increase with increasing concentration, the calculated values of Λ_c being even negative in some cases at higher concentrations.

The curves obtained by plotting log Λ_c against log C for different salts in different solvents are found to be straight lines. A sudden change in the slope of log Λ_c, log C curves for different salts in water is observed at higher concentrations.

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* The experimental work has been carried out entirely by Mr. H. N. Desai under the direction of the other two authors.

concentration range N/500, while in others a tendency to ionic association is observed even in dilute solutions.

In the present investigation measurements of conductance of various electrolytes have been made in water and in methyl, ethyl and *n*-propyl alcohols. The conductance has been studied over a wide range of concentration, specially with a view to find out the behaviour of electrolytes in solutions beyond the concentration of the applicability of Debye-Hückel-Onsager theory to almost saturation point.

EXPERIMENTAL.

(*a*) *Preparation of solvents.*—The conductivity water for the experiments was prepared in the usual manner. As far as possible fresh conductivity water was used in all experiments. The specific conductivity of the water used in these measurements was $0\cdot1\times10^{-5}$ r.o. The methyl, ethyl and *n*-propyl alcohols supplied by E. Merck were kept over freshly burnt lime for two to three days to remove traces of water that might be still present. The mixture was distilled and the portion of the distillate at the respective boiling points of alcohols was collected for purposes of these experiments. The viscosity of the sample so prepared was found to be practically the same as given in Standard Physical Tables. The specific conductivity of methyl, ethyl and *n*-propyl alcohols was $0\cdot3\times10^{-5}$ r.o., $0\cdot9\times10^{-6}$ r.o. and $0\cdot2\times10^{-5}$ r.o. respectively. In all the conductivity measurements solvent correction has been applied in order to eliminate the effect of the conductivity of the solvent itself.

(*b*) *Preparation of salt solutions.*—All the salts used in these experiments were Merck's analytical reagents. The concentration of saturated stock solutions which were prepared by dissolving weighed amounts of salts was further estimated by suitable volumetric or gravimetric estimation. Dilute solutions were prepared from the concentrated stock solutions by the method suggested by Whetham [4] by adding measured amounts of the stock solution to the measured amount of solvent. The pipettes used in these measurements were calibrated previously. The glass vessels used were of resistance glass.

(c) *Measurement of conductivity*.—The resistance of the electrolyte was measured by the Wheatstone bridge arrangement. An amplifying circuit similar to the one used by Lyrenz and Klauer [5] was also used in these measurements. Two thermionic valves instead of one were used to amplify the sound and get a sharp null point.

The source of alternating current was a small induction coil having a high-frequency hammer. The wire of the metre bridge was calibrated by the Griffith's double-circuit method and a graph was drawn of the length of wire against its actual resistance. In the usual method to find the resistance of electrolytes the ratio of lengths of wire is taken; in this case however the ratio of the two exact resistances corresponding to two lengths on either side of null point was taken so that no further correction due to non-uniformity of wire was necessary. The resistance used in these experiments was also calibrated previously. To avoid the direct excitement of telephone by the sound of the induction coil, the coil was put in a sound-proof box specially prepared for the purpose.

The conductivity cell used for these experiments was of the type described by Kohlrausch.[6] The polarisation effect was reduced to a minimum by often platinizing the electrodes and by using the alternating current of high frequency as stated before. The electrodes after platinizing were dried and moistened with absolute alcohol and then kept standing

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[4] Phil. Trans., 194, 321 (1900).

[5] Z. Anorg. Chem., 136, 121 (1924); also see Physical Chemistry by Taylor, Vol, I, Second Edition (1930), p. 646.

[6] Fig. 6 on page 15 of "Kohlrausch und Holborn, Leitvermogen der Electrolyte."

in water in order to avoid the difficulty of wetting due to a layer of air that might be on the surface of platinum.

The experiments were carried out in an electrically heated thermostat at a temperature of $30 \pm 0 \cdot 05°C$, this temperature being most convenient for adjustment in a place like Bombay. Before taking readings, solutions were allowed to remain in the thermostat for some time to attain its temperature. As the alternating current was passed for less than a minute, the unnecessary heating of the solution due to passage of the electric current was avoided.

The constant of the cell was determined by measuring the resistance of potassium chloride solutions of known concentrations. Taking the data of KCl at 18°C from the Standard Tables the values of specific conductivity of the solution at 30°C was calculated by using Kohlrausch's temperature co-efficient formula. The value of the constant was tested at intervals during the work to find out variation, if any. The cell constant did not vary to any appreciable extent during the period of experiments.

RESULTS AND DISCUSSION.

In Fig. 1 are plotted the values of $\wedge_c$ against $\sqrt{C}$ for NH_4I in different solvents. It will be seen that the curves so obtained are not straight lines. The nature of the curve in water is the same as that obtained by Noyes and Falk.[7] It will be observed that the initial slope of the curve for water is considerably smaller than the curves for alcohols. Also the difference is greatest between water and methyl alcohol when compared with difference between different alcohols. Frazer and Hartley[8] have observed that in dilute solutions the slope of the $\wedge_c$, $\sqrt{C}$ curves for electrolytes in methyl alcohol is about four times greater than that in water. The results given here show that a similar tendency also exists even in

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[7] Journ, Amer. Chem. Soc., 34, 461 (1912).

[8] *Loc. cit.*

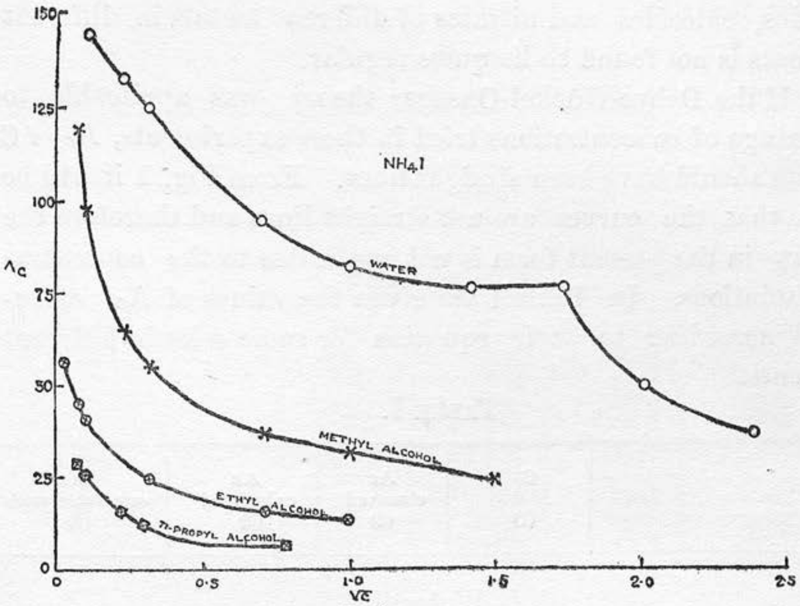
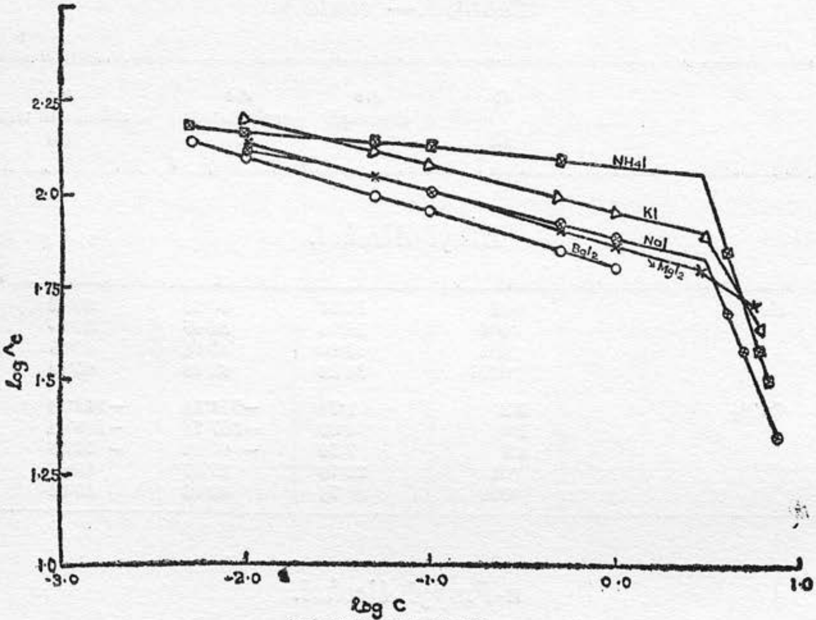


FIG. I

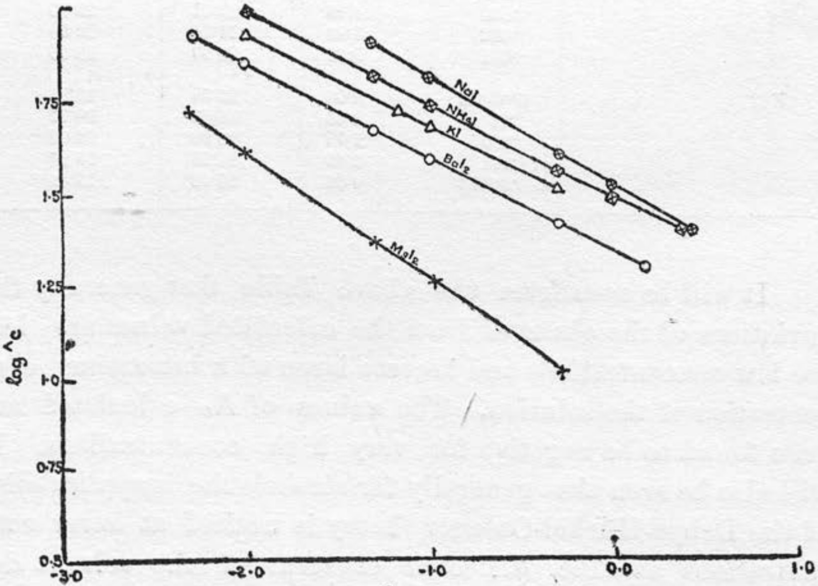
moderately concentrated solutions; in highly concentrated solutions however the Λ_c, $\sqrt{C}$ curves for NH_4I in water and methyl alcohol are parallel. The increase in the steepness of Λ_c, $\sqrt{C}$ curves would, according to Debye-Hückel-Onsager theory, indicate less and less ionisation or more and more incomplete dissociation. Also the curves for different solvents retain a common likeness suggesting that the same type of inter-ionic forces might be responsible for changes in conductivity with concentration.

In the case of water a sudden break occurs in Λ_c, $\sqrt{C}$ curve at a concentration of about 3 N. In the case of other iodides in water a break also occurs at about the same concentration. This sudden break at higher concentrations is however not observed in other solvents.

The nature of Λ_c, $\sqrt{C}$ curves of other salts in different solvents is found to be the same with the difference that the sudden break which occurs at higher concentrations in the case of iodides in water is practically not noticed at all in the case of chlorides and nitrates. The variation in the slope of

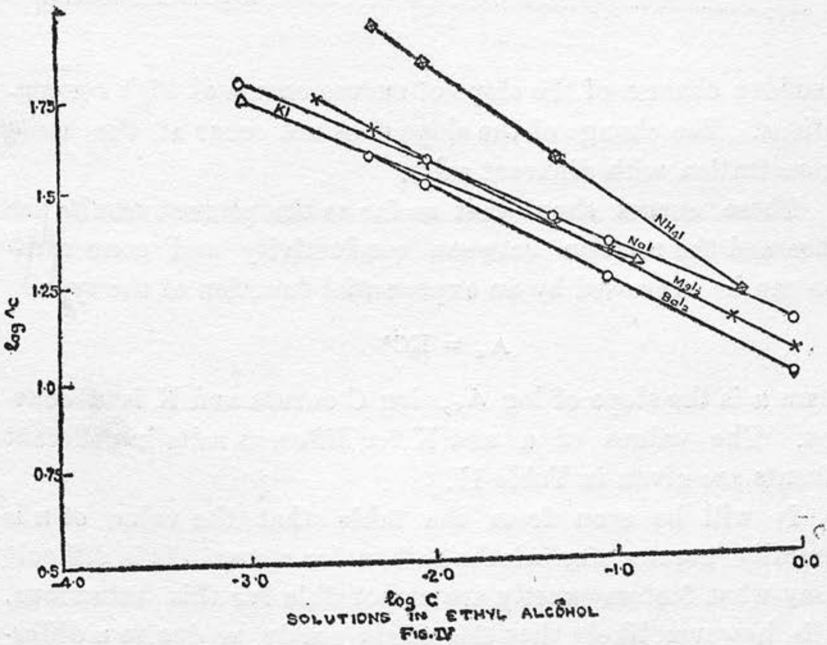


SOLUTIONS IN WATER
FIG. II



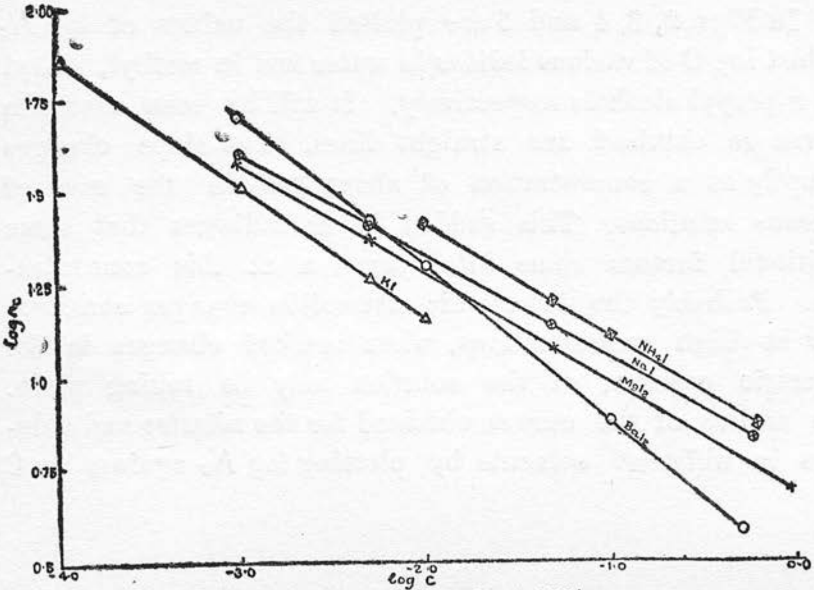
SOLUTIONS IN METHYL ALCOHOL
FIG. III

In Figs. 2, 3, 4 and 5 are plotted the values of log Λ_c against log C of various iodides in water and in methyl, ethyl and *n*-propyl alcohols respectively. It will be seen that the curves so obtained are straight lines. The slope changes abruptly at a concentration of about 3 N in the case of aqueous solutions. This sudden break indicates that some additional factors come into operation at this concentration. Probably the inter-ionic attraction changes considerably at high concentrations, when marked changes in the dielectric constant of the solution may be taking place. The nature of the curves obtained for the nitrates and chlorides in different solvents by plotting log Λ_c against log C is exactly similar to those obtained with iodides. This method of plotting the results however reveals one interesting thing namely that even in the case of nitrates and chlorides in water



SOLUTIONS IN ETHYL ALCOHOL

FIG. IV



SOLUTIONS IN n- PROPYL ALCOHOL
FIG V

a sudden change of the slope of curves occurs at high concentrations. The change of the slope does not occur at the same concentration with different salts.

These curves show that as far as the present results are concerned the relation between conductivity and concentration can be expressed by an exponential function of the type

$$\Lambda_c = KC^n$$

where n is the slope of log Λ_c, log C curves and K is a constant. The values of n and K for different salts in different solvents are given in Table II.

It will be seen from the table that the value of n is generally greater for alcohols than for water. It is difficult to say what factors exactly are responsible for this behaviour. It is, however, likely that this might partly be due to a difference in the dielectric constant of water and alcohols, which might affect the inter-ionic forces to different extents. The variation in the value of n for different salts in different alcohols does not show any regular behaviour.

TABLE II.*

Values of n and K.

	Water.	Methyl Alcohol.	Ethyl Alcohol.	n-Propyl Alcohol.
NaCl	n −·1864 K 66·21	−·2227 30·38	−·1500 7·854	−·1584 1·791
KCl	n −·0691 K 88·67	−·2083 30·66	−·3000 1·778	−·1764 0·3405
NH_4Cl	n −·0531 K 88·49	−·3011 23·96	−·3000 6·916	−·2925 2·448
$MgCl_2$	n −·0817 K 58·65	−·4289 14·83	−·3853 4·009	−·3727 1·809
$BaCl_2,2H_2O$	n −·1310 K 66·06	−·3200 8·718	−·2583 2·316	−·4717 0·2222
$CaCl_2$	n −·1459 K 63·92	−·3678 18·4	−·3803 3·992	−·4564 1·478
$NaNO_3$	n −·1344 K 61·48	−·2208 25·61	−·3000 5·689	−·3050 1·928
KNO_3	n −·0778 K 56·11	−·1838 19·81	−·0423 19·49	−·3267 0·1538
NH_4NO_3	n −·1257 K 74·89	−·3111 26·40	−·2425 11·61	−·3000 3·715
$Mg(NO_3)_2$ $6H_2O$	n −·08999 K 55·03	−·3141 17·86	— —	— —
$Ba(NO_3)_2$	n −·2281 K 43·25	— —	−·0706 11·73	−·6000 0·0282
$Ca(NO_3)_2$	n −·1332 K 40·61	−·4000 10·0	— —	— —
NaI	n −·1282 K 74·11	−·1343 53·99	−·2230 13·20	−·2804 5·738
KI	n −·1151 K 89·91	−·2375 28·83	−·2143 12·80	−·3411 3·054
NH_4I	n −·1615 K 88·23	−·2510 31·32	−·3561 10·52	−·3037 6·418
MgI_2	n −·1442 K 70·39	−·3551 15·95	−·2308 11·40	−·2937 5·052
BaI_2	n −·1414 K 66·62	−·3790 7·65	−·2584 9·740	−·2187 3·733

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* In the case of aqueous solutions only the value of n and K for the curves for concentrations before the break occurs are given. The values of n and K for the portion of the curves after the break will generally be higher than the values given in the table.

The variation of K for different salts in water and in alcohols is found to be quite regular. The value of K for all the salts generally decreases with a decrease in the dielectric constant of the solvent.

Attempts were also made to see how far the empirical equation of Furguson and Vogel[9] and the Lattey[10] are valid in concentrated solutions. It was observed that they do not satisfactorily express the relation between Λ_c and C beyond concentrations 0·5 to 1·0 N. Some of the formulae proposed by other investigators[11] were also tried but they were also not found to be valid over a large range of concentration.

Fuoss and Kraus[12] have devised equations taking into consideration the inter-ionic effect as well as the mass action effect; their equations give a better picture of the process than the empirical equations proposed by other investigators. The most important of their equations are

$$\Lambda_c = \gamma\,(\Lambda_\circ - \bar{a}\sqrt{C\gamma}) \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1)$$

$$-\log f = \beta\sqrt{C\gamma}/\,(1-\delta\sqrt{C\gamma}) \qquad \ldots \qquad \ldots \qquad \ldots \qquad (2)$$

$$C\gamma^2 f^2/1-\gamma = K \qquad \ldots \qquad \ldots \qquad \ldots \qquad ,,, \qquad (3)$$

where γ is the degree of dissociation, α is the slope of the Λ_c, $\sqrt{C}$ curve, f is the activity co-efficient, β and f are factors to be calculated according to Debye's method and K is the dissociation constant. The values of γ (the average fraction of solute free to carry the current calculated to determine the value of K (the dissociation constant) were found to be quite absurd, they being sometimes even higher than unity and in other cases even negative. It may be mentioned here that in calulating $\Lambda_\circ$ and K according to their equations, one has to utilise the actual value of $\Lambda_\circ$ itself. Thus 'a' the ionic

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[9] Phil. Mag., 4, 12 (1927).

[10] Phil. Mag., 4, 83 (1927).

[11] Taylor, Physical Chemistry, Vol. I, Second Edition, 1930, p. 657.

[12] Journ. Amer. Chem. Soc., 55, 476 (1933).

radius, which is necessary for using equation (2) above, is to be calculated from the limiting conductance Λ_0 by means of Stokes' Law and the value of α is also to be computed by Onsager's method using the actual value of Λ_0, so that one has to know actually in the beginning the value of Λ_0 before their equations can be applied.

It will not be out of place to refer here to the extension of the Onsager equation for moderately concentrated solutions discussed by Davies.[13] He considers that the deviation D of the experimental from the calculated value can be regarded as a close approximation as depending on Λ_0 in precisely the same way as does the $\sqrt{C}$ term. It is not clear how the deviation will depend upon the value of conductivity at infinite dilution, for as will be seen from Table I, the deviations of the experimental from the calculated values for different salts at the same concentration are quite irregular. Moreover by adding a factor like D to the Onsager equation any data can be made to fit in with the inter-ionic theory.

The most important factors which are responsible for the inapplicability of Debye-Hückel-Onsager theory to concentrated solutions are (1) variation in the dielectric constant of the solution, (2) variation in the viscosity of the solution, and (3) a decrease in the degree of dissociation and the complex ion formation. According to Walden [14] the dielectric constant of solution of small concentrations is lower than that of the pure solvent. Walden, Ulich and Werner [15] have observed a lowering of the dielectric constant proportional to concentration; but after the initial decrease they found that the dielectric constant increased with a further increase of concentration. Hückel [16] has shown that changes in the dielectric

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[13] Trans. Faraday Soc., 23, 354, 1927; also see Conductivity of Solution by Davies, 1930 Edition, pp. 114-116.

[14] Z. physik. Chem. 110, 44 (1924).

[15] Z. physik. Chem., 116, 261 (1925).

[16] Phys. Zeit., 26, 93 (1925).

constant with changing salt concentration make the self-potential of the ion, which has been neglected in the Debye-Hückel theory, appear as a significant quantity in the domain of concentrated solutions. In solvent media with smaller dielectric constants than water the increased electric forces will cause larger deviations from the ideal laws of solutions. The tendency of ions to associate, which increases with increasing charge and under equal conditions with decreasing size, will make itself more marked for such solvents.

The effect of viscosity on the mobility of ions can be ignored in very dilute solutions, but it will become more and more pronounced with an increase in the concentration of the solution. In the Debye-Hückel-Onsager theory for dilute solutions the viscosity of the solvent is used instead of the viscosity of the solution. One may be inclined to think that if the term for electrophoretic effect, which contains the viscosity factor, is corrected for variation in viscosity with concentration, the deviations from the theory may become less marked in concentrated solutions. Column 4 of Table I contains the values of Λ_c calculated from the Debye-Hückel-Onsager equation by using the actual viscosity * of solutions. It will be seen that the effect of the viscosity correction is most pronounced in highly concentrated solutions. But it is clear that this correction does not explain completely the deviations of the experimental from the calculated values. This might be partly due to the effect of viscosity on inter-ionic forces as pointed out by Onsager.[17] It thus appears that if the theory is to be extended to concentrated solutions, probably the viscosity factor should also be introduced in the first term of their equation, *viz.*, the relaxation factor.

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* Viscosity was measured by means of an Ostwald viscometer at 30°C.

[17] Trans. Faraday Soc., 23, 356 (1927).

Using the values of Λ_o at 33°C for different salts in different solvents[18] the value of the ratio Λ_c / Λ_0 was also calculated in different cases. It was found that in aqueous solutions the discussion is not quite complete even in solutions having concentrations as low as 0·05 N, the degree of dissociation decreasing appreciably with an increase in concentration. It was observed that generally the degree of dissociation at a particular concentration is less in alcohols than in water, it being least in the case of *n*-propyl alcohol. It should however be noted that in some cases for certain concentrations (especially in highly concentrated solutions) the percentage dissociation is found to be more in alcohols than in water. This is probably due to the fact that the value of Λ_o is considerably less in alcohols than in water, while the differnece between the values of Λ_c in the two cases is not in the same proportion. In what way a decrease in the degree of dissociation will affect the inter-ionic attraction is difficult to say. It is quite possible that the effect of inter-ionic attraction may be negligible in concentrated solutions when compared with a decrease in the concentration of ions which act as carriers of electricity in a solution.

In what way the undissociated salt exists in solution is not quite clear. It is however certain that the tendency for the formation of associated ion pairs, electrically neutral doublets or unionised molecules is sure to be present to a marked degree in concentrated solutions where the distance between oppositely charged ion of an electrolyte is reduced. In the case of non-aqueous solutions the dielectric constant will play an important part in that the lower the dielectric constant the greater will be the electrostatic attraction between oppositely charged ions and the smaller will be the dissociation constant. This view seems to be supported by the degree of dissociation in various alcohols. Also there is a possibility of inter-action

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[18] These were calculated by using Lattey's equation (Phil. Mag., 6, 258 (1928).

between solvent and ions; this tendency is more marked in the case of aqueous solutions, especially when one is dealing with electrolytes which are not neutral.

The formation of complex ions is sure to be well marked in concentrated solutions. This is sufficiently clear from the results of McBain and Rysselberge[19] and of Neis.[20] This effect will considerably influence changes in equivalent conductivity with increasing concentration.

In concentrated solutions the effect of solvation may be of much less importance when compared with the effect of the other factors considered before.

The authors wish to thank Professors Normand and Taylor for their interest in the work and for some valuable suggestions.

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[19] Journ. Amer. Chem. Soc., 50, 3009 (1928).

[20] (Zeit. physik. Chem., 138, 447 (1928).

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VISCOSITY OF MODERATELY AND HIGHLY CONCENTRATED SOLUTIONS OF SOME ELECTROLYTES IN WATER AND METHYL, ETHYL AND n-PROPYL ALCOHOLS AND A DISCUSSION OF RELATION BETWEEN CONDUCTANCE AND FLUIDITY

BY

H. N. DESAI*, D. B. NAIK AND B. N. DESAI

In a previous paper (H. N. Desai, D. B. Naik and B. N. Desai, Indian J. Physics, *8*, 323, 1934) we have given results of conductance of solutions of some electrolytes in water and methyl, ethyl and n-propyl alcohols. Simultaneous measurements of viscosity of those solutions at 30°C were also made with an Ostwald viscometer. In the present paper it is proposed to give some of the viscosity results of moderately and highly concentrated solutions and also to discuss the relation between conductance and fluidity.

The time required for the flow of solution between the two marks on the Ostwald viscometer was accurately noted by means of a previously calibrated stop watch reading upto one-tenth of a second. The time of flow for conductivity water was first determined to find out the constant of the viscometer. A number of readings were taken in each case and the mean value calculated. The density measurements were made by means of a pyknometer. The viscosity was calculated by using Poiseuille's formula. In the calculations the viscosity of water at 30°C was taken as 0·008007 dynes sec/cm^2.

RESULTS AND DISCUSSION

(*a*) *Relation between viscosity and concentration.*

It was found that in aqueous solutions chlorides, iodides and nitrates of potassium and ammonium show negative viscosity within a certain range of concentration with an increase in concentration of salt solution. The general nature of the viscosity-concentration (gram equivalent/litre-C) curves in these cases is similar to that

---

*The experimental work has been carried out entirely by Mr. H. N. Desai under the direction of the other two authors. The detailed results are to be submitted shortly in the form of a thesis for the M.Sc. degree of the Bombay University.

of the curves for KI and NH_4I given in Fig. 1. The results of KI agree within 1% with those of Getman (J. de Chem. Phys., *5*, 344, 1907.) and of KCl and NH_4Cl very closely with those of Simon

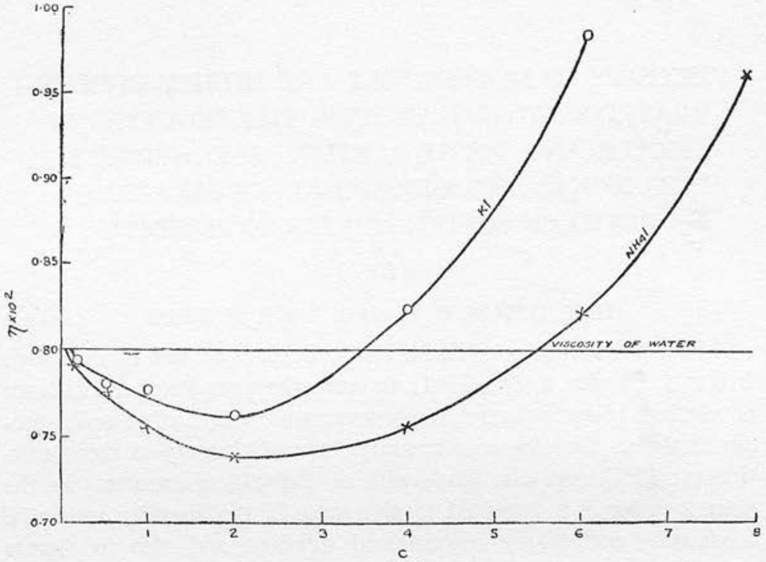


Fig. 1

(C. R., *176*, 437, 1923). In the case of methyl and ethyl alcohols only potassium and ammonium chlorides show negative viscosity (Figs. 2 and 3). In these cases it is observed that the range of

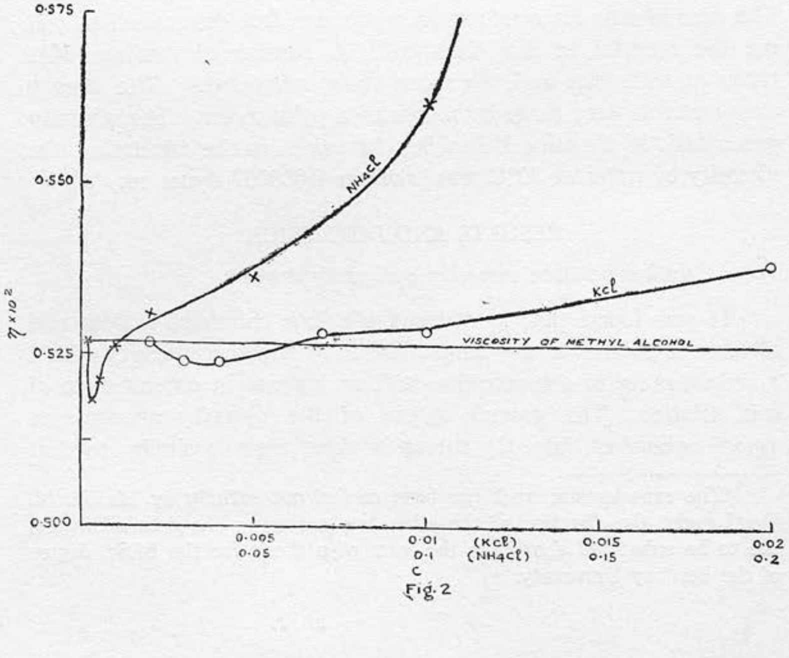


Fig. 2

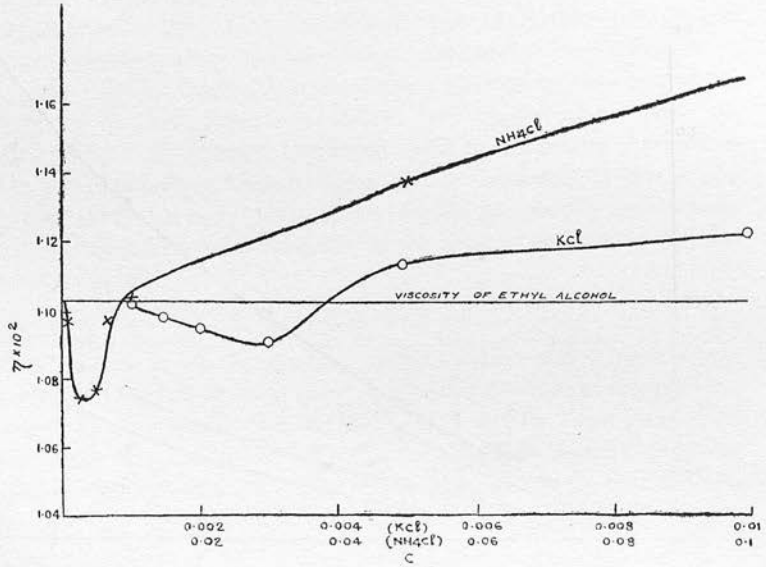
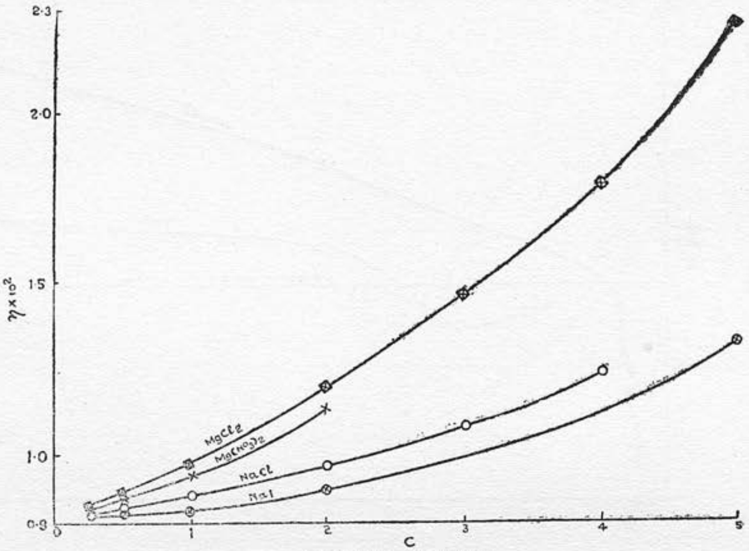


Fig. 3

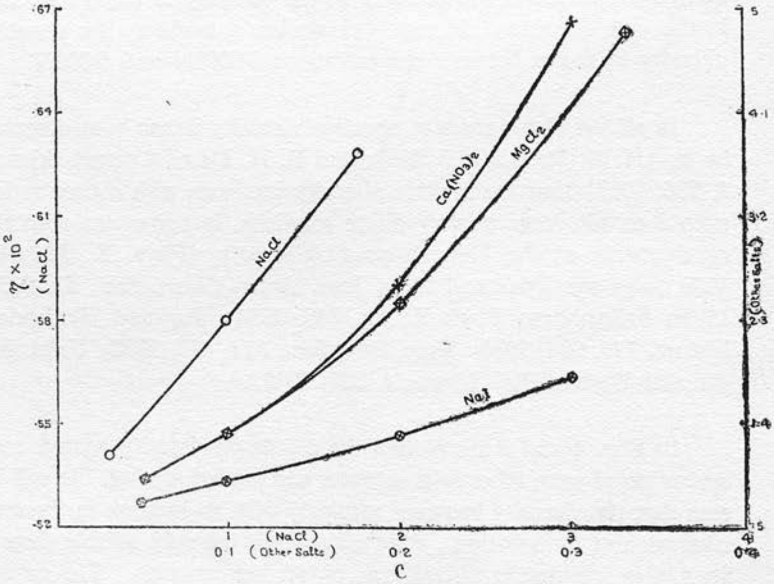
concentration over which viscosity decreases with concentration as well as the extent of the decrease in the viscosity is much less than in the case of water. In n-propyl alcohol a tendency for negative viscosity is shown between concentrations 0·0008N and 0·002N.

In all the above cases of negative viscosity it has been observed by us (H. N. Desai, D. B. Naik and B. N. Desai, Current Science, *2*, 206, 1933) that the relative viscosity increases with concentration upto a certain stage in very dilute solutions, in agreement with the requirements of the Falkenhagen-Dole theory (Phys. Z., *30*, 611, 1929 ; also see Jones and Dole, Jour. Amer. Chem. Soc., *51*, 2950, 1929 ; Falkenhagen Phys. Z., *32*, 745, 1931 ; Joy and Wolfenden, Nature, *126*, 994, 1930 ; Proc. Roy, Soc., *314*, 413, 1932 ; Falkenhagen and Vernon, Phil. Mag., *14*, 537, 1932).

In Figs. 4 and 5 are plotted the results of viscosity against concentration of some other salts in water and methyl alcohol. It will be seen that the viscosity increases regularly with an increase in the concentration of the solution. Also salts which are very soluble show a very large increase in viscosity at high concentrations. The nature of curves for other salts used in these experiments (except those which show negative viscosity) in all the four solvents is exactly similar to that of the curves given in Figs. 4 and 5.



SOLUTIONS IN WATER
Fig. 4.



SOLUTIONS IN METHYL ALCOHOL
Fig. 5.

Grinnell Jones and Malendel Dole (Jour. Amer. Chem. Soc., 51, 2950, 1929) have proposed an equation connecting viscosity with concentration. They have stated that it is applicable only upto a concentration of 0·5 N in case of $BaCl_2$ in water. For other salts it is valid only for very dilute solutions (also see in this connection paper by Grinnell Jones and Talley, Jour. Amer. Chem. Soc., *55*, 4124, 1933). An attempt was made to fit in the results obtained in this investigation, in various types of equations and it was found that the following equation could be applied successfully over a wide range of concentration, especially in moderately and highly concentrated solutions :—

$$\eta_c = \eta_0 + D_1C^2 + D_2C^3$$

where η_c and η_0 are the viscosity of the solution and solvent respectively, C is concentration in gram equivalents per litre of solution and D_1 and D_2 are constants for the particular salt. In Table I are given the values of η_c calculated according to the above equation for some salts in different solvents. The values of constants D_1 and D_2 were calculated by the method of least squares.

TABLE I

	C.	$\eta_c \times 10^2$ Observed	$\eta_c \times 10^2$ Calculated.	$[\frac{\eta_c}{\eta_0}-1]/c$
	WATER			
NaI ...	7·9	2·6630	2·7432	0·294
	5·0	1·3310	1·4459	0·133
$D_1 = 0{\cdot}01661 \times 10^{-2}$ ...	2·0	0·8945	0·8818	0·059
	1·0	0·8285	0·8192	0·035
$D_2 = 0{\cdot}001839 \times 10^{-2}$ ...	0·5	0·8245	0·8051	0·060
	0·1	0·8194	0·8009	0·230
BaI_2 ...	3·2	1·0290	1·0433	0·089
	1·0	0·8480	0·8471	0·059
$D_1 = 0{\cdot}05674 \times 10^{-2}$ ...	0·5	0·8217	0·8136	0·052
	0·1	0·8048	0·8013	0·050
$D_2 = -\ 0{\cdot}01033 \times 10^{-2}$ ...	0·01	0·8019	0·8007	0·120

METHYL ALCOHOL

$CaCl_2$ ...	4·0	9·3970	8·9739	4·21
	3·0	5·0470	5·4931	2·86
$D_1 = 0{\cdot}6232 \times 10^{-2}$ ...	2·0	2·4650	2·8293	1·84
	1·0	1·2410	1·1263	1·35
$D_2 = -\ 0{\cdot}0238 \times 10^{-2}$ ...	0·5	0·8206	0·6827	1·11
	0·1	0·6141	0·5331	1·66
	0·05	0·5746	0·5285	1·82
	0·01	0·5400	0·5275	2·50

ETHYL ALCOHOL

$MgCl_2$ ...	2·9353	7·690	7·533	2·03
	2·0	4·676	5·918	1·62
	1·0	2·404	2·790	1·13
$D_1 = 2{\cdot}172 \times 10^{-2}$ ...	0·5	1·779	1·585	1·23
	0·1	1·272	1·124	1·53
$D_2 = -\ 0{\cdot}4855 \times 10^{-2}$ ...	0·05	1·191	1·108	1·60
	0·01	1·145	1·103	3·80

n - PROPYL ALCOHOL

NaI ...	0·6	2·531	2·5020	0·80
	0·1	1·877	1·9172	0·97
$D_1 = 24{\cdot}18 \times 10^{-2}$ ...	0·05	1·803	1·7559	1·08
	0·01	1·752	1·7124	2·40
$D_2 = -\ 36{\cdot}63 \times 10^{-2}$ ...	0·005	1·726	1·7106	1·80
$CaCl_2$ ...	2·0	12·220	13·4460	3·07
	1·0	4·816	5·6110	1·82
$D_1 = 5{\cdot}118 \times 10^{-2}$ ...	0·5	3·034	2·8369	1·55
	0·1	2·042	1·7600	1·93
$D_2 = -\ 1{\cdot}217 \times 10^{-2}$ ...	0·01	1·818	1·7105	6·30
	0·005	1·778	1·7101	8·00

It will appear from the Table that in all the cases there is on the whole a fairly good agreement between the observed and the calculated values of viscosity for concentrated salt solutions. A still better agreement between the observed and the calculated values can be obtained if in determining the values of constants one uses a very large number of observations taken at very short interval of concentrations. It will appear from the form of the equation that the term D_1C^2 is large when compared with the term D_2C^3 for relatively dilute solutions, while the term D_2C^3 is also important for higher concentrations.

In column 4 of Table I are also given the values of factor $[(\eta_c/\eta_0)-1]/C$ for some salts. It will be found that in all the cases given in the Table except NaI in n-propyl alcohol, a minimum value is found to occur. It will be obvious that the values of this factor for cases of negative viscosity will also show a minimum. The minimum in the viscosity increment-concentration values observed here thus supports the results of Grüneisen (Wiss, Abh. d. Phys., Tech. Reichsanst., *4*, 239, 1905), Appleby (Journ. Chem. Soc., *97*, 2000, 1910) and Merton (Journ. Chem. Soc., *97*, 2454, 1910). According to Grüneisen this effect might be due to dissociation of salt molecules in solution. The present results do not support the observation of Tower (Journ. Amer. Chem. Soc., *38*, 833, 1916) according to whom the values of the factor are tolerably constant for alcoholic solutions. The causes of a maximum in the values of the factor in the case of NaI in n-propyl alcohol are not quite clear.

Adolph and Rabinovich (Journ. Amer. Chem. Soc., *64*, 954, 1922) consider that of all the factors the following may have a deciding influence on changes in viscosity with concentration : (1) Influence of the viscosity of the solution on the internal friction of solution ; (2) Changes in hydration of ions in dilute solutions ; (3) Formation of complex ions and molecules—specially well pronounced in moderately and highly concentrated solutions—will increase viscosity if the volume of the complex ion is larger than the sum of the volumes of the simple ions composing it and decrease the viscosity in the opposite case ; (4) Depolymerisation of the solvent on addition of electrolytes and depolymerisation of the solute by the solvent and (5) Influence of electric field due to ions.

The present results seem to support the assumption of Jones and Veazey (Jour. Amer. Chem. Soc., *37*, 405, 1906) about the specific effect of cation in lowering the viscosity with an increase of the concentration of the solution, for if the negative viscosity is as a result of the specific effect of the anion, all the chlorides, nitrates and iodides should have lowered the viscosity within a certain range of concentration in the case of aqueous solutions. The non-observance of negative viscosity with nitrates and iodides in methyl, ethyl and n-propyl alcohols might be due to lower dielectric constant of the solvent. These results show that the tendency for negative viscosity decreases with the dielectric constant of the solvent. This effect of relatively low dielectric constant on negative viscosity appears somewhat like the effect of relatively high temperature on the same, for as observed by Sprung (Ann. Phys. Chem., *1*, 159, 1876), negative viscosity effect becomes less marked with an increase of temperature and disappears at high temperatures [also see in this connection Getman (loc. cit.) and Joy and Wolfenden (loc cit.)]. According to Happart (reference from Landolt and Börnstein, 4th edition, p. 288) the volume changes on the addition of solute to solvent might be partly responsible for negative viscosity in certain cases.

From the results obtained by us it has been found that the percentage increase in viscosity for the same concentration of the solution is greater in ethyl alcohol than in methyl alcohol, while that in n-propyl alcohol is greater than either in the case of methyl or ethyl alcohols. These results thus support the view that the increase in viscosity with an increase in concentration of solution becomes more marked the lower the dielectric constant of the solvent.

(*b*) *Relation between equivalent conductivity and fluidity.*

It has hitherto been the general practice to discuss the relation between equivalent conductivity and fluidity ($1/\eta$) instead of equivalent conductivity (Λ_c) and viscosity itself. In Figs. 6 and 7 are

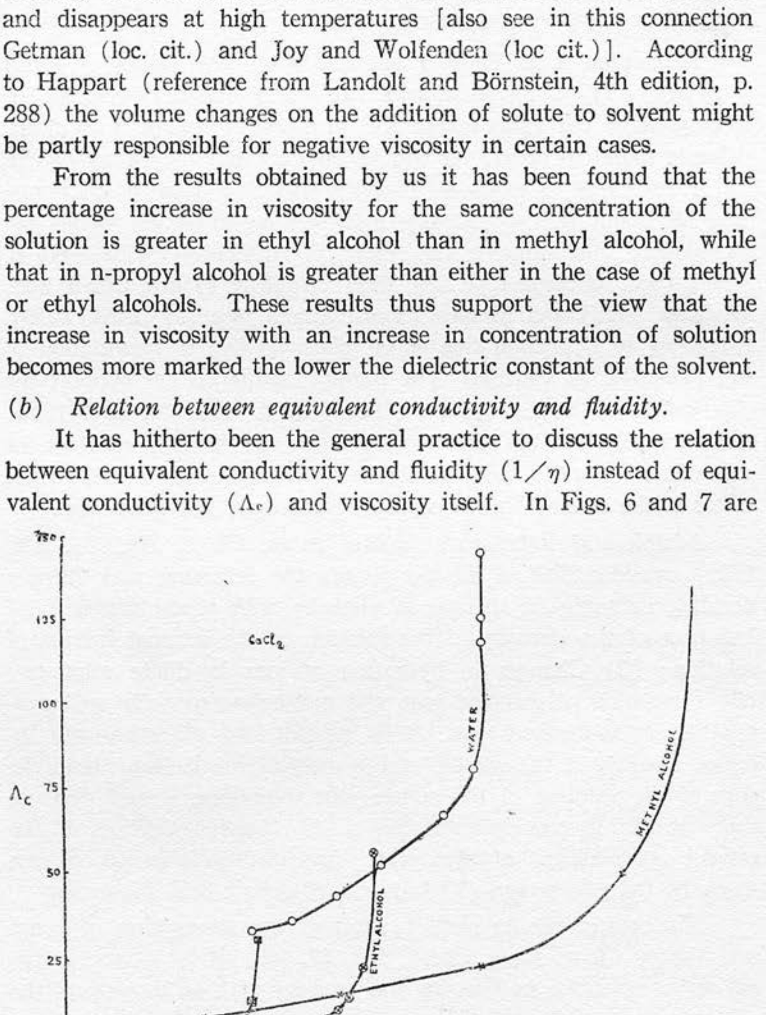


Fig. 6.

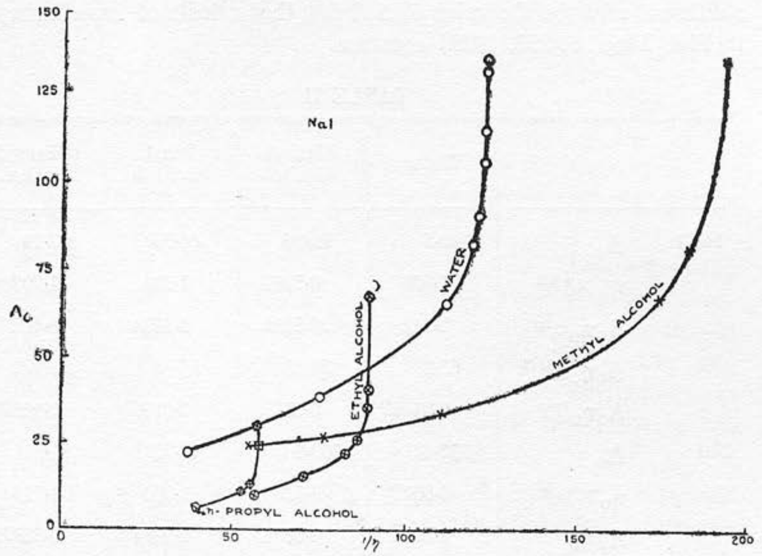


Fig. 7.

plotted the values of Λ_c [given in our previous paper (loc. cit.)] against $1/\eta_c$ for solutions of $CaCl_2$ and NaI respectively in different solvents. The nature of the curves in other cases, except those where negative viscosity is shown, is exactly similar. It will appear that for small decrease in fluidity of solution the equivalent conductivity decreases very rapidly for relatively dilute solutions, while in the concentrated solutions the decrease in the equivalent conductivity is much less than the decrease in the fluidity of the solution.

Walden (Z. physik. Chem., *55*, 207, 1906 ; *78*, 257, 1912 ; Z. f. Electrochemie, *26*, 67, 1920) has collected a large amount of data and come to the conclusion that the conductivity at infinite dilution of an electrolyte is inversely proportional to the viscosity of the solvent. It must be stated that only a rough parallelism between the viscosity of a solvent and the resistance it opposes to the passage of ions can be drawn from the results of Walden. From his data it becomes clear that in the majority of cases $\Lambda_0\eta_0$ only approximates to constancy in solvents whose dielectric constant is low ; directly one comes to solvents like water for which the dielectric constant is high, larger values of $\Lambda_0\eta_0$ are obtained. It thus appears that $\Lambda_0\eta_0$ is a function of the dielectric constant. According to Walden (loc. cit.) the factor $\Lambda_0\eta_0 M^{1/2}$, where M is the molecular weight of the solute, is also constant for different solvents. In Table II are given the values of the above factors for NaCl, NaI and $NaNO_3$ in different solvents, the value of Λ_o being that calculated from Lattey's (Phil. Mag., *6*, 258, 1928) equation.

TABLE II

		Water.	Methyl Alcohol.	Ethyl Alcohol.	n-Propyl Alcohol.
NaCl	Λ_o	143·5	99·36	44·55	27·19
	$\eta_o \times 10^2$	0·8007	0·5269	1·103	1·702
	$\Lambda_o\eta_o$	1·149	0·5235	0·4914	0·4627
	$\Lambda_o\eta_o M^{1/2}$	67·28	30·63	28·75	27·07
	$\Lambda_o\eta_o/D$	0·01497	0·01779	0·01997	0·02207
NaI	Λ_o	138·4	109·2	49·72	31·21
	$\eta_o \times 10^2$	0·8007	0·5206	1·060	1·710
	$\Lambda_o\eta_o$	1·109	0·5684	0·5271	0·5337
	$\Lambda_o\eta_o M^{1/2}$	166·3	85·27	79·07	80·05
	$\Lambda_o\eta_o/D$	0·01444	0·01932	0·02142	0·02537
$NaNO_3$	Λ_o	144·0	109·6	49·65	31·09
	$\eta_o \times 10^2$	0·8007	0·5206	1·060	1·670
	$\Lambda_o\eta_o$	1·153	0·5707	0·5262	0·5192
	$\Lambda_o\eta_o M^{1/2}$	98·02	48·51	44·73	44·13
	$\Lambda_o\eta_o/D$	0·01502	0·01939	0·02138	0·02468

It will appear that the two sets of values are quite different for water and methyl alcohol. It will thus be apparent that knowing the value of Λ_o for a salt in one solvent, it will not be possible to get even a rough value of Λ_o for the same salt in another solvent whose chemical nature is different. However the agreement of the value in different alcohols is fairly close.

Table II also contains the values of the factor $\Lambda_o\eta_o/D$, where D is the dielectric constant of the solvent. It will be seen that the value of this factor is very nearly the same in water as well as in methyl alcohol, the difference being less than 25% in this case, while it is about 100% in the case of values of the factor $\Lambda_o\eta_o$. It will also be seen that the value of the factor $\Lambda_o\eta_o/D$ rises continuously as the dielectric constant decreases. The value of Λ_o for NaCl in n-propyl alcohol calculated from the value of the factor for water comes to 18·51. The actual value calculated from Lattey's equation is 27·19. The calculated value of Λ_o for NaCl in n-propyl alcohol is lower than the actual value which will be observed in that solvent for the same salt probably because of the fact that the solvation of ions in n-propyl alcohol is less than in water. If the solvation of ions in n-propyl alcohol is less than in water, other things being taken into consideration, the smaller effective radii of ions in the former solvent will give higher value of Λ_o than the value of Λ_o calculated from the data for water on the assumption that the effective ionic radius is the same in both the solvents.

Grüneisen (loc. cit.) has observed that the expression $[(\eta_c/\eta_o)-1]/m = A\alpha + B(1-\alpha) + Cm$, where A, B and C are constants, α is the degree of dissociation, m is the concentration in gram-equivalents and η_c and η_o are the viscosities of solution and solvent respectively, fitted the experimental observations upto concentration several times normal. On applying his expression to the present results, it was not found to be valid at all.

Bousfield and Lowry (Phil. Trans., *204*, 289, 1903) suggested that the measured activities should be multiplied by the relative viscosity in order to account for the effect of fluidity on the mobility of the ions. The values of $\Lambda_c \, \eta_c/\eta_o$ for some of the salts in different solvents have also been calculated. It is found that in all the cases in water there occurs a minimum in the corrected conductivity at higher concentrations. In the case of alcohols the minimum in the corrected Λ_c also occurs at higher concentrations in those cases where the solubility is large ; in cases where the solubility is small the minimum is not observed. According to Kraus (Jour. Amer. Chem. Soc., *36*, 35, 1914) in cases of large negative viscosity effect the corrected value of Λ_c decreases in a regular way with increasing concentration. His observation is completely supported by all the cases of negative viscosity mentioned in this paper. Two explanations have been advanced for the occurrence of the minimum in the corrected values of Λ_c :—

(1) According to Franklin (Journ. Phys. Chem., *15*, 683, 1911) who investigated KI in liquid sulphur dioxide at 0°C, there occurs first a minimum point and then a maximum point in the Λ_c, C curve. Walden (Bull. Akad. Sci. Petersb., 1083, 1913) has stated that for any salt there exists a relationship between the position of minimum and the dielectric constant of the solvent. The causes of the minimum at higher concentration in the corrected Λ_c values might be similar to those of minimum in the value of Λ_c (experimental) observed in some non-aqueous solutions (Franklin, loc. cit.).

(2) According to Washburn (Journ. Amer. Chem. Soc., *33*, 1463, 1911) Λ_c has been over corrected and that it should be multiplied by the mth power of relative viscosity, where m is less than 1

and varies from ion to ion. Rabinovich (Z. physik. Chem., *99*, 338, 417, 1921) also considers that $\Lambda_c \, \eta_c/\eta_o$ figures are over corrected. It should however, be stated that the over correction does not wholly explain the facts.

It has also been found from our results that the viscosity corrected values of α (degree of dissociation) are in some cases higher in concentrated solutions than in dilute ones. This is certainly against all the known facts of physical chemistry.

It is difficult to say how much reliance should be placed on these corrections of viscosity. In concentrated solutions, where alone viscosity effects are large, there also exist undissociated molecules besides the ions. These three will be present in varying proportions and will presumably exert each its own individual effect on the viscosity of the solution. Moreover the mobilities of the ions may be differently affected by each of the three factors.

SUMMARY.

Measurements of viscosity of chlorides, nitrates and iodides of solutions of alkali metals and alkaline earths over a large range of concentration have been made using water and methyl, ethyl and n-propyl alcohols as solvents.

Chlorides, nitrates and iodides of potassium and ammonium in aqueous solutions show negative viscosity within a certain range of concentration; in methyl and ethyl alcohols KCl and NH_4Cl alone show negative viscosity, while in n-propyl alcohol only a tendency for negative viscosity is marked in the case of KCl alone. In other cases the viscosity increases continuously with concentration, the increase being more marked in concentrated solutions. An equation connecting viscosity with concentration has been suggested. These results have been discussed from points of view advanced by various investigators.

A discussion of relation between conductance (results of simultaneous measurements of conductance given in a previous paper) and fluidity has also been made. It has been observed that for relatively dilute solutions a small decrease of fluidity is accompanied by a very rapid decrease of Λ_c, while in concentrated solutions the decrease in Λ_c is much less than the decrease in fluidity. The same behaviour is shown by all salts in different solvents where fluidity decreases regularly with an increase in concentration. Applicability of Walden's rule has been discussed.

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

Part III. Colloidal Prussian Blue.

BY

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IN papers published by Desai and collaborators[1] it has been shown that changes which are produced in the charge on colloidal particles during dialysis are not so simple as is usually supposed and that the results of viscosity and stability cannot always be utilised for getting an idea about the charge on colloid particles. The results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric and thorium hydroxide have been given in Parts I (Desai and Borkar[1]) and II (B. N. Desai and A. K. Desai[1]) respectively. It will be seen from the results that the behaviour of both the sols as regards dialysis, dilution and critical potential is similar; the viscosity changes on dialysis and in presence of electrolytes have, however, been found to be different. In the present paper similar simultaneous measurements taken with colloidal prussian blue are presented.

Experimental.

Prussian blue was precipitated by adding slowly and without stirring a 2% solution of potassium ferrocyanide to a 2% solution of ferric chloride.[2] The precipitate was allowed to stand for about 15 minutes, filtered and peptised by shaking vigorously with a 2% oxalic acid solution in one case and a 5% oxalic acid solution in the other. The sol so obtained was filtered four times through a double-fold of filter in order to attain as far as possible uniformity of particle size and better constancy of conductivity.[3]

The sol was dialysed in parchment paper bags which were previously kept soaked in distilled water for 3 to 4 days. The outer water was changed once a day. No prussian blue passed out during dialysis; oxalic acid and traces of ferric chloride were however detected in the dialysate. Dialysis was carried out in dark room in order to avoid effect of light on the sol. The amount of prussian blue in the sol did not change to any appreciable extent during dialysis.

The cataphoretic speed was measured by Mukherjee's improved U-tube method. The dialysate made equi-conducting by addition of potassium chloride in the initial stages of dialysis and by addition of oxalic acid in the later stages was found to be quite satisfactory as an upper liquid. The difference between the direct and reverse movements of the boundary was never more than 3 to 4%. In all the tables of results, the cataphoretic speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre × 10^5. The concentration of the electrolytes is expressed in millimoles per litre.

Viscosity was measured by using an Ostwald viscometer. The results of viscosity have been expressed in terms of the viscosity of distilled water at the temperature of the experiment as unity.

The stability was determined by finding out the amount of the electrolyte necessary to give instantaneous coagulation. The flocculation values are expressed in millimoles of the electrolyte in total volume, *i.e.*, 30 c.c.'s in this case.

All the measurements of cataphoretic speed and viscosity were made at a temperature of 30° C.

Results and Discussion.

A. Effect of ageing.—Sols dialysed for 6 and 25 days were removed and stocked in resistance glass flasks covered with black paper and the cataphoretic speed (cat. speed) was determined at different periods. The results are given in the following table :—

TABLE I.

Sol dialysed for 6 days		Sol dialysed for 25 days	
Age in days	Cat. speed	Age in days	Cat. speed
0	39·20	0	38·60
30	37·00	20	38·30
40	36·90	38	31·55
143	36·90	104	27·90
216	36·60	173	27·40
262	36·00	218	27·20

It will appear that in the case of the sol dialysed for 6 days, the cat. speed first decreases and then remains constant for a certain period after which it again decreases, while for the sol dialysed for 25 days, the cat. speed first decreases very slowly, then rapidly and afterwards again slowly when kept for longer periods. The decrease in the cat. speed on ageing might possibly be due to preferential adsorption of the coagulating ions.

In order to minimise the effect of ageing, all the experiments were carried out in as short a time as possible.

B. Changes in cataphoretic speed, stability and viscosity with the progress of dialysis.—The results of these experiments are given in Tables II and III.

TABLE II.

Sol peptised with 5% oxalic acid solution.

Period of dialysis in days	Cat. speed	Relative viscosity	Flocculation values with KCl
3	38·10	1·027	7·06
6	41·60	1·000	5·80
10	42·05	0·996	4·20
12	42·90	1·005	2·74
15	50·30	1·008	1·20
19	21·50	1·009	0·50
23	13·10	1·014	0·10

TABLE III.

Sol peptised with 2% oxalic acid solution.

Period of dialysis in days	Cat. speed	Relative viscosity	Flocculation values with KCl
4	39·00	1·014	4·84
9	41·10	1·009	4·20
14	44·10	1·004	2·64
18	43·60	1·005	1·28
27	38·00	1·012	..
30	27·00	1·014	..
34	19·50	..	..

It will appear from Tables II and III that with the progress of dialysis the cat. speed first increases and reaches a maximum after which it gradually decreases, while the relative viscosity first decreases and reaches a minimum after which it gradually increases. The stability as determined by flocculation values with KCl continuously decreases with the progress of dialysis.

Desai and co-workers[1] have explained a first increase and then a decrease in the cat. speed with dialysis by assuming that the process of dialysis (during which the amount of peptising agent in the sol continuously decreases) can be considered roughly as a reverse of the process of adding small increasing amounts of the peptising agent to the colloid so far as the influence of the electrolyte on the cat. speed is concerned. If this analogy is correct one would expect that on adding small increasing amounts of oxalic acid, which is the peptising agent in the present case, to the prussian blue sol, the cat. speed should first increase and then decrease. That this is actually the case will be clearly seen from the results given in Table IV.

TABLE IV.

Cat. speed of colloidal prussian blue (peptised with 2% oxalic acid solution and dialysed for 25 days) in the presence of varying amounts of oxalic acid.

Amount of oxalic acid	Cat. speed
0·000	26·95
0·013	35·00
0·037	37·50
0·125	39·40
0·250	40·80
1·250	35·70
3·750	31·90
12·500	30·70

It will also appear that the cat. speed and the stability do not apparently go hand in hand till the maximum value of charge is reached during dialysis as in the case of ferric and thorium hydroxide sols investigated by Desai and co-workers.[1] In the present case, the decrease in the flocculation values with the progress of dialysis in spite of an increase in charge might be due to an increase in the preferential adsorption of the stabilising (oxalate) ions in the presence of KCl (electrolyte added for flocculation value determinations) as well as a change in the size of the colloid particles during dialysis.

According to v. Smoluchowski,[4] the greater the electric charge on the colloidal particles the greater will be the viscosity of the sol, while according to Dhar and co-workers,[5] other things being identical, a decrease in electric charge on colloid particles causes an increase in hydration and necessarily in the viscosity of the sol. From the results given in Table III it will appear that the viscosity and cat. speed changes with the progress of dialysis completely support Dhar's view, but in the case of the sol peptised with 5% oxalic acid the maximum in the cat. speed and minimum in viscosity have not occurred at the same stage of dialysis—a fact against Dhar's view. The results do not support v. Smoluchowski's view.

On comparing the results given in Tables II and III it will appear that a higher value of cat. speed is obtained for the sol peptised with 5% oxalic acid solution than for the one peptised with 2% oxalic acid solution. There is an advantage in peptising prussian blue with concentrated solution of oxalic acid in that sols so obtained have finer particles and are more stable than those obtained by using dilute solutions of oxalic acid. The sols peptised with concentrated solutions of oxalic acid are, however, not suitable for charge measurements as the boundary becomes diffused due to the disturbances caused by vigorous electrolysis once the current is passed through the sol. In the experiments to be described further only prussian blue sols prepared by using 2% oxalic acid solution have therefore been used.

C. Changes in the cataphoretic speed and stability of colloidal prussian blue dialysed and diluted to different extents.—Sols of different concentrations were prepared by adding requisite amounts of conductivity water to the original dialysed sol. The original sol has dilution 1; dilutions of other sols have been obtained from the value of the ratio $\frac{\text{total volume of the diluted sol}}{\text{actual volume of the original sol}}$. The results of these experiments are given in the following table.

TABLE V.

Figures in columns 'a' and 'b' give values of cat. speed and flocculation (with KCl) respectively.

Period of dialysis in days	Dilution										
	1		1·33		2		4		5·33	8	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*a*	*b*
3	38·70	5·20	40·30	4·70	42·50	4·16	39·00	3·36	35·75	30·10	3·16
8	40·60	4·32	41·10	4·04	41·10	3·50	37·70	2·58	35·00	30·10	2·20
13	43·20	3·24	42·20	2·84	40·50	2·20	36·10	1.12	33·80	28·60	0·36
17	42·50	1·70	40·90	1·28	38·70	0·66	35·00	0·14	32·50	27·00	..
21	41·05	..	40·00	..	37·60	..	33·60	..	31·30	25·90	..
26	37·10	..	35·40	..	32·30	..	24·20	..	22·30	21·50	..
30	27·50	..	25·80	..	23·05	..	21·00	..	20·60	..	..

The following conclusions can be drawn from the results given in the table :—

(1) With the progress of dialysis the cat. speed (vertical columns '*a*') first increases and then decreases for sols having dilutions 1 and 1·33, while it continuously decreases for sols having dilutions 2, 4, 5·33 and 8.

(2) On diluting the sol, the cat. speed (values given in columns '*a*'—horizontal rows) first increases and then decreases for sols dialysed for 3 and 8 days, while it continuously decreases for sols dialysed for 13, 17, 21, 26 and 30 days.

(3) The stability of the sol as determined by flocculation values (given in columns '*b*') continuously decreases with the progress of dialysis (vertical columns) and dilution (horizontal rows).

These results are thus exactly similar to those obtained with colloidal ferric and thorium hydroxide.[1] The changes in cat. speed on dilution have been explained by Desai and co-workers[1] by assuming similarity between processes of dilution and dialysis so far as the changes in the amount of the peptising electrolyte are concerned (the amount of the electrolyte in the sol decreases both during dialysis and dilution). According to this view samples of the sol which contain initially an amount of the peptising electrolyte more than that corresponding to the maximum in the cat. speed—concentration curve with that particular electrolyte (in this case the curve obtained by plotting results given in Table IV) will show first an increase and then a decrease in cat. speed on further dialysing or diluting the sol; samples of sol which contain initially an amount of the peptising electrolyte equal to or less than that corresponding to the maximum in the cat. speed concentration curve of the colloid with that particular electrolyte will show a continuous decrease in cat. speed on further dialysing or diluting the sol. Further according to their view the maximum value of the cat. speed should occur at smaller and smaller dilution with the progress of dialysis and that the maximum value of cat. speed on dialysis should not differ appreciably from the maximum value of cat. speed on dilution. The present results completely support their view-point because (i) the maximum value of cat. speed on dialysis having occurred either on the 13th day or betwen the 8th and 13th day, the cat. speed on dilution has first increased and then decreased in the case of sols dialysed for 3 and 8 days and continuously decreased for sols dialysed for 13 days or longer, (ii) there is no appreciable difference between the maximum value on dialysis, *i.e.*, 43·20 and dilution, *i.e.*, 42·50, and (iii) the maximum value of the cat. speed has occurred at dilution 2 for sol dialysed for 2 days, and between 1·33 and 2 for that dialysed for 8 days.

It is also clear from the results that changes in stability on dilution and dialysis do not always give an idea about changes in cat. speed of the colloidal particles.

It may be mentioned here that for prussian blue dialysed for 3, 8 and 13 days, on diluting the sol the viscosity is found to decrease first rapidly and then slowly and afterwards shows a tendency to become constant. In the case of sols dialysed for periods longer than 13 days, on diluting the sol the viscosity first decreases and then increases. From changes in the cat. speed on dilution of sols dialysed to different extents (Table V) it will be clear that neither the view of Dhar[5] nor of v. Smoluchowski,[4] can individually explain the changes in cat. speed and viscosity observed in these experiments. As stated by Desai and co-workers,[1] one should also consider changes in hydration, the amount of electrolyte and the shape and size of particles to explain these results.

D. Measurements of cataphoretic speed from the point of view of critical potential.—A summary of results obtained in these experiments is given in Table VI.

TABLE VI.

Electrolyte	Initial cat. speed	Initial increase of cat. speed	Cat. speed at which coagulation begins	Concentration of electrolyte at which coagulation begins
HCl	38·70	3·60	27·50	0·125
KCl	37·30	7·30	26·20	2·500
$MgCl_2$*	37·05	nil	27·85	0·075
	36·35	nil	26·75	0·750
$MgSO_4$*	27·90	nil	22·20	0·125
	36·90	nil	24·50	1·250

* Results taken with two different samples of sol.

It will appear from the results that in the case of the electrolytes with univalent coagulating ions the cataphoretic speed first increases and then decreases when small increasing amounts of electrolyte are added to the sol, while with electrolytes with bivalent coagulating ions, the initial increase is not noticed at all. The initial increase in cat. speed is due to preferential adsorption of the similarly charged ions as stated before. The preferential adsorption of the similarly charged ions is not observed with $MgCl_2$ and $MgSO_4$ because of the bivalency of the coagulating ions.[1] Further as H-ions act as better coagulating agent than K-ions the initial increase in the cat. speed is smaller in the former case than in the latter.

The value of the cat. speed at which coagulation begins in different cases lies between 22·20 and 27·85, the maximum difference in the initial cat. speed being 10·80. According to Powis[6] coagulation begins only when the electrokinetic potential or the electric charge is lowered to a certain absolute value characteristic of each colloid. Mukherjee and co-workers[7] have, however, concluded that there is no critical potential characteristic of coagulation of a colloid by an electrolyte as suggested by Powis. Desai and co-workers[1] have observed that in the case of the colloidal ferric and thorium hydroxide coagulation begins at about the same value of the cat. speed for different electrolytes although the concentration of the electrolyte corresponding to that cat. speed is quite different in different cases. The present results also support the idea of critical potential at least for the electrolytes tried in this investigation because coagulation has begun at about the same value of cat. speed in different cases ; slight variations in the critical values might be due to the differences in the nature of the stabilising ions as suggested by Desai and co-workers.[1]

E. Influence of sunlight on cataphoretic speed of colloidal prussian blue dialysed to different extents.—For these experiments equal volumes of sol were removed in resistance glass beakers (of same capacity) which were kept covered with glass plates and exposed to sunlight for different periods. Any loss due to evaporation was made good by addition of conductivity water. The results of these experiments are given in Table VII.

TABLE VII.

Sol dialysed for 10 days		Sol dialysed for 21 days	
Exposure in hours	Cat. speed	Exposure in hours	Cat. speed
0	44·30	0	42·70
1	43·90	1	37·80
3	37·90	2	36·20
		5	34·10
		10	33·60
		29	27·60

It will appear from the results that the cat. speed decreases on exposure to sunlight. According to Miss S. Roy and Dhar[8] the prussian blue sol becomes more stable (stability as determined by flocculation values) on exposure to light. They have further stated that the greater stability is due to agglomeration as inferred from the absorption-spectra of sol exposed to sunlight. It is not clear how stability can increase as a result of agglomeration because ordinarily one would expect that the greater the size of particles the smaller the stability of the sol as a smaller amount of electrolyte would be required to reach a given degree of turbidity when the particles are big than when they are relatively small. The fact that agglomeration takes place on exposure will also be supported by the following observations.

TABLE VIII.

Period of dialysis in days	Time after which sol coagulates on exposure
0	1 to 1·5 mins.
1	2·5 to 3 ,,
7	17 ,,
10	3 to 4 hours
21	> 29 ,,

It will appear that in the first four cases exposure has given rise to agglomeration, *i.e.*, coagulation. Agglomeration has however resulted in a decrease of stability—a fact not agreeing with observations of Miss S. Roy and Dhar.[8] In the case of the sol dialysed for 21 days no sign of coagulation appears even on exposing it for 29 hours.

According to Laderer and Hartleb,[9] Berlin blue hydrosols are decolourised when exposed to visible light. It may be stated that in our case no decolourisation of the sol was noticed upto an exposure of 29 hours to sunlight, in the case of sol dialysed for 21 days. They have, however, stated that electrolytes decrease the time of flocculation by irradiation. This observation is supported by the results given in Table VIII because the sol dialysed for 21 days and containing very little of oxalic acid does not coagulate even on exposure of 29 hours, while sols dialysed for shorter periods and containing relatively large amounts of oxalic acid coagulate on exposure to sunlight even for very short periods.

The changes in cat. speed on exposure are probably due to action of sunlight on oxalic acid which gives rise to a change in the nature of the intermicellary liquid.

It may be mentioned that viscosity of the sol is found to decrease on exposure to sunlight—a fact which would seem to support v. Smoluchowski's view.

Summary.

The cat. speed of colloidal prussian blue (prepared by peptisation with oxalic acid) with the progress of dialysis first increases and then decreases, while the stability as determined by flocculation values with KCl

continuously decreases. The cat. speed on dilution first increases and then decreases in some cases while it continuously decreases in others; the stability on dilution is found to decrease continuously in all the cases. These results of dialysis and dilution are exactly similar to those obtained with colloidal ferric and thorium hydroxide investigated by Desai and co-workers.

The changes in the cat. speed and viscosity under different conditions show that neither the view of Dhar nor of v. Smoluchowski can individually explain the results.

The idea of critical potential is supported.

The cat. speed of the sol decreases on ageing and exposure to sunlight, sols dialysed for short periods even coagulating when exposed to sunlight for a couple of minutes.

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CONDITION OF SPARINGLY SOLUBLE SUBSTANCES IN GELS.

Part I. Silver Chromate in Gelatine.

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Williams and Mackenzie,[1] Bolam and co-workers[2] and Desai and Nabar[3] have shown from conductivity and e.m.f. measurements that prior to the appearance of red colour the yellow mixture of silver nitrate and potassium chromate in gelatine contains silver chromate in supersaturated solution and that the red colour is due to the actual formation of the solid phase, and not to the coagulation of a solid phase which is already present in the form of colloidal particles. Dhar and collaborators[4] have, on the other hand, shown from conductivity and diffusion experiments that the yellow mixture contains particles which are negatively charged through adsorption of chromate ions, while the red substance is a less stable sol containing particles which are positively charged through adsorption of silver ions. Naik, Desai and Desai[5] have observed that whatever changes in the conductivity are to occur take place immediately the solutions of silver nitrate in gelatine and potassium chromate in gelatine are mixed and that there is no gradual decrease of conductivity with changes in the colour of the mixures—observation against the views of Bolam and co-workers. The cataphoretic experiments did not show presence of any charged particles either in the yellow or red mixtures—observation against the view of Dhar and co-workers. They have suggested that immediately the solutions are mixed some insoluble substance is produced, the particles of which are in a very highly dispersed condition—probably in molecular condition—and that changes in the colour of the mixtures are due to growth of these very fine particles into larger ones.

The present work was undertaken to find out causes of differences in the results of various investigators about the condition of silver chromate in gelatine.

Experimental.

The gelatine used in these experiments contained 1·177% ash and 18% moisture and its p_H (determined colorimetrically) was 5·45. Samples of gelatine having different p_H were prepared by adding suitable amounts of acetic acid and sodium acetate. The conductivity experiments were carried out exactly in the same manner as done by Naik, Desai and Desai.[5] N/100 solutions of $AgNO_3$ and K_2CrO_4 and 3% solution of gelatine were used throughout. The reacting mixtures ($AgNO_3$ in gelatine and K_2CrO_4 in gelatine) were allowed to attain the required temperature by placing them in an electrically heated thermostat and then mixed by passing from tube to tube several times in a uniform manner; the mixture was then transferred to the conductivity cell, which was immediately kept in the thermostat for conductivity measurements. The total volume of the mixture in each experiment was 16 c.c. The time when colour change took place was carefully noted. The percentage of silver chromate in ionic condition was calculated exactly in the same manner as before.[5]

On allowing the gelatine solution to stand for different periods it was observed that its inhibitive power (power to prevent appearance of red coloured precipitate of silver chromate from yellow mixture) is not affected to any appreciable extent even when the mixture of gelatine and reactants is kept standing for 72 hours.

Results and Discussion.

A. Changes in the inhibitive power of gelatine and condition of silver chromate at different temperatures.—In Fig. 1 are plotted the values of conductivity (observed) of silver chromate alone at different times for 4·5 c.c. of reactants at different temperatures. The curves for other concentrations of the reactants are exactly similar. It was observed that in each case the conductivity did not change further on allowing the mixture to stand even for 24 hours or more. A summary of the results of all these experiments is given in the following table.

TABLE I.

Concentration of gelatine = 3%, p_H of gelatine = 5·45.
Total volume = 16 c.c. [2X c.c. of electrolyte + 4·4 c.c. of 3% gelatine + (16 − 2X − 4·4) c.c. conductivity water].

c.c. of electrolyte (X)	Temperature °C.	% of Ag_2CrO_4 in ionic condition before red colour appears	% of Ag_2CrO_4 in ionic condition after appearance of red colour and when conductivity does not change further on standing	Time for appearance of red colour in minutes	Time when conductivity begins to decrease in minutes
3·5	20	91	59	200	215
	30	87	69	300	330
	35	86	75	430	470
	40	84	84	600	>720
4·0	20	88	49	29	30
	30	87	57	45	47
	40	85	65	90	94
	50	84	80	305	340
	55	83	83	460	>650
4·5	20	87	39	5	5·5
	30	85	44	8	8·5
	40	84	51	15	16
	50	82	61	28	30
	60	80	75	120	160
	65	78	78	200	>600
5·0	20	77	30	2	2·5
	30	76	35	3	3·5
	40	75	41	4	4·5
	50	74	47	5	6
	60	73	53	6	7
	65	72	55	7	9

The following conclusions can be drawn from the results :—

(1) The inhibitive power (time for appearance of red colour) increases with a rise of temperature.

(2) The difference between the times of appearance of red colour and the decrease of conductivity increases with a rise of temperature, the colour change and conductivity decrease occurring more or less simultaneously at relatively low temperatures.

(3) The temperature at which the conductivity does not decrease in spite of colour change even when the mixture is allowed to stand

for 24 hours or more is higher for mixtures containing larger amounts of reactants than those containing smaller amounts.

(4) For each concentration of the reactant the % of Ag_2CrO_4 in ionic condition before the appearance of red colour decreases with a rise of temperature, while that after the appearance of the red colour and when conductivity does not decrease any further on standing increases at the same time.

(5) For each temperature the smaller the amount of reactants, the larger the % of Ag_2CrO_4 in ionic condition before and after the appearance of red colour.

(6) If the difference between the amounts of silver chromate in ionic condition before and after the appearance of red colour is taken roughly as a measure of degree of supersaturation, it is seen that the degree of supersaturation decreases with an increase of temperature.

(7) In each case at relatively low temperatures the conductivity first remains constant, then decreases for some time and remains constant afterwards (Fig. 1).

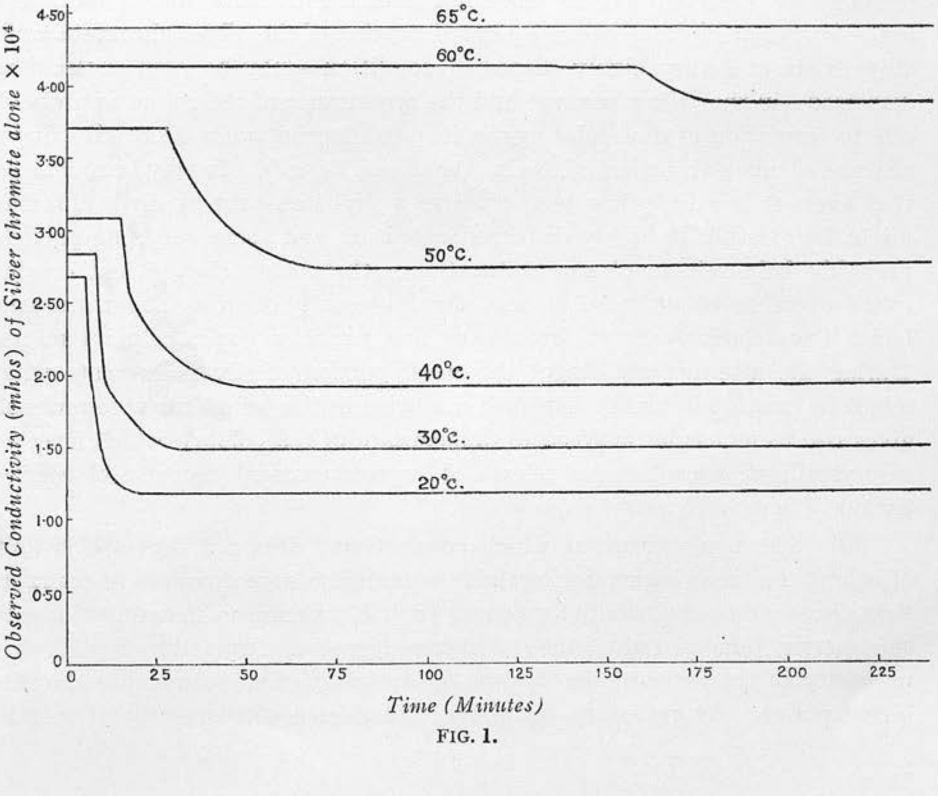

FIG. 1.

It is now proposed to discuss the above changes. (1) One might consider that the increase in the inhibitive power with a rise of temperature might be due to a change in the p_H of gelatine. The measurements of p between temperatures 20° C. and 70° C., however, showed that p_H changes, if any, are very insignificant and therefore cannot be considered to have any appreciable influence on the large inhibitive power of gelatine at relatively high temperatures. An increase in the solubility of Ag_2CrO_4 with a rise of temperature cannot also alone explain these changes because although the solubility of Ag_2CrO_4 in water at 60° C. is about $2\frac{1}{2}$ times that at 20° C., the inhibitive power has become more than $2\frac{1}{2}$ times within this temperature range as will be seen from Table I. It is likely that the degree of dispersity of gelatine might have increased with a rise of temperature, resulting in an increase of inhibitive power.

(2) At relatively low temperatures the colour change and decrease in conductivity take place more or less simultaneously probably because most of the silver chromate in those cases exists in ionic condition at first and a part of it is thrown out later as red Ag_2CrO_4 due to release of supersaturation (*cf.* Bolam and co-workers[2] and Desai and Nabar[3]). In each case at a certain temperature the conductivity does not decrease in spite of appearance of red coloured precipitate because a small portion of the silver chromate probably exists in a very highly dispersed condition—may be even molecularly dispersed—in the yellow mixture and the appearance of red colour is probably due to formation of molecular aggregates, conductivity not decreasing due to absence of supersaturation (*cf.* Naik, Desai and Desai[5]). It may be mentioned that even at relatively low temperatures a slight amount of silver chromate might be existing in highly dispersed condition and these very fine particles probably help release of supersaturation ; the colour change and conductivity decrease occur more or less simultaneously because supersaturation being also relatively great, even very fine particles could help its release. During the intermediate stages the small portion of silver chromate which might be existing in highly dispersed condition in the yellow mixture probably gives rise to molecular aggregates (appearance of red colour), which later act as crystallisation centres for release of supersaturation (decrease of conductivity).

(3) The temperature at which conductivity does not decrease in spite of colour change is higher for mixtures containing large amounts of reactants than those containing smaller amounts probably because the amount of gelatine having remained the same, a higher degree of dispersity of gelatine is necessary in the former case than in the latter in order to increase the inhibitive power. As stated in (1) above, the degree of dispersity of gelatine

probably increases with temperature; a higher temperature is therefore necessary for mixtures having larger amounts of reactants than those containing smaller amounts, other conditions having remained the same.

(4) The % of Ag_2CrO_4 in ionic condition in the beginning and before the appearance of red colour decreases with a rise of temperature probably because the degree of dispersity of gelatine having increased [see (1) above], a relatively large amount of Ag_2CrO_4 might have either been adsorbed by, or chemically interacted with, gelatine at relatively high temperatures.

The % of Ag_2CrO_4 in ionic condition after appearance of red colour increases with a rise of temperature probably because of an increase in the (*a*) solubility of Ag_2CrO_4 [see (1) above] and (*b*) inhibitive power of gelatine. As stated in (1) above the increase in inhibitive power is probably due to greater degree of dispersity of gelatine at higher than at lower temperatures; this effect seems to be similar to that of hydrolysis studied by Desai and Nabar,[3] where it was noticed that the final values of the activity of the silver ion increase with an increase in hydrolysis.

(5) This is probably due to the fact that a greater amount of Ag_2CrO_4 has either been adsorbed by, or chemically interacted with, gelatine in mixtures containing larger amounts of reactants than those containing smaller amounts.

(6) The degree of supersaturation with an increase of temperature has decreased but the inhibitive power of gelatine increased at the same time. Obviously, as stated by Naik, Desai and Desai,[5] the inhibition experiments cannot always be utilised to give an idea about the degree of supersaturation although they can be in some cases and under certain circumstances. The decrease in the degree of supersaturation with a rise of temperature might probably be due to an increase in the solubility of Ag_2CrO_4. The increased adsorption by, or chemical interaction with, gelatine of Ag_2CrO_4 at high temperatures might also to a certain extent decrease supersaturation.

(7) The conductivity-time curves are similar to the activity of Ag ion-time curves obtained by Desai and Nabar[3] except for the fact that the point at which the conductivity commences to decrease does not in every case correspond with the first appearance of red colour.

B. Influence of changes in p_H of gelatine on the condition of silver chromate.—The nature of the curves obtained on plotting the values of conductivity (observed) of silver chromate alone at different times is similar to that of the conductivity-time curves given in Fig. 1. A summary of the results of these experiments is given in the following table.

TABLE II.

Concentration of gelatine = 3%.

Temperature of experiments = 30° C.

Total volume = 16 c.c. [2X c.c. of electrolyte + 4·4 c.c. of 3% gelatine + (16 − 2X − 4·4) c.c. conductivity water].

c.c. of electrolyte (X)	p^H of gelatine	% of Ag_2CrO_4 in ionic condition before red colour appears	% of Ag_2CrO_4 in ionic condition after red colour appears and when conductivity does not change further on standing	Time of appearance of red colour in minutes	Time when conductivity begins to decrease in minutes
3·5	5·45	87	69	300	330
	5·75	81	58	180	190
	6·00	77	64	240	267
	6·25	73	73	300	>600
4·0	5·25	87	60	120	124
	5·45	87	57	45	47
	5·75	68	45	24	25
	6·00	66	50	32	40
	6·25	63	55	43	60
	6·50	60	60	65	>240
4·5	5·00	84	51	50	54
	5·25	85	47	22	23
	5·45	85	44	8	8·5
	5·75	58	32	4·5	5
	6·00	56	37	5	8
	6·25	53	42	6	15
	6·50	50	50	10	>180

The following conclusions can be drawn from these results :—

(1) For all the concentrations of reactants the inhibitive power of gelatine is minimum for p_H 5·75, it being greater for higher or lower values of p_H.

(2) The difference between the times of appearance of red colour and the decrease of conductivity increases with p_H for samples of gelatine having p_H greater than 5·75; for gelatine samples of p_H smaller than 5·75 this difference increases with decrease of p_H only in those cases where the concentration of the reactants is not too large and the inhibitive power is proportionately great.

(3) For samples of gelatine having p_H greater than 5·75 the greater the concentration of the reactants the higher is generally the p_H at which the colour change appears but the conductivity does not decrease at all.

(4) For each concentration of the reactants the % of Ag_2CrO_4 in ionic condition before the appearance of red colour generally decreases regularly with an increase of p_H; the % of Ag_2CrO_4 in ionic condition after the appearance of red colour and when conductivity does not decrease any further on standing is lowest for p_H value 5·75 for 3·5 and 4·5 c.c. of reactants, and for p_H value 5·45 for 4·0 c.c. of reactants, it being greater for higher or lower values of p_H.

(5) For each value of p_H the smaller the amount of the reactants, the larger the % of Ag_2CrO_4 in ionic condition before and after the appearance of red colour.

(6) If the difference between the amounts of silver chromate in ionic condition before and after the appearance of red colour is taken roughly as a measure of degree of supersaturation, it is seen that the supersaturation is highest for p_H value 5·75. for 3·5 and 4·5 c.c. of reactants, and for p_H value 5·45 for 4·0 c.c. of reactants, it being smaller for higher or lower values of p_H.

The causes of these changes may now be discussed.

(1) The results support the observation of Desai and Naik[6] that the inhibitive power of gelatine with reference to p_H 5·75 is minimum, it being higher for samples of gelatine having greater or smaller p_H. The causes of minimum inhibitive power for p_H 5·75 are not clear. It may be that the degree of dispersity of gelatine at this p_H might be lowest.

(2) The colour change and decrease in conductivity occur more or less simultaneously in all cases for p_H 5·75. It will appear from conclusion (6) that the degree of supersaturation is also highest in samples of gelatine having p_H near about 5·75. It is likely that a small amount of Ag_2CrO_4 which might be present in molecularly dispersed condition from the beginning helps in releasing supersaturation. For higher or lower values of p_H the degree of supersaturation decreases; at sufficiently low or high values of p_H characteristic of each concentration of the reactants, there will not be any supersaturation and therefore the colour changes which will occur in these cases will be due to formation of molecular aggregates from Ag_2CrO_4 which probably exists in molecularly dispersed condition from the beginning. It is clear from these results that for each concentration of the reactants the colour change and decrease in conductivity will occur more or less simultaneously for p_H 5·75; *i.e.*, the p_H is gradually lowered below or raised

above 5·75, the difference between the times of colour change and decrease of conductivity will continuously increase, and ultimately at certain values of p_H higher and lower than 5·75—characteristic of each concentration of the reactants, the conductivity will not decrease at all in spite of colour change.

(3) This is probably due to the fact that for relatively high concentrations of the reactants, the amount of gelatine having remained the same, the p_H will have to be increased relatively to a large extent in order to increase the inhibitive power. From the trend of the present results it appears that for samples of gelatine having p_H smaller than 5·75, the higher the concentration of the reactants the lower will generally be the p_H at which the colour change will occur but the conductivity will not decrease at all.

(4) The % of Ag_2CrO_4 in ionic condition before the appearance of red colour decreases with increase of p_H probably because a relatively large amount of Ag_2CrO_4 might have either been adsorbed by, or chemically interacted with, gelatine at relatively high values of p_H.

The % of Ag_2CrO_4 in ionic condition after the appearance of red colour is lower for p_H 5·75 probably because the inhibitive power being minimum, a relatively large amount of Ag_2CrO_4 is thrown out in condition other than ionic.

(5) The causes of this might be similar to those given under (5) in Section (A).

(6) The fact that gelatine samples of p_H near about 5·75 show higher supersaturation than those with higher or lower p_H in spite of minimum inhibitive power support the view stated before, namely, that the experiments on inhibitive power should not be utilised to get idea about degree of supersaturation.

On page 876 of their paper, Bolam and Donaldson[2] have calculated the degree of supersaturation according to the theory of von Weimarn and found that the degree of supersaturation increases slightly as the p_H decreases from 5·7 to 5·0, and then falls off more rapidly as the p_H is further decreased. They conclude that the degree of supersaturation and therefore the inhibitive action of gelatine, probably has an optimum value at p_H 5·0. The present results do not support the conclusion of Bolam and Donaldson.

C. Determination of temperatures at which colour change occurs but conductivity does not decrease at all in mixtures of silver chromate in gelatine of different p_H.—The results of these experiments are given in the following table.

TABLE III.

Concentration of gelatine = 3%.

Total volume = 16 c.c. [2X c.c. of electrolyte + 4·4 c. c. of 3% gelatine + (16 − 2X − 4·4) c.c. conductivity water].

c.c. of electrolyte (X)	p_H of gelatine	Temperature at which red colour appears but conductivity does not change
3·5	5·45	40° C.
	5·75	50
	6·00	40
	6·25	30
4·0	5·25	50
	5·45	55
	5·75	60
	6·00	50
	6·25	40
4·5	5·00	55
	5·25	60
	5·45	65*
	5·75	65
	6·00	55
	6·25	45

* The temperature, at which colour change occurs but conductivity does not decrease might be about 62° to 63° C. in this case.

It will appear from the table that for each concentration of the reactants the temperature at which no change in conductivity will occur in spite of a change in colour is highest for gelatine of p_H 5·75, it being lower for higher or lower values of p_H. It has been stated in Section B that the inhibitive power of gelatine is minimum for p_H 5·75. In Section A it is suggested that the degree of dispersity of gelatine might be increasing with a rise of temperature. It thus appears possible that the degree of dispersity of gelatine might be smallest for p_H 5·75—hence minimum inhibitive power—because the temperature at which colour change occurs but conductivity does not decrease is highest for that value of p_H. There is, however, no direct evidence to support this statement.

In each case for temperatures lower than those given in Table III, the conductivity will decrease either simultaneously with a change of colour or sometime after it.

D. Influence of changes in concentration of gelatine on the conductivity of silver chromate.—The results of these experiments are given in Table IV.

TABLE IV.

Temperature of experiments = 30° C.

p_H of gelatine = 5·45.

Total volume = 16 c.c. [2X c.c. of electrolyte + 2Z c.c. of 3% gelatine + (16 − 2X − 2Z) c.c. of conductivity water].

c.c. of electrolyte (X)	c.c. of 3% gelatine (Z)	% of Ag_2CrO_4 in ionic condition before red colour appears	% of Ag_2CrO_4 in ionic condition after red colour appears and when conductivity does not change further on standing	Time for appearance of red colour in minutes	Time when conductivity begins to decrease in minutes
3·5	1·0	95	43	5	6
	1·5	92	51	52	54
	2·0	89	60	225	250
	2·2	87	69	300	330

It will appear that the time for the appearance of red colour increases with an increase in the amount of gelatine and that although the colour change and decrease in conductivity occur more or less simultaneously when the amounts of gelatine are relatively small, the conductivity decrease occurs later and later than colour change as the amount of gelatine increases. These changes become intelligible if we examine the values given in columns 3 and 4 of the table ; the degree of supersaturation, as judged roughly from the difference in the values of % of silver chromate in ionic condition before and after the appearance of red colour, has decreased with an increase in the amount of p_H.

From the trend of the values given in columns 3 and 4 it will be clear that for a certain amount of gelatine (more than that contained in 4·4 c.c. of 3% gelatine solution), the % of silver chromate before and after the appearance of red colour will be the same, *i.e.*, the conductivity will not decrease in spite of appearnce of red colour. This amount of gelatine will be different for different concentrations of the reactants.

The percentage of silver chromate in ionic condition before the appearance of red colour decreases with an increase in the amount of gelatine. This is due to the fact that as the amount of gelatine increases the amount of silver chromate removed by it either as a result of adsorption or chemical interaction also increases.

The continuous increase in the percentage of silver chromate in ionic condition after the appearance of red colour with an increase in the amount of gelatine is due to the fact that a relatively large amount of silver chromate is thrown out when the amount of gelatine is relatively small.

Summary.

Changes in the conductivity and colour of silver chromate in gelatine solution have been studied. It is observed that by suitable adjustment of the (i) temperature of the experiments, (ii) p_H of gelatine, (iii) concentration of the reactants ($AgNO_3$ and K_2CrO_4) and (iv) amount of gelatine, the conductivity may (*a*) not decrease at all till the colour remains yellow, (*b*) decrease sometime after the colour change or (*c*) not change at all in spite of the colour change.

In the end we would like to mention that our preliminary experiments on the precipitation of lead iodide in agar have shown that the (*a*) temperature at which the experiments are carried out, (*b*) p_H of agar, (*c*) amount of agar and (*d*) concentration of the reactants [Pb $(NO_3]_2$ and KI) have a very marked influence upon the times when the colour change and decrease in conductivity take place[7] as in the case of precipitation of silver chromate in gelatine.

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CONDUCTIVITY AND CATAPHORETIC SPEED MEASUREMENTS OF BENZOPURPURIN 4B, CONGO RED AND SKY BLUE F.F.

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ALTHOUGH the dyeing of cotton by direct dye-stuffs has been practised for a long time, their action on the fibres has not been clearly understood. The substantive dye-stuffs have very high molecular weights and in aqueous solutions, they exist in the form of colloidal electrolytes.[1] In view of the colloidal chemical nature of the solutions of the direct dyes and the necessity of the presence of salts while dyeing, many investigators have studied their coagulation by and diffusion in the presence of different electrolytes. Benzopurpurin 4B, Congo Red and Sky Blue F.F. have already been the subject of numerous physico-chemical investigations and it was therefore decided to determine their conductivity and cataphoretic speed to see if these particular results can throw any light on the mechanism of dyeing by the substantive dye-stuffs.

Experimental.

It is a well-known fact that the technical dye-stuffs contain electrolytic and organic impurities, and for any investigational work, it is of fundamental importance to use the dyes in their purest form. Their purification is however not very simple as they are of complex nature and may contain their isomerides and homologues which are difficult to remove. Many methods which have been used for purification are open to objection as the dye is produced in a different state. The method adopted by Robinson and co-workers[2] was used for the precipitation of the dyes employed in this investigation as it is free from objections. The relative viscosity at 30° C. and the pH of solutions of the dyes so purified were as given below :—

Dye	Concentration	Relative Viscosity	pH
Benzopurpurin 4B ..	0·5%	1·039	7·10
Congo Red ..	0·4%	1·096	7·18
Sky Blue F.F. ..	0·4%	1·044	7·00

Conductivity water was used for preparing all the solutions.

The conductivity was measured by the usual method using an amplifying circuit similar to the one used by Lorenz and Klauer,[3] the details of the method being the same as those given by Desai and co-workers.[4]

The cataphoretic speed was measured in the same way as done by Desai and Borkar.[5] The upper liquid in these measurements consisted of a solution of sodium chloride having the same conductivity as the dye solution.

Benzopurpurin 4B was also subjected to dialysis in parchment paper bags and its cataphoretic speed measured at different stages of dialysis.

All the measurements of conductivity and cataphoretic speed were carried out in an air thermostat at a temperature of 30° C.

Results.

The results of these experiments are given in the tables below. The cataphoretic speed readings have been corrected for viscosity by taking the viscosity of water as unity. The concentration of the electrolyte is expressed in mols per litre of the mixture.

TABLE I. *Benzopurpurin 4B.*

Dye Conc. %	Cataphoretic speed × 10^5						
	Period of dialysis						
	0	4 days	8 days	12 days	16 days	20 days	24 days
0·025	17·54	30·50	28·32	25·20	17·01	16·45	15·89
0·05	19·62	33·61	30.19	27·18	18·12	17·51	16·91
0·10	26·39	36·63	33·21	27·78	27·18	27·00	26·15
0·20	32·57	39·25	39·66	30·80	28·01	27·78	26·70
0·30	38·04	42·33	44·39	36·54	32·24	29·68	27·18

TABLE II. *Benzopurpurin 4B.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed × 10^5
0·1795	125·65	17·54
0·3592	107·75	19·62
0·7184	99·30	26·39
1·4368	92·75	32·57
2·1552	85·05	38·04

TABLE III. *Benzopurpurin 4B.*
(Conc. 0·7184 N).

Conc. of NaCl	Cat. speed × 10^5
0·000	26·39
0·684	33·81
1·368	30·19
2·052	22·64
2·736	21·74

TABLE IV. *Congo Red.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed × 10^5
0·3453	116·20	22·64
0·6906	102·90	23·54
1·3812	97·30	36·23
2·0718	90·65	40·76
2·7624	90·15	45·50

TABLE V. *Congo Red.*
(Conc. 0·6906 N).

Conc. of NaCl	Cat. speed × 10^5
0·000	23·54
0·342	25·60
0·684	27·50
1·368	36·23
2·052	30·53
2·736	23·54

TABLE VI. *Sky Blue F.F.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed × 10^5
0·063	342·5	17·21
0·126	342·0	18·57
0·252	342·3	27·09
0·504	342·3	33·06
0·756	342·3	36·69
1·008	280·3	..

TABLE VII. *Sky Blue F.F.*
(Conc. 0·252 N).

Conc. of $BaCl_2$	Cat. speed × 10^5
0·0	27·09
0·2	31·57
0·4	41·93
0·6	31·73
0·8	14·49

Discussion.

(*a*) *Changes in cataphoretic speed during dialysis.*—It will appear from Table I that with the progress of dialysis (horizontal rows) the cataphoretic speed first increases and then decreases in all the cases. It will also be noticed that there is a tendency for the cataphoretic speed to remain constant when the dye solution is subjected to dialysis for long periods. The changes in the cataphoretic speed with the progress of dialysis are similar to those observed by Desai and co-workers in the case of colloidal gold,[6] ferric hydroxide,[5] thorium hydroxide[7] and Prussian blue.[8]

As stated before, the pH of the pure Benzopurpurin 4B dye solution was 7·1; the dye therefore does not hydrolyse in aqueous solution. Matters, however, become different when the solution of the dye is dialysed against pure water. As a result of the influence of the parchment membrane the dye will hydrolyse[9] and some NaOH pass out in the dialysate. The solution in the parchment bag will contain the undissociated dye [if the dye (salt) is not completely dissociated], the dye ions, Na-ions and H-ions.

For spherical particles obeying Stokes' law the following equation holds good :—

$$U_0 = \frac{E}{6\pi\eta r}$$

where U_0 = Cataphoretic speed under unit potential gradient.
E = Total charge on the particle.
r = Radius of the particle.
and η = Viscosity.

The total charge being proportional to the total surface area, *i.e.*, the square of the radius, the cataphoretic speed would be greater for the larger particles assuming that the shape of the particles does not change materially during aggregation and the frictional resistance does not increase with aggregation at the same rate as the total surface charge. The initial increase in the cataphoretic speed with the progress of dialysis is therefore due to the formation of large ionic micelles. The turbidity of the dye solution was found to increase during dialysis thus showing that aggregation of the dye ions to form ionic micelles had taken place.

In view of the increase of turbidity (*i.e.*, of the size of the ionic micelles) of the dye solution with the progress of dialysis, the cataphoretic speed should have continuously increased instead of only upto a certain stage of dialysis. The subsequent decrease of cataphoretic speed may probably be due to the following causes :—

(1) The increase in the hydration of the ionic micelles during dialysis will decrease the cataphoretic speed to a certain extent.

(2) The 'inclusion effect,'[10] *i.e.*, the inclusion of the gegenions (oppositely charged ions) will increase on standing during dialysis and the cataphoretic speed will decrease. This inclusion effect can be taken to mean preferential adsorption of the oppositely charged ions (gegenions).

It is considered that the influence of the second factor is mainly responsible for the subsequent decrease of the cataphoretic speed.

In the early stages of dialysis the inclusion effect will also be there but the cataphoretic speed increases because the effect of aggregation is more pronounced than that of inclusion.

The tendency for the cataphoretic speed to remain constant on dialysing the solution for long periods is probably due to effect of aggregation and inclusion being about the same.

It may be mentioned that the explanation which Desai and collaborators[5,6,7,8] have advanced for the ∩-shaped cataphoretic speed-dialysis curves for the hydrophobic sols cannot be utilised in the present instance because in the former case the charge on the particles is due to preferential adsorption of the ions of the peptising electrolyte whose amount continuously decreases during dialysis, while in the latter case the dye ion itself represents the micelle ion.

(*b*) *Changes in conductivity and cataphoretic speed with dilution.*—It will appear from Tables II and IV that in the case of Benzopurpurin 4B and Congo Red the equivalent conductivity continuously decreases, while the cataphoretic speed continuously increases on increasing the concentration of the dye solution. In the case of Sky Blue F.F. (Table VI) on increasing the concentration of the dye solution the equivalent conductivity remains more or less constant at first and decreases later while the cataphoretic speed continuously increases as in the case of the other dyes.

In his extensive researches on soap solution McBain[11] observed a remarkable increase of equivalent conductivity with increasing concentration in the aqueous solutions of soaps at about N/10 and higher concentrations. He ascribed the increase in equivalent conductivity to the aggregation of ions of one kind to form ionic micelles. As discussed by Moilliet, Collie, Robinson and Hartley[10] if 'm' ions aggregate to form ionic micelles, their velocity will be multiplied by $m^{\frac{2}{3}}$ and as they carry the same amount of electricity as before their contribution to the conductivity will be multiplied by the same amount. The above arguments however apply only in the case of very dilute solutions in which the 'inclusion effect' of Robinson and others and the ' atmosphere effect ' of Debye, Hückel-Onsager theory are both negligible. It is likely that even in most dilute dye solutions multivalent ionic micelles will be there and the 'inclusion effect ' and the ' atmosphere effect ' will be very large as compared with the ordinary electrolytes. Thus the increase in conductivity due to Stokes' law effect of aggregation—termed primary effect—will be levelled out by the inclusion and atmosphere effects —termed secondary effects—which will decrease the conductivity. The decrease of conductivity due to the secondary effects will increase with the increase in the number of ions aggregating to one micelle, *i.e.*, with concentration. The dye solutions tried here are generally moderately concentrated and the conductivity has decreased with increase in concentration probably due to the fact that the secondary effects are more pronounced than the primary effect. In the case of Sky Blue F.F. the conductivity has remained constant between concentrations 0·063 N and 0·756 N ; this is probably due to the fact that the primary effect and the secondary effects balance each other. For the same equivalent concentration the conductivity of Sky Blue F.F. is greater than that of either Benzopurpurin 4B or Congo Red ; this perhaps indicates relatively high mobility of the dye ion in the case of Sky Blue F.F.

From Tables II, IV and VI it will appear that the cataphoretic speed has increased with concentration for all the three dye solutions. In view of the arguments discussed in section (*a*) the increase in the cataphoretic speed is due to aggregation of the dye ions to form ionic micelles. The cataphoretic speed results thus show that the size of the particles increases with concentration for Benzopurpurin 4B, Congo Red and Sky Blue F.F.

The next question to be considered is why the conductivity results do not give evidence of aggregation although the cataphoretic speed results definitely indicate formation of large micelles. Moilliet, Collie, Robinson and Hartley[10] have discussed the difficulties of obtaining information regarding aggregation from conductivity measurements as a result of secondary effects mentioned above. They have also pointed out that the secondary effects might be less marked if mobilities or transport numbers of the ionic micelles are determined instead of conductance. They have shown that the atmosphere effect will decrease both mobility and transport number as conductance ; the inclusion effect though tending to decrease the mobility slightly and conductance greatly will actually increase the transport number quite markedly. The transport number will not however increase due to aggregation to the same extent as mobility and conductance. Robinson[12] observed that the mobility of *meta*-Benzopurpurin increases with increase in concentration in dilute solutions although the conductivity measurements under the same conditions did not give evidence of aggregation. He also found that the mobility of Benzopurpurin 4B decreases with increase in concentration from 0·004 N to 0·01 N. Moilliet, Collie, Robinson and Hartley[10] however determined transport numbers of the 4B dye and found evidence of aggregation with increase in concentration from about 0·001 N to 0·012 N. From the present results (Table II) it will appear that the cataphoretic speed gives evidence of aggregation with increase in concentration from 0·1795 N to 2·1552 N. The cataphoretic speed determinations would thus appear to be more important than the transport number measurements for getting an idea about aggregation of ionic micelles.

The fact that ionic micelles aggregate on increasing the concentration of the 4B dye is further supported from stability determinations. It is found that the flocculation value with NaCl decreases as the concentration of the dye is increased. If aggregation of ionic micelles had not taken place, the amount of NaCl required to produce a given degree of turbidity in a certain time would be greater for a concentrated than for a dilute solution.

(*c*) *Changes in cataphoretic speed in the presence of salts.*—It will appear from Tables III, V and VII that on adding small increasing amounts of salts to the dye solutions the cataphoretic speed increases in the beginning but decreases later. Robinson and Moilliet[13] also found an increase in the cataphoretic speed of the particles of Benzopurpurin 4B on the addition of electrolytes.

The initial increase in the cataphoretic speed on the addition of salt can be due to (i) preferential adsorption of the similarly charged ions and (ii) aggregation of the ionic micelles. It is considered that the increase in the cataphoretic speed is mainly due to the second factor. The increase in the turbidity of the dye solution on the addition of salt would also support aggregation of the particles. It is likely that some oppositely charged ions might also be preferentially adsorbed but the decrease in the cataphoretic speed on account of this is not perceptible owing to the marked effect of aggregation.

As the dye solution actually coagulates (increase in the size of the particles) on the addition of large amounts of salt one would expect an increase in the cataphoretic speed throughout. It will however appear that the cataphoretic speed has actually decreased on adding relatively large amounts of salts. This is probably due to the marked preferential adsorption of the gegenions which does not allow the effect of aggregation to be noticed at all.

These results are similar to those obtained by Valkó[14] who determined the diffusion coefficients by the porous plate method of the 4B dye, Congo

Red and Chicago Blue 6B (identical with the Sky Blue F.F.) in the presence of different small amounts of NaCl and found that the particles aggregate in all the cases.

(*d*) *Bearing of the present results on the mechanism of dyeing by direct dye-stuffs.*—A very interesting and important discussion on the various theories on dyeing by direct dye-stuffs took place at London in September 1934 under the auspices of the Faraday Society, and it is proposed to examine some of the views expressed there in the light of the present results and conclusions. Morton[15] has stated that in the presence of small amounts of NaCl the degree of dispersion of pure dye increases although on adding relatively large amounts of salt the degree of dispersion decreases. Our results do not support the view that the degree of dispersion of the dye particles increases in the presence of salt. The results of diffusion experiment of Valkó[14] also show that the degree of dispersion of the ionic micelles does not increase on raising the salt concentration.

Neale and others[16] have measured the adsorption of the dye-stuffs by fibres and observed that it increases with increase of salt concentration at least upto a certain concentration. They have calculated the rate of diffusion by the application of Hill's[17] equation and found that the rate of diffusion first increases, reaches a maximum and then decreases. Their diffusion coefficients so calculated do not therefore agree with the results of Valkó.[14] according to whom the diffusion coefficients continuously decrease on adding increasing amounts of salt. It must however be stated that the adsorption results of Neale and co-workers[16] can be easily understood even on the basis of continuous increase in the size of the dye ions on the addition of increasing amounts of salt. Greater adsorption of the dye with the increase in salt concentration might probably take place in spite of a decrease in the diffusion coefficient, because relatively larger ionic micelles will be adsorbed instead of smaller ones (with little or no salt) as long as the ionic micelles are not bigger than the capillary pores of the cellulose. Once the micelles become of the same size as or larger than the capillary pores, further aggregation will not increase adsorption. Thus there will be an optimum concentration of salt for dyeing at which maximum dye can be adsorbed ; smaller or larger amounts of salts than the optimum will mean less adsorption of the dye. The experience of the practical dyer that too much of the salt causes a waste of dye is to be explained on the basis that some of the ionic micelles reach such a large size that they cannot be adsorbed by the fibre.

Robinson[18] has suggested that the effect of the negative charge in the viscose capillaries, which will oppose the passage of the dye whose ionic micelles are also negatively charged, will be almost completely suppressed by the presence of the salt and hence the dye will be allowed to pass freely. According to him the effect of salt on the degree of dispersion of the dye is only of secondary importance. It may however be stated that increased adsorption of the dye in the presence of salt can easily be explained, as pointed out above, on the basis of aggregation and that it is not necessary to consider the effect of charge on the viscose capillaries on the adsorption of the dye whose micelles are also negatively charged.

Neale[19] has also stated that it is difficult to be dogmatic with regard to the importance of aggregation in dyeing with direct cotton colours. His view is that there is only slight aggregation and that at the elevated temperatures (usually 90° C.) used in his experiments aggregation of the dye is of little or no importance except at exceptionally high concentrations of the added salts. We would like to mention that although there will be considerably less aggregation of the dye at 90° C. than at ordinary temperatures, it has been shown by Morton[15] that the direct dyes are dissolved colloidally to some extent even at 75° C. In view of this it is highly probable that even at the " boil " the addition of small amounts of salts would produce appreciable aggregation of dye micelles, although certainly less than at ordinary temperatures.

It is now possible to explain in a simple manner the process of dyeing by substantive dye-stuffs in the presence of salts on the basis of aggregation of dye ions. If salt is not added to the bath, the size of the dye ions may be so small (amicronic size or even smaller) that they may come out from the fibre on washing, *i.e.*, the colour will not be fast to wash. If two much of salt is added, the size of the ionic micelles will become very large and only a small amount of the dye will be adsorbed, some dye actually remaining in the bath as stated before. The advantage of dyeing at higher temperatures instead of at ordinary temperatures is that as a result of the swelling of the fibre relatively large sized dye micelles are adsorbed in the presence of salt in the former case and when the ordinary temperature is attained the dye becomes so fixed in the fibre due to shrinking of the latter that it cannot be washed out easily (colour fast to washing). If salt is not present in the dye bath only small sized micelles will be adsorbed at relatively high temperatures as the degree of dispersion of the dye increases with temperature and the fastness to washing will be less unless a very large amount of the dye is added to increase the size of the micelles adsorbed, but a considerable amount of dye will be wasted in that case. Dyeing at ordinary temperatures even if salt is present in the bath will also not give desired fastness as the micelles adsorbed will be easily washed out due to absence of shrinking of the fibre.

Summary and Conclusions.

Measurements of conductivity and cataphoretic speed of pure Benzopurpurin 4B, Congo Red and Sky Blue F.F. have been made and it is found that on increasing the concentration of the dye solutions although the equivalent conductivity continuously decreases the cataphoretic speed increases regularly. The cataphoretic speed of Benzopurpurin 4B first increases and then decreases with the progress of dialysis. On adding small increasing amounts of sodium chloride to Benzopurpurin 4B and Congo Red and barium chloride to Sky Blue F.F. the cataphoretic speed first increases and then decreases. The changes in conductivity and cataphoretic speed are explained on the basis of aggregation of the dye ions to form ionic micelles. It is shown that the process of dyeing of cotton fibre by substantive dyestuffs in the presence of salt can be easily understood on the basis of aggregation of dye ions.

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

Part IV. Colloidal Arsenious Sulphide.

BY

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

Part IV. Colloidal Arsenious Sulphide.

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In previous papers we have given the results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric hydroxide,[1] thorium hydroxide,[2] and prussian blue[3] dialysed and diluted to different extents; in the case of prussian blue cataphoretic speed measurements on ageing and on exposure to sunlight have also been given. In the present paper the results of similar measurements of colloidal arsenious sulphide as well as of changes in its composition under different conditions are presented.

Experimental.

Hydrogen sulphide gas was bubbled through four litres of distilled water till saturation. While the gas was still passing one litre of 15 per cent. solution of arsenious oxide was gradually added, stirring the mixture all the time. Hydrogen sulphide was bubbled through the mixture till it contained no free arsenious acid. The excess of hydrogen sulphide was removed by bubbling hydrogen through the sol. In the end the sol was also filtered a number of times. The colour of the sol so obtained was orange yellow with a peculiar greenish fluorescence. All exposures to light and air were avoided as far as experimental conditions could permit (see Section *E*). Dialysis was carried out in a dark room as before[3] and experiments with each sample were completed in as short a time as possible in order to minimise effect of ageing (see Section *D*).

The cataphoretic speed (cat. speed) was measured as before. An equi-conducting solution of HCl was found to be a satisfactory upper liquid.[4] The difference between the direct and reverse movements of the boundary never exceeded 3 to 4 per cent. In all the tables of results, the cat. speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre $\times 10^5$. The concentration of the electrolytes is expressed in millimoles per litre.

The stability was measured by finding out the amount of electrolyte necessary for instantaneous coagulation. The flocculation values are expressed in millimoles of the electrolyte in total volume, *i.e.*, 30 c.c. in this case.

The composition of the sol was determined by finding out the (i) total amount of arsenic, (ii) total amount of sulphur, and (iii) free arsenious acid. For the estimation of total arsenic and sulphur the method adopted was the one used by Chaudhury and Kundu.[5] For the amount of free arsenious acid, the sol was first coagulated by adding an excess of KCl and the coagulum removed by filtration and washed thoroughly with conductivity water; the amount of free arsenious acid was then estimated iodometrically.[6] The total amount of arsenic and sulphur and the amount of free arsenious acid in terms of arsenic are expressed in all the tables in gm. per litre of the sol.

For ageing experiments the sol was kept in a resistance glass flask wrapped in black paper. Portions of sol were removed after different periods of standing and the various properties were studied after filtering the sol in order to remove precipitates formed as a result of ageing.

For light experiments equal volumes of colloidal arsenious sulphide were kept in resistance glass beakers (of the same capacity) covered with glass plates. A 500 C. P. tungsten filament lamp was used as the source of artificial light; the lamp was kept vertically above the beaker containing the sol. In the case of sunlight experiments the beakers containing the sol were directly exposed.

Results and Discussion.

A. Changes in cataphoretic speed, composition and stability with progress of dialysis.—The results of these experiments are given in Table I.

TABLE I.

Period of dialysis in days	Total As	Free arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	$MgCl_2$
0	2·172	0·0000	2·194	66·52	1·230	0·0202
2	2·156	0·0045	2·145	56·98	1·365	0·0190
5	2·137	0·0135	2·095	32·25	1·605	0·0172
8	2·128	0·0300	2·053	18·23	1·830	0·0156
11	2·090	0·0195	2·040	33·25	1·575	0·0166
14	2·070	0·0120	2·029	38·15	1·425	0·0180
20	2·032	0·0120	2·012	42·75	1·350	0·0187
28	2·013	0·0120	2·002	52·40	1·275	0·0193
31	1·994	0·0120	1·996	10·55	0·825	0·0080

It will be seen from the results that with the progress of dialysis

(1) the amount of arsenic in the sol continuously decreases ;

(2) the amount of free arsenious acid increases upto a period of 8 days after which it decreases till 14 days when it does not change any more during further dialysis ;

(3) the amount of sulphur continuously decreases ;

(4) the cat. speed decreases upto 8 days after which it increases till 28 days when it decreases again ;

(5) the stability with reference to KCl increases upto 8 days and decreases continuously thereafter ;

(6) the stability with reference to $MgCl_2$ decreases upto 8 days after which it increases till 28 days when it decreases again.

The changes in the composition of the sol suggest that a portion of arsenious sulphide hydrolyses during dialysis giving rise to arsenious acid and hydrogen sulphide. A part of the arsenious acid passes out in the dialysate—this accounts for a decrease in the amount of arsenic in the sol (see 1 above). A portion of the hydrogen sulphide escapes as gas and of that which remains in the dissolved condition, a certain amount must also be passing out in the dialysate—these two causes account for a decrease in the amount of sulphur in the sol (see 3 above). Some of the dissolved H_2S may get oxidised giving rise to SO_2 which may react with H_2S producing polythionic acids and sulphur. The sulphur might absorb polythionate ions and pass into colloidal sulphur (*cf.* Freundlich and Nathansohn[7]). The changes in the amount of arsenious acid suggest that upto 8 days the rate of its production by hydrolysis is greater than that of its passing out in the dialysate and that between 8 and 14 days the rate of passing out of arsenious acid in the dialysate is greater than that of its production, while after 14 days both the rates of production of arsenious acid and its passing out in the dialysate are about the same. The rate of hydrolysis is faster in the beginning and slower towards the end possibly because the sol does not contain to start with any free electrolytes and later on complications are introduced due to production of colloidal sulphur as well as changes in the distribution of the preferentially adsorbed ions on the surface of the colloidal particles as a result of introduction of electrolytes in the sol.

The amounts of total arsenic and sulphur in the freshly prepared sol are not according to the formulæ As_2S_3. This is probably due to the fact that during the preparation of the sol a portion of hydrogen sulphide gets oxidised ultimately giving rise to colloidal sulphur as stated above ; the arsenious sulphide sol thus contains some colloidal sulphur also from the beginning. The composition of colloidal arsenious sulphide prepared in different ways has been represented as $X_2As_2S_3$, $H_2As_2S_4$ by Pauli and Semler,[8] $m.As_2S_3$, H_2S by Linder and Picton[9] and As_2S_3, H_2S by Chaudhury and Kundu[5] (also see Burton and Annetts[10] and Krestinskaya[11]).

The initial cat. speed changes during dialysis in this case (see 4 above) are not similar to those observed with colloidal gold,[12] ferric hydroxide,[1] thorium hydroxide[2] and prussian blue.[3] This is due to the changes in the composition of this sol during dialysis.

The fact that the amount of free arsenious acid in the sol increases upto a dialysis of 8 days and decreases thereafter upto 14 days, while the cat. speed decreases upto 8 days and increases thereafter upto 28 days suggests that the variation in the amount of free arsenious acid upto 14 days might have some bearing on the changes in the cat. speed during that period. In the following table the result of changes in the cat. speed when small increasing amounts of arsenious acid are added to the sols dialysed for different periods are presented.

TABLE II.

Sol. dialysed for 5 days		Sol. dialysed for 25 days		Sol. dialysed for 31 days	
Concentration of arsenious acid	Cat. speed	Concentration of arsenious acid	Cat. speed	Concentration of arsenious acid	Cat. speed
0·000	30·35	0·000	65·10	0·000	47·10
0·025	34·15	0·009	65·35	0·009	43·05
0·125	41·45	0·047	64·60	0·094	42·90
0·250	43·55	0·940	54·70	0·469	41·55
1·250	22·50	9·400	51·50	4·687	40·50
12·500	20·95	46·875	41·20		
170·000	15·75	139·350	35·60		

It will appear from the results that the cat. speed first increases and then decreases in the case of sol dialysed for 5 days. In the case of the sol dialysed for 25 days only a slight rise occurs in the presence of small amounts of arsenious acid, while for sols dialysed for longer periods the cat. speed continuously decreases. S. N. Mukherjee[13] observed that the cat. speed of arsenious sulphide diminishes on the addition of arsenious acid, while Mukherjee, Raichaudhuri and Rajkumar[14] noticed that the cat. speed of As_2S_3 sol increases in the presence of small amounts of H_3AsO_3 although it decreases when larger amounts of the acid are added to the sol. Our results support both the observations. The difference in the behaviour in different cases is due to a difference in the composition of the sol, the preferential adsorption of the ions being affected to different extents on account of differences in the nature and amounts of electrolytes present in each sol.

From Table II, it will appear that the initial rise of cat. speed increases with a decrease in the period of dialysis. A greater initial rise of cat. speed on addition of small increasing amounts of arsenious acid is therefore likely to occur in the case of the freshly prepared sol containing no free arsenious acid than that of the sol dialysed for 5 days and containing some free arsenious acid from the beginning. The fact that the cat. speed of the freshly prepared sol first increases and then decreases on the addition of small increasing amounts of arsenious acid will incline one to the view that the cat. speed of the sol might have increased immediately after keeping the sol for dialysis and before 2 days, *i.e.*, as soon as traces of arsenious acid were produced as a result of hydrolysis—this might have occurred during the first couple of hours of dialysis and hence not noticed in the experiments described here. Leaving aside this particular point, it is clear that the decrease in the cat. speed upto 8 days is due to an increase in the amount of arsenious acid in the sol. Between 8 and 14 days the cat. speed has increased and this is due to a decrease in the amount of arsenious acid (Table I) during that period. Thus the cat. speed changes upto 14 days' dialysis are primarily due to changes in the amount of arsenious acid in the sol which affect the preferential adsorption of the ions on the surface of the colloidal particles.

The cat. speed changes between 14 and 31 days, *i.e.*, first an increase (between 14 and 28 days) and then a decrease (between 28 and 31 days) can be explained as done by Desai and co-workers[1,2,3] by considering the process of dialysis as a reverse of the case of adding small increasing amounts of the peptising electrolyte to the colloid. In the present case, the sol is probably peptised by sulphide and hydrosulphide ions. Although it has not been possible to take measurements of cat. speed of As_2S_3 sol on adding small increasing amounts of hydrogen sulphide, it is highly probable that, as in the case of other peptising agents and sols, in this case also the cat. speed will first increase and then decrease on adding small increasing amounts of hydrogen sulphide. The amount of total sulphur has continuously decreased between 14 and 31 days as before 14 days. This decrease is due to escape of H_2S as gas and in the dialysate as stated earlier. The amount of the peptising ions must therefore be continuously decreasing between 14 and 31 days and therefore the cat. speed should first increase and then decrease as stated by Desai and co-workers.[1,2,3] Thus the cat. speed changes between 14 and 31 days of dialysis are primarily due to changes in the amount of the peptising ions in the sol which alter the distribution of the ions on the surface of the particles.

Upto a dialysis of 8 days stability has increased although cat. speed has decreased. This might perhaps be due to replacement of arsenious acid from the surface of the particles by KCl, which process will increase the cat. speed (from a comparison of the results given in Table II with those for KCl given in Section *C*, it will appear that the initial increase in the cat. speed is greater in the presence of KCl than arsenious acid) and hence a larger amount of KCl would be required for coagulation of sols dialysed for relatively long periods than in the beginning when the amount of arsenious acid is relatively small. The stability changes with reference to KCl (Table I) between 8 and 28 days might be primarily due to preferential adsorption of similarly charged ions (Cl-ions) as in the cases of ferric and thorium hydroxide and prussian blue where the stability also decreased in spite of increase of cat. speed. The stability changes between 28 and 31 days are primarily due to changes in cat. speed during that period.

The stability changes with reference to $MgCl_2$ are primarily due to changes in the cat. speed—greater cat. speed greater stability and *vice versa* because the preferential adsorption of the similarly charged ions is probably not allowed to take place in the presence of bivalent coagulating ions.[1,2,3] The productions of slight turbidity on the addition of $MgCl_2$ to the sol containing free arsenious acid does not seem to have any marked influence on the stability of the sol.

B. Changes in cataphoretic speed and stability of arsenious sulphide sol dialysed and diluted to different extents.—Sols of different concentrations were prepared by adding requisite amounts of conductivity water to the original sol. The original sol has dilution 1 ; dilutions of other sols have been obtained from the value of the ratio $\frac{\text{total volume of the diluted sol}}{\text{actual volume of the original sol}}$. The results of these experiments are given in the following table :—

TABLE III.

Period of dialysis in days	Dilution												
	1			1·33	2			4			8		
	Cat. speed	Flocculation values		Cat. speed	Cat. speed	Flocculation values		Cat. speed	Flocculation values		Cat. speed	Flocculation values	
		KCl	$MgCl_2$			KCl	$MgCl_2$		KCl	$MgCl_2$		KCl	$MgCl_2$
0	50·65	1·620	0·016	40·75	33·60	1·89	0·020	21·70	2·40	0·023	17·40	3·15	0·028
4	34·15	1·935	0·012	30·30	24·85	2·52	0·016	17·55	3·37	0·017	14·35	4·26	0·021
8	26·10	2·160	0·010	24·05	20·85	2·84	0·011	15·65	3·96	0·012	13·25	5·25	0·012
17	39·25	1·635	0·016	38·30	36·15	2·40	0·022	33·30	3·06	0·025	33·45	4·02	0·030
23	45·70	1·530	0·020	45·80	46·10	2·02	0·024	48·30	2·58	0·030	54·25	3·30	00·39
29	36·00	1·260	0·014	33·30	28·40	1·62	0·017	31·80	1·95	0·019	43·70	2·34	0·022
31	21·40	0·610	0·007	22·65	24·80	0·81	0·009	29·00	0·93	0·009	41·20	1·05	0·010

It will be seen from the table that on diluting the sol the cat. speed (horizontal rows), (*a*) continuously decreases for sols dialysed for 0, 4 and 8 days, (*b*) first decreases and then shows a tendency of increase for sol dialysed for 17 days, (*c*) continuously decreases for sols dialysed for 23 and 31 days and (*d*) first decreases and then increases for sol dialysed for 29 days; however in all the cases, the stability with reference to KCl and $MgCl_2$ continuously increases (horizontal rows) on diluting the sol. For all the samples of the sol having different dilutions, the cat. speed during dialysis first decreases and then increases after which it again decreases (vertical columns) (*cf.* Section *A*); the results of stability with reference to KCl and $MgCl_2$ (vertical columns) are also exactly similar to those given before in Section *A*.

From the above results, it is quite clear that in the case of arsenious sulphide sol the changes in cat. speed on dilution of sols dialysed for different periods are not regular as in the case of colloidal ferric and thorium hydroxide and prussian blue.[1,2,3] This is due to the fact that the composition of the sol continuously changes during dialysis which affects distribution of the ions adsorbed on the surface of the colloidal particles as shown in Section *A*; hydrolysis of arsenious sulphide will also perhaps increase with dilution of the sol, the size of the particles decreasing at the same time. Peculiar changes in cat. speed on dilution of As_2S_3 sol observed by Mukherjee and co-workers[15] are also probably due to a difference in the composition of the various samples tried by them. Mukherjee and Ganguly[16] also observed as has been done by us that the stability as determined by flocculating values with electrolytes increases on dilution. It may be concluded that the results of stability and cat. speed measurements of colloidal arsenious sulphide should not be utilised either to prove or disprove any of the existing ideas about coagulation of colloids in view of considerable differences that are likely to be produced as a result of changes in the composition of different samples of the sol.

C. Measurements of cat. speed of arsenious sulphide sol (dialysed for different periods) from the point of view of critical potential.—The results of these experiments are given in the following table :—

TABLE IV.

Electrolyte	Period of dialysis	Initial cat. speed	Initial rise in cat. speed	Cat. speed at which sol begins to coagulate	Concentration of electrolyte at which sol begins to coagulate
HCl	5 days	28·60	33·80	15·90	25·00
	25 ,,	65·50	24·00	26·90	12·50
	31 ,,	46·80	nil	28·50	17·50
KCl	5 ,,	29·20	22·40	25·40	50·00
	25 ,,	63·10	23·75	25·85	37·50
	31 ,,	45·35	nil	29·50	25·00
$MgCl_2$	5 ,,	26·25	nil	12·80	0·25
	25 ,,	63·70	nil	14·15	0·37
	31 ,,	45·35	nil	18·20	0·25
K_2SO_4	5 ,,	17·30	36·20	27·65	25·00
	25 ,,	62·40	14·35	25·00	18·75
$MgSO_4$	5 ,,	15·95	nil	10·40	0·37

It will be seen from the results that the initial rise in the cat. speed when small increasing amounts of electrolytes are added to the sol does not occur in those cases where the electrolyte contains a bivalent coagulating ion.[1,2,3] Further, even in the case of electrolytes with univalent coagulating ions, the initial rise is not noticed with those samples of the sol which are dialysed for long periods. The initial increase in the cat. speed is due to preferential adsorption of the similarly charged ions and this may not be noticed when the coagulating ion is multivalent. The non-observance of initial rise even with the univalent coagulating ions for sols dialysed for longer periods is due to changes in the composition of the sol as stated before.

Mukherjee and co-workers[17] observed that the cat. speed of As_2S_3 sol continuously decreases on adding small increasing amounts of HCl, while Nanitski and Proskurnin[18] got first an increase and then a decrease with HCl. Freundlich and Zeh[19] observed that when KCl is added to As_2S_3 sol the cat. speed continuously decreases, while Kruyt and co-workers[20] got a continuous increase with this electrolyte; Mukherjee and co-workers[21] got with KCl results similar to those of Freundlich and Zeh as well as of Kruyt and co-workers and further observed that in some cases the cat. speed with KCl first decreases and then increases. From what has been stated above it is clear that the differences in the results of different investigators working with the same electrolytes are probably due to differences in the composition of the As_2S_3 sols tried by them.

From the table it will appear that the value of cat. speed at which coagulation takes place lies between 10·40 and 29·50. It would thus appeal that these results as a whole do not support the idea of critical potential.[22] The variation in the value of critical cat. speed for individual electrolytes is, however, generally small. The results show that generally the value of critical cat. speed at which coagulation begins is lower for bivalent coagulating ions than for univalent ones (*cf.* Powis[23] and Chaudhury[24]).

The variation in the value of the critical cat. speed in different cases is due to preferential adsorption of the stabilising ions which is considerably modified by the valency of the coagulating ions as suggested by Desai and co-workers.[1,2,3] In the case of colloidal As_2S_3 the differences are further increased as a result of changes in the composition of the sol—varying amounts of arsenious acid, H_2S and colloidal S.

D. Influence of ageing on the cataphoretic speed, stability and composition of the arsenious sulphide sol.—The precipitates formed as a result of ageing were removed by filtration before studying the various properties. The results of these experiments are given in the following table :—

TABLE V.

Age in days	Total As	Free arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	$MgCl_2$
0	1·306	0·00263	1·426	37·05	1·70	0·0252
15	1·287	0·03300	1·412	34·95	2·02	0·0228
30	1·191	0·04175	1·379	29·35	2·22	0·0189
45	1·110	0·05228	1·341	20·50	1·86	0·0168
60	1·093	0·05689	1·282	18·15	1·66	0·0153
90	1·026	..	1·148	16·30	1·60	0·0147

It will appear from the results that the amount of total As and S continuously decreases on ageing, the amount of free arsenious acid in the sol increasing at the same time. These changes are due to decomposition of the arsenious sulphide sol as stated in Section *A*. The decrease in the total amount of As and S (besides that due to escape of H_2S as gas) is due to removal of the precipitate. Arsenious acid and polythionate ions will have stabilising as well as destabilising effect on both colloidal As_2S_3 and S; the formation of precipitate is due to latter effect.

The decrease in the cat. speed is due to an increase in the amount of arsenious acid with an increase in the age of the sol.

The initial increase in the stability with reference to KCl in spite of a decrease of cat. speed is due to preferential adsorption of the stabilising ions as stated in Section *A*. In the case of $MgCl_2$ the stability has continuously decreased with cat. speed as the preferential adsorption of the similarly charged ions has not been probably allowed to take place as a result of bivalency of the coagulating ion.

E. Effect of artificial light and sunlight on the cat. speed and composition of the arsenious sulphide sol dialysed for different periods.—In these experiments also as in the ageing experiments the precipitate formed on exposing the sol to light was removed by filtration before all measurements were made. Any decrease in volume on exposure was made good by adding conductivity water. The results of these experiments are given in Tables VI, VII and VIII.

TABLE VI.

Artificial Light.

Period of exposure in minutes	Total As	Free Arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	$MgCl_2$
0	1·306	0·0028	1·482	37·05	1·70	0·025
50	1·306	0·0214	1·473	31·05	1·76	0·024
100	1·306	0·0337	1·462	27·20	1·85	0·023
150	1·296	0·0416	1·456	23·60	1·72	0·022
200	1·290	0·0484	1·448	21·85	1·60	0·021
300	1·286	0·0536	1·431	19·50	1·18	0·019
500	1·284	0·0623	1·405	17·00	0·86	0·013
900	1·283	.	1·371	15·38	0·58	0·008

TABLE VII.

Sunlight.

Undialysed Sol.

Period of exposure in minutes	Total As	Free arsenious acid in terms of As	Total S	Cat. speed
0	1·529	0·0000	1·467	50·10
30	1·519	0·0024	1·458	51·25
70	1·514	0·0362	1·450	48·35
150	1·500	0·0569	1·425	43·80
300	1·452	0·0825	1·338	34·05
450	1·422	0·1075	1·326	32·05
1,200	1·403	0·1781	1·312	29·85

TABLE VIII.

Sunlight.

Values in columns 1 *and* 2 *refer to sols dialysed for* 25 *and* 35 *days respectively.*

Period of exposure in minutes	Total As		Free arsenious acid in terms of As		Total S		Cat. speed	
	1	2	1	2	1	2	1	2
0	1·471	1·413	0·0437	0·0437	1·422	1·390	41·40	36·20
60	1·442	1·374	0·1000	0·1812	1·373	1·308	35·20	30·05
300	1·307	1·219	0·2256	0·5563	1·222	1·120	21·45	17·40
600	1·258	1·132	0·2751	0·4625	1·169	1·049	18·85	14·25
1,200	1·210	1·074	0·4282	0·6437	1·100	0·967	17·15	11·45

It will appear that on exposing the sol to light the amount of total As and S decreases while that of free arsenious acid continuously increases. These changes are due to hydrolysis of a part of As_2S_3 into arsenious acid and H_2S. H_2S is photochemically oxidised to SO_2 which further reacts with H_2S giving rise to polythionic acids and S. The latter adsorbs polythionate ions and passes into colloidal sulphur (Freundlich and Nathansohn[7]).

The cat. speed decreases on exposure as the amount of arsenious acid increases except for the undialysed sol where it first increases slightly and then decreases. As stated before (Section *A*) the cat. speed first increases and then decreases on adding small increasing amounts of arsenious acid in the case of sols dialysed for short periods and the initial increase in the cat. speed of the undialysed sol is due to this effect.

The stability with reference to KCl first increases and then decreases on exposing the sol to artificial light (same changes were also noticed with sunlight) (*cf.* Miss Shila Roy[25]), while that with reference to $MgCl_2$ continuously decreases. The stability changes on exposure to light are thus exactly similar to those observed on ageing (Section *D*) and can be explained in the same manner.

Summary.

The cat. speed of colloidal arsenious sulphide with the progress of dialysis decreases upto 8 days after which it increases till 28 days when it decreases again ; the amount of total arsenic and sulphur continuously decreases, while that of free arsenious acid increases at first and then remains constant. The stability with reference to KCl first increases and then decreases, while that with reference to $MgCl_2$ changes exactly as the cat. speed. It is shown that changes in cat. speed are as a result of changes in the composition of the sol with the progress of dialysis which in turn affect to different extents the preferential adsorption of the ions on the surface of the colloidal particles.

The changes in cat. speed on dilution of sols dialysed for different periods are not regular as in the case of colloidal ferric and thorium hydroxide and prussian blue. The stability with reference to KCl and $MgCl_2$ increases regularly on dilution.

The idea of critical potential is not supported in the case of this sol.

The cat. speed decreases generally on ageing and exposure to light ; the amount of total arsenic and sulphur (excluding that in the precipitate) decreases, while that of free arsenious acid increases at the same time. The stability with reference to KCl first increases and then decreases, while that with reference to $MgCl_2$ regularly decreases both during ageing and exposure to light.

It is shown that the results with As_2S_3 sol should not be utilised either to prove or disprove any of the existing ideas about coagulation of colloids because changes in the composition of the sol introduce considerable compli cations.

In the end it may be mentioned that our cataphoretic speed measurements given in the four papers of this series support the physical point of view (based on the adsorption of the ions of the peptising electrolytes by the colloidal particles)[26] about the origin of charge ; the chemical point of view[27] about the origin of charge which is based on the dissociation of the ionogenic complex is not supported by our results. These points will be discussed in detail in a later publication (Paper to be published in September 1936 number of the *Journal of the Bombay University*).

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A DISCUSSION OF CONDUCTIVITY AND CATAPHORETIC SPEED MEASUREMENTS OF COLLOIDAL PRUSSIAN BLUE AND ARSENIOUS SULPHIDE FROM THE POINT OF VIEW OF ORIGIN OF CHARGE ON COLLOIDAL PARTICLES.

By

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According to the physical point of view the charge on colloidal particles is due to the adsorption of the ions of the peptising electrolytes on the surface of the particles (Mukherjee, *Koll. Zeit.*, 67, 178, 1934 and other papers by Mukherjee and co-workers ; Rabinovitch and Kargin, *Trans. Faraday Soc.*, 31, 50, 1935), while according to the chemical view the charge is due to the dissociation of the ionogenic complex attached to the surface of the colloidal particles (Pauli and Valko' *Electrochemie der Kolloide*—1929 ; Pauli, *Trans. Faraday Soc.*, 31, 11, 1935).

In previous papers published from our laboratory emphasis has been laid on the necessity of making simultaneous measurements of various properties of colloidal solutions under varying conditions, and it has been shown that the results can be easily understood by taking into consideration the changes in the preferential[1] adsorption by the colloid particles, of both the similarly and the oppositely charged ions as well as in the amount of electrolytes in the intermicellary liquid. In the present paper it is proposed to discuss some of the results of cataphoretic speed given in two of our previous papers (one by Mankodi, Barve and Desai and the other by Joshi, Barve and Desai, both in course of publication in the Proc. Indian Acad. Sci.[2]) and the simultaneous measurements of conductivity made at that time from the point of view of origin of charge on colloidal particles.

The conductivity was measured by the same method as that used by Desai and co-workers (*Indian J. of Physics*, 8, Part IV, 323, 1934).

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[1] The word " preferential " indicates that the ions are adsorbed in the inner sheet of the double layer.

[2] Mankodi, Barve and Desai, *Proc. Indian Acad. Sci.*, 4 (4), 480, 1936 ; Joshi, Barve and Desai, Ibid, 4 (5), 1936,

RESULTS AND DISCUSSION

(a) *Changes in specific conductivity and cat. speed during dilution.*

In the following tables are given the cat. speed and specific conductivity on dilution of the prussian blue and arsenious sulphide sols dialysed for different periods.

TABLE I.

NOTE :—Readings in columns " a " and " b " refer to prussian blue sol dialysed for 3 days and 26 days respectively.

Dilution.	Cat. Speed × 10^5		Sp. Conductivity × 10^6	
	a	b	a	b
1	38·70	37·10	31630	270·9
2	42·50	32·30	16020	119·3
4	39·00	24·20	9194	72·8
8	30·10	21·50	4586	33·3

TABLE II.

NOTE :—Readings in columns " a " and " b " refer to arsenious sulphide sol undialysed and that dialysed for 31 days respectively.

Dilution.	Cat. Speed × 10^5		Sp. Conductivity × 10^6	
	a	b	a	b
1	50·65	21·40	226·3	212·0
2	33·60	24·80	115·5	105·8
4	21·70	29·00	51·7	45·5
8	17·40	41·20	28·9	30·4

The prussian blue sol dialysed for 3 days contained appreciable amounts of the peptising electrolyte (oxalic acid) as well as traces of ferric chloride, while that dialysed for 26 days contained only inappreciable amounts of the peptising electrolyte. Although the results with the sol dialysed for 26 days (Table I) would not seem to be against the chemical theory of the origin of charge, those with the one dialysed for 3 days cannot be reconciled with the same view, as although the sp. conductivity has decreased with dilution, the cat. speed has first increased and then decreased. It has been shown in our previous paper (Mankodi, Barve and Desai, *loc. cit.*) that the changes in the cat. speed on dilution for both the short period and long period dialysed sols are due to changes in the amount of the active electrolyte in the sol which alter the distribution of the preferentially adsorbed ions on the surface of the particles. The changes in the sp. conductivity of the sol are mainly due to changes in the amount of the electrolyte contained in the intermicellary liquid and in the number of colloid particles per c.c., the influence of the size of the particles, the viscosity of the sol, the thickness of the double layer and the cat. speed being comparatively less marked (*Colloid and Capillary Chemistry* by Freundlich, Eng. Translation, 1926—p. 395).

In the case of the arsenious sulphide sol, (Table II) the sp. conductivity has decreased with increase of dilution for both the undialysed sol and the sol dialysed for 31 days. The undialysed sol did not initially contain any free arsenious acid, while the sol dialysed for 31 days contained some free arsenious acid as a result of hydrolysis of arsenious sulphide during dialysis (Joshi, Barve and Desai, *loc. cit.*). Arsenious sulphide may hydrolyse slightly during dilution. The changes in the sp. conductivity during dilution in the case of both the dialysed and undialysed sols are however considered to be mainly due to the changes in the number of colloid particles per c.c. of the sol.

The changes in the cat. speed on dilution of the undialysed arsenious sulphide sol (Table II) are probably mainly due to changes in the distribution of the preferentially adsorbed ions on the surface of the particles. In the case of the sol dialysed for 31 days the amount of free arsenious acid which is there in the sol, as a result of hydrolysis during dialysis, decreases on dilution ; the increase in the cat. speed with dilution instead of decrease as in the case of the undialysed sol is probably mainly due to a decrease in the amount of arsenious acid (Joshi, Barve and Desai, *loc. cit.*). The chemical view point of Pauli and Valko' (*loc. cit.*) about the dissociation of the ionogenic complex on the surface of arsenious sulphide particles cannot explain satisfactorily the changes in sp. conductivity and cat. speed with dilution in the case of the sol dialysed for 31 days.

(b) *Changes in sp. conductivity and cat. speed during dialysis.* The results of these experiments are given in Tables III & IV.

TABLE III.
Prussian blue sol.

Period of dialysis in days.	Cat. speed × 10^5	Sp. Conductivity × 10^6
3	38·70	31630·0
8	40·60	8780·0
13	43·20	2156·0
17	42·50	1116·0
21	41·05	554·4
26	37·10	270·9

TABLE IV.
Arsenious sulphide sol.

Period of dialysis in days.	Cat. speed × 10^5	Sp. Conductivity × 10^6
0	50·65	226·3
4	34·15	181·1
8	26·10	167·0
17	39·25	284·5
23	45·70	213·1
29	36·00	209·6

From Table III it will appear that with the progress of dialysis of prussian blue sol the sp. conductivity decreases as during dilution. The decrease in the sp. conductivity with the progress of dialysis is mainly due to a decrease in the amount of the peptising electrolyte and in the number of particles per c.c. because the turbidity of the sol increases during dialysis. The changes in the cat. speed during dialysis are, as stated in our previous paper (*loc. cit.*), due to changes in the amount of the peptising electrolyte which alter the distribution of the preferentially adsorbed ions on the surface of the particles. It is thus not possible to account for the variations in the cat. speed as arising out of changes in the ionic strength as assumed by Pauli and Valko' (*loc. cit.*).

The changes in the sp. conductivity with the progress of dialysis of arsenious sulphide sol are very interesting (Table IV). It will appear that the sp. conductivity first decreases and reaches a minimum, then increases and reaches a maximum after which it again decreases on carrying the dialysis to extreme. As stated above this sol initially did not contain any free arsenious acid. With the progress of dialysis however, arsenious sulphide hydrolyses and the amount of free arsenious acid in the sol increases upto a dialysis of 8 days, decreases between 8 and 14 days and remains constant thereafter (Joshi, Barve and Desai, *loc. cit.*). One would ordinarily expect that the sp. conductivity with the progress of dialysis of arsenious sulphide should first increase and then decrease and remain practically constant thereafter if the changes in the amount of free arsenious acid in the sol during dialysis were controlling it. The changes in the sp. conductivity of this sol with dialysis are therefore due to some other factors. As a result of hydrolysis the number of particles of arsenious sulphide per c.c. will decrease but the number of particles of colloidal sulphur, produced as a result of oxidation of H_2S, will increase at the same time. It is likely that the decrease in the sp. conductivity in the early stages and later stages of dialysis might have mainly been due to a greater rate of decrease of the number of arsenious sulphide particles than of increase in the number of sulphur particles. The intermediate increase in the sp. conductivity (Table IV) is perhaps due to the fact that as a result of decrease in the amount of free arsenious acid, the peptisation of the sol takes place, thus giving rise to a greater number of particles per c.c. It should be mentioned that the above explanations of changes in the sp. conductivity of arsenious sulphide during dialysis are only tentative and some other causes might also be responsible for these peculiar changes. These points are being investigated. The changes in the cat. speed during dialysis have been explained in our previous paper (*loc. cit.*) as being due to changes in the amount of electrolytes in the sol, resulting in a change in the distribution of the preferentially adsorbed ions on the surface of the particles.

(c) *Changes in sp. conductivity and cat. speed during ageing.*

TABLE V.

Prussian blue sol dialysed for 25 days.

Age in days.	Cat. speed × 10^5	Sp. Conductivity × 10^6
0	38·60	65·3
20	38·30	63·6
38	31·55	41·9
104	27·90	34·2
173	27·40	33·4
218	27·20	32·7

TABLE VI.

Arsenious sulphide sol.

Age in days.	Cat. speed × 10^5	Sp. Conductivity × 10^6
0	37·05	145·0
15	34·95	160·3
30	29·35	196·1
45	20·50	236·2
60	18·15	191·9
90	16·30	114·8

It will appear from Table V that the changes in both the sp. conductivity and cat. speed of prussian blue are more marked during the first thirty days than afterwards. The changes in the sp. conductivity in the beginning may be mainly due to a preferential adsorption of the oppositely charged ions from the intermicellary liquid which possibly gives rise to a slight increase in the size of the particles, thus decreasing their number per c.c. at the same time. The decrease in the cat. speed is also probably due to a preferential adsorption of the oppositely charged ions from the intermicellary liquid.

In the case of arsenious sulphide sol (Table VI), the changes in the sp. conductivity and cat. speed on ageing are not in the same direction for the first 45 days. The amount of arsenious acid in the sol increases with age (Joshi, Barve and Desai, *loc. cit.*) and the initial rise in sp. conductivity might be probably mainly due to this increase in the amount of free arsenious acid. The decrease of sp. conductivity after 45 days in spite of an increase in the amount of free arsenious acid suggests that some other influences are also at work. As a result of increase in the amount of free arsenious acid in the sol, the preferential adsorption of the oppositely charged ions will increase resulting in an increase in the size of the particles and consequently a decrease in their number per c.c. Freundlich (*Zeit. f. Physik. Chemie,* 80, 566, 1912 ; also see Krestinskaya, *Koll. Z.* 66, 58, 1934) has emphasised the coarsening of the particles in the arsenious sulphide sol on ageing (cf. R. S. Krishnan, *Proc. Indian Acad. Sci.* 1,44 & 211, 1934 ; 717, 1935). It thus appears that after 45 days, the influence of the decrease in the number of particles per c.c. on the sp. conductivity becomes so marked that the increase in the same which results due to an increase in the amount of arsenious acid is not allowed to be noticed at all. The decrease in the cat. speed on ageing is due to an increase in the preferential adsorption of the oppositely charged ions on account of an increase in the amount of arsenious acid in the sol. It must be mentioned here that the chemical theory of the origin of charge (Pauli and Valko', *loc. cit.*) cannot explain the simultaneous changes observed by us in the sp. conductivity and cat. speed on ageing of the sol.

(d) *Changes in sp. conductivity and cat. speed on exposure to sunlight.*

The results of experiments are given in Tables VII & VIII.

TABLE VII.

Prussian blue sol dialysed for 21 days.

Exposure to sunlight in hours.	Cat. speed × 10^5	Sp. Conductivity × 10^6
0	42·70	154·5
1	37·80	27·2
2	36·20	31·4
5	34·10	33·0
10	33·60	41·3
29	27·60	127·1

TABLE VIII.

Arsenious sulphide sol.

NOTE :—Readings in columns "a" and "b" refer to arsenious sulphide sol undialysed and that dialysed for 35 days respectively.

Exposure to sunlight in minutes.	Cat. speed × 10^5		Sp. conductivity × 10^6	
	a	b	a	b
0	50·10	36·20	259·2	425·9
30	51·25	...	281·5	...
60	...	30·05	...	653·1
70	48·35	...	287·8	...
150	43·80	...	359·8	...
300	34·05	17·40	754·8	1434·0
450	32·05	...	1128·0	...
600	...	14·25	...	1825·0
1200	29·85	...	1920·0	...

The changes in the sp. conductivity and cat. speed on exposing the prussian blue sol to sunlight are not in the same direction except for the first one hour (Table VII). The changes in the cat. speed on exposure are probably due to action of sunlight on oxalic acid which gives rise to a change in its amount in the intermicellary liquid and in the distribution of preferentially adsorbed ions on the surface of the particles. The initial decrease in the sp. conductivity is probably due to the fact that agglomeration of the particles results, giving rise to a decrease in their number per c.c. The subsequent increase in the sp. conductivity is perhaps due to desorption of the preferentially adsorbed similarly and oppositely charged ions, thus increasing the amount of free electrolyte in the intermicellary liquid. Small changes in the cat. speed after 1 hour's exposure, in spite of a marked increase in sp. conductivity, suggest that almost an equal amount of similarly and oppositely charged ions is desorbed thus keeping the excess of the preferentially adsorbed similarly charged ions to the preferentially adsorbed oppositely charged ions about the same.

In the case of the undialysed arsenious sulphide sol (Table VIII) as well as the sample dialysed for 35 days the sp. conductivity has continuously increased while the cat. speed decreased at the same time except for the former sol on short exposures when the cat. speed has actually somewhat increased. It has been found that the amount of free arsenious acid in the sol continuously increases on exposing it to sunlight (Joshi, Barve & Desai, *loc. cit.*). On exposure the size of the particles increases and their number per c.c. decreases and the specific conductivity should have decreased due to this effect. The continuous increase in sp. conductivity in spite of this is probably due to the fact that the influence of the increase in the amount of free arsenious acid in the sol is so marked that the decrease due to aggregation of particles is not allowed to be noticed at all. The initial increase in the cat. speed for the undialysed sol which does not contain any free arsenious acid in the beginning, is due to production of free arsenious acid in the sol which increases the preferential adsorption of the similarly charged ions.

The sol dialysed for 35 days already contained appreciable amount of free arsenious acid from the beginning and hence production of further arsenious acid on exposure to light did not show an initial increase in the cat. speed. The decrease in the cat. speed is due to an increase in the preferential adsorption of the oppositely charged ions due to a continuous increase in the amount of free arsenious acid in the sol.

SUMMARY AND CONCLUSIONS.

From a discussion of results of simultaneous measurements of specific conductivity and cataphoretic speed of colloidal prussian blue and arsenious sulphide during dilution, dialysis, ageing and exposure to sunlight, it is shown that the changes in conductivity and cat. speed can be easily understood if it is assumed that the charge on the particles is due to preferential adsorption of the ions of the electrolytes present in the sol. The chemical view point about the origin of charge which is based on the dissociation of the ionogenic complex on the surface of the particles is not supported by our results.

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A STUDY OF THUNDERSTORMS IN POONA IN 1930

By

B. N. Desai, M.Sc., Ph.D., B.A., LL.B.

(*Received on 24th February 1931.*)

In his paper on hailstorms in India during the period 1883-97, Eliot (*Indian Meteorological Memoirs, Volume VI, page 237*) has mentioned that hailstorms in the Bombay Presidency occur chiefly in the Deccan districts of Poona, Dharwar, Belgaum, Bijapur and Khandesh in the hot weather months of March, April and May, the maximum frequency being in the month of April, and are entirely absent during the southwest monsoon period, *i.e.*, from July to November. Eliot (*loc. cit.*) has summarised the conditions that accompany and appear to be essential to the formation of thunderstorms and hailstorms as under :—

1. High temperature,
2. Large diurnal range of temperature.

The large ascensional movement necessary for the formation of hailstorms were supposed to be produced either (*a*) by exaggerated hot weather conditions giving rise to vigorous convection, or (*b*) by a strong dry land current advancing seawards and passing under a sea current and forcing the latter upwards, or (*c*) by air movement from the plains across lines of hills.

In the present paper, thunderstorms that passed over or very near Poona during the year 1930 have been discussed with a view to study how far the morning local upper air conditions indicate subsequent development of a thunderstorm.

It will not be out of place to give here the chief physical features of Poona. The following description of the physical features of Poona is taken from the *Indian Meteorological Memoirs, Volume IX, page 127* :—

> " Poona, Lat. 18° 28′ N and Long. 74° 10′ E and about 1,850 feet above mean sea-level, is situated about 30 miles from the edge of the Deccan plateau. It stands on the right bank of the Mutha river, near the confluence of the Mutha and Mula rivers, both of which are small tributaries of the Bhima. In the vicinity of Poona, the Mutha river runs from southwest to northeast, but, after combining with Mula, it takes an easterly direction. The country around is rugged. A range of hills culminating in the fort of Sinhgarh runs from west to east at a distance of about 8 miles to the south of Poona."

Normal mean monthly directions of surface winds and of upper winds up to 6 km. above sea-level at Poona are given in the Departmental *Memoirs, Volume IX (pages 247, 248)* and *Scientific Notes, Volume I, No. 7*, respectively. The effect of diurnal variation is a general tendency to superpose a more and more westerly component during the day up to about 3 km. in all months. This tendency is strongest in March, April and May, less so from November to February and very little from June to September.

For facility of discussion, the thunderstorms have been classified into different types. The classification into different types is based on the mean direction (eight points of the compass) from which the wind was blowing at the time of the thunderstorm. This wind has been called the "*prevailing wind*" in what follows. Humphreys (*Physics of the Air, 1929 edition, page 333*) has pointed out that the direction from which the wind is blowing when the thunderstorm is on is also the direction from which the thunderstorm has approached the station. This was found to be true for most of the thunderstorms discussed in this paper. Thus if the wind was blowing from NW when the thunderstorm was on, it has been called a thunderstorm of the northwesterly type, *i.e.*, a thunderstorm which came from the northwest and moved in a southeasterly direction.

In *Table I* below are given the details about thunderstorms in 1930 as seen from the autographic records at the Meteorological Office, Poona. A Dines Anemograph, Thermograph and Hygrograph are installed at the top of the tower, which is about 120 feet above the ground level. The Hyetograph is kept in an enclosure in the compound and is to the southeast of the tower at a distance of about 100 feet from it. In what follows, the word "*surface*" has been used to mean the top of the tower.

Information about weather at different places round about Poona in the Deccan for those days on which thunderstorms occurred in Poona is given in *Table II*. In some cases observers reported times of commencement and cessation of rain and thunderstorm, and these times are given along with the respective weather remarks in order to bring out any relationship that may exist between the weather conditions at different places on the same day.

In *Table III* are given the directions (in sixteen points of the compass) of morning upper winds at 1·0, 2·0, 3·0, 4·0 and 6·0 km. above M. S. L. as well as of clouds over Poona on those days on which thunderstorms occurred.

Besides the days given in *Table I* on which thunderstorms passed over or very near Poona, thunder was also heard on some other days although all the other characteristics of thunderstorms were not well marked. *Table IV* contains directions of morning upper winds (in sixteen points of compass) as well as of clouds over Poona on those days when thunder was heard but no appreciable (less than 10 cents) rainfall occurred at the time.

TABLE I_3

Date.	Time of commencement of prevailing wind.	Time of cessation of prevailing wind.	Maximum velocity in gust.	Temperature-fall with coming of prevailing wind and before rain.	Relative humidity increase with coming of prevailing wind and before rain.	Time of commencement of rain.	Time of cessation of rain.	Amount of rain.
	H. M.	H. M.	M. P. H.	°F.	%	H. M.	H. M.	Cents.
				Northeasterly Type.				
17th April 1930 ..	21—30	00—40	36	5	..	..	..	*Nil*
28th May 1930 ..	23—15	23—30	22	3	6	23—30	23—50	2
25th September 1930	17—00	17—50	30	3	10	17—07	17—30	33
7th October 1930 ..	18—30	18—45	33	..	..	18—30	18—40	2
10th October 1930 ..	16—30	17—30	44	11	38	17—10	17—40	29
20th October 1930 ..	19—02	19—30	66	16	40	19—25	19—55	40
4th November 1930 ..	15—45	18—00	26	8	25	16—15	16—45	10
				Southeasterly Type.				
14th April 1930 ..	17—35	18—00	60	..	..	17—37	18—00	126
22nd May 1930 ..	18—10	19—10	54	6	14	18—20	19—15	48
6th September 1930 ..	16—40	17—10	25	..	..	16—44	17—30	120
2nd October 1930 ..	17—40	17—55	29	..	..	17—40	17—55	40
9th October 1930 ..	15—10	16—35	13	5	9	15—50	16—20	12
28th October 1930 ..	18—40	19—50	34	..	..	18—50	20—00	29
				Southwesterly Type.				
21st May 1930 ..	14—40	15—35	58	..	..	15—25	16—00	55
2nd September 1930 ..	13—45	15—30	50	6	34	14—38	15—15	135
3rd September 1930 ..	15—35	..	30	9	15	16—32	16—45	29
7th September 1930 ..	15—55	17—25	22	7	7	..	..	*Nil*
5th October 1930 ..	14—45	16—10	29	7	12	..	..	*Nil*
5th December 1930 ..	15—20	15—35	24	..	..	15—20	15—35	20
				Northwesterly Type.				
22nd March 1930 ..	18—05	18—45	22	5	8	..	..	*Nil*
9th June 1930 ..	16—35	..	33	2	17	16—45	19—10	88
14th September 1930	17—20	18—45	34	..	..	17—20	18—35	78
21st October 1930 ..	16—38	17—15	42	16	38	17—07	17—55	99

NOTE.—In some cases, the barograph showed a rise in pressure of the order of 0·070″ with the coming of the prevailing wind and before the commencement of rain. The steady fall in pressure that is expected before the coming of the thunderstorm was not well pronounced. Dots in columns 3, 5 and 6 denote occasions when the sudden changes were not noticed in the autographic records.

TABLE II.*

Date.	Malegaon.	Aurangabad.	Ahmednagar.	Sholapur.	Gulbarga.	Bijapur.	Belgaum.
17th April 1930	..	..	T (night)	..	..	..	..
28th May 1930	..	..	..	..	..	..	T
25th September 1930	..	..	..	..	..	..	..
7th October 1930	..	..	..	r	..	..	r (18·30 to 20·00)
10th October 1930	..	..	..	r	r (14·45 to 15·30)	r	r (19·00 to 19·30)
20th October 1930	..	..	..	..	..	..	..
4th November 1930	..	..	..	..	..	..	..
14th April 1930	..	..	..	..	..	..	T, r (evening)
22nd May 1930	r	..	..	..	..	..	T, r (15·30 to 18·30)
6th September 1930	r	..	r (22·30 to 23·00)	r, l	r	r	..
2nd October 1930	T (15·50 to 16·55)	..	r (20·30 to 23·00)	r	..	r	r (15·00 to 16·30)
9th October 1930	..	..	..	r	r (20·00)	r	T, r
28th October 1930	r	r (day)	r, l (14·30 to 14·45)	r	r	..	r
21st May 1930	..	r (21·00)	l	T, r	..	r	T, r (14·00 to 15·30)
2nd September 1930	r	r	r (20 to 22)	r, l	r	r	T
3rd September 1930	r (15·50 to 16·30)	..	r (16·15 to 17·30)	..	..	l	T, r
7th September 1930	..	r	r (16 to 17, 20 to 22)	r, l	r	r	r (17·30)
5th October 1930	r	r (night)	r (14 to 15, 21 to 22)	..	..	r	r (13·00 to 20·00)
5th December 1930	r	r	r	..	..	..	..
22nd March 1930	..	..	..	T	..	..	T (15·30 to 18·00)
9th June 1930	r	r	r (20 to 21)	r	..	..	r
14th September 1930	..	..	..	..	..	..	..
21st October 1930	..	..	..	..	..	..	..

*T—Thunderstorm.
r—Rain.
l—Lightning.

TABLE III.

Height (Km.)→	1·0	2·0	3·0	4·0	6·0	Remarks.
Northeasterly Type.						
17th April 1930	WNW	E	SE	E	SSW	CK from SSW.
28th May 1930	WNW	NNE	E	E	..	..
25th September 1930	WNW	E	ENE	E	..	SK from ESE AK from S.
7th October 1930	ENE	ENE	E	E	..	..
10th October 1930	SE	E	E	ESE	ESE	AK from SE.
20th October 1930	ESE	ESE	E	NNE	..	AK from ENE.
4th November 1930	ENE	*CALM*	..	..	..	N from NE.
Southeasterly Type.						
14th April 1930	SE	SE	ESE	S	N	..
22nd May 1930	NNW	NW	SSW	S	W	CK from NNW.
6th September 1930	NW	N	..	..	..	S from N.
2nd October 1930	N	ENE	E	SE	..	AK from SSE.
9th October 1930	ESE	E	E	SE	..	AK from SE.
28th October 1930	ESE	..	..	..	..	S from SSE.
Southwesterly Type.						
21st May 1930	W	E	SSE	SSE	WNW	..
2nd September 1930	ESE	SE	SSE	E	N	FK from E. CK from NNE.
3rd September 1930	SE	NNE	NNW	..	..	S from SE.
7th September 1930	WNW	ENE	*CALM*	E	..	S from WSW.
5th October 1930	E	SSE	WSW	SW	..	AK from SW. CK from SW.
5th December 1930	SW	S	SSW	SW	SW	..
Northwesterly Type.						
22nd March 1930	NW	S	S	ESE	NW	AK from SSW.
9th June 1930	N	E	SE	..	..	AK from SSE.
14th September 1930	WSW	W	NW	..	..	SK from WNW. AK and AS from NE.
21st October 1930	ESE	E	ENE	N	NW	C from WSW.

TABLE IV.

Height (Km.)→	1·0	2·0	3·0	4·0	6·0	Remarks.
Northeasterly Type.						
6th October 1930	NNE	E	E	..	..	SK from ENE. N from ENE.
Southeasterly Type.						
24th May 1930	WNW	NNW	WNW	WSW	WNW	..
7th June 1930	SW	ESE	NNW	SE	NNE	C from ESE.
Southwesterly Type.						
26th August 1930	W	SSW	SSW	SSW	ENE	FK from W. C from ENE.
1st September 1930	N	ESE	..	..	..	SK from ESE.
8th September 1930	W	N	NE	ENE	..	N from NE. AK from NE.
15th September 1930	W	..	..	..	..	N from W.
23rd September 1930	W	ESE	SSE	ESE	WSW	C from ENE.
3rd October 1930	ENE	E	ENE	ENE	..	SK from SSE.
4th October 1930	E	E	NE	W	..	S from SE.
2nd November 1930	E	SSW	W	..	..	S from SSE.
Northwesterly Type.						
18th April 1930	ESE	S	S	SSW	WSW	AK from SW.
19th April 1930	ESE	WNW	S	SSE	SSW	..
6th May 1930	WNW	NE	N	NE	WNW	..
19th May 1930	WNW	SW	SE	S	NW	..
20th May 1930	W	NNE	ENE	..	..	N from SE.
23rd May 1930	NNW	ENE	SSE	S	SW	..
16th June 1930	W	WSW	SE	SSE	SW	K from WSW. C from ENE.
17th June 1930	W	..	..	..	..	SK from WSW.
18th June 1930	WSW	ENE	WSW	..	..	K from WSW. AK from E.
9th September 1930		No ascent due to rain.				
18th September 1930	WNW	W	..	..	..	SK from W.
6th December 1930	E	S	WNW	W	WSW	..

NOTE.—In some cases a fall of temperature of the order of 10° to 15° F., and a rise in relative humidity by 30 to 40 per cent., was also observed although no sharp change in wind direction was noticeable.

Details about some Thunderstorms.*

(a) *Northeasterly Type.*

25th September 1930.—The trajectories of the morning and afternoon pilot balloon ascents together with the cloud directions are shown in *fig. I*. In the morning, Alto-Cumulus was coming from S, while in the afternoon even Strato-Cumulus was coming from that direction. This shows that the southerly or the moist current had descended since morning. The surface wind, which was blowing from some direction between W and N up to 4-20 P.M., had veered to SE in the next thirty minutes, but again backed to NE at 5 P.M. With this, weather became squally and the thunderstorm accompanied with rain passed over the Observatory. One noticeable feature about the passage of this thunderstorm over the Observatory was that, although during the period 5·07 P.M. and 5·25 P.M. it was raining, the temperature rose by 2°F. and the relative humidity at the same time decreased by 3 to 4 per cent.

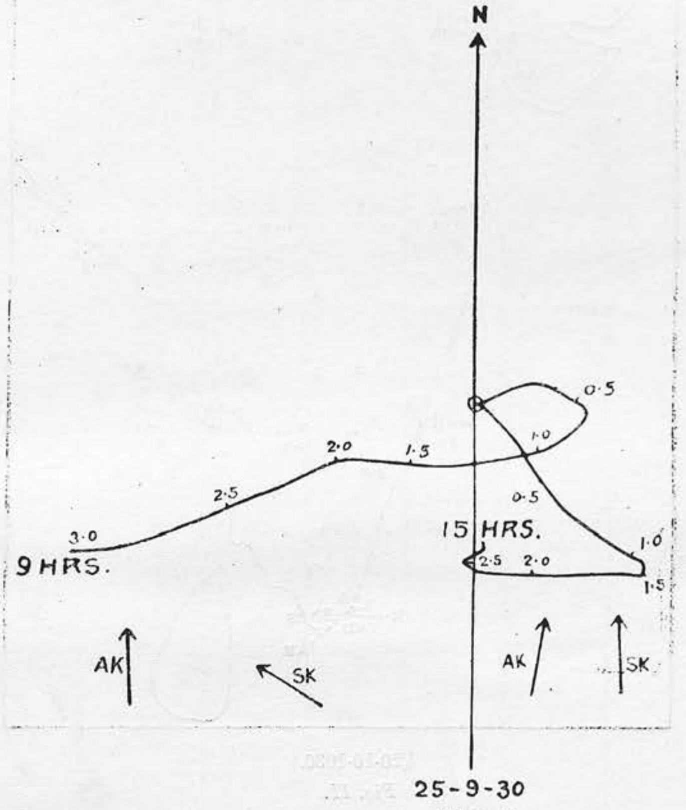

FIG. I

20th October 1930.—Temperature was above normal in the north Bombay Deccan and adjoining parts of Gujarat. Upper winds over the Peninsula on that

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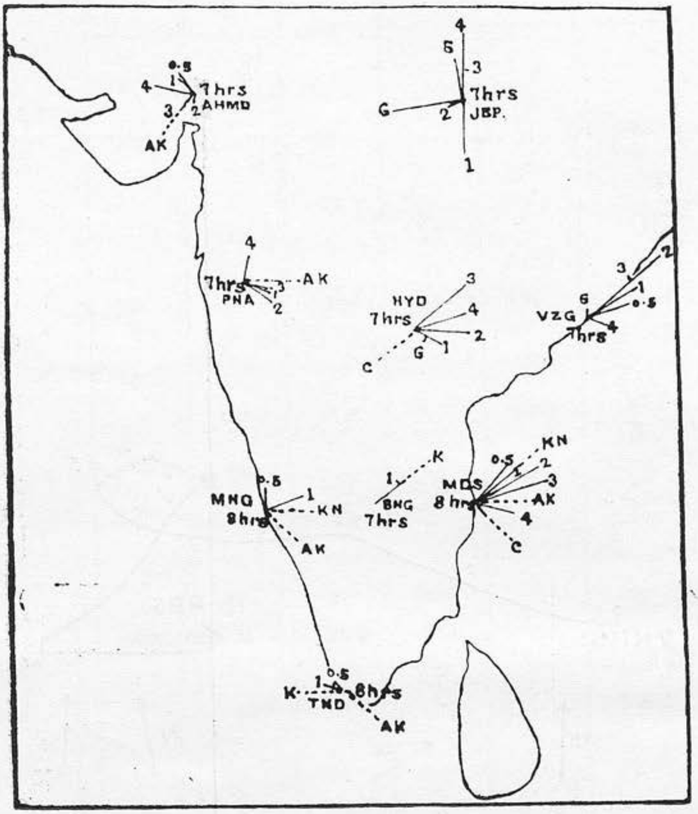
* Some details about weather on these days have been taken from weather diaries maintained by Mr. Ramkrishnan of the Upper Air Section, Poona, and the Chief Observer of the Observatory.

morning are given in *fig. II*. In the morning there was very little cloud, but it

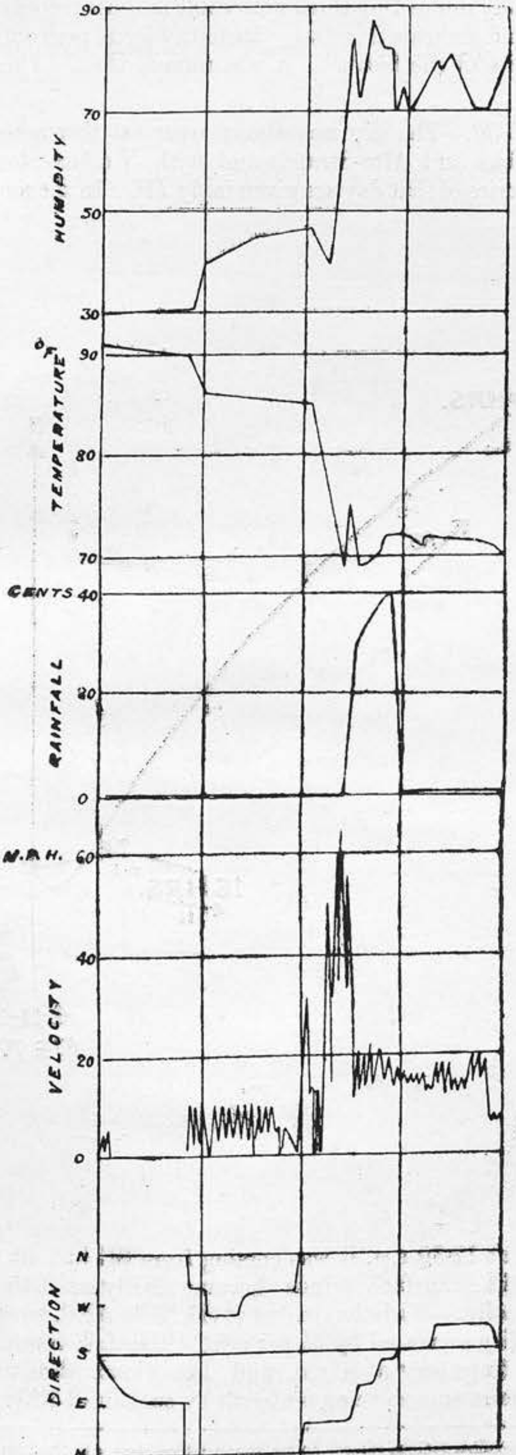


(20-10-1930.)

Fig. II.

gradually increased. There was Cirrus and Alto-Cumulus (about 5), at noon. By 4-30 P.M. the cloud amount increased to 7, but still there was very little low cloud. However, Alto-Cumulus which was coming from N78E in the morning had changed its direction by 4-30 P.M., when it was coming from S65E. The cloud then gradually lowered and at 7 P.M. the surface wind suddenly veered to NE and there was a vigorous squall with the coming of the thunderstorm, the squall lasting up to 7-30 P.M.

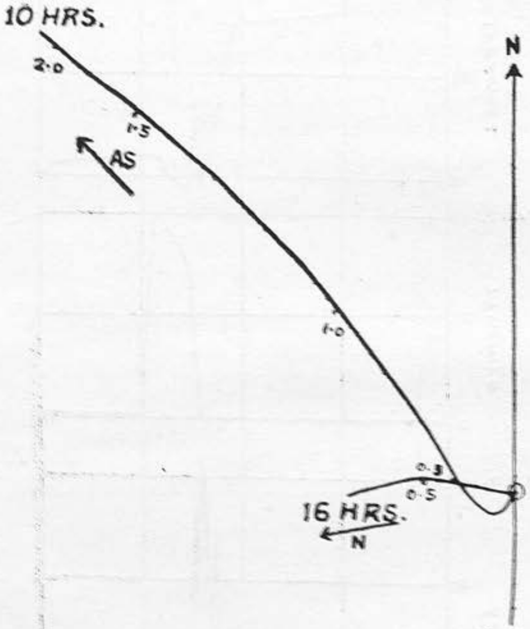
The autographic records of that day are reproduced in *fig. III*. It will be seen that,



20·10·30
FIG. III

before the rain commenced, temperature fell by 16°F., with the coming of the north-easterly wind. A very interesting thing noticeable in these records is the rising of temperature by 6°F. and decrease in relative humidity by 11 per cent. between 7-24 P.M. and 7-30 P.M. in spite of the fact that it was raining then. This point will be discussed later.

4th November 1930.—The sky was almost overcast throughout the day, in the morning with Nimbus and Alto-Stratus and with Nimbus alone at 4 P.M. The pilot balloon trajectories of that day are given in *fig IV*. In the morning, Nimbus was coming from NE; at 12-30 P.M. it was coming from SE but at 4-00 P.M. it was moving from N81E. Surface winds became NEly at 3-45 P.M. and, with it, weather became squally. With the coming of the NEly wind, temperature fell by 8°F. and relative humidity increased by 25 per cent. Rainfall commenced at 4-15 P.M. The pilot balloon trajectory at 4 P.M. and the cloud direction at that time indicate that the moist air was being undercut by cool air of NEly origin*.



4-11-30
FIG. IV

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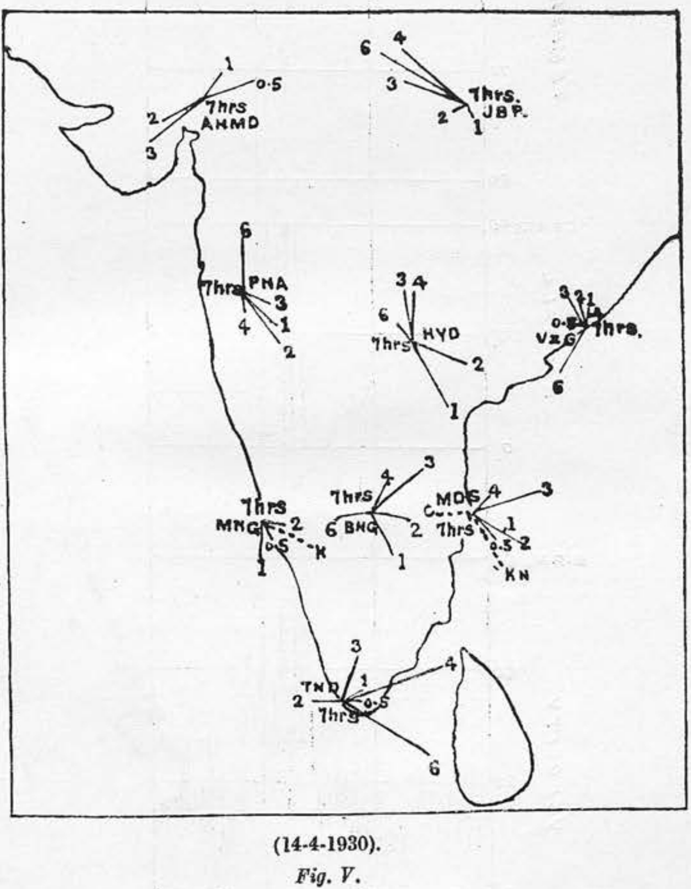
* In the absence of sounding balloon records on the thunderstorm days discussed in this paper, an assumption has been made throughout that winds from Sly directions are moister than those from Nly directions. This assumption has been found to be generally valid for those occasions when Sly winds were associated with the formation of cloud.

(b) *Southeasterly Type.*

14th April 1930.—Upper winds over the Peninsula on that morning are given in *fig. V.* Weather was fine and clear in the morning. Cumulus began to form after

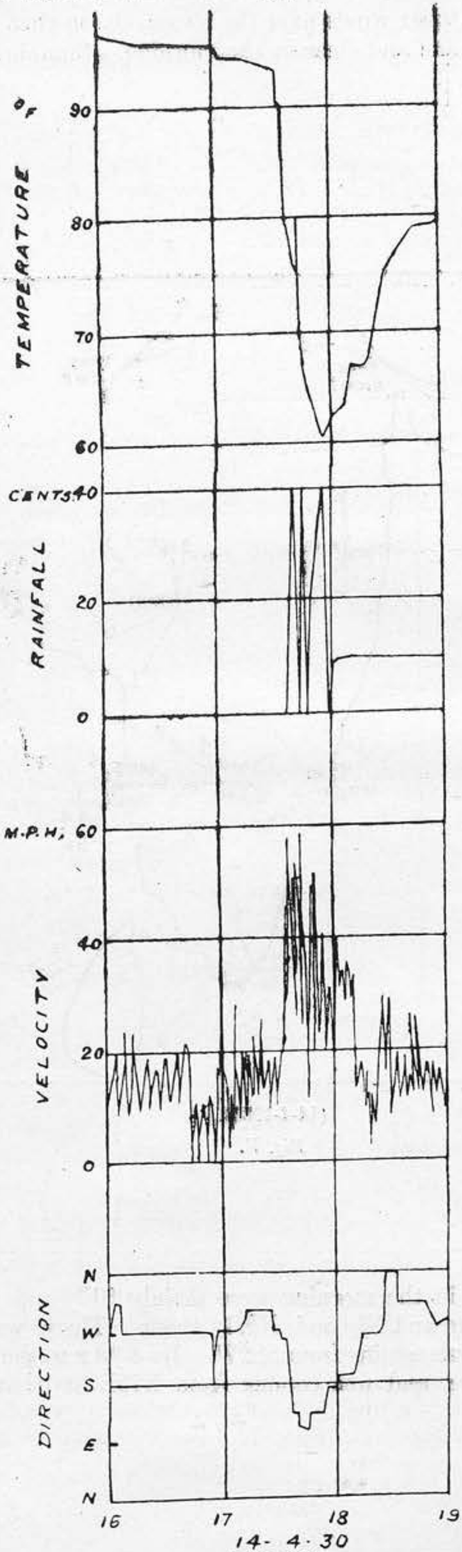


(14-4-1930).

Fig. V.

10 A.M. Upper winds in the morning were mainly SEly up to 3·5 km., Sly between 3·5 and 4·0 km. and Nly and NWly above. There was Cumulus (about 6) at 12-30 P.M. and it was coming from S52W. By 4-30 P.M. the cloud had changed to Cumulo-Nimbus type, and was coming from N75E at that time. The auto-

graphic records for that day are reproduced in *fig. VI*. At 5-35 P.M. the surface wind



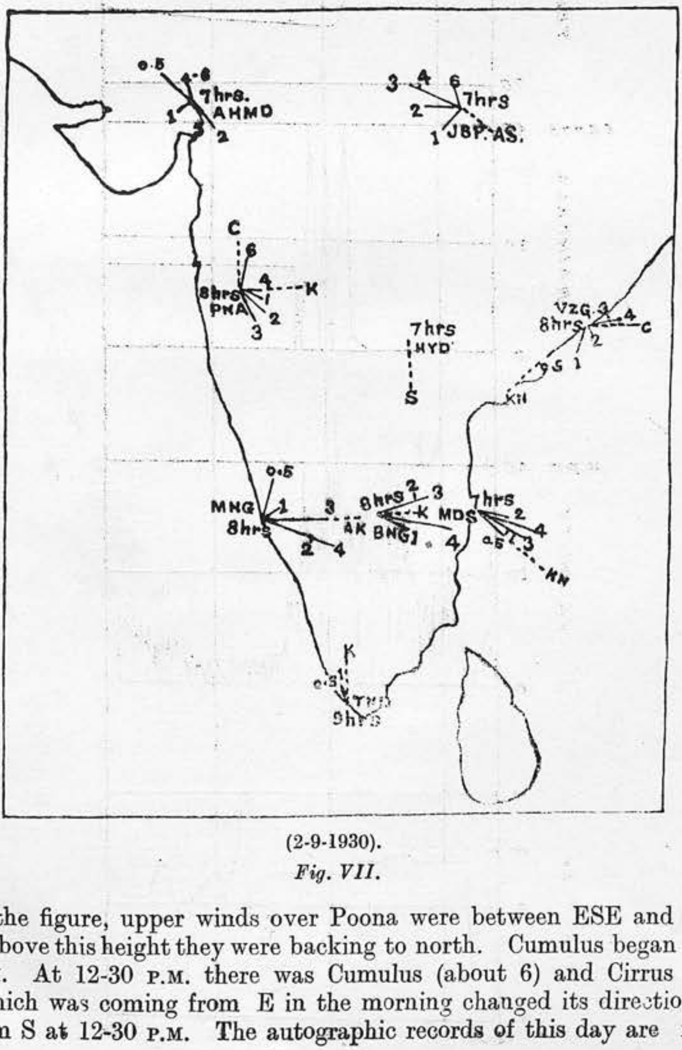
14- 4 · 30

FIG. VI

backed to SE and the coming of the SEly was accompanied by a very vigorous squall and raising of dust in front of the thunderstorm. It could be seen that dust was raised to almost the low cloud level. Due to dust, visibility was considerably reduced, objects within 50 yards being invisible. This was followed by rain which commenced at 5-37 P.M. In the beginning, rain drops were being whirled and tossed by the strong wind. Afterwards, steady and heavy rain fell, the amount being 120 cents. between 5-37 and 5-57 P.M. The sky cleared after 6 P.M. The most interesting thing about this thunderstorm was the rise in temperature of 5° at 5-44 P.M. in spite of the fact that it was raining heavily at that time. Between 5-35 and 5-55 P.M. there was cooling of the order of 34°F. Belgaum had also a thunderstorm and rain on that day. The instability in this case was presumably associated with the over-running of moist air by dry and potentially cold air.

(c) *Southwesterly Type.*

2nd September 1930.—The sky was practically clear in the early morning. Upper winds over the Peninsula on that morning are shown in *fig. VII.* As will be



(2-9-1930).

Fig. VII.

seen from the figure, upper winds over Poona were between ESE and SSE up to 4 km. and above this height they were backing to north. Cumulus began to increase after 8 A.M. At 12-30 P.M. there was Cumulus (about 6) and Cirrus (about 3). Cumulus which was coming from E in the morning changed its direction and was coming from S at 12-30 P.M. The autographic records of this day are reproduced in *fig. VIII.* It will be seen from them that with the coming of the WSWly wind th

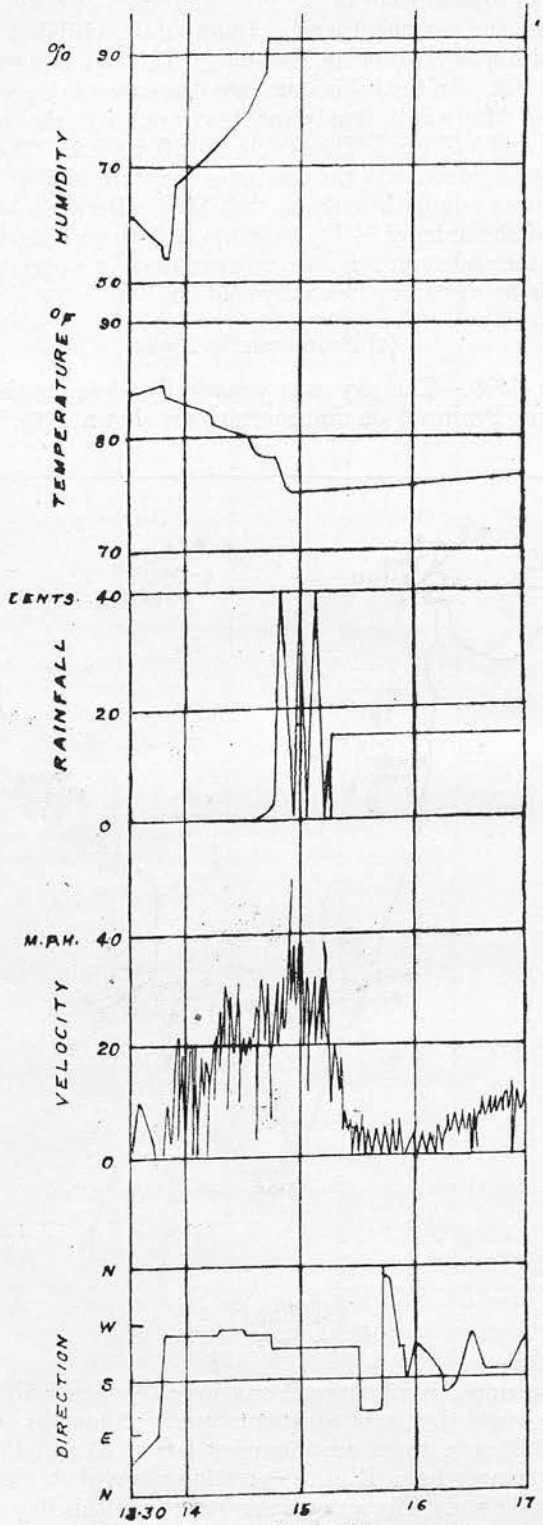
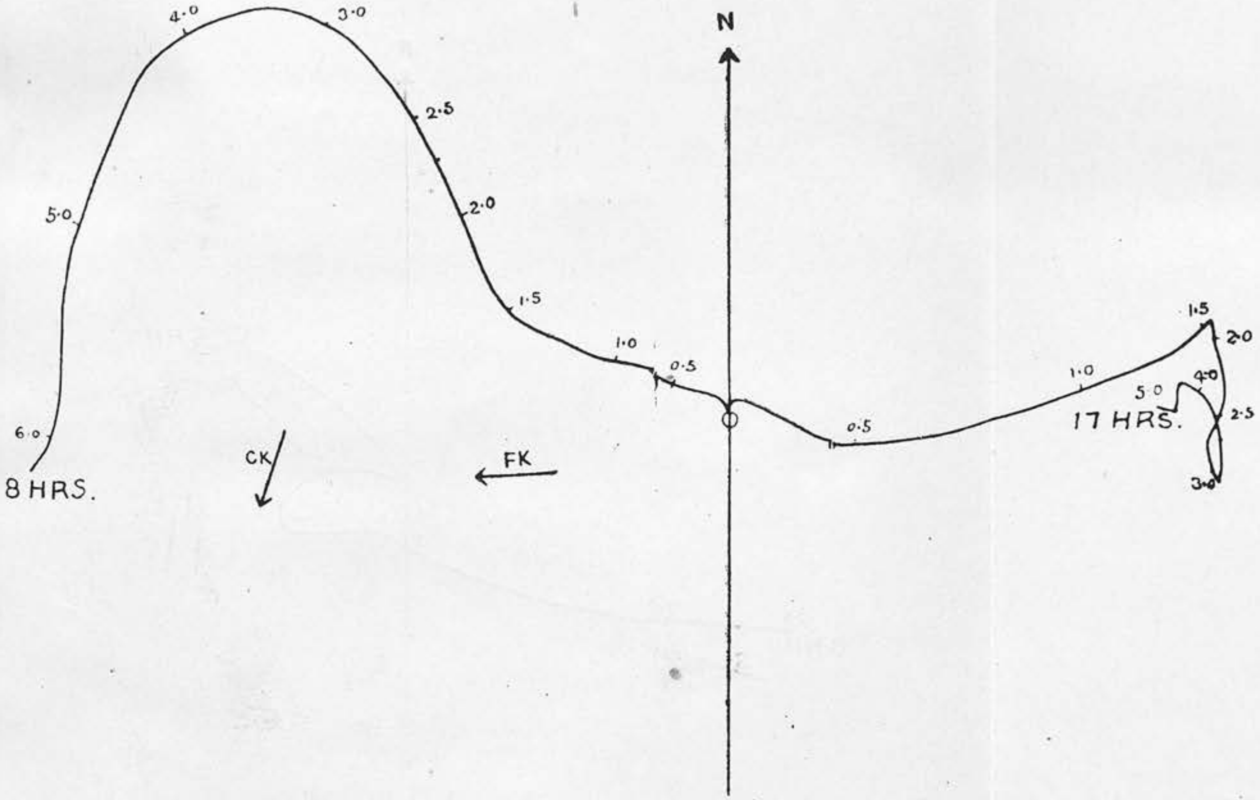


FIG. VIII

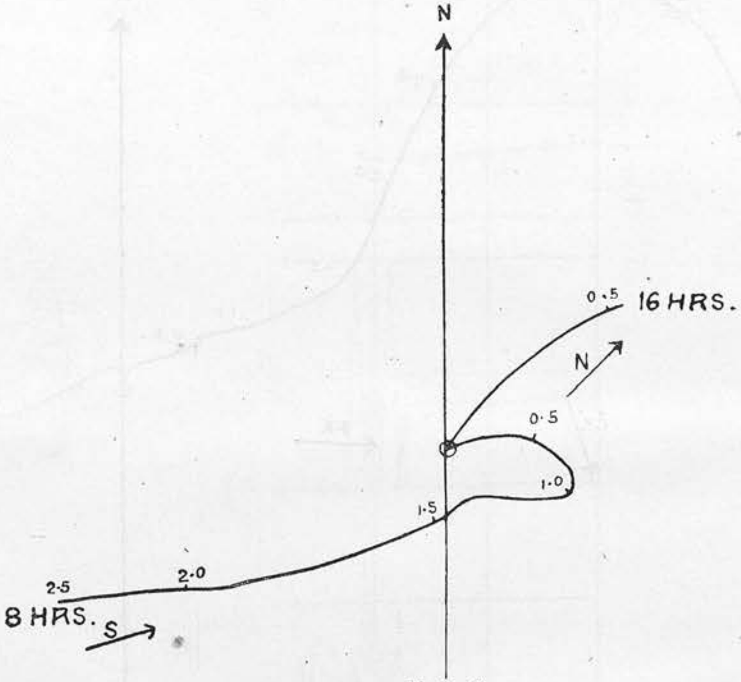
temperature began to fall and the relative humidity began to increase. The wind gradually backed to SW, strengthening at the same time. At 2 P.M. the sky was threatening towards southwest and thunder began to be heard. At 2-15 P.M. dust was seen being raised towards southwest. At 2-45 P.M. with the approach of the thunderstrom, heavy rain began to fall. The trajectories of the pilot balloon ascents in the morning (before thunderstorm) and in the afternoon (after the thunderstorm) are given in *fig. IX*. The instability seems to have been associated with the over-



2-9-30
FIG. IX

running of moist air by dry and potentially cold air. The afternoon pilot balloon trajectory gives an idea about the confused state of air in the upper layers after the passage of the thunderstorm.

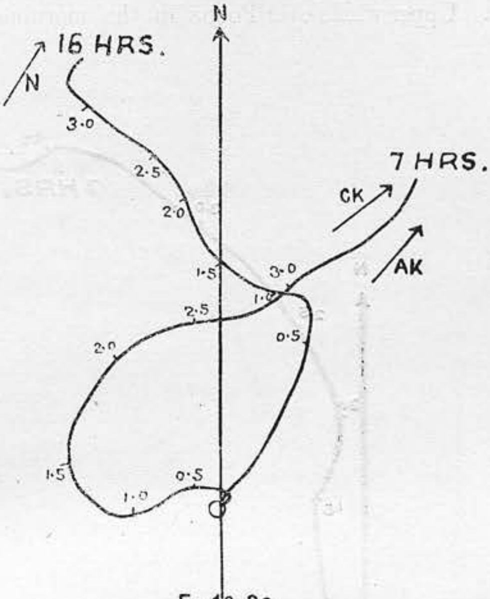
7th September 1930.—There was some Stratus in the morning coming from S72W. Later on, cloud increased and Cumulus formed. At 12-30 P.M. there was Alto-Cumulus (about 3) covered by low cloud, Stratus (about 4) coming from N68W and Cumulus (about 2) at low angle. Thereafter, the cloud changed to Nimbus. Surface wind which was coming from NW after 2 P.M. backed thereafter, and at 3-55 P.M. began to blow from SW, becoming more gusty at the same time. By this time, the sky had become threatening and the thunderstorm approached the Observatory, as shown by the fall of temperature and increase in relative humidity. There was, however, no rain. The pilot balloon trajectories for that day, morning (before thunderstorm) and afternoon (after thunderstorm), are given in *fig. X.* At 4-30 P.M. sky was covered with Alto-Stratus (about 3, a uniform sheet,) and Nimbus, (about 7,) the latter coming from SSW. The absence of rain in Poona on this day may have been due to the moist current being very shallow before the thunderstorm occurred.



7-9-30

FIG. X

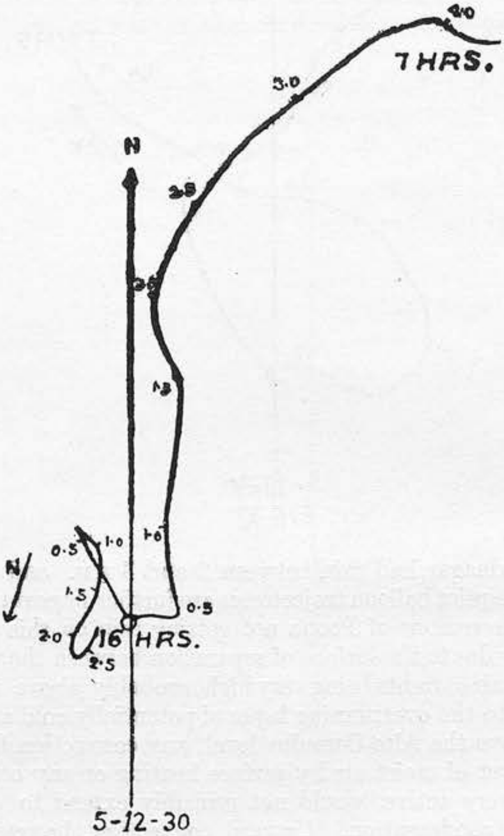
5th October 1930.—There was Cirro-Cumulus and Alto-Cumulus (about 7) in the morning and they were coming from SW. Later on Cumulus began to form and at 12-30 P.M. there was Cumulus (about 8) coming from SW. Surface wind was from NE upto 2-45 P.M. Peals of thunder were heard after 2 P.M. The surface wind veered to SW at 2-45 P.M. and also strengthened. The thunderstorm apparently approached the Observatory at this time as shown by the fall in temperature and an increase in relative humidity, but it did not give any rain. Pilot balloon trajectories for the morning and for the afternoon at the time of the thunderstorm are given in *fig. XI*. They show definitely that the SWly wind had descended since morning.



5-10-30
FIG. XI

On that day, Ahmednagar had rain between 2 and 3 P.M. and Belgaum between 1 and 2-30 P.M. The pilot balloon trajectories are further important in that they help us to understand the reasons of Poona not getting rain on this day. The absence of rain was probably due to the surface of separation between the warm moist and the dry potentially cold air currents being very high, probably above Alto-Cumulus level. In such a case, due to the overrunning layer of potentially cold and dry air with high lapse rate being above the Alto-Cumulus level, any convection that may be started within the lower layer of moist air by surface heating or any other cause, provided that these are not very active, would not probably extend to a height sufficient to produce marked condensation. Upward convection, however, could be maintained from and above the level of the surface of separation of the warm moist and the potentially cold dry air resulting in the formation of Cumulus cloud with high base. As most of the moist air would be below the level of active upward convection, there would be but a very limited quantity of moisture available for condensation, and the little precipitation that may occur may not be sufficient to reach the ground owing to evaporation during descent from the high level of condensation. This conclusion is further supported by the fact that on days when there is a moist current of great depth, *i.e.*, right up to the cirrus-level, we do not get any thunderstorm unless there is very strong surface heating to give rise to convection. Without strong surface heating or the cold dry current above the moist current in lower levels (below 6 km.) or undercutting by cold air, it does not appear possible to produce sufficient convection to give a thunderstorm.

5th December 1930.—Temperature was above normal in the Bombay Deccan. The sky was clear in the morning. Cloud began to appear later on and at 12-30 P.M. there was Cirro-Cumulus (about 3) coming from S78W and Cumulus (about 4) coming from S9W. Later on, the sky became more and more threatening. At 3 P.M. the wind which was then Ely began to veer and, with the coming of the SWly at 3-20 P.M., weather became squally and it began to rain. The rain continued till 3-35 P.M. The cloud thereafter began to decrease. The pilot balloon trajectories in the morning (before thunderstorm) and in the afternoon (after the thunderstorm) are given in *fig. XII*. Upper winds over Poona in the morning were Sly to SWly upto 8 km, (full trajectory not shown). The trajectory of the pilot balloon in the afternoon shows how weak and indefinite in direction the winds in the upper atmosphere become after the passage of a thunderstorm. This thunderstorm also supports what has been said about the instability in the previous case, *i.e.*, about the thunderstorm on 5th October 1930. In this case also upper winds up to Cirrus-level being Sly to SWly were not favourable for giving rise to a marked convection and rain due to absence of dry and potentially cold air above the moist wind, (below 6 km.). There was, however, another factor operative in this case, *viz.*, the surface heating as shown by high temperatures over the Bombay Deccan, which gave rise to marked vertical convection and consequently the thunderstorm. It also appears that in spite of Sly upper winds up to 8 km., there was not much rain because the convection produced by heating is not so strong as in the case of overrunning of moist air by dry and potentially cold air.



5-12-30

FIG. XII

(d) *Northwesterly Type.*

9th June 1930.—The morning and afternoon pilot balloon trajectories are given in *fig XIII*. The sky was practically clear in the morning. Later on, Cumulus

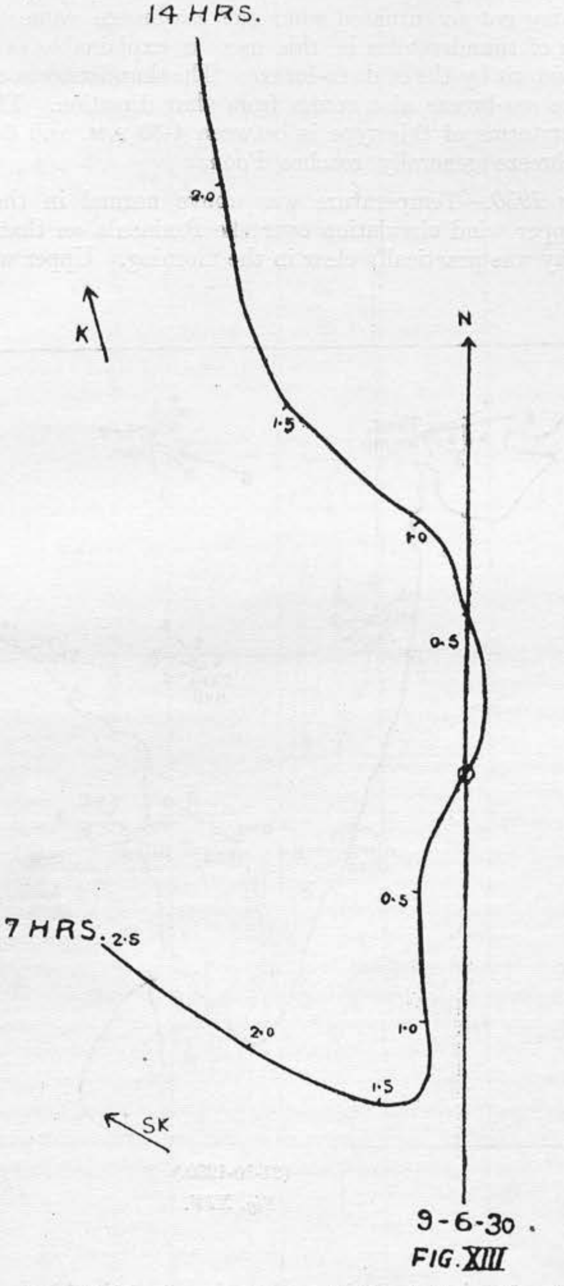
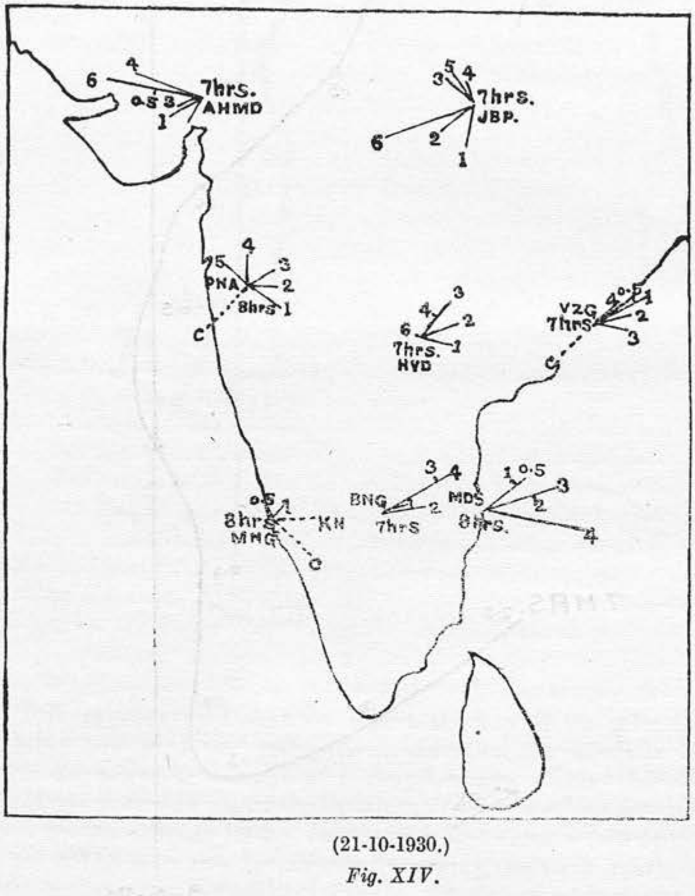


FIG. XIII

and Cumulo-Nimbus formed, the former (amount about 8) coming from N85E at 12-30 P.M. Surface wind which was coming from ESE up to 2 P.M. veered to SW at 2-10 P.M. Thunder was heard at a distance after 2 P.M. there being also slight rain at 2 P.M. After 2-45 P.M. the wind backed to SE, but at 4-30 P.M. it became variable. Cumulus (about 8) was coming from S21E at 4-30 P.M. At 4-45 P.M.

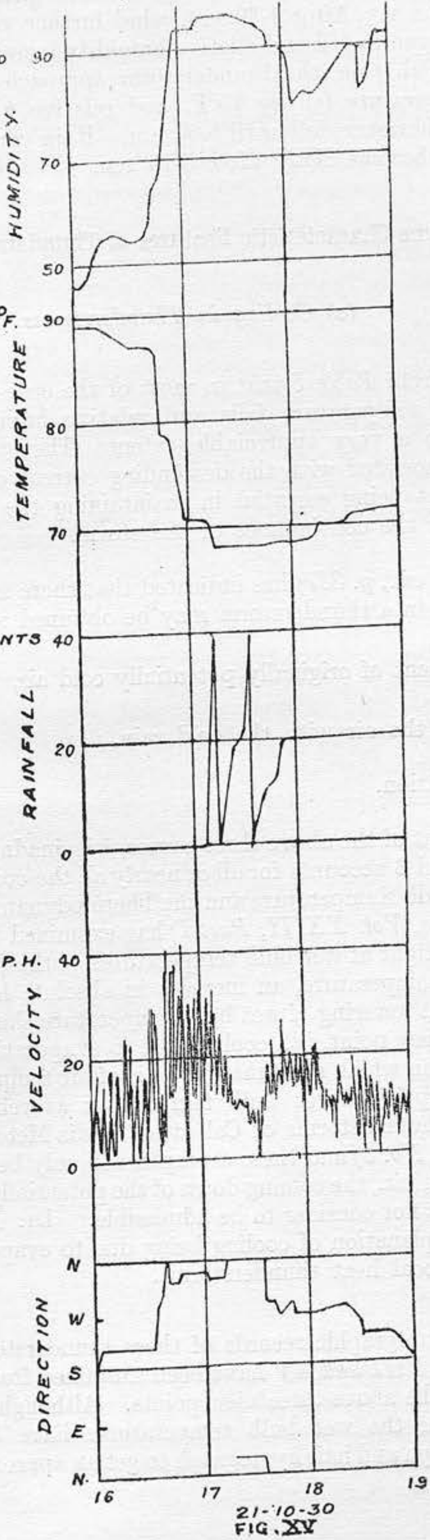
wind began to blow from between NW and W and became very gusty. With this, the thunderstorm approached and passed over the Observatory. Rain also began at 4-45 P.M. The pilot balloon trajectories show how the moist current descended with the advance of the day. The convection produced by gradual heating with the advance of day got accentuated when the sea-breeze came. The mechanism of the formation of thunderstorm in this case is explainable as being due to the lifting of the moist air by the cold sea-breeze. The thunderstorm comes from north-west because the sea-breeze also comes from that direction. The time of occurrence of thunderstorms of this type is between 4-30 P.M. and 6-30 P.M., *i.e.*, the time when sea-breeze generally reaches Poona.

21st October 1930.—Temperature was above normal in the north Bombay Deccan. The upper wind circulation over the Peninsula on that day is shown in *fig XIV*. The sky was practically clear in the morning. Upper winds at that time were ESEly up to 1·9 km. and above that they were backing and were Wly at 6·5 km. Cirrus was coming from S62W. Cloud increased later on. At 12-30 P.M. Alto-Cumulus (about 2) and Cumulus (about 3) were coming from S23E and N86E respectively. At 4-30 p.m. Cumulus (about 3) was coming from N45W. There was also Cumulo-Nimbus (about 2) and Cirro-Stratus (about 2) at that



(21-10-1930.)
Fig. XIV.

time. Autographic records for that day are given in *fig. XV*. As will be seen from the



21-10-30
FIG. XV

figure, surface wind veered and became SWly and more gusty after 4 P.M. Thunder was also heard at 4 P.M. After 4-30 P.M. wind further veered to between N and NW, temperature began to fall and relative humidity increased rapidly, and weather became squally. With this, the thunderstorm approached and passed over the Observatory. Temperature fell by 15°F. and relative humidity increased by 40 per cent. No rain, however, fell until 5-07 P.M. Rain continued up to 5-50 P.M., although wind had become NEly after 5-15 P.M.

Some Characteristic Features of Thunderstorms.

(a) *Cooling in Thunderstorms.*

It will be seen from *Table I* that in most of the cases with the coming of the prevailing wind the temperature falls and relative humidity increases, in some cases rapidly and to a very appreciable extent. These changes in temperature and humidity are associated with the descending current of air in a thunderstorm, the descending current being essential in maintaining the strong upward vertical current necessary for the continuance of the storm.

Humphreys (*loc. cit., p. 337*) has indicated that there are three possible ways by which the cooling in a thunderstorm may be obtained :—

1. By the descent of originally potentially cold air,
2. By chilling the air with the cold rain,
3. By evaporation.

He has argued that of the above three causes, 1 is inadmissible, 2 is but a minor contributing factor and 3 accounts for all or nearly all the cooling. Dr. Normand in his paper on "Wet-Bulb Temperature and the Thermodynamics of the Air" (*Indian Meteorological Memoirs, Vol. XXIII, Part I*) has examined these three view points of Humphreys' in the light of wet bulb temperatures of the descending air mass and shown that a fall in temperature, an increase in absolute humidity in the surface layers and a very slight lowering of wet bulb temperature should be the consequence if Humphreys' third view point, *i.e.*, cooling due to evaporation is correct. He has, however, quoted cases in which most marked falls of air temperature were generally accompanied by a sharp fall of wet bulb temperature as well, (*Cf.* fig. 6 Mr. V. V. Sohoni's paper on "Thunderstorms of Calcutta," India Meteorological Department, *Scientific Notes, Vol. I, No. 3*) and these examples can only be explained on the basis of the first view point, *viz.*, the coming down of the potentially cold air, an argument which Humphreys does not consider to be admissible. Dr. Normand (*loc. cit.*) has also shown that the explanation of cooling being due to evaporation alone can only hold good in cases of local heat thunderstorms.

The data of the autographic records of these thunderstorms which have been reproduced in *figs. III, VIII and XV* have been examined from the point of view of testing the validity of the above three view points. Although there was no dry and wet bulb thermograph, the wet bulb temperatures have been calculated from the dry bulb thermograph and hair hygrograph to get an approximate idea about the probable nature of air masses. These results have been given in the following table :—

TABLE V.

Date.	Time.	Dry bulb.	Wet Bulb.	Vapour Pressure.
	H.—M.	°F.	°F.	″
20th October 1930	18—00	86·0	68·2	·50
	18—30	85·5	69·4	·55
	19—00	85·3	69·6	·56
	19—05	85·2	69·3	·55
	19—14	78·0	62·1	·39
	19—20	72·9	64·4	·52
	19—24	69·0	65·7	·60
	19—30	75·0	68·7	·64
	19—33	69·0	64·8	·57
	19—45	70·0	66·2	·61
	20—00	72·0	65·1	·55
2nd September 1930	13—30	83·5	72·3	·68
	13—45	84·5	71·6	·64
	14—00	83·0	74·7	·78
	14—15	81·0	74·7	·80
	14—30	80·0	74·8	·81
	14—45	78·0	77·0	·93
21st October 1930	16—00	89·0	72·3	·62
	16—30	87·0	74·7	·73
	16—45	79·0	70·5	·66
	17—00	71·0	70·0	·73
	17—07	71·0	70·0	·73
	17—15	68·0	66·9	·65

It will be seen from the above table that on 20th October 1930 and 21st October 1930, with the falling of the dry bulb in the beginning, the wet bulb also fell, thus showing that the initial fall in temperature in these cases was due to the coming of a potentially cold air mass. It also appears from the vapour pressure values that the air which descends in the beginning is relatively drier. On 2nd September 1930, we, however, find that, although the dry bulb fell, the wet bulb rose. From *fig. VIII* we also find that wind was coming from a WSWly direction since 1-45 P.M. The fall in dry bulb temperature is also seen to be gradual and not rapid as in other cases. The rise in wet bulb temperature and the fall in dry bulb temperature are apparently associated with the coming of cool moist air (higher vapour pressure as seen from *Table V*) from the direction of the Western Ghats.

(*b*) *Rise in Temperature during a thunderstorm when it is raining.*

From the autographic records of the thunderstorm on 20th October 1930, *fig. III*, we find that between 7-24 P.M., and 7-30 P.M., although it was raining, the dry bulb rose by 6°F. and relative humidity decreased by 11 per cent. The autographic records of 14th April 1930, *fig. VI*, also show a very sudden rise in temperature of 5°F. in spite of the fact that it was raining heavily. Unfortunately the hair hygrograph on that day (14th April 1930) went out of order during the thunderstorm and hence it is not possible to get an accurate idea about the corresponding change in relative humidity. From *Table V* we find that on 20th October 1930 this rise in the dry bulb also corresponds to a rise in the wet bulb and an increase in vapour pressure, the rise in the wet bulb being of the order of 7°F. Mr. Sohoni (*loc. cit., fig. 7*) has given an example in which also the dry bulb temperature rose during a thunderstorm. In the case given by him, the wet bulb, however, fell. He says that such cases were associated with little or no rain. The behaviour of dry and wet bulb thermometers in such cases can probably be explained on the assumption that the dry cold air descends and in doing so is adiabatically heated up. The consequences will be a rise in dry bulb and a fall in wet bulb temperature. The rise in dry bulb will be specially marked owing to absence of cooling due to precipitation. The same explanation can not, however, be applied in the case considered here, because wet bulb temperature has also risen. The changes in the present case can be explained on the basis of the following assumptions :—

While a potentially cold and drier air mass is descending through the region where condensation is taking place, it has brought with it some air from the level of condensation ; this air being warmer and moister than the originally descending air mass, the consequences would be a rise in both dry and wet bulb temperatures and an increase in vapour pressure. This rise will stop no sooner the main descending air mass, (potentially cold), asserts its influence. The fact that when the dry bulb was maximum, the wet bulb was more or less the same as the wet bulb of the ascending air mass (about 69°F.) supports the assumptions made above. The dry bulb did not rise to the same value as that of the originally ascending air mass (about 85°F.) because the air got cooled by evaporation of rain drops.

Discussion.

From *Table I*, we find that thunderstorms occurred in Poona at any time of the year and that generally one particular type of thunderstorm was not confined to any particular season (except for the limitations indicated on page 113). We have seen that the thunderstorms considered here have been produced by one or the other of the following three mechanisms (*cf.* Humphreys' " Physics of the Air ", 1929 edition, p. 309) :—

1. Strong surface heating (generally southwesterly type),
2. The undercutting and consequent uplift of a moist current of air by a dense layer (northwesterly and northeasterly types),
3. The overrunning of a moist layer of air by a cold layer of air (generally southeasterly or southwesterly, but sometimes also northwesterly).

From the discussion of his results, it appears that Eliot (*loc. cit.*) did not consider the third condition given above as capable of producing vertical currents. This third condition can exist in any season, winter, summer or monsoon months ; in the last named season, however, the chances will be less due to the greater depth of the moist current (southwest monsoon current).

Table I further shows that thunderstorms of a southwesterly type occur generally earlier during the afternoon than those of the other types and that the time of their occurrence is very near the time of the maximum temperature. It may be that surface heating also plays a greater part in producing convection in this case than in other cases. We also find that the rain giving capacity of the southeasterly and southwesterly type of thunderstorms is generally more than those of other types and that the northeasterly type of thunderstorms generally give a small amount of precipitation. As for the wind velocity during the different types of thunderstorms, it appears that the velocity is relatively smallest in the northwesterly type.

Conclusions.

(A) The conditions favourable for occurrence of thunderstorms in Poona as brought out by the study of thunderstorms there in the year 1930 can be summed up as under :—

(1) Winds having a Sly component from the surface up to 3 or 4 km. or between 1 and 4 km., the winds above this height having a Nly component and being potentially colder and relatively drier or practically dry, with surface temperature (*a*) above normal, (*b*) normal, or even slightly lower.

(2) Winds with Sly component from surface upwards to 6 km. or even higher and surface temperature above normal.

The depth of the Sly component generally increases with the advance of the day. The rain giving capacity of the thunderstorms will depend upon the strength of the Nly. component and the depth of the Sly component.

The presence of any of the conditions (1) or (2) mentioned above in the morning on any day can be taken as indicating the possibility of a thunderstorm that afternoon.

(B) When conditions mentioned in *1* (*a*) in (*A*) above existed the thunderstorm had a greater tendency to be of a southwesterly type.

When conditions mentioned in *1* (*b*) in (*A*) above existed the thunderstorms were either of a southeasterly or southwesterly type in most of the cases ; in some cases they were even of northwesterly or northeasterly types.

When conditions were as mentioned in *1* (*b*) in (*A*) above but the Nly. component above 3 or 4 km. was weak, the thunderstorm was in most of the cases of a northeasterly type.

When conditions mentioned in *2* in (*A*) above were present the thunderstorm was generally of a northwesterly type in a season of marked sea-breeze in Poona.

It may be pointed out here that if on any day in the morning the winds had a ly. component right upto 6 km. or above and surface temperature was normal or elow it, a thunderstorm did not generally occur on that day.

The direction of the slope of the surface of discontinuity between the moist and the potentially cold dry air currents in the neighbourhood of Poona can also probably help in deciding the type of any individual thunderstorm.

I have great pleasure in thanking Dr. K. R. Ramanathan for criticising the paper. I also wish to thank Mr. S. Basu and Dr. Sobhag Mal for some useful suggestions.

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BY

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and
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A STUDY OF THE STRUCTURE OF THE BAY STORM OF NOVEMBER 1926.

BY

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and

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(Received on 18th March 1931.)

Summary.—The authors have analysed a storm which formed in the Bay of Bengal in November 1926. The study is specially interesting in view of the fact that the structure of the storm resembles one of middle latitudes discussed by J. Bjerknes in which he finds " back-bent occlusion " acting as another cold front ; the characteristics of the different fronts and sectors in the storm are described.

The storm tracks compiled by Dr. Normand (1) show that generally in the month of November storms originating to the east and in the neighbourhood of Ceylon travel northwestwards, the cases of those travelling northeastwards being very few. The study of the present cyclone (2) was taken up with a view to find out the causes of its unusual movement in a northeasterly direction and whether it had a structure similar to those of middle latitudes.

Brief description of the movement of the Cyclone.

Although cyclonic circulation was not established till the 21st, signs of weather becoming disturbed in the southeast of the Bay were noticeable in a strengthening of the upper winds at Port Blair on the 19th and in a gradual increase in the amount of precipitation at Sabang after the 16th, as shown in Table I.

TABLE I.

In 24 hours ending at 8 hrs. on	Amount of precipitation in cents.
18	10
19	25
20	150
21	25

The continuous precipitation at other places in the Bay as reported by ships on the 19th also points to the same fact. The 8 hrs. charts of the 19th to 26th as

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(1) C. W. B. Normand, " Storm tracks in Bay of Bengal ", India Met. Dept., 1925.

(2) A general account of the cyclone is given in the 'Annual Summary' for 1926 published by the India Met. Dept.

well as charts at other hours on some of the days are given in *Figs.* 1 to 17. The shading within the smaller circles indicates the cloud amount, full black representing low cloud and line shading medium or high cloud. The hatchings indicate the probable areas of frontal rain at the time of observation, full lines representing continuous and broken lines passing or occasional rain. The following symbols have been used to denote various fronts and characteristics of weather at the time of observation :—

Warm front	◠◠◠◠◠◠◠◠
Principal cold front	▲▲▲▲▲▲
Secondary cold front	▲ ▲ ▲ ▲
Occlusion	◠▲◠▲◠▲
Drizzle	—+—
Shower	▽
Rain	•
Heavy Rain	⁝
Squally	y
Heavy squalls	yy
Heavy rain squalls	⁝y
Thunderstorm	☈
Frequent	ǁ
Occasional	0
Passing	P

For the land stations, the dry bulb temperature (in degrees F.) and the rainfall (in inches) during the past 24 hours have also been shown in *Figs.* 1 to 17.

The track of the cyclone is given in *Fig.* 18. It will be seen from it, that the region of disturbed weather moved more or less in a northwesterly direction up to the 21st, after which the direction of movement changed to northeast. The broken line corresponds to the stage when the disturbance had not developed into a storm. The storm weakened rapidly while approaching the Arakan coast, and on the 26th morning nothing but a feeble surface of discontinuity was noticeable.

The barometric deficiency at the stations on the Arakan coast when considered with the barometer readings of ships nearest the centre indicate that the pressure deficiency at the centre of the storm on the 25th morning was probably between 0·5″ and 0·6″. It is quite likely that the barometric depth at the centre may have been greater than the above value between the 22nd and the 25th when the storm was most severe.

The origin and development of the disturbance.

The signs of a feeble warm sector near Lat. 4° N. and Long. 94° E. were noticeable on the 19th morning. It is difficult to fix the position of the fronts accurately on that day because of lack of information. However, the movement and the sequence of clouds as well as the upper winds at Port Blair (Table II) show that the warm front had already begun affecting that place in higher .evels on the 18th.

TABLE II.

Date.	Time. (Hrs.)	0·5 km. above station		1 km. a. s .1		2 km. a. s. 1		3 km. a. s. 1		4 km. a. s. 1		6 km. a. s. 1		Clouds.		
		D*	V*	D	V	D	V	D	V	D	V	D	V	D	Kind.	Amount.
16	7	85	6	95	9	100	6	105	9½	95	8	..		80	Cu-Nb	10
														115	Ci	
17	6	60	7½	80	7	90	5	80	6	75	8½	50	9½	..	..	..
	16	40	6½	55	6	..		..		..		..		40	Cu-Nb	5
18	7	45	7½	55	9	80	9	95	11	..		..		SE	Ci	
19	7	65	11	70	14½	80	14	85	15½	85	17	..		65	Cu-Nb	10
														155	Ci-St	
20	7	70	15	90	16½	95	17	..		..		..		..	..	..

S. S. "Holland Maru" (Lat. 1°47′ N. and Long. 88° 46′ E.) and S. S. "Alipore" (Lat. 5° 35′ N. and Long. 99° 18′ E.) were also experiencing light rain at 8 hrs. on the 19th morning. The development of the warm sector in this case was probably due to an incursion of a tongue of warm and moist southeasterly air in the cold easterly to northeasterly air of land origin.

The movement of the warm sector during that day is shown by continuous precipitation at Sabang (1½″) and Car Nicobar (2″) and the veering of upper winds at 1, 2 and 3 km. at Port Blair on the 20th morning as seen from Table II above This veering of the upper winds at Port Blair also indicates that the warm front had already reached that place at 2 km. and above, a fact further supported by rainfall at Port Blair during late that night and early next morning.

On the morning of the 20th, the area of rainfall had also increased. This was probably due to a strengthening of the northeasterly winds in the west half of the Bay and an extension of the warm sector in the upper air over that area, the warm sector getting also strengthened by the continuous supply of warm and moist winds.

An idea about the position of the warm front on the 21st morning is given by the amount of precipitation on the 20th at Sabang which had decreased since the previous day, showing thereby that the station was in the warm sector for the most part of the 20th. Comparison of the rainfall at Car Nicobar (Table III) on the 20th, 21st and 22nd shows that the warm front had passed that station by some time between 8 and 19 hrs. on the 21st.

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*D—denotes direction and V—velocity of the wind in metres/sec.

TABLE III.

In 24 hours from	Amount of precipitation in cents.
8 hrs. 20th to 8 hrs. 21st	400
8 hrs. 21st to 8 hrs. 22nd	300
8 hrs. 22nd to 8 hrs. 23rd	25

The existence of another front between S-ly to SSE-ly and SW-ly winds on the 21st morning is evident from the log of S. S. "Alipore" (see Appendix). The wind shift and changes in the characteristics of weather experienced by this ship between 8 hrs. and 16 hrs. on that day indicate definitely that she was crossing a front and entering a sector which had quite different properties from those of the sector in which she was before. The characteristics of the different sectors will be discussed later.

The movement of the region of disturbed weather from the 19th to 21st morning, as seen from *Figs.* 1 to 3, was more or less in the direction of movement of the air in the warm sector. This agrees well with the investigations of movement of cyclones of temperate latitudes by Bjerknes and Solberg (1) and by Palmén (2), and the cyclones of lower latitudes by Ramanathan and Narayana Iyer (3). The movement of the present disturbance also agrees well with the upper winds in the warm sector up to cirrus level in conformity with Hesselberg's (4) conclusions about the movement of cyclones of European latitudes.

With the strengthening of the westerlies and the northeasterlies in the west half of the Bay and the development of a sector with SW-ly winds, the disturbance intensified rapidly. S. S. "Badarpur" (Rangoon to Karachi 8 hrs. position Lat 9° 52′ N. and Long. 86° 18′ E.) experienced ENE wind with overcast sky and drizzle at 4 hrs., ESE wind with occasional heavy rain squalls at 8 hrs., showery weather with SSE-ly to S-ly wind between 8 and 16 hrs. and WSW wind with occasional squalls at 20 hrs. These wind shifts together with strong winds experiences by S. S. "Alipore" after 12 hrs. on the 21st indicate that a storm had formed by that evening.

The position of the warm front at 8 hrs. on the 22nd can be fixed by—

(1) A veer in the wind at Port Blair since the previous day (SSE from E)

(2) A rise in the dry bulb temperature at Port Blair from 79°F. to 82°F. (See Table IV).

(3) Continuous precipitation at Port Blair (2″) since the 21st morning.

(4) Heavy rain squalls experienced by S. S. "Singu" after 8 A.M. on the 21st and by S. S. "Chindwara" after 8 A.M. on the 22nd (Logs are given in the Appendix). The squally character of the weather is an indication of the approach and passage of the warm front (5).

TABLE IV.

Day.	22	23	24	25	26
Dry Bulb	79·0	82·0	82·0	81·0	77·6
Wet Bulb	77·4	78·0	78·2	74·2	75·0

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(1) Bjerknes and Solberg—Geof. Pub., Oslo., Vol. III, No. 1.

(2) E. Palmén—Soc. Scient. Fennica Comment. Phys. Math. II, Helsingfors, 1923.

(3) Ramanathan and Iyer—Ind. Met. Dept., Scientific Notes, Vol. III, No. 18, p. 8.

(4) Th. Hesselberg, Die Luftbahnen im Cirrusniveau, Geoph. Institut. Leipzig, 2. Serie, Bandi, Heft 2.

(5) Ramanathan and Iyer, *loc. cit.* p. 9.

The position of the front separating the sector of southerlies to southeasterlies from the sector of southwesterlies is defined by the weather experienced by S. S. "Aungban" and S. S. "Indo Maru". The former steamer experienced squally weather at 8 hrs. and the latter S-ly wind (force 6) near Lat. 5°47′N. and Long. 90°57′E. at 8 hrs. on the 22nd and a SW-ly wind (force 7) with occasional rain squalls 4 hrs. later near Lat. 5°47′N. and Long. 90°27′E., showing that both these steamers were approaching the front. Squally weather is one of the characteristics of the southerwesterly wind sector as will be shown later.

S. S. "Alipore" (Singapore to Colombo), 8 hrs. position on 22nd Lat. 6°19′N and Long. 87°47′E., was experiencing SW-ly winds (force, 7-8, see Log in the Appendix), while S. S. "Chyebassa" (Rangoon to Bombay), 8 hrs. position on the same day Lat. 6°06′N. and Long. 87°E., was having a W-ly wind force 6. These wind changes as well as the change of weather experienced by S. S. "Alipore" indicate the presence of a third front on this morning separating the SW-ly wind sector from the W-ly wind sector. The position of this front has been shown in the 8 hrs. and also in the 3 hrs. chart (***Figs.*** 5 & 6) of the 22nd. Its position on the 21st could not be located exactly for want of ships' observations in that area; but it is most likely that it developed some time by the 21st morning and its probable position has been indicated by the broken line in ***Figs.*** 3 & 4.

The position of the warm front at 8 hrs. on the 23rd can be fixed by—

(1) A rise in dry bulb temperature by 4°F. at Diamond Island between 8 hrs. on the 22nd and the 23rd.

(2) 1″ rain each at Diamond Island and Rangoon on 22nd-23rd night. Neither of these stations had any rain before.

(3) Rain squalls experienced by S. S. "Chilka" after 12 hrs. on the 23rd (Log given in the Appendix).

The position of the front separating the region of southerlies from that of the southwesterlies is defined by—

(1) Veering and strengthening of the wind of S. S. "Singu" after 8 hrs.

(2) Veering and strengthening of winds of S. S "Chindwara" after 12 hours.

Upper winds at Port Blair on the 23rd morning were strong SSE-ly up to 1 km. and Nimbus was also moving from the same direction, showing that the SW-ly winds had not still arrived at those levels.

The position of the third front is fixed with the help of—

(1) *a*. Sequence of weather experienced by S. S. "Alipore"

b. A veering in her wind after 16 hrs. of the 22nd.

(2) Veering and weakening of the wind experienced by S. S. "Aungban" between 8 hrs. of the 23rd and the 24th (from WSW force 11 to W force 7).

Tables V, VI and VII give the dry bulb, wet bulb and the amount of rainfall recorded at 8 hrs. on different days as well as the times of occurrence of rainfall during the previous 24 hours at Rangoon, Kyaukpyu and Akyab.

TABLE V.

Rangoon.

Day.	23	24	25
Dry Bulb	76·4	77·0	83
Wet Bulb	75·1	76·0	77
Rainfall in cents	103	164	13
Time of occurrence	22nd-23rd night	cont. rain between 8 hrs. 23rd and 24th.	during day time on 24th.

TABLE VI.

Kyaukpyu.

Day.	24	25	26
Dry Bulb	72·2	76·8	73·6
Wet Bulb	71·9	76·5	73·2
Rainfall in cents	455	135	423
Time of occurrence	cont. rain between 8 hrs. 23rd and 24th.	cont. rain between 8 hrs. 24th and 25th.	cont. rain between 8 hrs. 25th and 26th.

TABLE VII.

Akyab.

Day.	24	25	26
Dry Bulb	73·0	78·1	75·3
Wet Bulb	72·1	72·2	72·2
Rainfall in cents	311	244	223
Time of occurrence	cont. rain between 8 hrs. 23rd and 24th.	intermittent rain during past 24 hrs.	occasional rain during past 24 hrs.

The sequence of weather as well as the rise in the dry bulb (Table V) indicate that the warm front passed Rangoon some time between 8 hrs. on the 23rd and the 24th. The heavy falls at Kyaukpyu (Table VI) and Akyab (Table VII) during 24 hours ending at 8 hrs. on the 24th are apparently due to the nearness of the warm front as well as of the Arakan hills to these two stations. S. S. "Chilka", bound for Rangoon, experienced heavy rain and frequent hard squalls (see Appendix) after 12 hrs. of the 23rd as she was approaching the warm front. As shown by a veer in her wind, she passed the warm front at about 20 hrs. on the 23rd.

Port Blair again began to get more rain (2″ in 24 hours ending at 8 hrs. on the 24th) due to the nearness of the front separating the SW-ly air sector from the warm sector. This front actually passed Port Blair some time between 8 hrs. and 19 hrs. on the 24th as seen by—

(1) A veer in wind from S to SW.

(2) Sequence of weather—cessation of rain and decrease of cloud.

The SW-ly winds in the upper layers had already arrived at Port Blair before 8 hrs. on the 24th as shown by the movement of Nimbus (from SSW) at that time.

The veering and the weakening of the wind experienced by S. S. "Singu" after 16 hrs. on the 24th and by S. S. "Chindwara" after 12 hours on the same day help one to fix the position of the third front. Due to the northeastward movement of the storm, this front did not show itself at all at Port Blair.

It has been shown already that the front separating the SW-air sector from the warm sector passed Port Blair between 8 hrs. and 19 hrs. on the 24th. When we consider along with this fact the changes in the dry bulb and wet bulb temperatures at Port Blair recorded at 8 hrs. each day from the 22nd to 26th (see Table IV) an interesting feature is revealed. We find that during the 24 hrs. ending at 8 hrs. on the 25th the dry bulb had only fallen by 1°F., but the wet bulb fell by 4°F. This indicates that at Port Blair, after the passage of the cold front (separating SW-air sector and warm sector), an air mass had arrived which, though only slightly cooler than the air mass there on the 24th morning, was distinctly drier. The existence of a slightly colder air behind the primary cold front has been explained as being due to subsidence taking place at the foremost part of the advancing cold wedge resulting in a dividing up of the cold front into two(1). The air between the two cold fronts would have a temperature between that of the cold and warm currents. The greater the height from which the air had descended, the warmer it would be and the smaller the temperature contrast at the original cold front. This is exhibited in the present case by Port Blair, which while in the warm sector registered a temperature of 82°F. (8 hrs. 24th), and 81°F. (25th morning) just after the passage of the cold front. The temperature contrast has, therefore, been almost completely transferred to the second front which separates the descended cold air from the horizontally moving main cold current as shown in the present instance by a further fall of about 3°F in the dry bulb at Port Blair (77·6° at 8 hrs. on the 26th). On a hygrogram the air between the two cold fronts ought to appear drier than the air on both sides. This is shown in the present case by the successive changes in the dry and wet bulb temperature at Port Blair, the colder air at 8 hrs. on the 26th being moister than the descending air preceding it.

On the above diagnosis, the probable position of the secondary cold front has been shown in *Figs.* 12-15. There are, however, no more temperature or other available data to support this analysis.

The position of the warm front on the 25th morning is indicated by a rise in the dry bulb (about 5°F.) at Kyaukpyu and Akyab and the sequence of weather at these two places during the previous 24 hrs. (Tables VI and VII).

With the weakening of the SW-ly current, the northwesterly cold air mass began to move rapidly and the storm began to weaken thereafter. The weakening was presumably due to the cutting off of the supply of southwesterly air.

By the 26th morning, the storm had weakened rapidly and a shallow diffused low lay at 8 hrs. off the Arakan coast. No well defined fronts could be traced at that time, probably due to the disturbance having got occluded. What was left was a line of discontinuity of winds along which widespread rain had occurred during the previous 24 hrs.

Upper winds at Port Blair, which were SW-ly (about 30 m.p.h.) up to alto-cumulus level on the 25th morning, became light variable up to 1 km. and SW-ly (about 15 m.p.h.) above, up to 4 km. This also indicates the occlusion having taken place. On that morning, there were also indications of the seasonal low being established in the south of the Bay as seen by $\frac{1}{4}''$ of rain at Sabang.

General.

From our study of the present storm, we find that in its initial stages it consisted of two air currents of different temperatures, the warm and moist being represented by S-ly to SE-ly air and the cold by E-ly to NE-ly air. The tongue of warm air protruded into the cold air mass giving rise to a warm sector which had well defined surfaces of discontinuity [*Fig.* 19(*a*)] running through the centre of low pressure. The

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(1) J. Bjerknes,—Practical examples of Polar Front analysis—London Meteorological Office, Geoph. Memoirs No. 50. Page 13. Also R. S. Read,—Q. J. Roy, Met. Soc. Oct. 1925. Page 416.

direction of movement of the disturbance till it had developed into a cyclone (up to 21st morning) was the same as that of the air in the warm sector. During its northwestward movement, the disturbance was gradually strengthening due to its approaching the land, the distribution of land and water helping to make the contrast between the two air masses more marked than before.

J. Bjerknes and Solberg(¹) have pointed out that if a secondary cold front has a temperature and wind contrast much greater than that at the foremost boundary of the cold air, all the air contained between the warm front and the strong secondary cold front may act as a single large warm sector. This artificial enlargement of the warm sector means a greater store of potential energy and enables the cyclone to increase its kinetic energy. The appearance of a strong secondary cold front, therefore, indicates a reinforcement of the cyclone. In fact, even the occluded and apparently dying cyclones may get reinforced with the appearance of such a strong secondary cold front.

In the present case, we find that the disturbance intensified into a storm on the 21st with the appearance [*Fig.* 19(b)] of a second cold front separating the region of southwesterlies from that of the westerlies. The second cold front had a greater temperature and wind contrast than at the foremost boundary of the cold air. As this front did not pass Port Blair, only indirect evidence is available in support of the above statement. The W-ly air, the source of which should be traced to the neighbourhood of the Circars and the Orissa coast, would probably have a temperature of about 73°F. as shown by the temperatures recorded at the coast stations in that region from the 24th onwards; the SW-ly air, on the other hand, had a temperature of about 77·6°F. as recorded at Port Blair, which was in the SW-ly sector on the 26th morning. Hence the W-ly air was probably colder by about 5°F. than the SW-ly air. It has been shown already that the temperature contrast was only 1°F. at the foremost boundary of the cold air. The intensification of the disturbance on the 21st, therefore, seems to be due to the artificial enlargement of the warm sector in a manner pointed out by J. Bjerknes and Solberg(¹). In this connection, it is also interesting to note that as soon as the artificial enlargement of the original warm sector could not be maintained due to the cutting off of the supply of southwesterly air, the storm dissipated very rapidly as pointed out before.

Surface air trajectories in the Bay from the 21st to 25th drawn independently by Mr. S. Basu are reproduced in *Figs.* 20 to 24. They support very strikingly the facts discussed in this paper, *viz.*, that after the 21st morning the storm consisted of three different sectors, the air masses within each having different properties owing to their travel over different regions. These trajectories were drawn from 4 hourly observations of winds reported by ships in their logs and on the same lines as adopted by Shaw and Lempfert in their paper on " Life History of Surface Air Currents ".

Although during its initial stages the propagation of the cyclone had a close relation with the direction of the wind at the surface in the warm sector (in this case S to SE-ly), in the latter stages, however, it happened to agree with the wind direction in the SW-ly sector. This change in the direction after the 21st morning seems to be probably due to the arrival of the southwesterly air.

The foregoing considerations show that the structure of the storm was probably similar to that of the middle latitudes in which the front formed at the top of a backbent occlusion acts as an additional cold front(²).

(¹) Bjerknes and Solberg,—*loc. cit.*

(²) J. Bjerknes,—*loc. cit.*

The characteristics of the three different sectors as well as of the surfaces of discontinuity separating one from the other in this storm can briefly be summarised as under :—

1\. (*a*) *Tropical* Warm Front.*—This surface of discontinuity resembles the warm front of the cyclones of the middle latitudes in so far as the nature of the precipitation at this front is concerned. The precipitation is, however, more intense. We also find that with the approach and passage of this surface of discontinuity, squally weather, which is absent in the European cyclones, is experienced commonly.

(*b*) *Tropical Warm Sector.*—The characteristics of this sector are occasional light to moderate rain and absence of squalliness.

2\. (*a*) *Tropical Primary Cold Front.*—Heavy squalls often associated with heavy rain are experienced with the approach and the passage of this front. The wind change is sudden and the velocity of the wind increases with the veering of the wind. This front is similar in character to the primary cold front of the European cyclones, the only difference being in the greater intensity of the phenomena and the larger area of rainfall met with here.

(*b*) *Tropical Maritime Cold Sector.*—The characteristics of this sector are the high velocities, of the order of hurricane force, accompanied with frequent heavy squalls with or without rain. The air in this sector resembles in properties the southwest monsoon air, the fresh advance of which gives rise to depressions and storms in the Indian Seas during the monsoon season. In this case, however, in view of the evidence of the wet bulb and dry bulb changes at Port Blair, it seems that the air in this sector was really of northerly origin, but having had a long travel over the sea, probably round the south of the Peninsula, had acquired the properties of fresh monsoon air. The squally character, therefore, seems to be due to the lower layers getting heated by coming in contact with the sea. The temperature difference between the air in this sector and that in the warm sector is small as a result of subsidence at the primary cold front as well as due to the long travel of the air over the sea.

3\. (*a*) *Tropical occluded front acting as second cold front.*—This front has a temperature and wind contrast much greater than that of the primary cold front and probably resembles the second cold front as described by J. Bjerknes(1).

(*b*) *Tropical Continental Cold Sector.*—This resembles the cold sector of the cyclones of middle latitudes, the only difference being the absence of squally weather due to a shorter travel of the cold air over the sea.

The authors wish to express their thanks to Dr. K. R. Ramanathan and Mr. S Basu for their helpful suggestions and criticisms.

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*The word "tropical" is used in order to indicate that there are distinguishing characteristics in the tropics.

(1) See J. Bjerknes,—*loc. cit.*

APPENDIX

"*S. S. Alipore*".

Day.	Hour.	Lat.	Long.	Wind.		Cloud.	Remarks.
				Dir.	Force.		
		N.	E.				
21	4			S/W	4	Overcast.	Moderate S-ly swell; occasional light rain.
	6			S	4	Do.	Moderate S-ly sea and swell; occasional light rain.
	12	6°24′	90°16′	S	7	Do.	Rough S-ly sea and swell; frequent heavy rain squalls.
	16			SW	7	Do.	Considerable SSW-ly sea and swell.
	20			SW	7/8	Do.	Ditto.
	24			SW	7/9	Do.	Considerable SW-ly sea and swell. Frequent violent rain squalls.
22	4			SW	7	Do.	Considerable SW-ly sea and swell. Passing rain squalls.
	8	6°19′	87°47′	SW	7/8	Do.	Considerable SW-ly sea and swell. Passing violent rain squalls.
	12	6°18′	87°17′	SW	7	Do.	Considerable SW-ly sea and swell.
	16			WSW	7	Do.	Considerable SW-ly sea and swell. Passing rain squalls.
	20			SW/W	8/6	Do.	Considerable SW-ly sea and swell.
	24			WSW	6	Cloudy	Ditto.
23	4			WSW	7	Overcast.	Considerable SW-ly sea and swell.
	8	6°00′	85°17′	WSW	7	Cloudy.	Considerable WSW-ly sea and swell.
	12	5°57′	84°53′	WSW	7	Do.	Ditto.
	16			WSW	7	Do.	Considerable head sea and swell.
	20			WSW	4/3	Clear.	Moderate head sea; fine.
	24			W/S	4	Do.	Considerable swell; fine.

S. S. "Singu".

Day.	Hour.	Lat.	Long.	Wind.		Cloud.	Remarks.
				Dir.	Force.		
		N.	E.				
21	12	14°45′	93°53′	ENE	4		Moderate ENE sea.
	16			E	6	Cloudy.	Rough following sea; fine.
	20			SE	6		Rough sea; NE swell; heavy rain squalls.
	24			S/E	6	Cloudy.	Rough sea; heavy S-ly swell.
22	4	13°20′	91°45′	SE	5		Rough sea; heavy SE-ly swell; Heavy rain squalls.
	8			SE	6		Ditto.
	12	13°03′	91°10′	SSE	6		Rough sea; heavy S-ly swell; frequent heavy squalls of rain.
	16			S/E	5		Ditto.
	20			S	5		Rough sea; heavy SSW-ly swell; frequent heavy squalls of rain.
	24			S	5		Rough sea; heavy SSW-ly swell; frequent heavy squalls of rain.
23	4			S	7	Overcast.	Rough sea; heavy S-ly swell.
	8	11°30′	89°39′	S	7		Rough sea; heavy S-ly swell; light showers.
	12			W/S	8	Overcast.	Rough sea; heavy S-ly swell.
	16			SSW	9	cloudy	High sea; heavy swell.
	20			SW/W	9	Do.	Ditto.
	24			SW/W	10	Do.	High sea; very heavy swell; fine.
24	4			SW	10		High sea; very heavy swell.
	8	14°40′	89°29′	SW	10	Cloudy.	High sea; very heavy WSW swell.
	12			SW	10	Do.	Ditto.
	16	10°16′	89°12′	SW	8	Overcast.	Rough sea; heavy swell; fine.
	20			WSW	6		Moderate sea; heavy W-ly swell; clear.
	24			WSW	5	Cloudy.	Moderate sea; heavy W-ly swell.

S. S. "Chindwara"

Day.	Hour.	Lat.	Long.	Wind. Dir.	Wind. Force.	Cloud.	Remarks.
		N.	E.				
22	4			SE/E	4/6	Cloudy.	Moderate rough sea; occasional rain.
	8	13°48′	92°19′	SE	4/6	Overcast.	Rough sea and SSW-ly swell; frequent rain squalls.
	12	13°32′	91°46′	SE	5	Do.	Rough sea and heavy S-ly swell; frequent heavy rain squalls.
	16			SSE	6		Rough sea; dull; occasional sharp rain squalls.
	20			S/E	6	Do.	Rough sea; frequent heavy rain squalls.
	24			SSE	6	Do.	Rough sea and heavy swell; frequent violent squalls.
23	4			SSE	7/8	Cloudy.	Heavy sea and swell.
	8	12°14′	91°10′	S	7/8	Overcast.	Heavy sea and swell; occasional rain squalls.
	12	11°58′	91°03′	S	7/8	Do.	Ditto.
	16			S/W	8	Do.	Heavy sea; occasional rain squalls.
	20			SW/S	8	Do.	Rough high sea and heavy swell; occasional fierce heavy rain squalls.
	24			SSW	8/9	Do.	Very heavy sea and confused swell; occasional rain.
24	4			SSW	9	Do.	Very rough sea; frequent violent rain squalls.
	8	11°39′	90°27′	WSW	10/12	Do.	Very rough sea; high SW-ly swell.
	12	11°35′	90°20′	SW	9	Do.	Rough sea and confused swell.
	16			SW/W	8	Do.	Heavy steep sea; frequent rain squalls.
	20			SW/W	7	Do.	Rough high sea and heavy WSW-ly swell.
	24			SW/W	7	Do.	Rough sea; heavy WSW-ly swell.
25	4			WSW	6/7	Do.	Rough sea and very heavy WSW-ly swell.
	8	10°29′	88°57′	WSW	5	Do.	Ditto
	12	10°16′	88°41′	WSW	5	Do.	Ditto

S. S. "*Chilka*".

Day.	Hour.	Lat.	Long.	Wind. Dir.	Cloud.	Remarks.
		N.	E.			
23	8	16°56′	91°01′	SE		Fresh wind; moderate to rough sea; heavy confused swell.
	12	16°46′	91°30′	SE/E	Overcast.	Strong wind; rough sea; big swell ship labouring and spraying; torrential continuous rain.
	16			SE/E	Do.	Strong wind; rough sea; big swell; frequent hard squalls; torrential rain.
	20			SSE	Do.	Ditto.
	24			SSE	Do.	Strong wind; rough sea, heavy swell; ship labouring and spraying; frequent hard squalls; torrential rain.
24	4			SSE	Do.	Fresh to strong wind and rough sea big swell; frequent heavy rain.
	8	15°56′	93°40′	SSE	Do.	Strong wind, rough sea; big swell; heavy squalls; heavy rain.
	12	15°43′	94°04′	SSE	Do.	Gale, heavy sea and swell; frequent hard squalls; heavy rain.
	16			SE/S	Do.	Gale, heavy sea and swell; occasional rain.
	20			S/E	Do.	Ditto.
	24			SSE	Do.	Strong wind, rough sea, big swell; ship labouring and spraying.
25	4			S	Cloudy	Fresh to strong wind; moderate rough sea; moderate heavy swell; fine.
	8	Rangoon	..	SSE	Cloudy	Light to moderate wind; slight sea; fine.

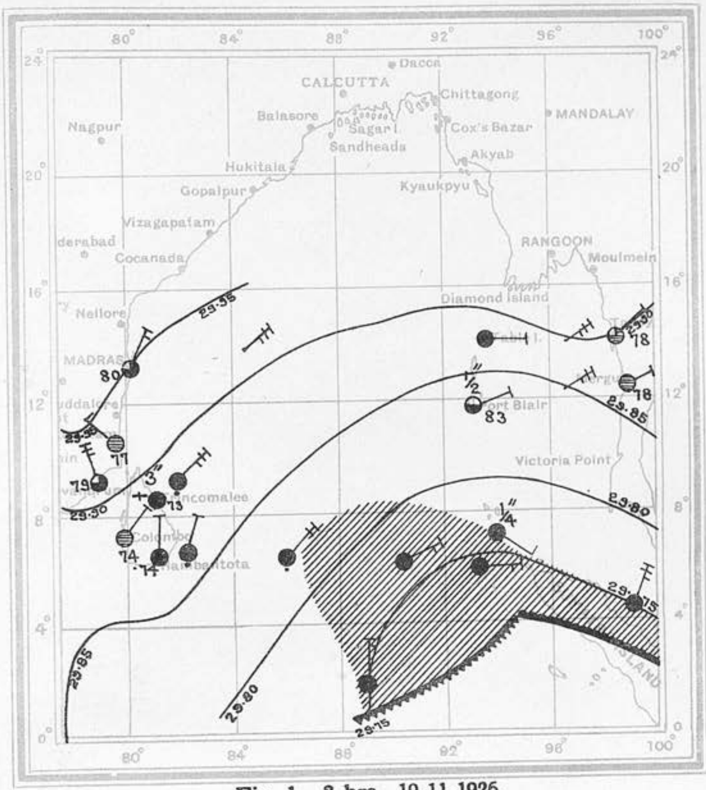

Fig. 1. 8 hrs., 19-11-1926.

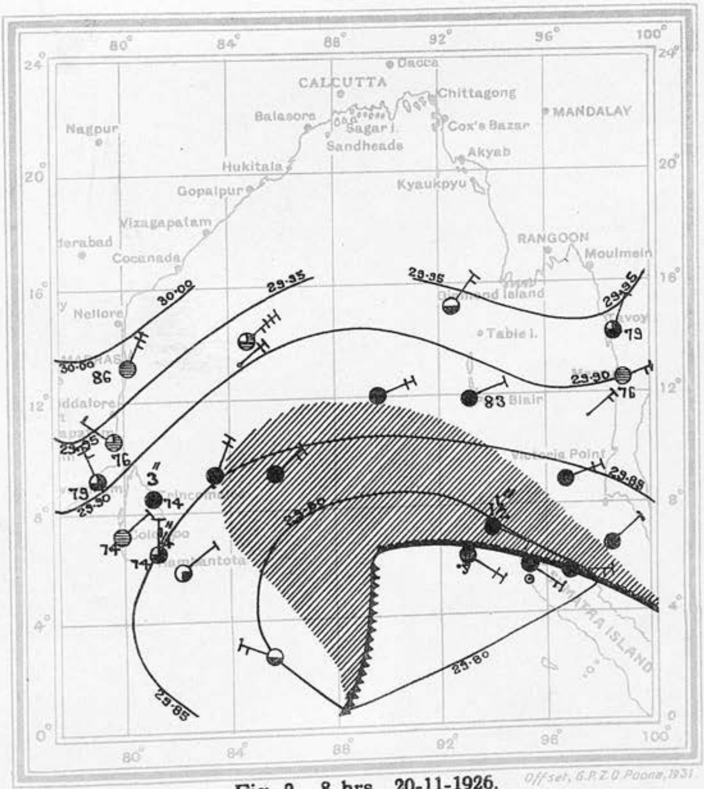

Fig. 2. 8 hrs., 20-11-1926.

Offset, G.P.Z.O. Poona, 1931

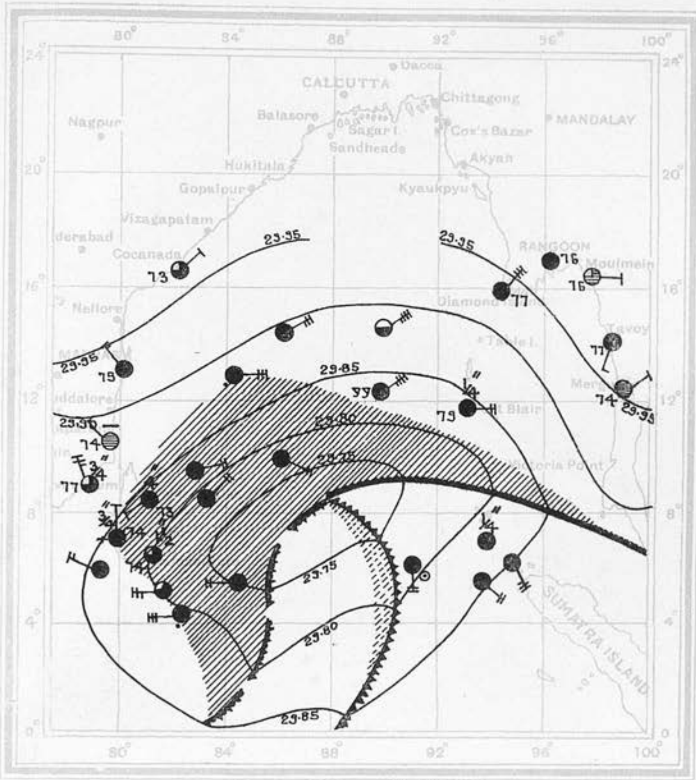

Fig. 3. 8 hrs., 21-11-1926.

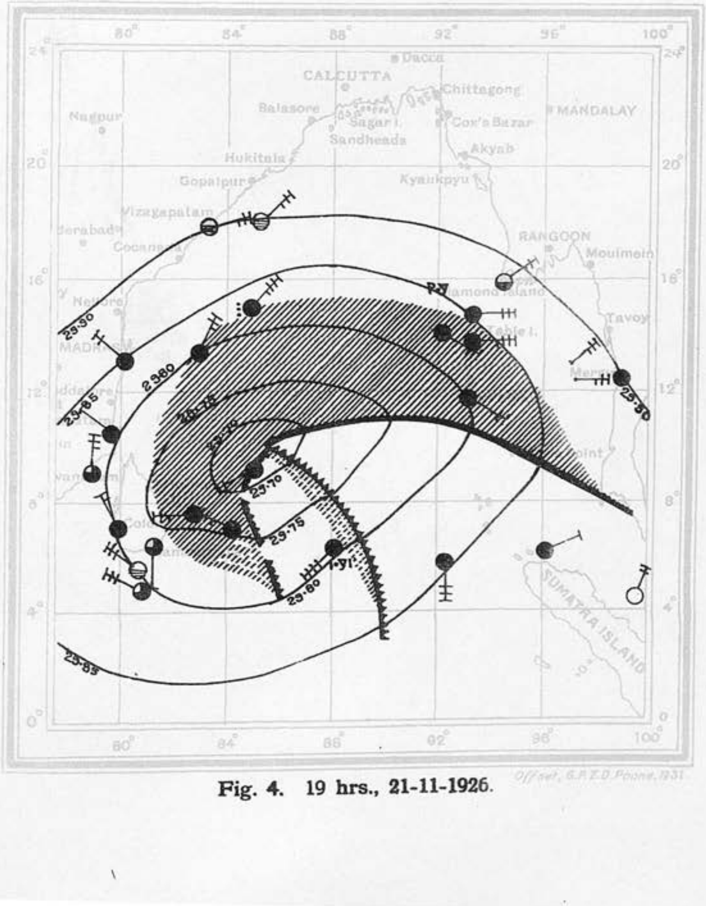

Fig. 4. 19 hrs., 21-11-1926.

Offset, G.P.Z.D. Poona, 1931.

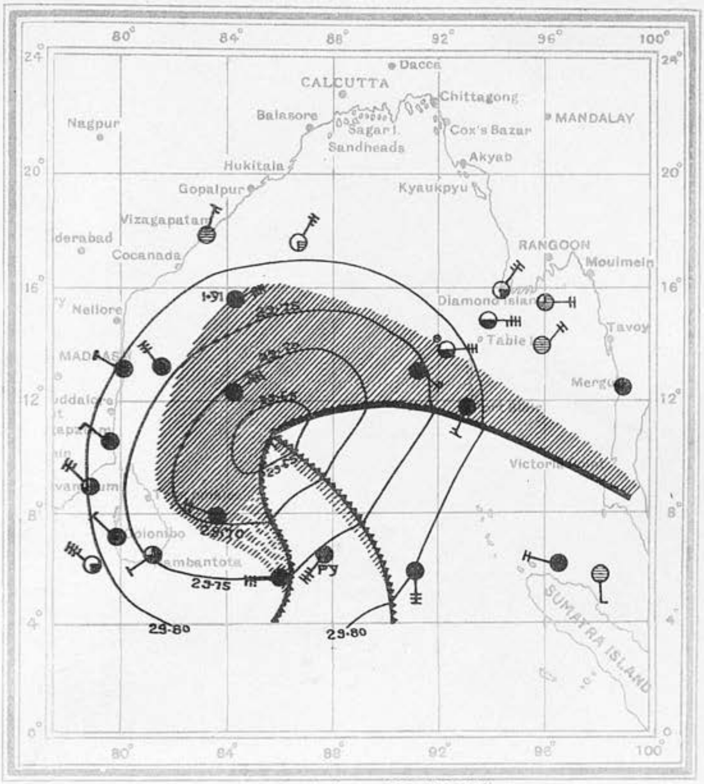

Fig. 5. 3 hrs., 22-11-1926.

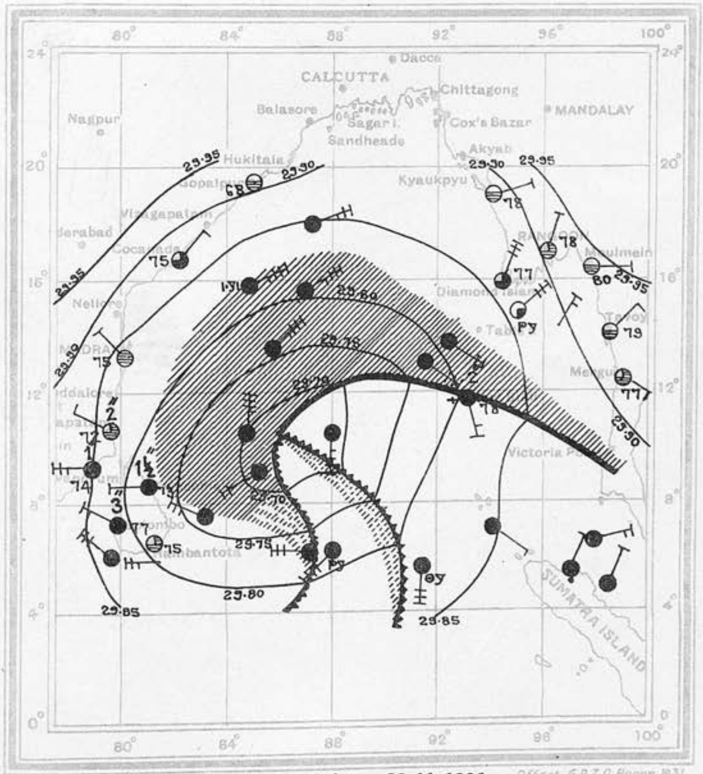

Fig. 6. 8 hrs., 22-11-1926.

Offset, G.P.Z.O. Poona, 1931.

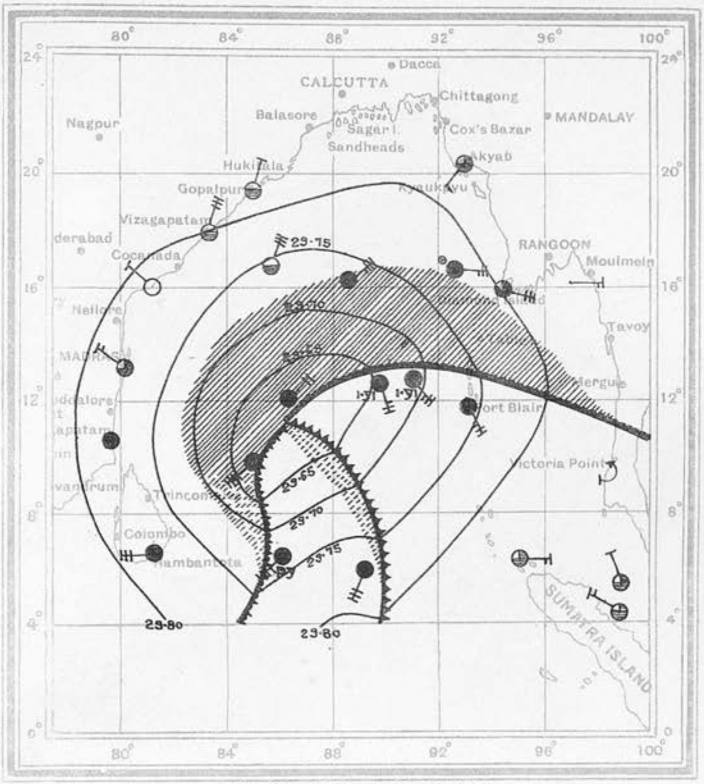

Fig. 7. 19 hrs., 22-11-1926.

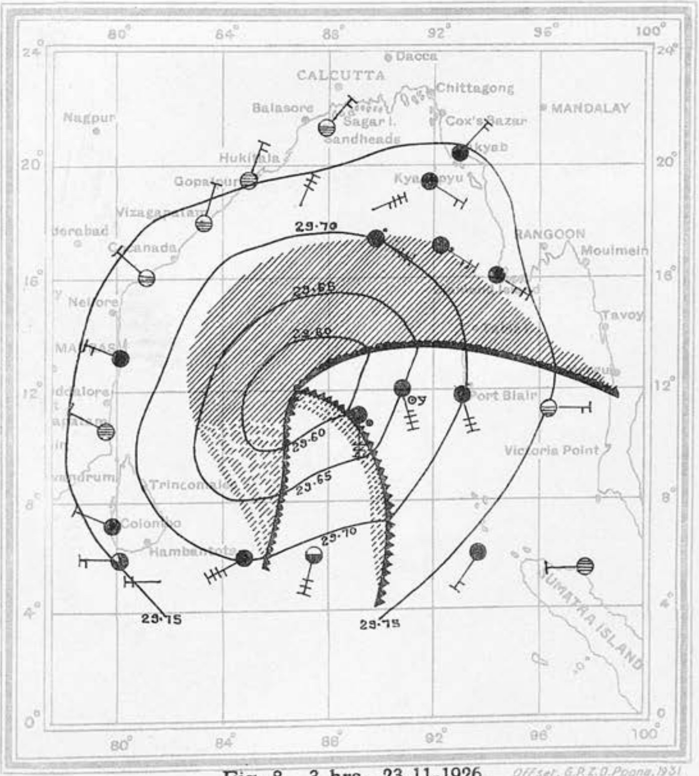

Fig. 8. 3 hrs., 23-11-1926.

Offset, G.P.Z.D.Poona, 1931

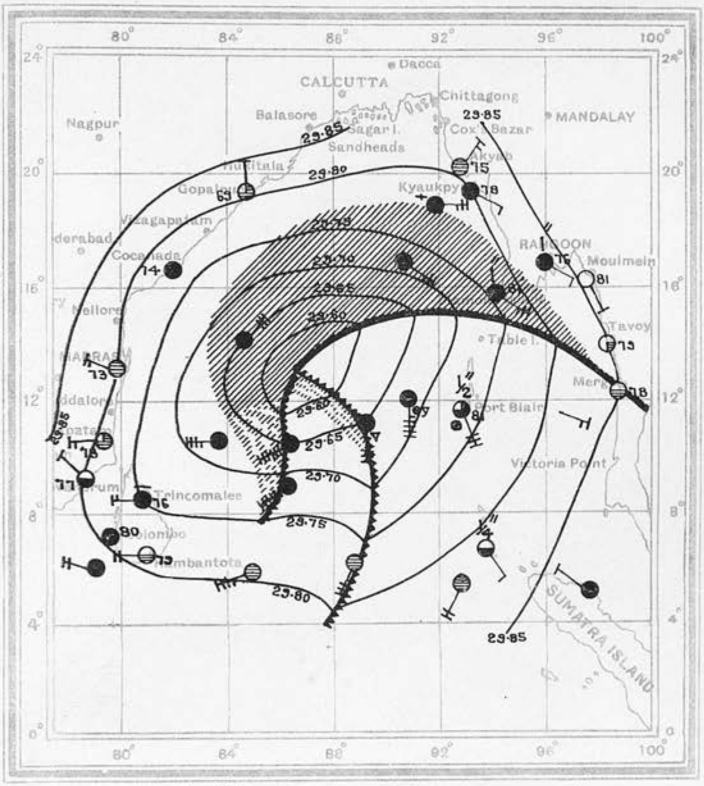

Fig. 9. 8 hrs., 23-11-1926.

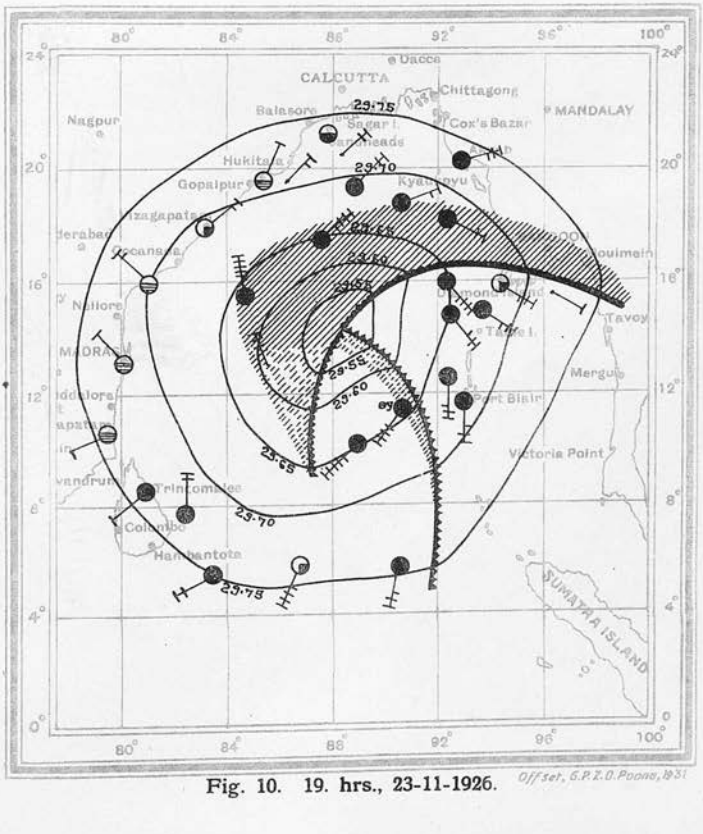

Fig. 10. 19. hrs., 23-11-1926.

Offset, G.P.Z.O.Poona, 1931

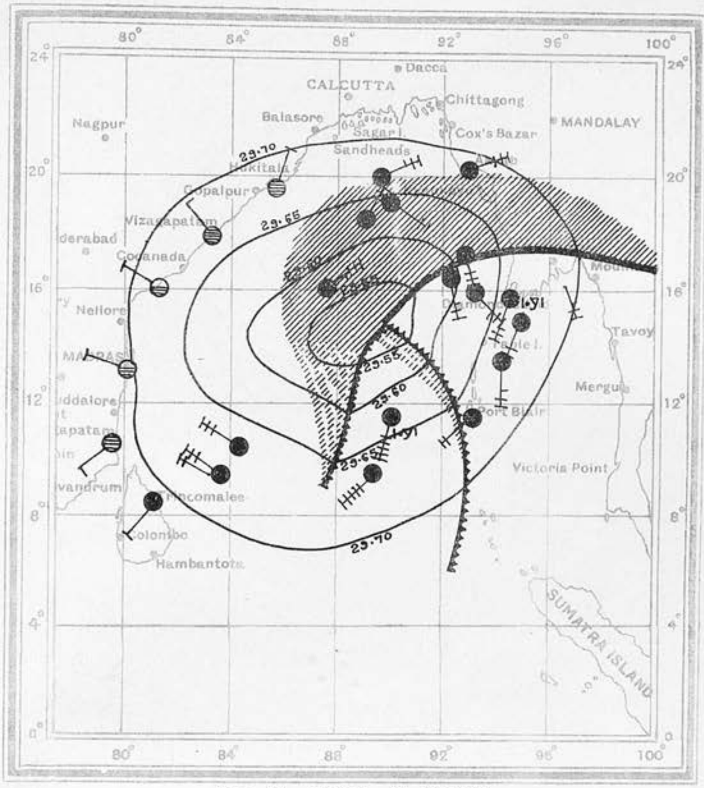

Fig. 11. 3 hrs., 24-11-1926.

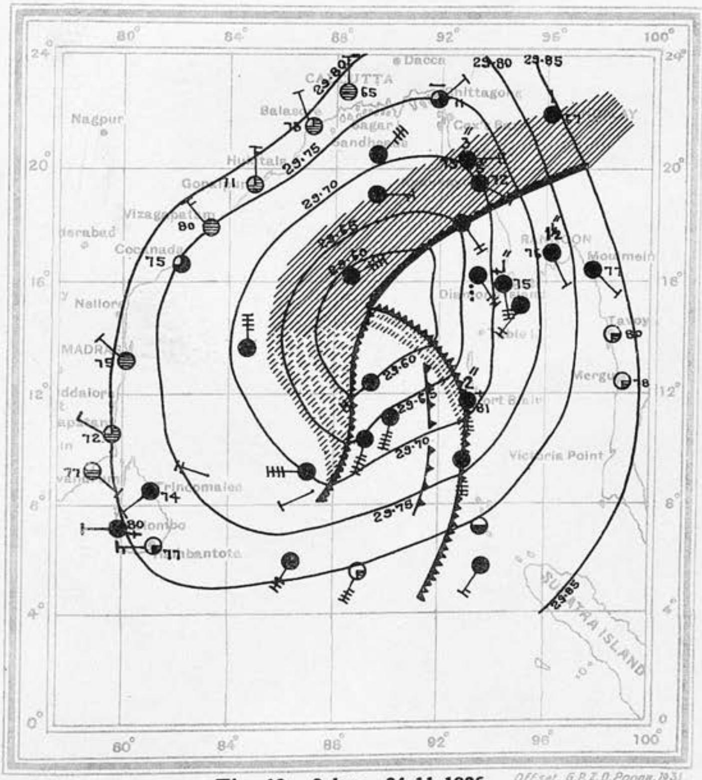

Fig. 12. 8 hrs., 24-11-1926.

Offset, G.P.Z.D.Poona, 1931

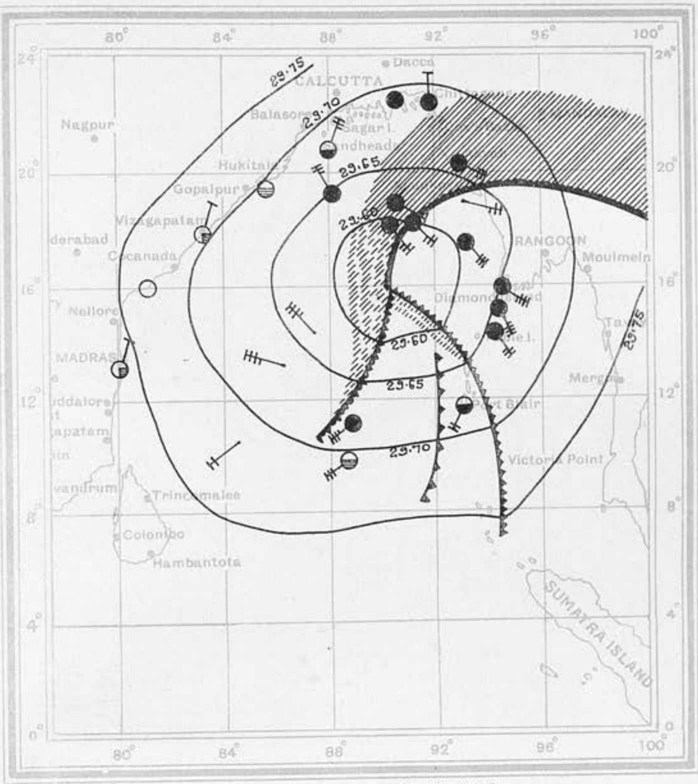

Fig. 13. 19 hrs., 24-11-1926.

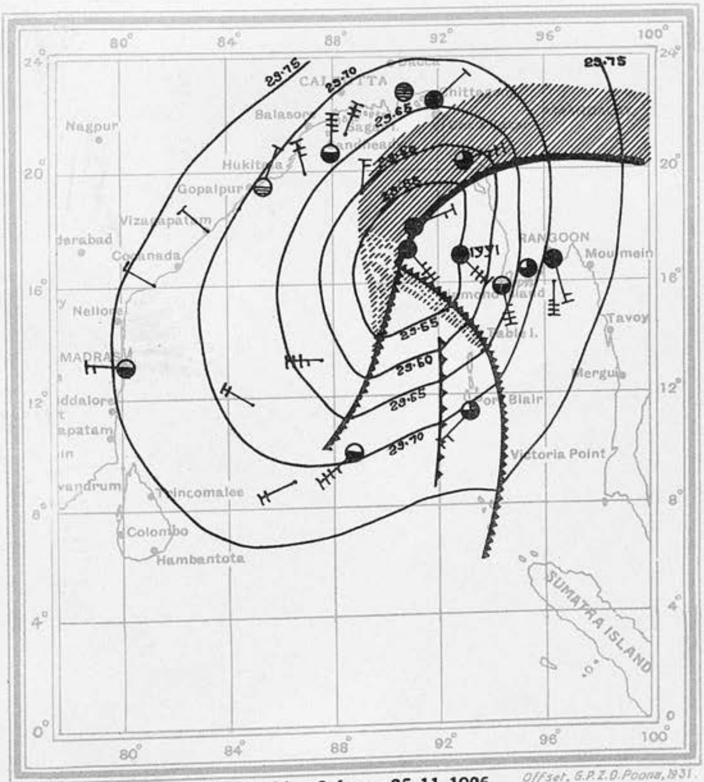

Fig. 14. 3 hrs., 25-11-1926.

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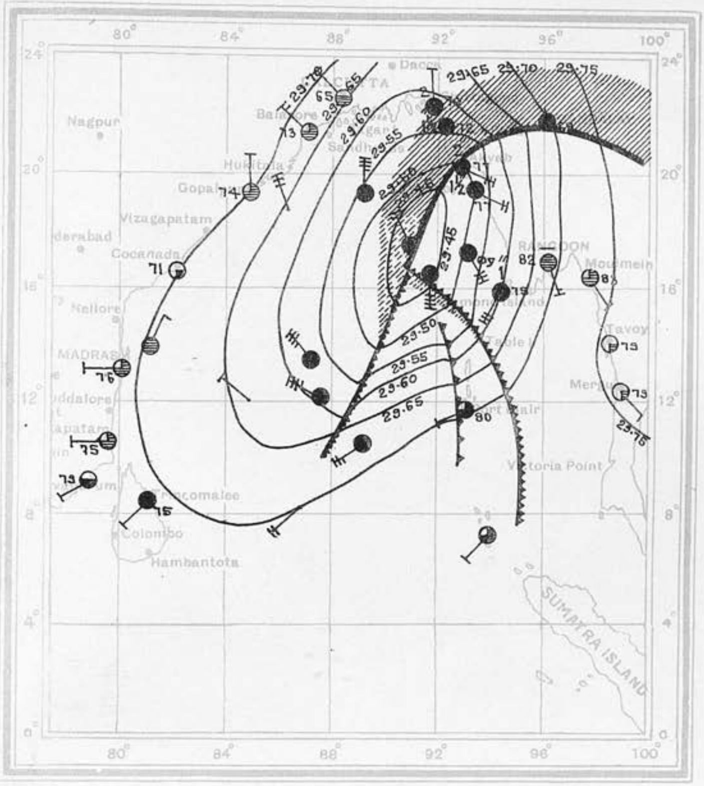

Fig. 15. 8 hrs., 25-11-1926.

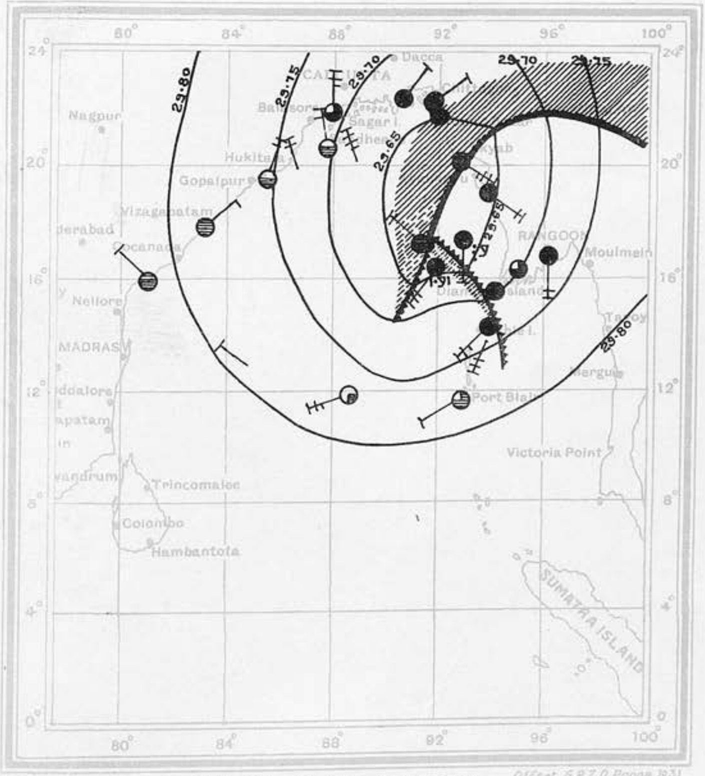

Fig. 16. 11 hrs., 25-11-1926.

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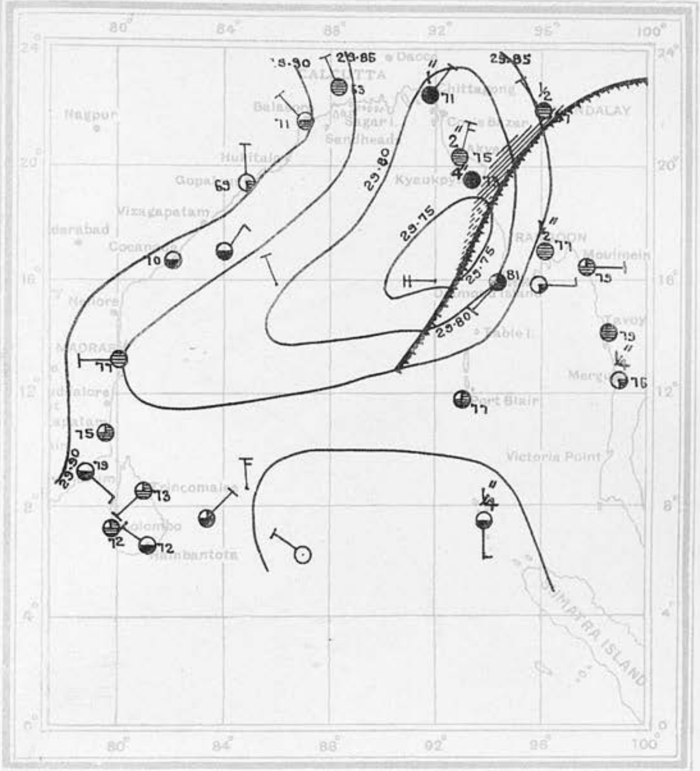


Fig. 17. 8 hrs., 26-11-1926.

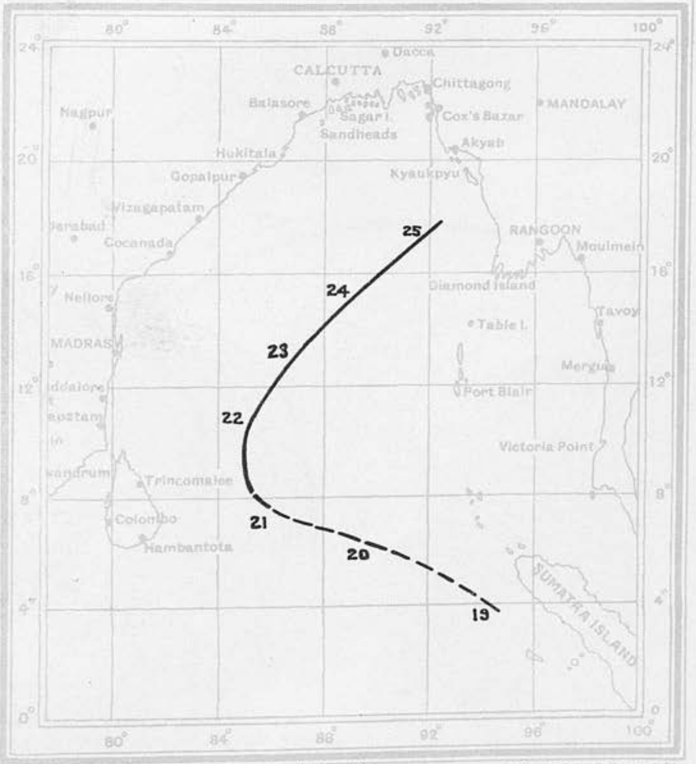


Fig. 18.

Offset, G.P.I.D Poona, 931

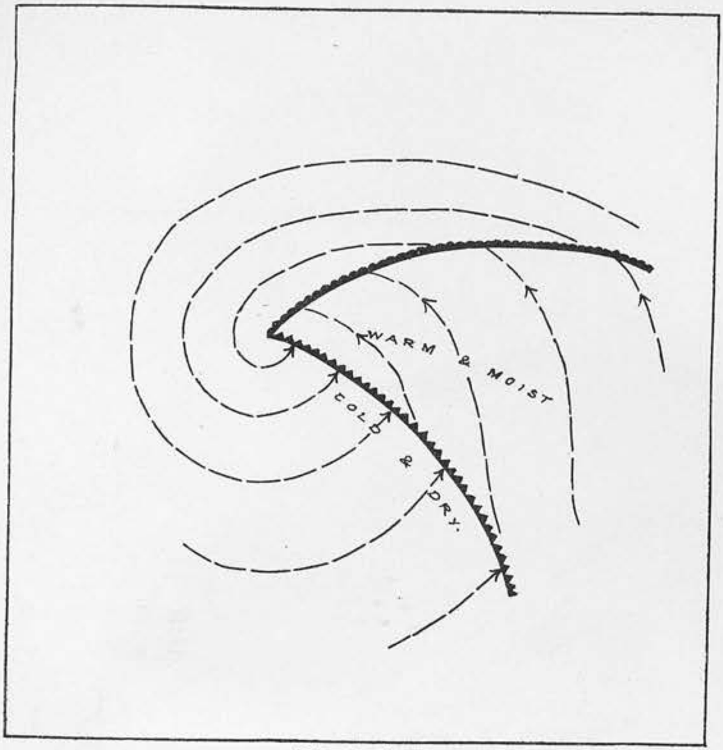
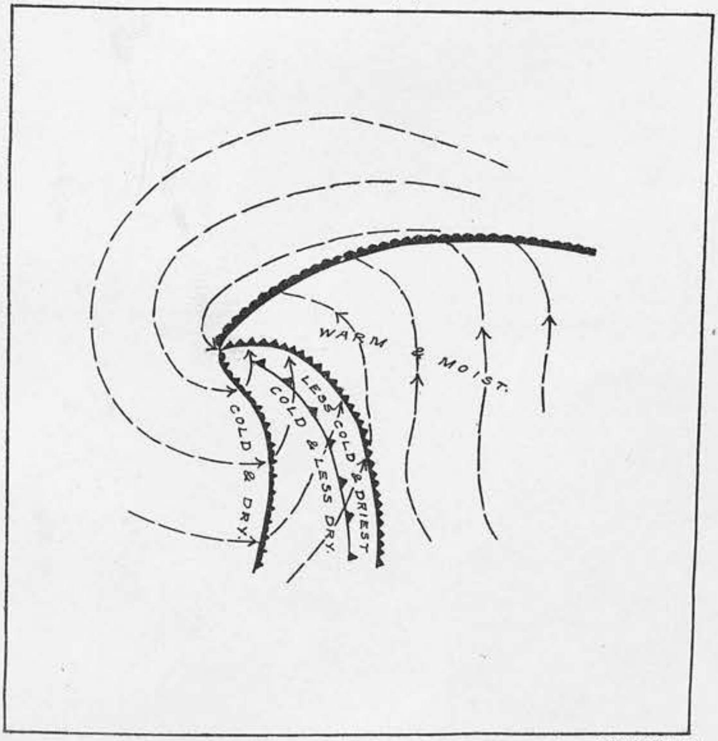
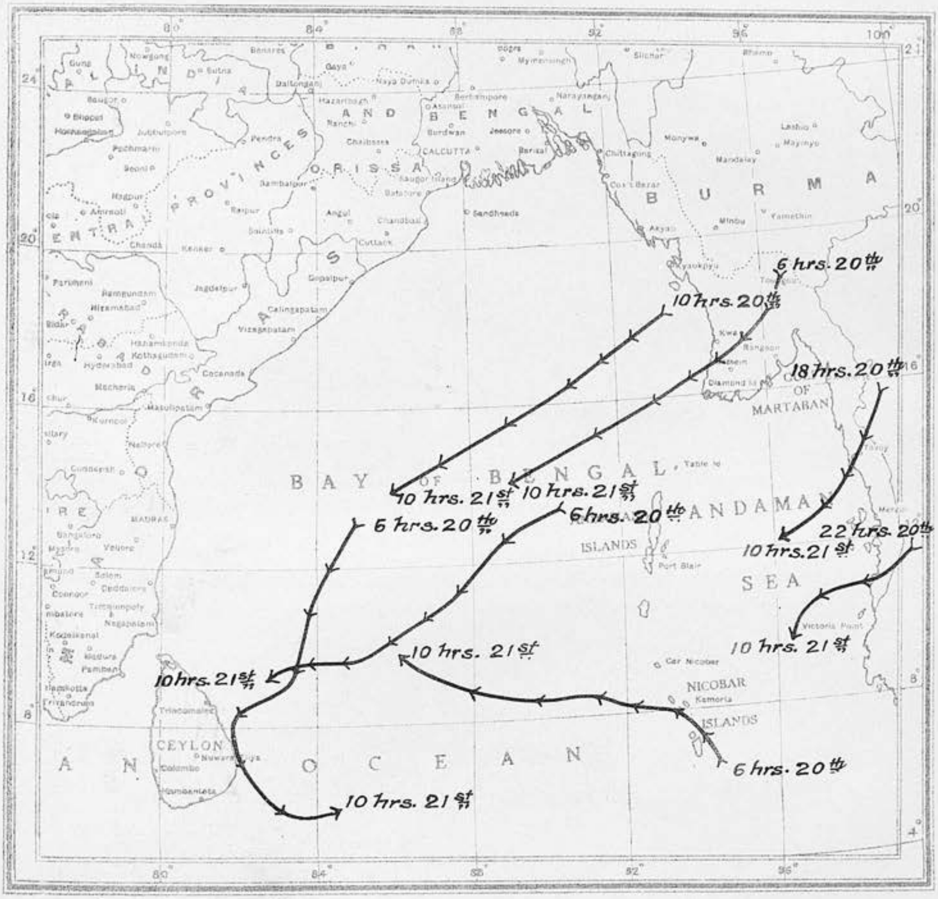


Fig. 19(a).



G.P.Z.O. POONA 1931.

Fig. 19(b)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BAY OF BENGAL
ANDAMAN SEA
ANDAMAN ISLANDS
NICOBAR ISLANDS
GULF OF MARTABAN
CEYLON
BURMA
BENGAL
ORISSA
CENTRAL PROVINCES
INDIAN OCEAN
CALCUTTA
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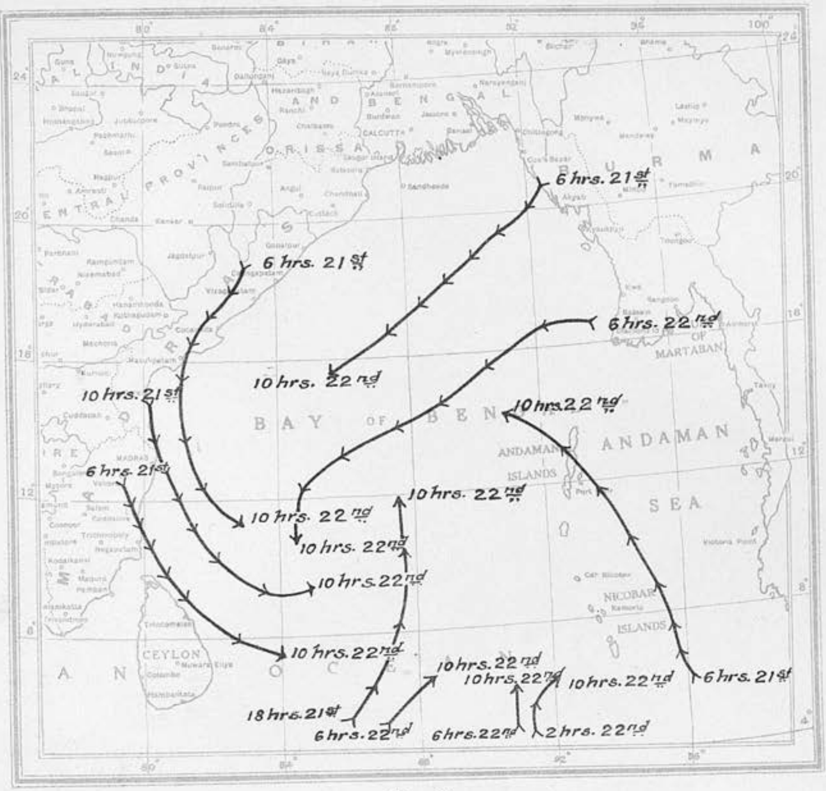
4

Fig. 20.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BAY OF BENGAL
ANDAMAN SEA
ANDAMAN ISLANDS
NICOBAR ISLANDS
CEYLON
GULF OF MARTABAN
BURMA
ORISSA
BIHAR AND BENGAL
CENTRAL PROVINCES
MADRAS
CALCUTTA
80°
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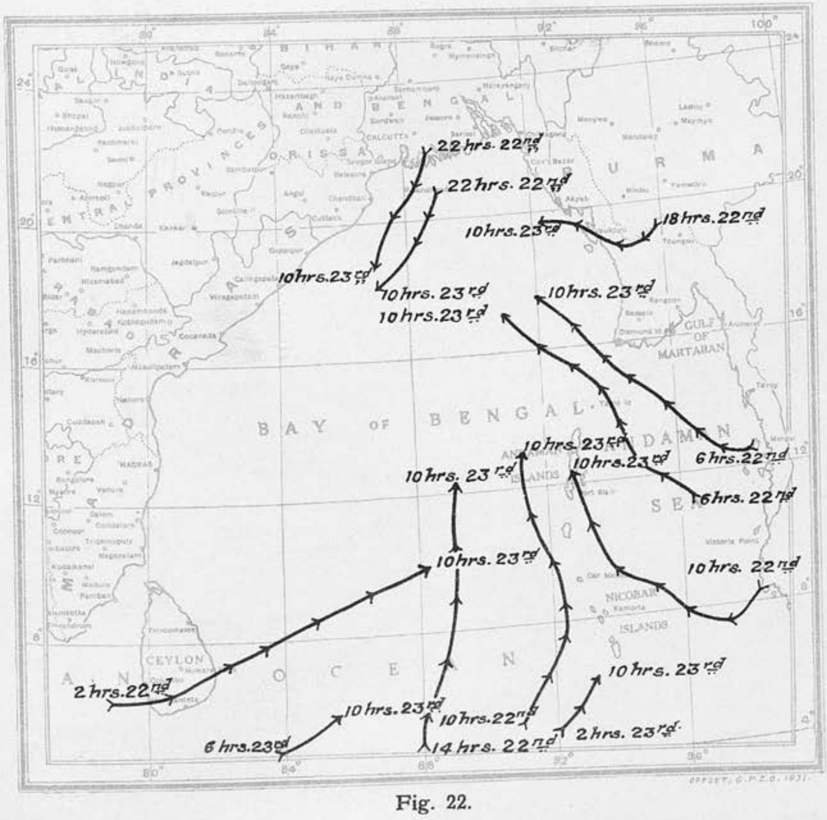
Fig. 21.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14 hrs. 22nd
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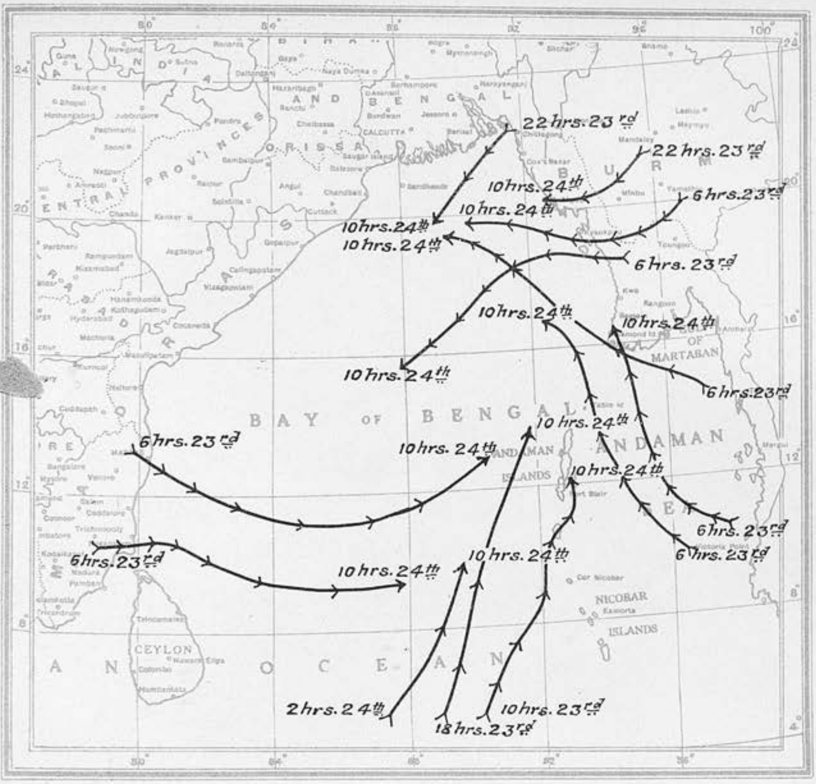
BAY OF BENGAL
ANDAMAN SEA
ANDAMAN ISLANDS
NICOBAR ISLANDS
CEYLON
GULF OF MARTABAN
BURMA
OCEAN
OFFSET, G.P.Z.O. 1931.
80°
84°
88°
92°
96°
100°

Fig. 22.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BAY OF BENGAL
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ANDAMAN ISLANDS
ANDAMAN SEA
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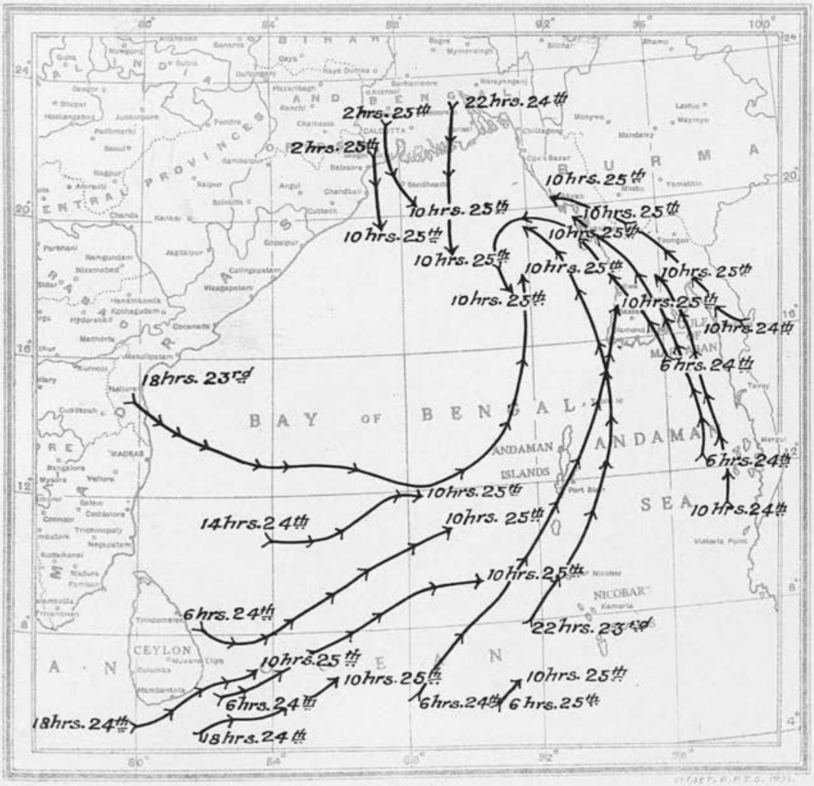
10 hrs. 24th
NICOBAR ISLANDS
CEYLON
OCEAN
2 hrs. 24th
10 hrs. 23rd
18 hrs. 23rd
GULF OF MARTABAN
BURMA
CALCUTTA

Fig. 23.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18 hrs. 23rd
BAY OF BENGAL
ANDAMAN ISLANDS
ANDAMAN SEA
6 hrs. 24th
10 hrs. 24th
10 hrs. 25th
14 hrs. 24th
10 hrs. 25th
10 hrs. 25th
6 hrs. 24th
22 hrs. 23rd
NICOBAR
CEYLON
10 hrs. 25th
10 hrs. 25th
10 hrs. 25th
6 hrs. 24th
6 hrs. 24th
6 hrs. 25th
18 hrs. 24th
18 hrs. 24th
BURMA
CALCUTTA

Fig 24.

3m

Reprinted from „Gerlands Beiträge zur Geophysik“ Vol. 35, pp. 68—81, 1932

NOCTURNAL ATMOSPHERIC RADIATION AT POONA — A DISCUSSION OF MEASUREMENTS MADE DURING THE PERIOD JANUARY 1930 TO FEBRUARY 1931

By

K. R. Ramanathan and B. N. Desai
Poona

(With 9 figures)

Akademische Verlagsgesellschaft m. b. H., Leipzig

Summary: Results of measurements of nocturnal radiation at Poona with an Ångström pyrgeometer extending over a year are analysed. The net radiation is maximum in February and March and minimum in the monsoon months July to September. Comparing the results with those obtained by W. H. & L. H. G. Dines in England, the net radiation in any particular month at Poona is greater than that at Benson. Comparing sky radiation, its value in winter at Poona is smaller than that at Benson in summer in spite of higher temperatures at Poona. This is probably due to the comparative dryness of the atmosphere over Poona. It is found that there is a general agreement between the observed values of sky-radiation and those calculated from Ångström's equation, although there are significant departures at high and low values of vapour-pressure. During the months May to October, the sky radiation on all clear days reaches a value about 0.75 of the black body radiation at the surface temperature — the maximum that may be expected if water-vapour is practically the sole radiating constituent. Tables are given showing the relation between night radiation and surface inversion at night. The marked influence of upper winds at Poona on sky radiation during winter months is pointed out.

Introduction.

The rapid drop in temperature at nightfall which is a characteristic feature of continental climates is very well-marked in North India during the months November to April and to a less degree in the Deccan. Actual measurements of sky-radiation in the tropics are, however, very rare and the measurements discussed in this paper were undertaken to provide some reliable data on the subject which will be of use in considering problems of radiation of the atmosphere.

The sky radiation was measured at night, generally between 20 and 22 hrs., with an Ångström's pyrgeometer. The instrument was obtained from Mr. G. Rose of Upsala. One of the two strips of constantan was coated with lamp-black and the other gilded. The instrument was exposed horizontally on the top of the tower of the Poona Meteorological Office. A calibrated Siemens and Halske milliammeter was used to measure the heating current and a mirror galvanometer to indicate the equality of temperatures of the thermo-couples soldered to the backs of the strips.

The pyrgeometer was tested in the following manner. A metal vessel was prepared with a hollow cylindrical dent at its bottom with a diameter of about 15 cm. The concave side of the cavity was coated with lamp-black. The vessel was filled with water at different temperatures below that of the room and supported over the pyrgeometer so that the instrument received radiation from the vessel over a solid angle 2π and the rate of loss of heat from the black strip was determined as usual from the heating current required to equalise the temperatures of the bright and black strips. The radiation loss was found to be practically proportional to $T^4 - T_1^4$ when T was the temperature of the strips and T_1 that of the water in the vessel.

If the black strip and the hollow radiator were assumed to be perfect absorbers for long-wave radiation and the bright strip to be perfectly reflecting, the mean value of STEFAN's constant came out to be $8.1 \cdot 10^{-11}$ in agreement with the accepted standard value $8.15 \cdot 10^{-11}$. The value obtained by calibration was used in all calculations. The vapour pressure of water at the time of measurement of night radiation was calculated from the readings of the wet and dry bulb thermometers exposed in a Stevenson Screen at the top of the tower. It was observed (as was noticed by ÅNGSTRÖM) that whenever the wind was markedly unsteady, the galvanometer did not have a steady zero. Movement of low or medium clouds, or change of their character caused fluctuations in the balancing current, which were largest when the clouds were overhead and least when they were near the horizon.

Results.

The daily values of radiation and weather elements at the time of observation together with relevant weather remarks will be published elsewhere.

In Table 1 are given the mean monthly values of air temperature and aqueous vapour pressure at the time of observation including both clear and cloudy days, black body radiation at the temperature of the instrument, net radiation and sky radiation as well as the number of observations on which the means are based.

Table 1.

Mean monthly values of night radiation (all days).

Month	No. of observations n	Air Temp. °A	Vapour pressure mm. of Hg	Black body radiation gcal/cm² min.	Net radiation gcal/cm² min.	Sky radiation gcal/cm² min.
Jan.	31	298	8.5	0.638	0.205	0.433
Febr.	34	297	8.1	.631	.215	.416
March	29	301	10.3	.670	.214	.456
April	27	302	11.6	.675	.194	.481
May	25	301	16.0	.669	.161	.508
June	20	300	17.3	.655	.114	.541
July	8	297	17.1	.633	.064	.569
August	17	297	16.4	.629	.115	.514
Sept.	8	298	18.1	.644	.097	.547
Oct.	17	300	15.9	.659	.117	.542
Nov.	26	298	11.6	.638	.176	.462
Dec.	28	298	9.9	.639	.184	.455

Table 2 contains the mean monthly values of the same quantities on clear days alone. The maximum and minimum net radiation from the instrument and of sky radiation on these days are also given in the Table. Days with high cloud or with medium or low cloud near horizon

Table 2.

Mean monthly values of radiation (clear days).

Month	No. of observations	Air Temp.	Vapour Pressure	Black body radiation	Net radiation gcal/cm² min.			Sky radiation gcal/cm² min.			$\frac{(9)}{(5)}$
(1)	n (2)	°A (3)	mm. of Hg (4)	cal/cm² min. (5)	Mean (6)	Max. (7)	Min. (8)	Mean (9)	Max. (10)	Min. (11)	(12)
Jan.	30	297	8.5	0.637	0.207	0.238	0.186	0.430	0.457	0.392	0.68
Febr.	34	297	8.1	.631	.215	.257	.173	.416	.462	.335	.66
March	25	301	9.9	.669	.225	.257	.200	.444	.474	.382	.66
April	20	301	11.0	.672	.214	.249	.183	.458	.498	.413	.68
May	16	301	16.5	.664	.171	.203	.138	.493	.528	.456	.74
June	6	300	16.7	.661	.173	.196	.144	.488	.518	.467	.74
July	1	297	17.2	.633	.152	—	—	.481	—	—	.76
Aug.	1	298	16.8	.641	.152	—	—	.489	—	—	.76
Sept.	2	298	17.9	.644	.149	—	—	.495	—	—	.77
Oct.	5	301	12.7	.667	.165	.176	.149	.502	.519	.488	.76
Nov.	22	297	10.3	.636	.191	.227	.147	.445	.490	.406	.70
Dec.	23	298	8.8	.639	.197	.244	.147	.442	.502	.378	.69

and amount less than one have been taken as clear days; even if the sky was completely covered with light high cloud, the day has been taken as a clear day as it was found that the balancing current was little affected by the presence of such cloud. In the last column are given the ratios of the mean sky radiation to the black body radiation at the same temperature.

Monthly and seasonal variation of sky radiation and net radiation.

The mean monthly values of sky radiation and vapour pressure on all days (Table 1) and on clear days (Table 2) are plotted in figures 1 and 2 respectivley.

From figure 1 we find that the sky radiation gradually increased from February to July, decreased in August, slightly increased again from August to October and thereafter decreased till February, when

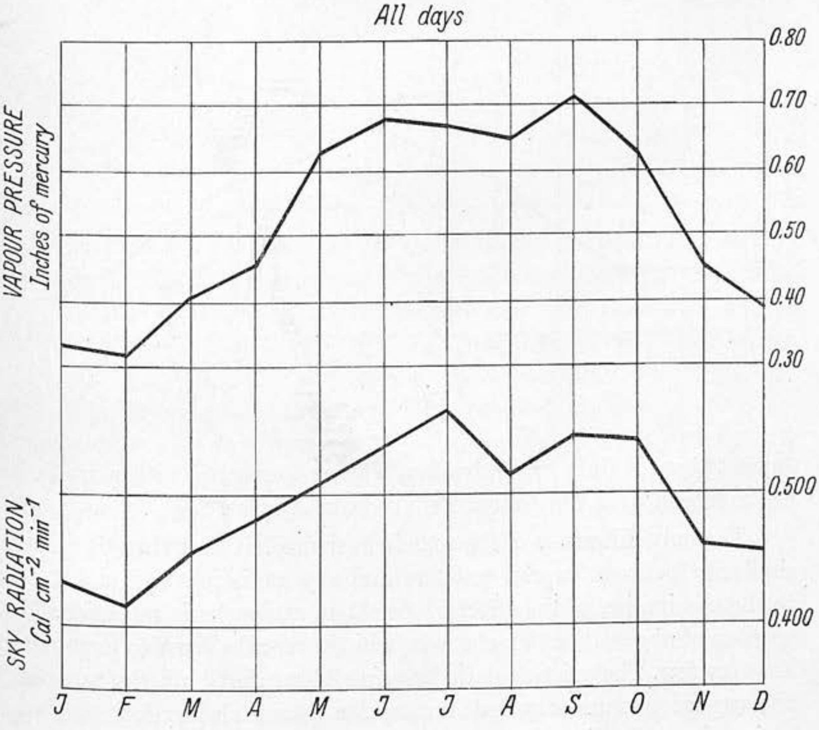

Fig. 1.

it was lowest. The vapour pressure curve also shows the same tendency. The number of observations in the months July and September are only 8 each, but on most of the other days in these months, it was either heavily clouded or was raining, so that their inclusion would only lead to an increase in the value of the sky radiation. One interesting feature of the curves is the smaller vapour pressure as well as sky radiation in August than in July or September. This is connected with a break in the monsoon over the Indian Peninsula in August.

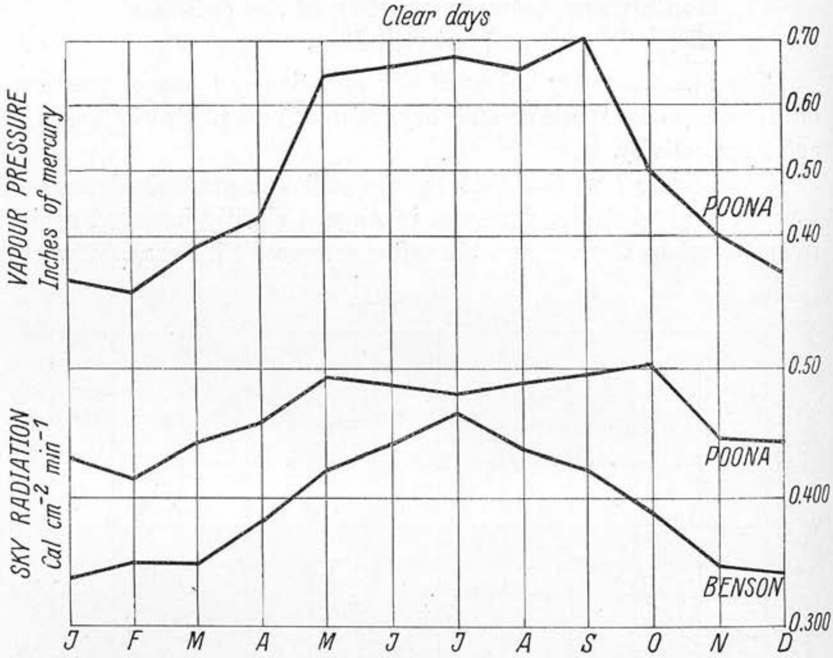

Fig. 2.

The only difference of figure 2 from figure 1 is that there is greater similarity between vapour pressure and sky radiation in figure 2 due to the elimination of the effect of clouds on atmospheric radiation. The number of observations on clear days in the months June to September are very few. The existing data, however, show that both sky radiation and vapour pressure vary little during these months when Southwesterly moist winds blow in the lower levels up to at least 2 km.

Comparison of monthly mean values of sky radiation with values over England.

In figure 2 is also given a curve showing mean monthly values of sky radiation on clear days at Benson (England) [1] [2]. The following points are of interest:

1. The sky radiation at Poona in any month is larger than that at Benson in the same month.

2. The sky radiation at Poona in winter is smaller than that at Benson in summer in spite of the fact that temperatures over Poona are higher. This is due to the great dryness of the atmosphere over Poona during winter, a fact supported by results of sounding balloon ascents.

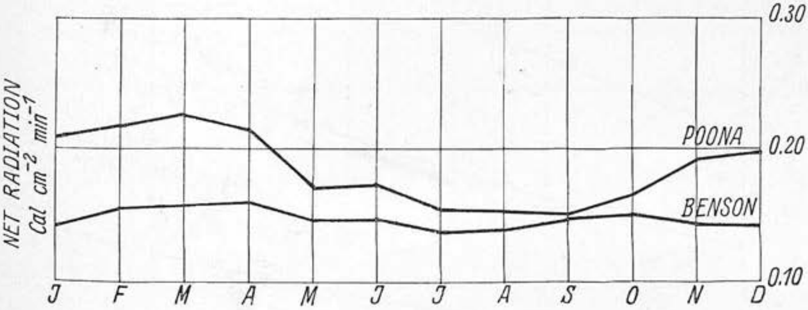

Fig. 3.

The monthly variation of net radiation at Poona and Benson is given in figure 3. The nocturnal radiation in any particular month at Poona is seen to be greater than that at Benson. This difference is large in winter and hot season. There is very little seasonal variation of net radiation over Benson. The difference in net radiation at Poona and Benson in different seasons is to be expected from the nature of the air supplies over the two places. The air supply of Poona during winter and hot season is land air from Northwest India, Baluchistan and Persia while from June to October, it is sea air from between south and west. The air supply over England is from the Atlantic throughout the year.

In his paper on "Further studies in Terrestrial Radiation", Simpson has calculated the limits of nocturnal radiation (maximum and minimum) for different temperatures from the absorption coefficients of water-vapour and carbon dioxide for different wave-lengths.

The values given in Table 5 of his paper have been plotted in figure 4 as thick curves. The curves have been extended to 305° A. The mean monthly and extreme values of net radiation on clear days in each month over Poona as given in Table 2 have been plotted in figure 4. The mean values are indicated by circles and the extreme values by dots. We find that all these values fall between the two extreme curves.

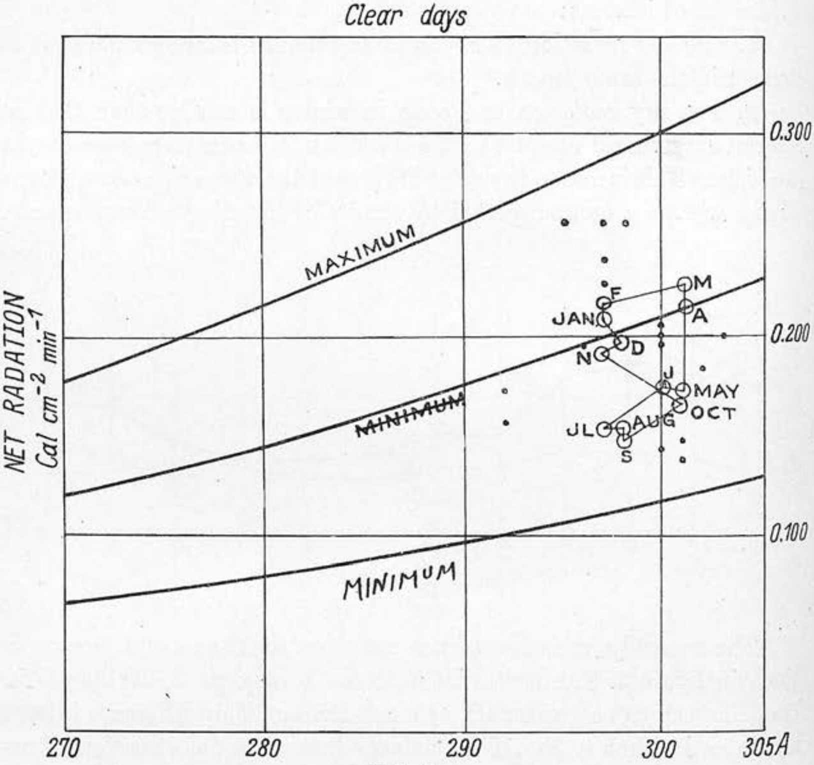

Fig. 4.

The net radiation in May is found to be less than that in March or April in spite of the fact that the air temperature in all the three months was the same. This is due to a gradual increase in water vapour content of the atmosphere from March to May. We also find that the drier the atmosphere, the higher the value of net radiation.

Relation between sky radiation, vapour pressure, and temperature.

From his studies of the radiation of the atmosphere, A. Ångström [3]) has deduced the following semi-empirical equation connecting sky radiation and the aqueous vapour pressure at the surface.

(1) $$E_a = S_t\,(0.75 - 0.32 \cdot 10^{-0.069p})$$

where E_a is the sky radiation and S is the black-body radiation at the temperature of the air at the surface and p the aqueous vapour pressure in millimetres of mercury. According to (1), the value of sky radiation from a clear sky will lie between 0.75 and 0.43 of that of a black body at the temperature of the atmosphere at the earth's surface. Table 3 compares the monthly means of the observed radiation on clear days with the values calculated according to (1).

Table 3.

Mean monthly values of sky radiation (clear days).

Month	Jan.	Febr.	Mar.	Apr.	May	Jun.	July	Aug.	Sept.	Oct.	Nov.	Dec.
E_a Calculated	0.425	.419	.453	.460	.486	.480	.463	.468	.468	.468	.431	.430
E_a Observed	0.430	.416	.444	.458	.493	.488	.481	.489	.495	.502	.445	.442

It is not quite correct to extrapolate the equation to zero value of humidity, but as has been explained by SIMPSON, owing to the very high absorptivity of water-vapour for some regions of long-wave radiation spectrum, the radiating power of the atmosphere is high even for exceedingly small quantities of moisture-content.

The daily values show that the limits of sky radiation on clear days at Poona lie between 0.77 and 0.58 of that of a black-body at the temperature of the atmosphere near the instrument and that the maximum value is reached on practically all clear days during the months May to October.

There is good agreement between the calculated and observed average monthly values in the drier part of the year. In the wet months July to October, the observed values are generally higher. This may be due either to the cloud haze that is often present in the atmosphere in these months or to the imperfect applicability of the formula when the vapour pressures are high. It should be remembered that the number of observations in these months is also small.

The individual values of sky radiation on clear days are plotted in figure 5 together with the curve of ÅNGSTRÖM's equation [1]) given above. The black dots which represent the values in the months June

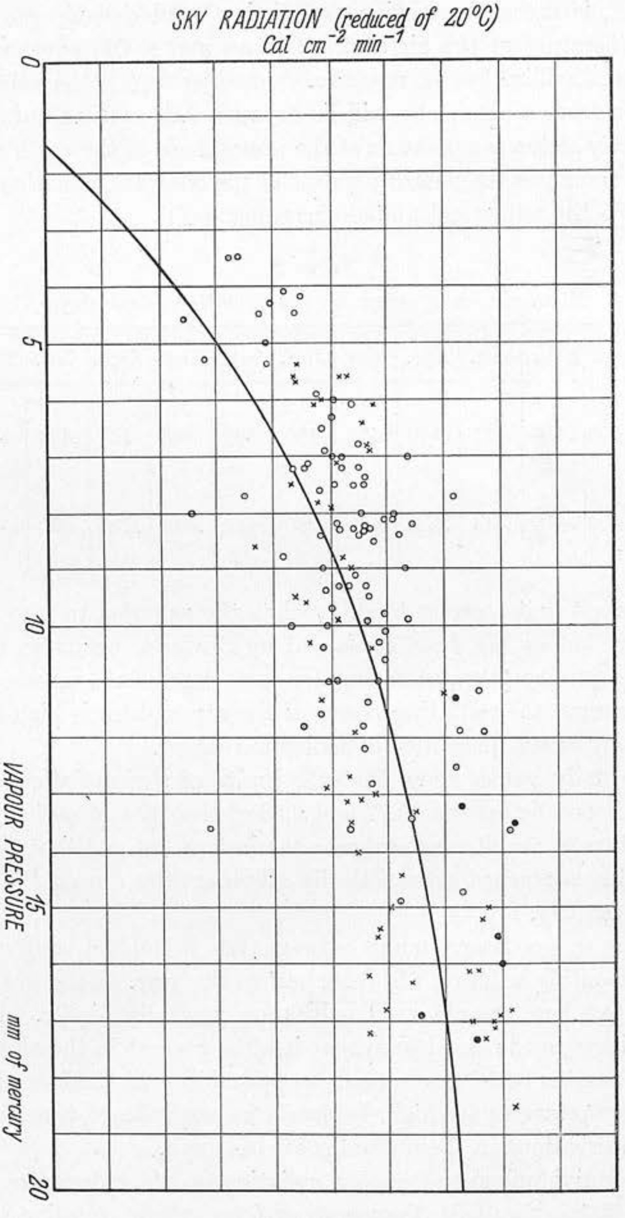
SKY RADIATION (reduced of 20°C)
Cal cm^-2 min^-1
0
5
10
15
20
VAPOUR PRESSURE
mm of mercury

Fig. 5.

to October are generally higher than those given by the curve. Also when the vapour pressure is below 7 mm. which usually occurs under anti-cyclonic condition in the months December—March, there is a tendency for the observed values to be higher than the calculated. This is not surprising as ANGSTRÖM's equation does not take into account variations of upper air temperatures and humidities.

Surface inversion and nocturnal radiation.

At the Poona Meteorological Office, thermographs are kept in Stevenson Screens supported on 4 ft. stands on the top of the tower and on the ground in the office compound. A grass minimum thermometer is also exposed near the ground Stevenson Screen. In Table 4 are given the number of occasions when the difference between the minimum temperatures recorded in the Stevenson Screen on the ground and by the grass minimum thermometer had various values ranging from 0° F to 12° F and the corresponding mean values of net radiation on the previous night.

Table 4.

Clear days.

Stevenson Screen minimum — grass minimum. $(S-G)$ °F.	2	3	4	5	6	7	8	9	10	11	12
Number of occasions.	2	3	9	18	22	20	22	27	25	8	1
Average net radiation gcal/cm² min.	0.038	0.153	0.152	0.174	0.191	0.208	0.207	0.209	0.224	0.223	0.242

Only clear nights or nights on which there was no appreciable alteration of high cloud amount (with no middle or low clouds) have been considered for the purpose of this table. In figure 6 are plotted the individual values of net radiation against the difference between the 4 ft. screen minimum and grass minimum. The mean values of net radiation for definite values of difference between the screen and grass minimum are also plotted as circles. It will be seen that the strength of the inversion grows at increasing rates as the net radiation increases. Radiation tends to produce stratification while turbulence tends to destroy it. For any value of eddy diffusivity there will be a definite value of radiation required to set up stratification; with increase of radiation in excess of this value, the stratification will increase in intensity.

In Table 5 are given the number of clear days on which the difference between the minimum temperatures recorded in the Stevenson Screens

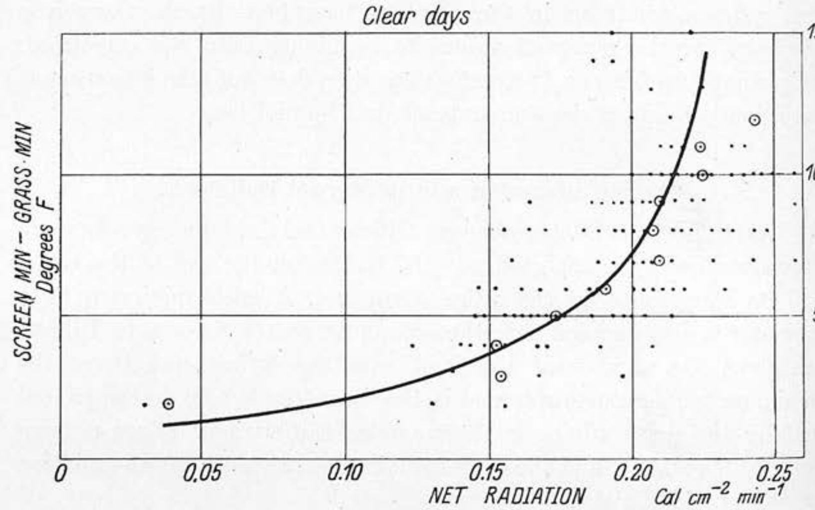

Fig. 6.

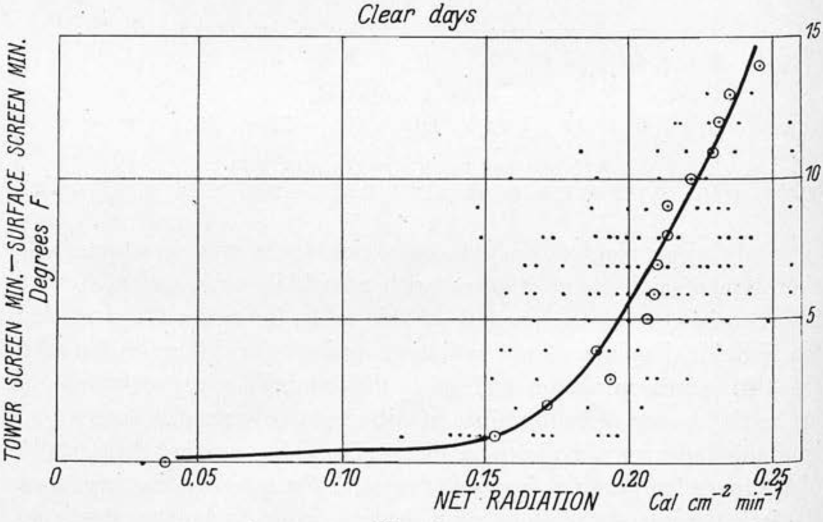

Fig. 7.

at a height of 4 ft. above ground (S) and on the top of the Tower (T) had values ranging from 0° to 14° F and the corresponding mean values of net radiation. The individual and mean values are plotted in figure 7.

Table 5.

Clear days.

Tower S. S. Min. — Surface S. S. Min. $(T-S)$ °F.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Average net radiation gcal/cm² min.	0.038	.153	.172	.194	.189	.207	.209	.210	.213	.213	.222	.229	.231	.235	.245
Number of occasions.	2	13	3	5	3	9	28	33	24	12	4	5	5	2	2

The inversion extends appreciably above 4 ft. only when the net radiation exceeds 0.150 gcal/cm² min.

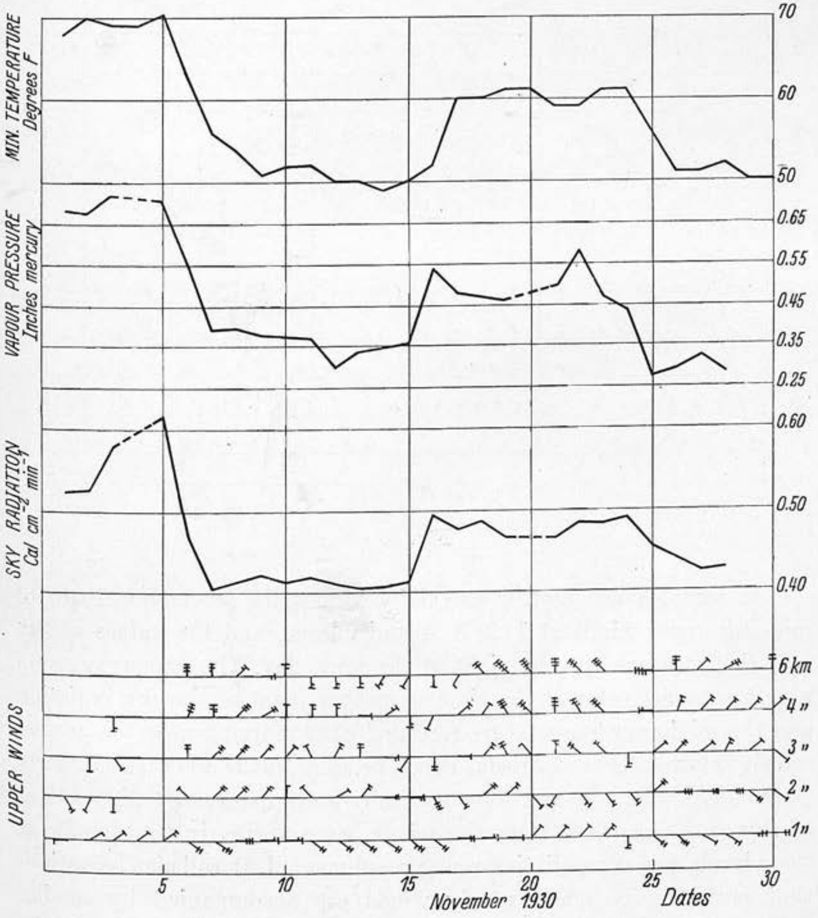

Fig. 8.

Sky radiation and upper winds.

As the intensity of the sky radiation is intimately connected with the moisture content of the atmosphere, it may be excepted that the source of supply of air in the upper atmosphere and hence the direction of upper wind will influence the sky radiation, especially in those seasons and days when the moisture near the surface is small.

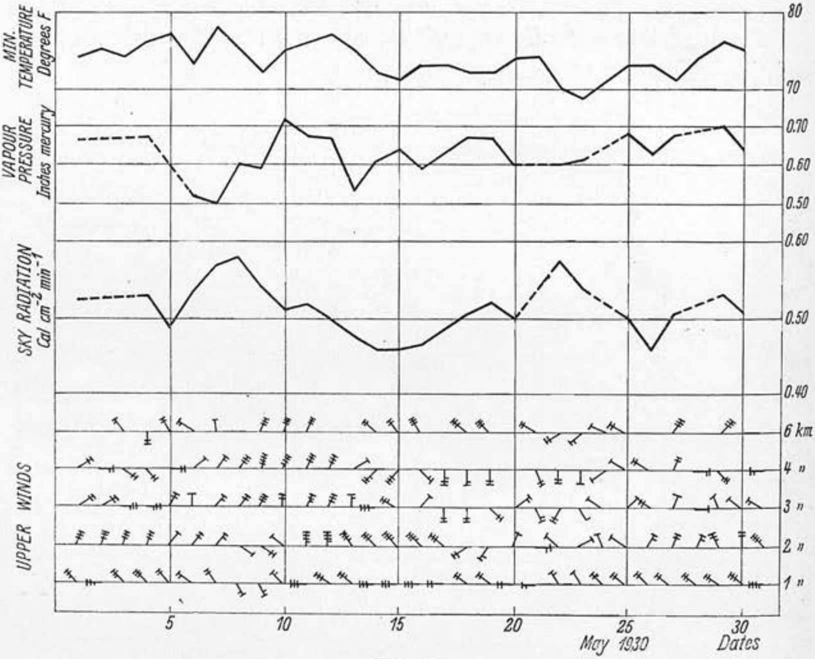

Fig. 9.

In figure 8 are plotted the daily values (in November 1930) of morning upper winds at 1, 2, 3, 4 and 6 kms., and the values of sky radiation measured on the night of the same day. The vapour pressure near the pyrgeometer at the time of measurement of the sky radiation and the minimum temperature recorded next morning near the ground are also plotted for comparison. It will be seen that winds with southerly components at 2 to 4 km. were generally accompanied by high values of sky radiation, and when the winds were northerly to easterly at these levels, the sky radiation was generally small. It will also be noticed that northerly to northeasterly winds are accompanied by smaller values of sky radiation than northwesterly winds. This is due to the fact that in the former case, Poona is situated to the southwest of the seasonal anticyclone which extends up to about 3 km. while northwesterly winds at 2 and 3 km. over Poona occur in the immediate rear of western disturbances moving eastward across N.India. The winds and radiation on the 8th to 15th show that the direction of wind at 6 km. and above has little influence on the radiation. A Southeasterly wind at 1 km. alone does not appear to be markedly different from an easterly at the same level. The wind at 2 km. gives the best index of an increase of moisture content. All the quantities skyradiation, vapour pressure, minimum temperature on the next morning, and direction of wind at 2 km. go together. The number of feathers in the arrows represents the wind velocity on the Beaufort Scale.

In the comparatively hotter and moister month of May the sky radiation is very little dependent on upper winds (figure 9).

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With 19 figures.

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With 19 figures.

I. *Introduction.*

The application of kite, balloon and aeroplane ascents to meteorology has shown that the variation of temperature with height in the free atmosphere is of a very complicated nature. Though on an average the rate of fall of temperature with height is about 6° C. per kilometre within the troposphere in all parts of the world, yet the fall is often very irregular in individual ascents, varying from super-adiabatic to zero (isothermal) or to a negative value (inversions). Owing to the important part played by these inversions in the atmospheric phenomena much work has been done on them recently, and in spite of several practical difficulties, many important papers discussing their structure from a qualitative as well as quantitative point of view have appeared in various journals. The names of Sverdrup, Douglas, Kopp and W. Peppler are particularly to be mentioned in this connection.

All surfaces of discontinuities in the atmosphere showing temperature inversions or isotherms have been mainly divided into two classes:

a) Fronts — in which the humidity after increasing continuously upwards, attains its maximum at the upper edge of the isothermal or inversion layer, remains constant for a certain height and then decreases. These surfaces of discontinuities are always inclined.

b) Dry inversions — in which the humidity after increasing continuously upwards, attains a maximum at the lower edge of the discontinuity and shows a sudden decrease at it. These surfaces of discontinuities are inclined when they occur at some distance below a frontal surface and horizontal when they occur in anticyclonic weather.

The present view about the development of dry horizontal inversions as due to a general slow descent of air from higher levels regards the appearance of the temperature discontinuity as a condition precedent to the development of humidity discontinuity in the form of a haze or cloud layer below it. Kopp, however, from his experience of aeroplane flights pointed out that after the passage of a cyclone, humidity discontinuity in the form of horizontal haze or cloud layer precedes the temperature discontinuity, the latter being probably brought into existence as a result of the radiation from the haze or cloud layers. The two views are contrary to each other as regards cause and effect. Accordingly it seemed advisable to make a detailed examination of some cases of marked inversions at the surface as well as in the free atmosphere, and to discuss the effects of the processes of subsidence and radiation quantitatively. The data used for this purpose are those obtained by instrumental observations at the surface observatories and by kite and aeroplane ascents at Lindenberg and Berlin.

II. *Present Classification of Surfaces of Discontinuity.*

Surfaces of discontinuity must be produced either a) at the boundaries of different air masses or b) within the same air mass. To class a) belong the "inclined" surfaces of discontinuity known as "fronts" which are produced by horizontal movements of air bringing moist air over drier and denser air. To class b) belong dry inversions of the following two types: —

1. Those associated with fronts, but occurring within the colder air mass and at some distance below the true frontal surface, known sometimes as "surfaces of subsidence". They are generally of limited extent and have a fairly definite angle of slope, usually less than 1 in 200.

2. Those connected with anticyclonic weather and which are horizontal and extend over wide areas. These inversions are usually stronger than those described under type 1 above.

III. *Results of aeroplane and kite ascents.*

Till lately it was believed that a dry surface of discontinuity owed its origin to a temperature discontinuity, the humidity maximum in the form of haze or cloud layer below it resulting from its presence. Consequently all attempts to explain its formation were directed to investigating those physical processes which give rise to a temperature discontinuity in the free atmosphere. That this is not always the case was pointed out recently by Kopp [1] in a paper where he has discussed his experiences of aeroplane flights. His results may be summarised as follows: —

1. That 90% of the aerological ascents show marked haze boundaries, the number of ascents showing significant temperature inversions at the upper surface of these haze boundaries being comparatively small.

2. That after the passage of a cyclone (when all previous inversions have dissolved owing to intense cyclonic convection) the atmosphere shows first the presence of haze boundaries and the temperature inversions follow later as a result of radiation from the solid particles constituting the haze layers.

3. That though strong inversions always show strong haze layering, the reverse is not true and that low and opaque haze layers are always connected with significant temperature inversions.

4. That a haze layer is always associated with a humidity discontinuity, the maximum humidity coinciding with the top of the haze layer[1]).

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[1]) The appearance of humidity discontinuity at the haze layer is due to absorption of water vapour by the hygroscopic particles constituting the haze and having the greatest concentration at its top. The humidity discontinuity is in some cases in the form of a cloud sheet.

To the above results, the following may also be added from the experience of one of the authors (Mal):—

5. That after the passage of a cyclone, the whole atmosphere gets divided up not by one, but a number of horizontal haze layers which occur more or less at equal intervals (see Fig. 1 which shows a number of inversions corresponding to a number of haze or cloud layers).

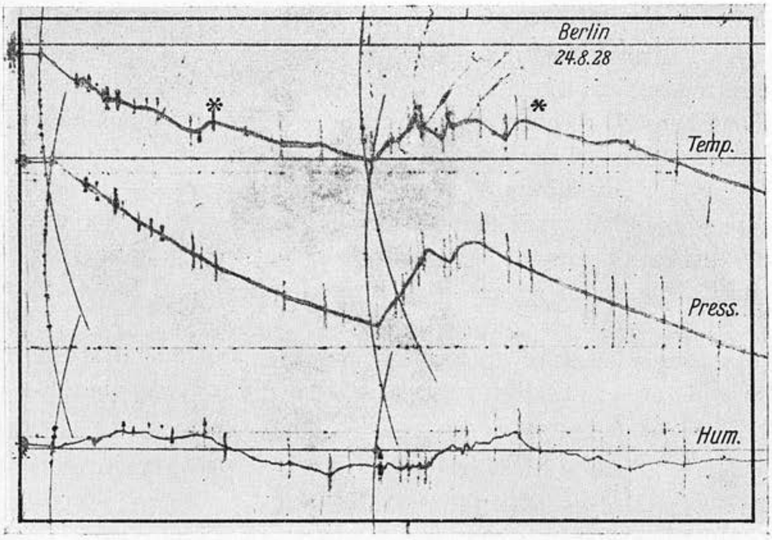

Fig. 1. A number of inversions in one single ascent.

6. That the intensity of haze layers falls with height.

7. That the heights of the haze layers do not change very much from day to day.

The observation of Kopp, 2. above, is the opposite of what one should expect if the discontinuity in humidity (as shown by the presence of haze or cloud layers) was primarily due to temperature discontinuity. In order to see how far the above observation is supported by actual facts, the aeroplane and kite ascents at Berlin and Lindenberg (during 1927, 1928, 1929) were examined in detail. Though the observations of most of these aeroplane and kite ascents (which were not very frequent and hence not very suitable for the purpose of studying the origin and growth of these inversions) would ordinarily lead one to think that the temperature discontinuity was responsible for the humidity discontinuity, yet more careful analysis revealed several cases which showed complete agreement with the conclusions of Kopp (see* in Figs. 2a and 2b, and Figs. 2c and 2d). Fig. 3a which represents the morning ascent at Lindenberg on 9. 3. 27 shows a humidity maximum in the form of a cloud layer at 1 km. height without any change in the temperature gradient; the later ascents, Figs. 3b and 3c, however, show the development of an isotherm and then a temperature inversion at a some-what lower level. Whether in all cases it is the horizontal haze discontinuity (as shown by a humidity discontinuity) which gives rise to horizontal temperature inversion is difficult

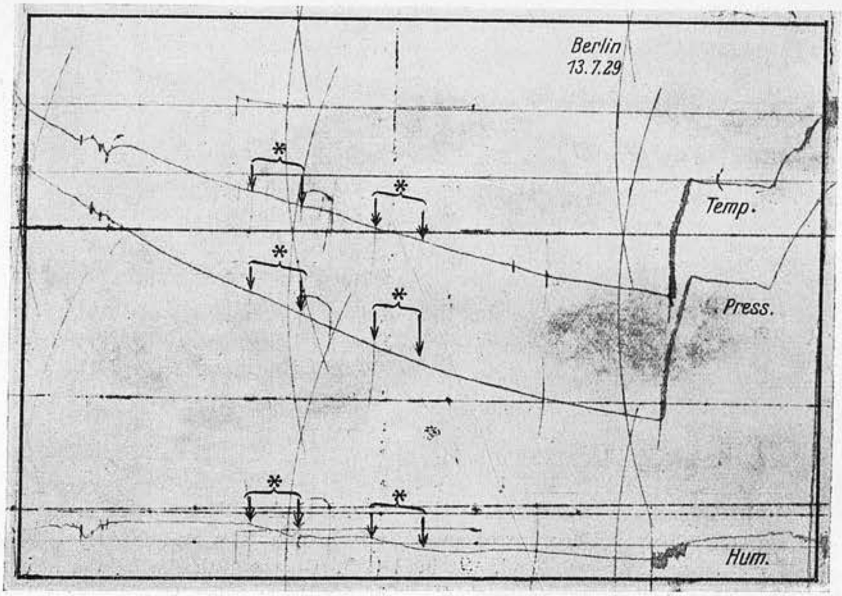

Fig. 2 a. Berlin in front of an anticyclone situated over the British Isles. The anticyclone moved eastwards over Berlin during the next two days.

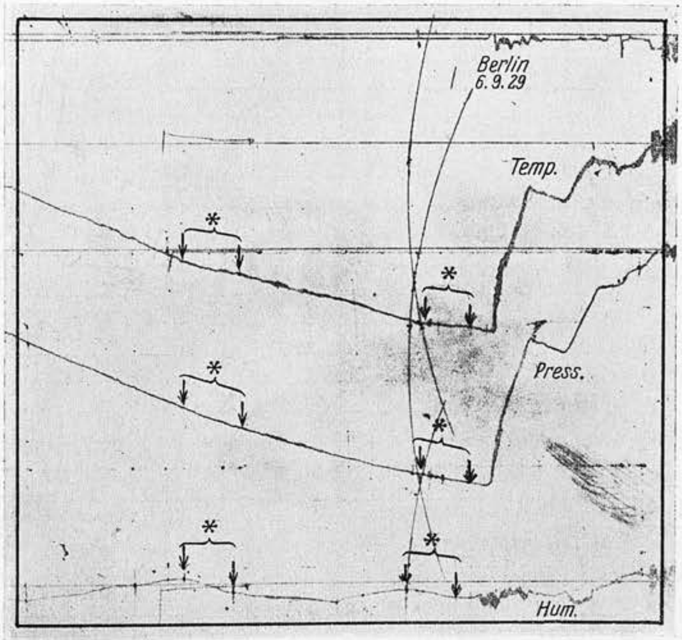

Fig. 2 b. In front of an advancing anticyclone which came over Berlin on the 8th.

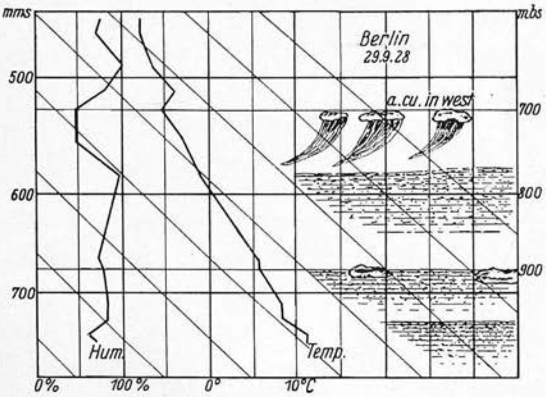

Fig. 2 c. On the 28th Berlin was situated in the rear of a cyclone which had rapidly passed over North Sea and was situated over Finland, and in front of another cyclone which was to the S. W. of the British Isles.

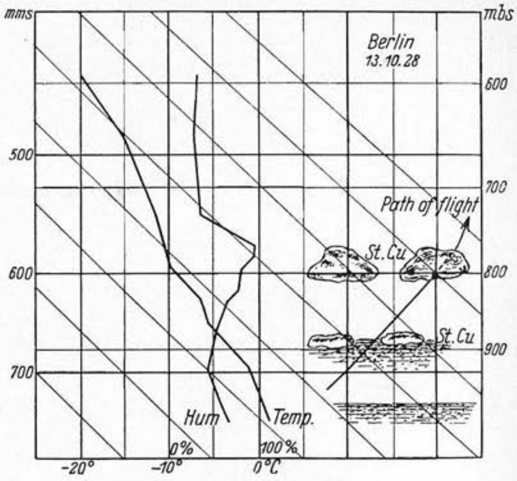

Fig. 2 d. A cyclone was situated to the west of the British Isles and rapidly filled up on the 12th. On the 13th Berlin was situated in front of an anticyclone which was advancing from Spain and was over Berlin on the 15th.

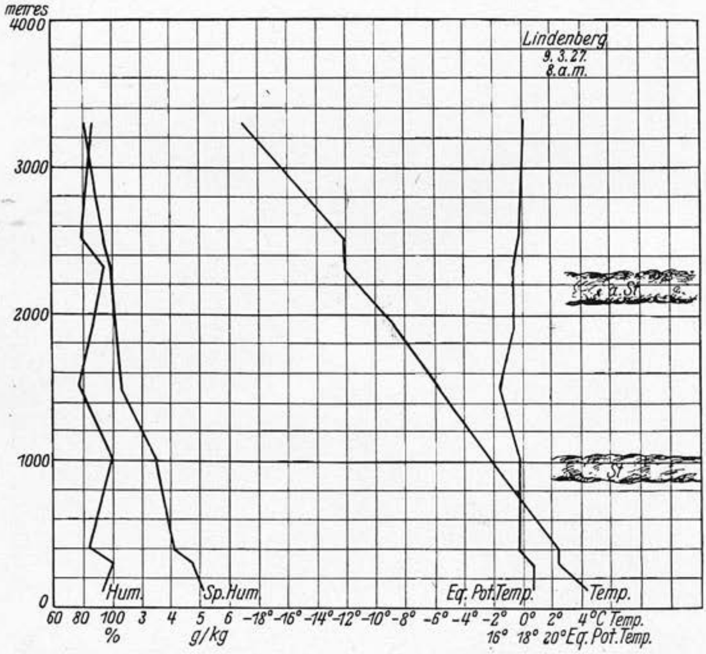

Fig. 3a.

to say, as the available data are inadequate for tracing the history of a surface of discontinuity. The only point to be laid stress on is that in the free atmosphere a horizontal temperature inversion can and does at times owe its origin to a haze or cloud discontinuity.

Hitherto it was customary to identify "surfaces of discontinuity" in the free atmosphere by temperature inversions or isotherms and then classify them according to the distribution of humidity which they show. From what has been stated above, one can easily realise that it is possible to have a discontinuity in moisture content as well as other chemical properties (dust and haze contents) without there being any discontinuity in temperature. In such cases therefore if one depends only on temperature for identifying various discontinuities one willcertainly miss them.

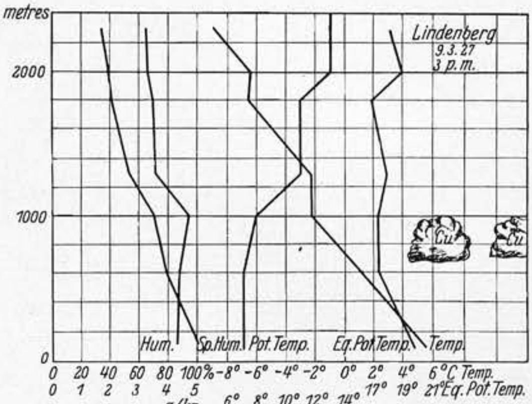

Fig. 3 b.

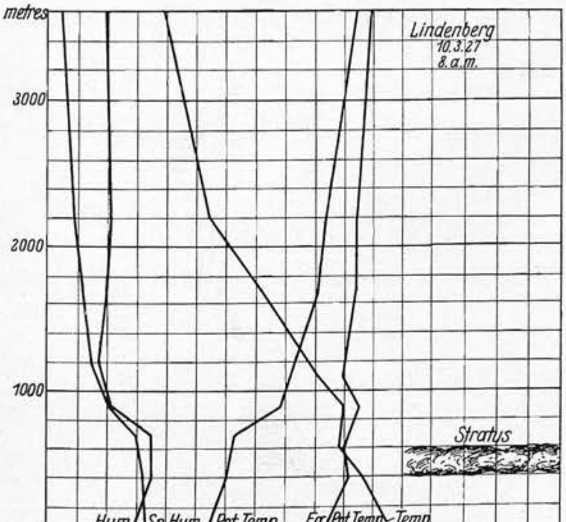

Fig. 3 c. An occluded front passed over Berlin on the 8th and the Observatory remained in maritime polar air on the 9th and the 10th.

IV. *Criteria for the identification of air masses.*

Before an attempt can be made towards a proper classification of surfaces of discontinuity, we need to know whether a particular discontinuity represents a boundary between two different air masses or occurs within one air mass. In order to be able to do this it is necessary to find out some conservative property of an air mass which will remain invariant during movements involving changes of pressure or environment.

Bergeron [2] has discussed the various thermal and chemical properties of an air mass from this point of view. From his discussion it will be seen that, with the exception of "opalescence", if a generalised potential temperature (e.g. pseudo pot. temp.) is introduced to cover cases of condensation also, then a function is obtained which is conservative over a considerable range of processes to which the elements of the air mass may be subject. **Normand** [3] has shown that wet bulb and equivalent potential temperature are such functions. If T_E represents the equivalent temperature of an air mass, we have

$$T_E = T + \frac{K}{b} e$$

where

T = the absolute temperature of the air,
e = the vapour pressure in mm,
b = the pressure in mm,
K = a constant which is equal to 1570 if moisture is condensed to water, and 1789 if condensed to ice.

If an air mass at pressure p and equivalent temperature T_E be brought adiabatically to a standard pressure p_0, its temperature Θ_E would be the "equivalent potential temperature" which remains constant under all adiabatic changes even if condensation occurs.

It must be remembered that the changes in the atmosphere are never adiabatic and therefore even the equivalent potential temperature is conservative only to a first approximation. So far, atleast in practical work, no function is known which is absolutely invariant under all conditions. The equivalent potential temperature however, when compared to other elements, does afford a better criterion for the identification of air masses.

V. *Application of equivalent potential temperature to the examination of theoretically possible cases of surfaces of discontinuity.*

After having decided upon the best available criterion, i.e., the equivalent potential temperature (denoted hereafter as Θ_E), for identifying air masses, we may now apply it to the theoretically possible cases of discontinuities in the atmosphere. In the case of discontinuities between two different air masses we should expect a sudden change in Θ_E at the surface of separation, its value remaining more or less the same within the respective air masses. In the case of discontinuities within the same air mass, the value of Θ_E on an average will remain more or less the same on either side of the discontinuity.

a) Discontinuities between two air masses. — The possibilities under this head are that the lighter ascending air may be 1. the moister and warmer of the two, 2. moister but colder of the two (the moisture content making it less dense) and 3. the drier and warmer of the two. 1. and 2. will give rise to fronts. In these cases, Θ_E will always show a marked increase in passing from the lower air mass through the front to the air mass above (see Fig. 4).

The case 3. will give rise to what may be called "dry fronts". In such cases Θ_E will in general show a sudden decrease at the surface of discontinuity (see Fig. 5a). In special cases, however, when the difference between the moisture contents of the two air masses is small, Θ_E will not show a sudden decrease but may be the same or even show a slight rise.

b) Discontinuities within the same air mass. — The formation and development of temperature inversions in the same air mass can be brought about either by 1. subsidence of air near fronts or 2. large scale subsidence as contemplated by Sverdrup and Douglas or 3. by radiation.

1. The surfaces of discontinuity produced by subsidence near fronts will be inclined and will be changing continuously with the movement of the front; they may appear, lose their identity and reappear during the various stages of development and movement of the front with which they are associated (see Bjerknes [4]). Since the descent of air takes place within the same air mass adiabatically, Θ_E will show practically no change (see Fig. 6).

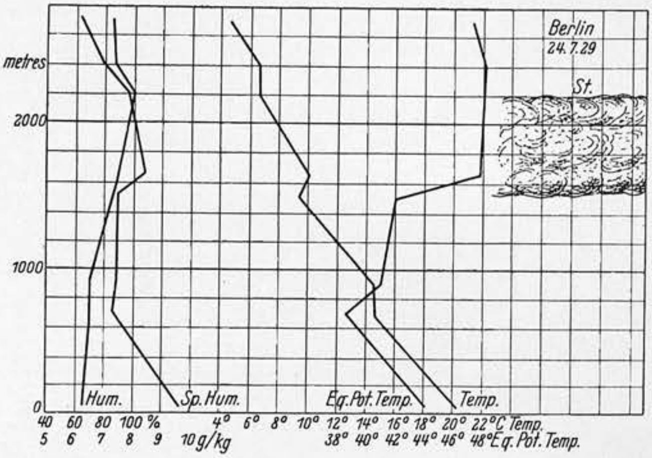

Fig. 4. Ascent through a cold front:
The Bergen synoptic chart shows a cold front passing just to the south of Berlin.

2. It will be shown later that large scale subsidence of air warming at the adiabatic rate cannot be considered to be of much importance in giving rise to horizontal dry inversions.

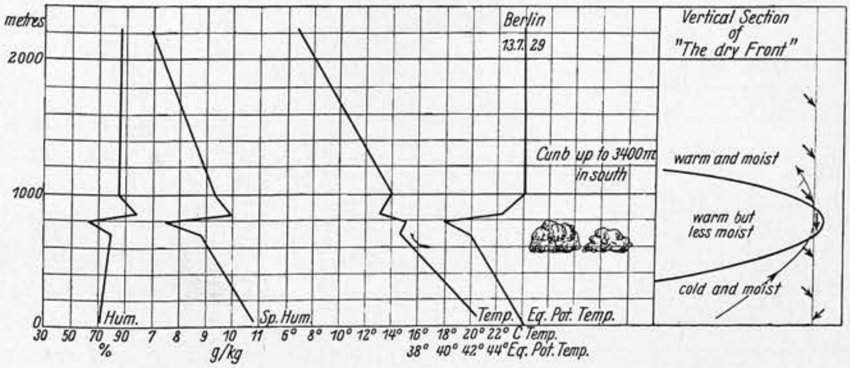

Fig. 5 a. Ascent through a dry front.
The Bergen synoptic chart shows an occlusion, between maritime polar air and continental air with higher temperature, running SW to NE through central Europe about 100 km to the north of Berlin.

3. The surfaces of discontinuity produced by radiation will be horizontal and their heights above the ground will remain practically the same from day to day. For their production, it is necessary to have initially a discontinuity in haze content (shown by humidity discontinuity) as shown by Kopp (see section 3.). In the case of a haze layer, it is known that its intensity continuously increases with height, reaches a maximum at the top and then suddenly falls to almost

nothing. As the intensity of haze is proportional to the number of solid particles, the cooling due to radiation will also increase with the intensity of the haze, and therefore Θ_E will steadily decrease upward upto the top of the haze boundary, reach a minimum there and will suddenly increase above and ultimately return to its original value (Fig. 7a). If the nocturnal radiation from the earth's surface is large, Θ_E may show a large fall in the lower layer near the surface (Figs. 7b and 7c).

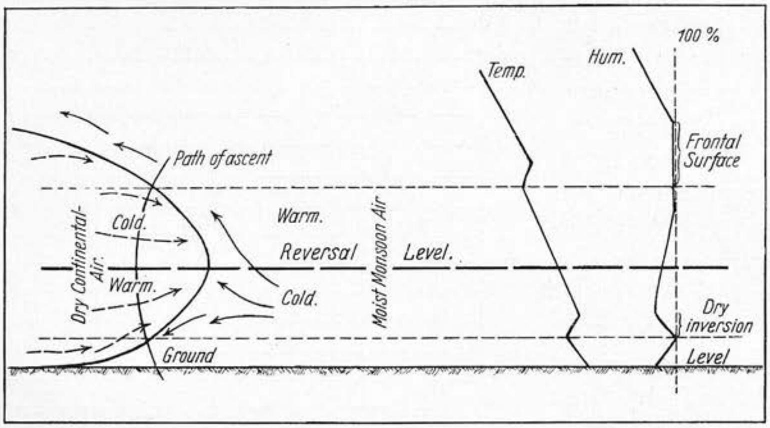

Fig. 5b.

In the case of a cloud sheet the intensity of haze increases with height upto the base of the cloud and is practically nothing above it. Θ_E will therefore at first continuously decrease with height till the base of the cloud is reached where it will suddenly increase due to absorption of radiation by the cloud base; within the cloud, Θ_E will again decrease and reach a minimum at the top due to the top of the cloud radiating like a black surface to the space above. Above the cloud, Θ_E will again increase and ultimately attain its original value at some height (see Fig. 8).

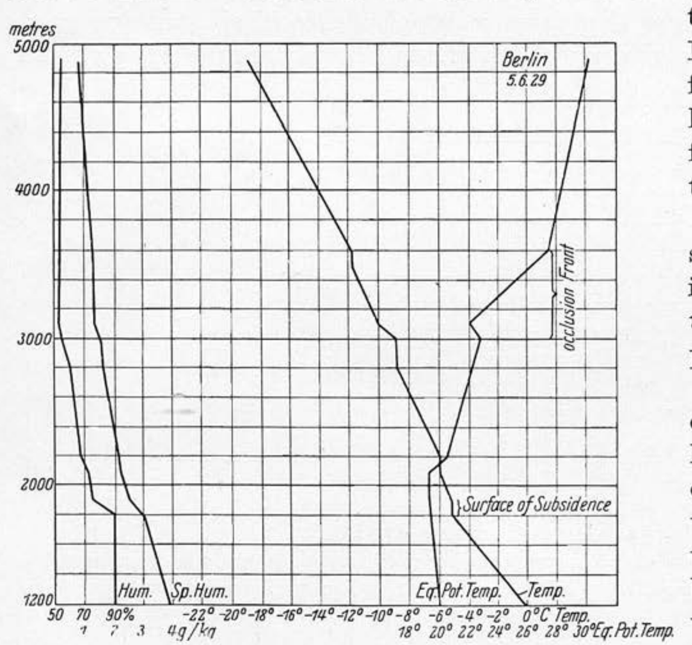

Fig. 6. Ascent through a surface of subsidence near an occlusion.

The Bergen synoptic chart shows an occlusion between maritime polar air and polar air running W to E through central Europe about 300 km to the south of Berlin.

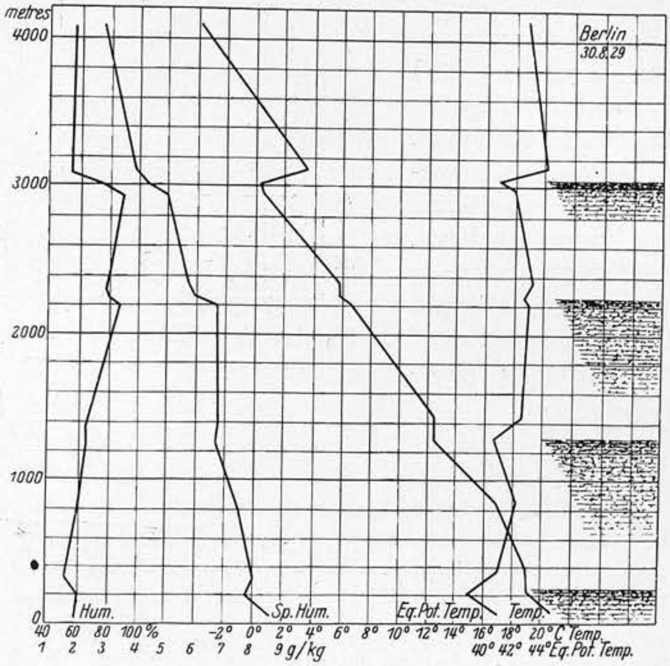

Fig. 7 a. Ascent through a number of haze layers (no effect of surface radiation).

The Bergen synoptic chart shows Berlin to be in the martime polar air within an anticyclone with its central region over Poland.

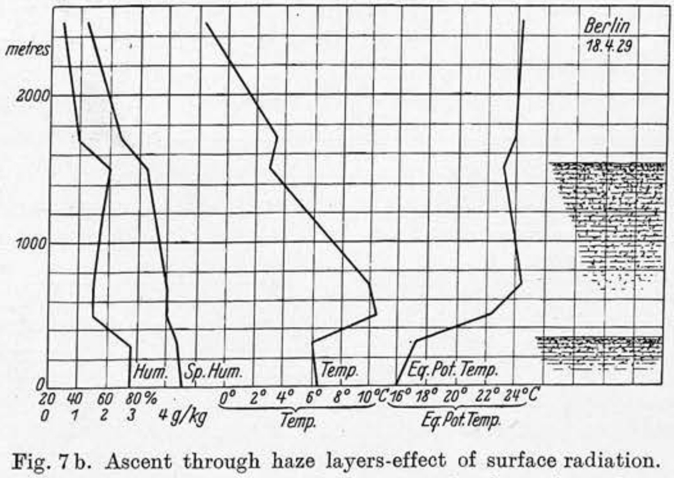

Fig. 7 b. Ascent through haze layers-effect of surface radiation. The Bergen synoptic shart shows an anticyclone situated to the northwest of Black Sea with central region near Lat. 47° N, Long. 25° E; the whole of central Europe was under the influence of continental cold air.

In order to test the validity of the theoretical considerations discussed above, a year's (1929) data of aeroplane ascents at Berlin and Lindenberg were examined. The occasions when marked temperature inversions or isotherms were met with were analysed, regard being paid to the moisture content of the air at different levels and to Θ_E. It was found that the inversions could be classified into the types shown in the table below. Curves for typical examples of each type (Figs. 4–8) have been already referred to.

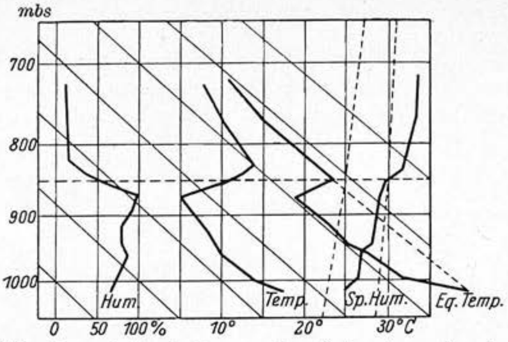

Fig. 7 c. A typical example of dry inversion in the same air mass (Robitzsch's paper)

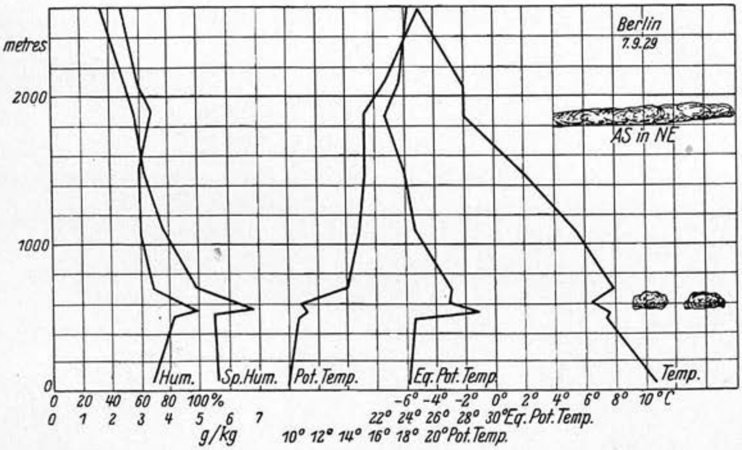

Fig. 8. Ascent through cloud sheets.

Surfaces of discontinuities

- A — Between two different airmasses (produced by horizontal movements of air)
  - a_1-fronts-inclined (see Fig. 4)
  - a_2-dry fronts-inclined (see Fig. 5a)
- B — In the same air mass
  - b_1-Inclined dry inversions (surfaces of subsidence near fronts) (see Fig. 6)
  - b_2-Horizontal dry inversions
    - By radiation at cloud layers (see Fig. 8)
    - By radiation at haze layers (see Figs. 7a, b and c)

VI. *Methods of formation of temperature inversions.*

There are five factors to be taken into account some or all of which may act simultaneously in varying degrees in producing dry inversions viz., a) horizontal movements bringing cold air below warmer dry air, b) 1. turbulence of mechanical origin, and 2. turbulence mainly of thermal origin with rising currents carried by their momentum slightly above their equilibrium position, c) subsidence and d) radiation. We shall now discuss these factors in detail and consider the role of each in the production of inversions.

a) Horizontal movements of air. — This factor [5] has usually been thought to be subsidiary in character in producing dry inversions, its effect being chiefly to intensify already existing inversions in certain cases. An example of dry inversion in the middle latitudes produced by horizontal movements of air is illustrated in Fig. 5a. In India, during the monsoon season however, we have striking examples of the dry inversions in lower layers being produced in this way by the ascent of surface heated dry continental air over the moist and cold (in the lower levels) monsoon air as shown in the schematic diagram Fig. 5b. The thermal relation of the two air masses become reversed aloft so that in higher levels the surface of discontinuity changes itself to a frontal type giving rise to warm and cold fronts.

b) Turbulence. — According to G. I. Taylor [6] if a current of air flows from a region of higher surface temperature to one of lower surface temperature, the temperature of the air layer in contact with the surface falls below that of the layers above it. This cooling of the air in contact with the surface extends upwards by eddy motion, and the longer the process continues the greater the height to which this cooling influence can be traced. The actual extent of cooling however will be decreasing upwards from the layers in contact with the surface. The upward transmission of cooling by eddy motion requires that the turbulence should be of mechanical and not of thermal origin. These conditions are frequent near the ground and the inversions so produced will be confined only to the lower layers of the atmosphere. The conditions mentioned above may however obtain higher up when there is an abnormally rapid change of wind with height. Douglas [7] has stated that in the case of the typical inversions above the lowest kilometre the strongest wind shearing is above the base of the inversion while the turbulence is below that level with a lapse rate upto the adiabatic. So that there is no conclusive evidence that this process is of great importance in producing inversions in higher levels.

2. About the importance of turbulence of purely thermal origin very little is known. Giblett [8] has however called attention to some observations made in Egypt where this factor probably predominates.

c) Subsidence. — Sverdrup [9] first pointed out that dry inversions in anticyclonic weather are caused in the free atmosphere by the sinking of the overlying air and its warming, and further by its spreading over the cold air below. He applied these ideas to the examination of an inversion over Frankfurt-a-Main, and assumed that the air at 1.5 km. (the top of the inversion) descended from the 4 km. level and that the specific humidity of the air remained constant throughout the descent. With these assumptions he found that if the air at the top of the inversion level had come down from a height of 4 km, the potential temperature at the inversion level ought to have been 30° C. Actually, however, the potential temperature was 19° C. In order to explain this, he assumed that the air had lost heat by radiation etc. during its descent, and hence concluded that in the centre of an anticyclone the potential temperature of the air during its descending movement in the lower part of the troposphere does not remain constant but that the air loses heat by radiation and other causes, and therefore the temperature changes are not truly adiabatic. No quantitative estimate has however been given to show how much cooling can in these circumstances take place by radiation and whether it is actually possible to explain a cooling of the order of 10° C in 24 hours.

This commonly accepted explanation of the maintenance of dry inversions in anticyclones by the descent of air cooled by radiation is untenable, firstly because the air at higher levels is potentially the warmer and it is least likely to be cooled by any process to descend spontaneously and secondly the descent of air due to the outflow of air at the bottom in stationary anticyclones takes place at the rate of 1 mm. per second or 86 metres in a day as has been calculated by Shaw [10]. For a local anticyclone over the British Isles on the 26th March 1907 the rate of descent came out to be 264 metres per day. Using the same method as adopted by Shaw, we have calculated the rate of descent in a few stationary anticyclones over middle Europe as well as over northwest India. The rates of descent found in some of these cases are 130 metres per day (9. 1. 29) and 106 metres per day (3. 2. 29) in the case of anticyclones over middle Europe, and 130 metres per day (3. 12. 30) and 144 metres per day (23. 12. 30) in the case of anticyclones over northwest India. The results show that if the air were to descend, as assumed by Sverdrup in the example cited by him, from 4 to 1.5 km. it will take 30 days to reach the inversion level. Further Sur and Roy [11] on the basis of Rossby's theory have made calculations for the changes in temperature due to vertical descent of layers of air during the period of existence of the anticyclone of 19th – 22nd December 1930 over northwest India the air over which had a rate of descent of 144 metres per day. Their calculation shows that the changes in temperature due to such slow vertical subsidence of air are of a negligible order.

Thus we see that the outflow of air from an anticyclone produces subsidence of the air column to the extent of a millimetre per second. The effect of this slow descent upon the physical conditions of the air is negligible in comparison with the effects due to more stirring events. The characteristics of an anticyclone are therefore not of air which has just accomplished a journey from the upper layers but of air which has time to take up local colour imposed by the surface and other conditions. In any case the descent is so slow that the effect of compression due to subsidence can be neglected in comparison with the effects of radiation and absorption as far as the origin and maintenance of dry inversions in the atmosphere are concerned.

Douglas [12], however, starts from another assumption. If air containing a cloud sheet subsides then owing to the different rates of adiabatic warming of the dry and moist air stability is increased at the upper surface of the cloud but is decreased at its lower surface. According to Douglas, the instability at the lower surface will tend to maintain the convection and therefore the cloud sheet if enough moisture were carried up to counteract the dryness caused by the general subsidence. For the supply of moisture to maintain the cloud, he contemplated the evaporation from the surface of the sea and the moisture taken upward by turbulence upto the region of instability already produced. This view, however, is not free from objections. It is common experience to meet with not only one dry inversion but as many as six or seven in one single aeroplane ascent. If all these inversions are to be explained by the general slow descent in the manner contemplated by Douglas, one will have to assume the presence of as many cloud sheets initially in the descending system as the number of inversions met with. If this is so, with the general slow descent of the whole system the cloud sheets will tend to evaporate. It is conceivable that moisture could be supplied upto the lowest cloud layer by evaporation from the sea and by turbulence, but it is difficult to imagine any process by which a supply could be maintained at all the cloud levels. Naturally therefore one should expect that when air having five or six cloud sheets begins to descend, all the cloud sheets will evaporate and after some time the whole system, except perhaps the lowest cloud layer, will behave as dry air, and the difference between the adiabatic rates of the warming of the moist and dry air will gradually disappear. In such circumstances one cannot possibly think how so many strong inversions will persist from day to day as is actually found to be the case. Further if these dry inversions are the result of slow subsidence of air, a natural consequence would be that they will not persist at about the same height from day to day, but would gradually sink. Again, it would be difficult for even the lowest inversion layer to be maintained from day to day if a mechanism of the type contemplated by Douglas for the supply of moisture is to be accepted. From experience we know that a Cumulus or Cumulo-Nimbus cloud will change to a sheet cloud only at its edges and not at the centre, where the ascending currents are strong enough to preclude any spreading unless there be initially a very strong inversion. If a general slow descent of the cloud sheet takes place the result will be, as pointed out before, stability at the upper surface and instability at the lower surface. The degree of instability will be more or less of the same order as the stability above, because the air above and below the cloud sheet will be less moist than the air in the cloud itself. As the ascending movements of air connected with the instability at the lower surface will be much stronger than the slow descent of the system itself, it is difficult to imagine how the descent and the inversion could be maintained once the instability is produced. Such an idea therefore cannot easily be accepted as being responsible for maintaining inversions for several days.

d) Radiation. — Radiation has been commonly used for explaining the surface inversions often met with in dry weather on clear winter nights. The importance of its role in producing inversions in the free atmosphere was recently emphasised in a qualitative manner by Mal [13]. He has stated that the haze layers composed of hygroscopic particles are warmed and cooled in a manner similar to the earth's surface, though not to the same extent, and thus produce inversions in the free atmosphere similar to the surface ones. According to him, therefore, if there is a humidity discontinuity marked by a haze or cloud boundary at its lower limit this by radiation will gradually change the temperature-height curve to an isotherm and ultimately to an inversion.

It is now proposed to discuss quantitatively the manner of formation of horizontal dry inversions in the free atmosphere by radiation during the night. A cloud sheet acts like a black body and the top and the bottom of the cloud layer, therefore, absorb and emit long wave radiation at their respective temperatures in accordance with Stefan's Law. Simpson [14] has further shown that a layer of air containing 0.3 mm. of precipitable water absorbs and radiates like a black body between the wave-lengths $5^1/_2\,\mu$ to $7\,\mu$ and from $14\,\mu$ onwards, is transparent to wave-lengths between $8^1/_2\,\mu$ to $11\,\mu$ (and therefore does not absorb or radiate between these wave-lengths, this energy being lost to space unless there be another cloud sheet above) and partly absorbs and partly emits radiation between the wave-lengths $7\,\mu$ to $8^1/_2\,\mu$ and $11\,\mu$ to $14\,\mu$.

The radiation leaving the cloud top at a temperature T° A. is given by

$$R_T = \sigma T^4 = [R_T]^{7}_{5^1/_2} + [R_T]^{8^1/_2}_{7} + [R_T]^{11}_{8^1/_2} + [R_T]^{14}_{11} + [R_T]^{\infty}_{14}. \qquad (1)$$

If the temperature of the next layer above the cloud containing 0.3 mm. of precipitable water is T_1, the radiation received back at the cloud top, provided there is no higher cloud, will be

$$R_{T_1} = [R_{T_1}]^{7}_{5^1/_2} + [R_{T_1}]^{\infty}_{14} + C_1 \qquad (2)$$

where C_1 is the part corresponding to the wave-lengths $7\,\mu$ to $8^1/_2\,\mu$ and $11\,\mu$ to $14\,\mu$; no part corresponding to $8^1/_2\,\mu$ to $11\,\mu$ occurs in this equation as the layer is transparent to radiation between these wave-lengths. Therefore the net loss of radiation at the top of the cloud is

$$H = R_T - R_{T_1} = [R_T - R_{T_1}]^{7}_{5^1/_2} + [R_T - R_{T_1}]^{\infty}_{14} + [R_T]^{8^1/_2}_{7} + C - C_1 \qquad (3)$$

where C stands for $[R_T]^{8^1/_2}_{7} + [R_T]^{14}_{11}$.

If the difference between T and T_1 is not large, the most important term in equation (3) will be $[R_T]^{11}_{8^1/_2}$, all other terms being small compared to it.

If there were another cloud layer at some height above, it would absorb and emit radiation between $8^1/_2\,\mu$ and $11\,\mu$ as a black body at the temperature of its lower surface. This emitted radiation will be received back at the top of the first (lower) cloud sheet and hence the net loss of radiation (H) found above will correpondingly decrease. The smaller the difference between the temperatures of the top of the lower cloud and the bottom of the higher cloud layer, the smaller will be the decrease.

The long wave radiation reaching the lower surface of the cloud from the earth's surface will also be absorbed and emitted back, the cloud base acting like a black body. The net effect of this will be, in general, a gain of heat at the lower surface of the cloud.

As soon as the cooling of the cloud begins, the effect will be transmitted above the cloud by radiative diffusion (k_R) and eddy conduction (k_E), and below by eddy conduction (k_E) with the progress of time[1]). For the height $\mathfrak{z}$ to which the cooling effect will extend in time t Taylor finds $\mathfrak{z}^2 = 2\overline{w}\,dt$; if we replace his $\frac{\overline{w}\,d}{2}$ in the fundamental turbulence equation by k, the eddy conductivity

$$\mathfrak{z} = 2\,(kt)^{1/_2}. \qquad (4)$$

---

[1]) The effect of turbulence (k_E) in transmitting the cooling upwards will probably be small unless there is a marked discontinuity in the wind.

Assuming different values for radiative and eddy diffusivity, it is possible to calculate from this equation the thickness of the layer to which cooling will penetrate in a certain time above and below the cloud. For the case in which the initial potential temperature Θ of the air is zero at all heights and the surface potential temperature Θ_0 decreases at a rate p° per second so that $\Theta_0 = -pt$, Taylor [15] finds that the fall in potential temperature at a height $\mathfrak{z}$ after a time t is

$$pt\,[(1+2u^2)(1-2\pi^{-\frac{1}{2}}\int_0^u e^{-\mu^2}d\mu)-2\pi^{-\frac{1}{2}}ue^{-\mu^2}] \quad (5)$$

where $u = \frac{1}{2}\,\mathfrak{z}\,(kt)^{-\frac{1}{2}}$. This equation has been graphically reprented in Fig. 9.

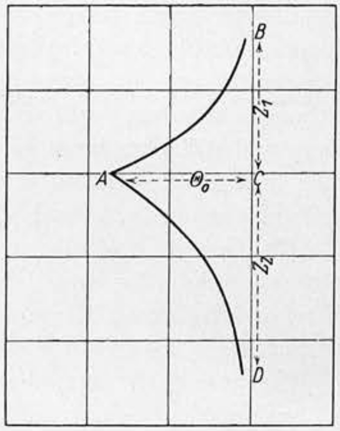

Fig. 9. Curve representing fall in potential temperature above and below the cooling surface according to equation (5).

The area ABD in Fig. 9 representing the total cooling in the entire affected layer will be proportional to the net loss of radiation (Ht) from the cloud. From these conditions the cooling ($\Theta_0 = -pt$) of the cloud surface can easily be calculated by drawing suitable diagrams.

Thus we see that radiation from a cloud to the clear sky at night cools the upper surface of the cloud and consequently the layer of air in contact with it; also the cooling spreads upwards by radiative diffusion and eddy conduction and below by eddy conduction and can be treated in a way similar to that worked out by G. I. Taylor according to which if Θ_1 be the potential temperature at any height $\mathfrak{z}$ above the cloud surface and Θ the initial potential temperature at all heights, then

$$\Theta_1 = \Theta - pt\,[(1+2\,u^2)\,(1-2\,\pi^{-\frac{1}{2}}\int_0^u e^{-\mu^2}\,d\mu) - 2\,\pi^{-\frac{1}{2}}ue^{-u^2}].$$

In a recent paper Brunt went through Taylor's analysis and came to the conclusion that Taylor's analysis holds good even if in the above equation potential temperature (Θ) of the air is substituted by ordinary temperature (T) of air, so that if the temperature of the air immediately in contact with the top of the cloud (at temperature T) falls at a uniforrm ate $\left(p = \dfrac{\Theta_0}{t}\right)$, then the temperature T' at any height $\mathfrak{z}$ above the cloud surface is gnive by

$$T' = T - \beta\,\mathfrak{z} - pt\,[(1+2\,u^2)\,(1-2\,\pi^{-\frac{1}{2}}\int_0^u e^{-\mu^2}\,d\mu) - 2\,\pi^{-\frac{1}{2}}\,ue^{-u^2}] \qquad (6)$$

where β is the temperature lapse rate. Thus knowing the cooling (Θ_0) by radiation at the top of a cloud layer, we can find out the temperatures at different heights above and below the cloud upto the maximum thickness that the cooling would extend, and thus draw the changed temperature height curves which will show inversions above the cloud. Such inversions will, in general, weaken during the day, and if not sufficiently strong ones, may disappear altogether due to absorption of solar radiation and evaporation at the cloud surfaces and increase of turbulence.

It may be pointed out that the cooling at the top of the cloud [17] will not cause a general sinking of the whole cloud sheet, but the cooling at the top and warming at the bottom of the cloud will diffuse downwards and upwards respectively within the cloud by eddy conduction with the progress of time. As a result, instability will set up within the cloud in layers near the top and the bottom. The distance to which the heating at the bottom and the cooling at the top will travel in time t will be given by equation (4). If the time t is such that the corresponding value of $2\mathfrak{z}$ is small compared with the thickness of the cloud itself, in that case, although turbulence will set up near the upper and lower boundaries of the cloud, there will still be a layer between them which will remain stable. If however t is such that $2\mathfrak{z}$ is comparable with the thickness of the cloud, the whole cloud sheet will become unstable and will break into St. Cu or A. Cu. type of cloud.

To illustrate the process of the development of an inversion in the free atmosphere by radiation from an initial cloud discontinuity, we give below examples of a few ideal cases. Examples have not been worked out in the case of haze discontinuities as no data on the absorption and radiation by haze layers are available.

Suppose there is a stratus cloud sheet at any height, say 1 km. which has

Thickness = 500 metres approx.
Temperature of the top $(T) = 273°$ A.
Lapse rate of temperature = 6° C/km.
Relative humidity in the cloud = 100%.
Relative humidity above the cloud = 40%.

The length of the air column in metres containing 0.3 mm. of precipitable water is given by

$$l = \frac{45 \cdot 9 m T_1}{e} \tag{7}$$

where

m = the amount of precipitable water in cms.,
T_1 = mean absolute temperature of the column, and
e = pressure of water vapour in millibars.

The length of the air column immediately above the cloud containing 0.3 mm. of precipitable water with humidity above the cloud as 40% will, therefore, be 150 metres approximately and hence the mean temperature of the column (T_1) will be 272° A. From equation (3), the net loss of radiation from the cloud top is given by

$$H = [R_T - R_{T_1}] = [R_T]_{8^1/_2}^{11} + a \text{ small quantity} = 0.071 \frac{\text{gm} \cdot \text{cal}}{\text{cm}^2 \cdot \text{min}} .$$

If the relative humidities above the cloud are assumed to be 20% and 60%, the mean temperature of the columns containing 0.3 mm. of precipitable water comes out to be 271.5° A. and 272° A. respectively and it is easily seen that the value of the net loss of radiation from the cloud is very little affected.

The values of k_R and k_E near a cloud surface are not definitely known. However in a recent paper, Brunt [18] calculated the value of k_R and found it to be of the order of 10^3 C.G.S. units. For calculations made here, the value of k_E below the cloud surface has been assumed to be 10^3 and 10^4 C.G.S. units. Table 2 gives the depths of the heated layer for $k = 10^3$ and $k = 10^4$ corresponding to different values of t.

Table 1.

t	$k = 10^3$	$k = 10^4$
10 minutes	15 metres	49 metres
1 hour	38 ,,	123 ,,
5 hours	84 ,,	270 ,,
10 hours	120 ,,	384 ,,

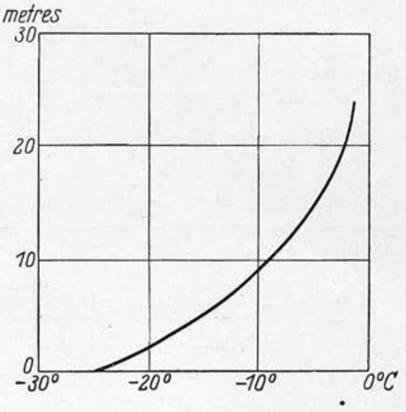

Fig. 10.

It has been pointed out before that the total area ABC (A_1) and ACD (A_2) (Fig. 9) would be proportional to the net loss of radiation from the cloud surface in a time t provided $\mathfrak{z}_1$ and $\mathfrak{z}_2$ were the corresponding limiting thicknesses above and below the cloud surface and Θ_0 was the actual cooling of the cloud surface in time t. Now if we draw another diagram for a case when the actual cooling is not Θ_0 but Θ' and the corresponding limiting depths above and below the cloud are $\mathfrak{z}_3$ metres and $\mathfrak{z}_4$ metres respectively in time t, then

$$Ht = 100\,\varrho\,\sigma \left(\frac{A_1 z_3}{z_1} + \frac{A_2 \mathfrak{z}_4}{\mathfrak{z}_2} \right) \frac{\Theta'}{\Theta} \qquad (8)$$

where

$H =$ the net loss of radiation in gm/cal/cm²/min.,
$t =$ time in minutes,
$\varrho =$ density of air,
$\sigma =$ specific heat of air at constant pressure.

In order to calculate the values of the cooling, a curve was drawn using equation (5) for an arbitrary value of Θ_0 say 25° C. and two thicknesses $\mathfrak{z}_1 = \mathfrak{z}_2$ 24 metres (see Fig. 10)[1]).

From this diagram the area $A_1 = A_2 = 212$ units.

In the example taken, if $t = 10$ hours and $k_R = k_E = 10^3$ C.G.S. units, we have $\mathfrak{z}_3 = \mathfrak{z}_4 = 120$ metres. Further the net loss of radiation in 10 hours is

$$Ht = 0.071 \times 10 \times 60 \text{ gm. cal/cm}^2.$$

Therefore from equation (8), $\Theta' = 17.7^\circ$ C. If however $k_R = 10^3$ and $k_E = 10^4$, we have $\mathfrak{z}_3 = 120$ metres and $\mathfrak{z}_4 = 384$ metres and $\Theta' = 8.6^\circ$ C.

If there is another cloud layer above with temperature of its base as 263° A., the net loss of radiation (H) reduces to .014 gm. cal/cm²/min. In the foregoing calculation, if H is taken to be .014, the corresponding values of Θ' come out as 3.5° C. and 1.7° C. respectively.

Using equation (6) and the values of cooling of the surface of the cloud (Θ') obtained above, the cooling at the various heights above and below the cloud was calculated. These values are given in Table 3.

---

[1]) Only the upper half of the curve is drawn as the lower half will be similar to the upper half $\mathfrak{z}_1$ being equal to $\mathfrak{z}_2 = 24$ metres.

The temperature height curves above and below the cloud using these values are shown in Fig. 11.

Table 3.

Ratio $\frac{x}{\mathfrak{z}}$	Cooling in degrees C			
	One cloud sheet		Two cloud sheets	
	$k_R + k_E = 10^3$, $k_E = 10^3$	$k_R = k_E = 10^3$, $k_E = 10^4$	$k_R + k_E = 10^3$, $k_E = 10^3$	$k_R + k_E = 10^3$, $k_E = 10^4$
0	17,7	8,6	3,5	1,7
$\frac{1}{8}$	13,2	6,5	2,6	1,3
$\frac{1}{4}$	9,8	4,8	1,9	0,9
$\frac{3}{8}$	7,0	3,4	1,4	0,7
$\frac{1}{2}$	5,0	2,4	1,0	0,5
$\frac{5}{8}$	3,5	1,7	0,7	0,3
$\frac{3}{4}$	2,3	1,1	0,5	0,2
$\frac{7}{8}$	1,4	0,7	0,3	0,1
1	1,0	0,5	0,2	0,1

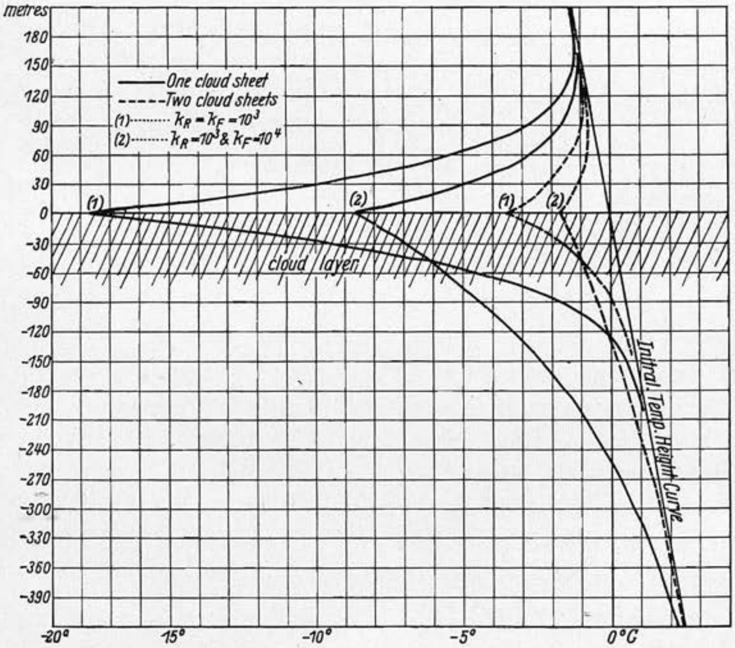

Fig. 11.

In the above calculations, no allowance has been made for the change in the value of H with time. It may be mentioned that as the surface cools, the value of H also decreases progressively and hence the net loss of radiation in a period of 10 hours will be some what less than what has been taken above. It will be seen, however, that by lowering the initial temperature of the radiating surface by 5° C., the value of the net loss of radiation is decreased by about 12%. This will, therefore, neither affect the arguments nor the form of the curves obtained.

The curves show that (1) a large part of the cooling is confined to a comparatively thin layer near the radiating surface and (2) the upper boundary is not sharp and the changed temperature curve merges gradually into the original curve. This is in agreement with the observed temperature height curves met with during aeroplane or kite ascents (see * in Fig. 1). It appears, therefore, that one should expect a smoothing of the temperature height curve rather than a sharp kink at the top of the inversion, and that this smoothing is not due to instrumental lag as has been generally regarded so far.

VII. *Mechanism of the production of haze layers in the atmosphere.*

The experience of aeroplane ascents has shown that the atmosphere gets divided into a number of horizontal stratified layers after the passage of a cyclone. A similar tendency to a manifold layering of the lower part of the troposphere has been pointed out by Peppler [19] in his paper on the discussion of Kite and Balloon ascents data at Lindenberg and Friedrichshafen. Peppler's conclusions are

1. That inversion layers tend to occur at certain distinct levels more frequently than at others.
2. That the levels of the maximum inversion frequency are little affected by changes of seasons.
3. That they coincide approximately with different cloud stages.
4. That the thickness of cloud layers [20] decreases with height.
5. That the intensity of inversions continuously decreases with height and strong inversions occur only in the lower levels, inversions of the value of more than 3° C. being absent above 3 km.

Clayton [21] was led to the same conclusion in his discussion of the cloud observations of the International year (1896–1897). His conclusions can be summarised as follows: —

1. There are certain distinct levels or stages in the atmosphere where clouds are formed more frequently than at others.
2. The maxima of cloud frequency occur practically at the same height at widely different places, thus indicating that they are neither local nor accidental.

Since there is an intimate relationship between the occurence of cloud and inversions, as been shown before, it is not at all surprising to find a general agreement between the results of Peppler and Clayton.

Mendenhall and Mason [22] have studied the stratification of powdered rock suspensions in water and found that the suspended material separates into layers when exposed to light altough tendency for stratification is found to be absent when the settling is allowed to take place in a dark room having uniform temperature. From a series of experiments, they have concluded that stratification only occurs when there is a lateral temperature gradient across the liquid and there is also a vertical density variation. Temperature gradients had to be within certain limit, higher gradients destroying the stratifications already formed with lower gradients. The vertical density variation is brought about automatically by a tendency of the suspended particles to settle according to Stokes' Law. According to them, lateral temperature gradient, in the presence of a vertical density variation, produces localised convective systems which are primarily responsible for stratified subsidence.

It is suggested that the observations of Clayton and Peppler regarding the existence of a number of haze layers after the passage of a cyclone (even in the absence of temperature inversions) may be explained on the analogy of Mendenhall and Mason's experiments. Both the essential conditions for stratification of suspended particles, namely the existence of vertical density variation and lateral temperature gradients, exist in the free atmosphere. As the atmosphere contains numerous particles of varying sizes and nature, after the passage of a cyclone, when vigorous convective processes have ceased and stable conditions established, the particles settle down in accordance with Stokes' Law and hence a vertical density gradient (density increasing downward) is established. Also a lateral temperature gradient generally exists in the atmosphere; it has been shown statistically by A. Peppler [23] that there are differences of temperature in the various quadrants of anticyclones. It is considered, therefore, that the reasoning applied by Mendenhall and Mason to explain stratification of particles suspended in water may also apply in the case of the atmosphere which would show a tendency to stratification due to the existence of the two conditions, provided the vertical temperature lapse rate is near the adiabatic (potential temperature remains practically constant). This will lead to manifold haze layers, leading to the development of humidity discontinuities at these layers, which in some cases may also give rise to cloud sheets. Once these haze discontinuities or cloud sheets are produced, temperature inversions follow, being produced by radiation in the manner already explained. Morrison [24] has studied the effect of light on the settling of suspensions and concluded that exposure to light brings about stratification. His photographs obtained in the laboratory resemble closely the appearance presented by the haze layers in the atmosphere.

Summary.

1. From an analysis of aeroplane and kite ascents of Lindenberg and Berlin evidence has been brought forward that after the passage of a cyclone haze discontinuities in the atmosphere precede temperature discontinuities, as pointed out by Kopp from his experience of aeroplane flights. An actual example which shows that temperature inversion follows as a result of radiation from the haze or cloud discontinuities has also been given.

2. The various processes of development of dry inversions have been discussed. It has been argued that slow subsidence of air cannot adequately explain the formation of the dry horizontal inversions within an anticyclone. Radiation has been discussed in detail and it has been shown that cooling of the top of a cloud or haze layer by radiation and the spreading upward and downward of this cooling effect by radiative diffusion and eddy conduction offers a satisfactory explanation for the formation of horizontal dry inversions both qualitatively as well as quantitatively.

3. On the analogy of Mendenhall and Mason's experiments on the "stratified subsidence of suspended particles", a mechanism has been suggested for the production of a number of haze particles in the atmosphere met with in one single aeroplane ascent after the passage of a cyclone.

Acknowledgments.

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EVIDENCE IN FAVOUR OF NON-SYMMETRICAL STRUCTURE IN THE INNER STORM AREA OF CYCLONES IN THE INDIAN SEAS.

By
B. N. Desai and **S. Basu**, Poona.

(With 6 figures.)

Summary at the end.

Introduction.

It has long been known that cyclonic storms of very great intensity form in the Indian seas only during the transition seasons before and after the southwest monsoon period of June to September. It has also been recognised that an interplay between two different currents of air of land and oceanic origin is responsible for initiating the development of a cyclonic circulation. Whatever may be the theories regarding the actual formation of these storms, there is no doubt that the storms do originate at a zone of separation or surface of discontinuity, generally not very sharply defined, between two different air masses. Perhaps the clearest indication of this is the fact that the average places of origin of cyclones in the Indian seas in different seasons roughly coincide with the boundary separating the southerly air of oceanic origin (monsoon air) from northerly air of land origin (continental air). The month to month shift in the places of the origin of storms corresponds with the forward or backward movement of one or the orther air current. Further, it has been noticed during the initial stages of a cyclone formation that a strengthening of the moist air current or its temporary excursion beyond its normal limit is almost an invariable precedent to the formation of the storm. Also a disturbance, when once started, is not maintained and does not intensify into a storm without the effective presence of the air current of land origin in the region of the disturbed weather.

Recent work (1) on the examination of the structure of storms in the Indian seas has shown that in a fully developed cyclone it is possible to distinguish different air masses and to recognise their effect in giving rise to well-marked "fronts" showing different characteristics of weather. It must be stated, however, that the fronts met with in the Indian latitudes have somewhat different, and some extra, characteristics from those of middle latitudes, most probably because of the greater moisture content of the monsoon air and consequently the greater intensity of the precipitation and its associated phenomena; the temperature contrast in the lower levels between the two air currents is much less than it is in the middle latitudes and may be entirely absent, or may even be reversed as in the case of the premonsoon storms when the air over the Indian continent is warmer than that over the adjacent sea upto about 1 to 2 km. above the surface. Hence to look for the fronts dividing different air sectors in the storm field, one has to depend mostly on wind discontinuities and associated weather and rainfall rather than on temperature contrast.

A tropical cyclone is generally considered to consist principally of three different parts — the outer region in which winds of force 6—9 prevail, the inner storm area with very rapidly falling barometer and winds of force 10—12 and the central calm area where pressure is lowest and winds are either light or even calm. In some of the papers regarding storm structure, it has been suggested that although one is able to recognise different air sectors and fronts within the comparatively less intense tropical storms, yet it is doubtful, if the same is true, in the case of the typical tropical cyclones which show the characteristic V-shaped barogram and the existence of the inner hurricane region (2) (3). The general impression gathered from other writers may be summed up in the following words (4): — While it is possible to locate different air sectors and fronts in a fully developed intense tropical cyclone in the region known as the outer storm area, it is doubtful if their existence can be accepted within the inner zone of hurricane winds and rapidly falling barometer and that within this area, the winds, rain and other meteorological elements must be symmetrically distributed round the centre or "eye" of the storm.

The question which naturally arises is: Are air sectors and fronts really absent within the inner storm area of a tropical cyclone or is the belief in the symmetrical distribution of weather round the centre of a cyclone based only on a lack of sufficient observations within the hurricane zone? Recent investigators in India (1) have not sufficiently stressed the weather phenomena very near and around the centre of a cyclone. The object of the present paper is to examine the available data, observations on land as well as on ships at sea from within inner storm areas of some typical tropical cyclones in the Indian seas, and to set forth what evidences may be deduced regarding the distribution of weather and rainfall in the inner zone of cyclones.

Examples of non-symmetrical structure in the inner storm area.

In Figs. 1—5 are given the observations of pressure, winds and weather remarks as recorded during the passage of a few notable cyclones (tracks shown in Fig. A) on steamers at sea or over coastal observatories. In what follows, rapid fall or rise of pressure and winds of force 10—12 have both been considered for defining roughly the limits of the inner storm area of each cyclone; these limits have been indicated by broken lines on the two sides of the barometric minimum in the figures.

Case 1. Arabian Sea Storm of 9th to 10th November 1925.

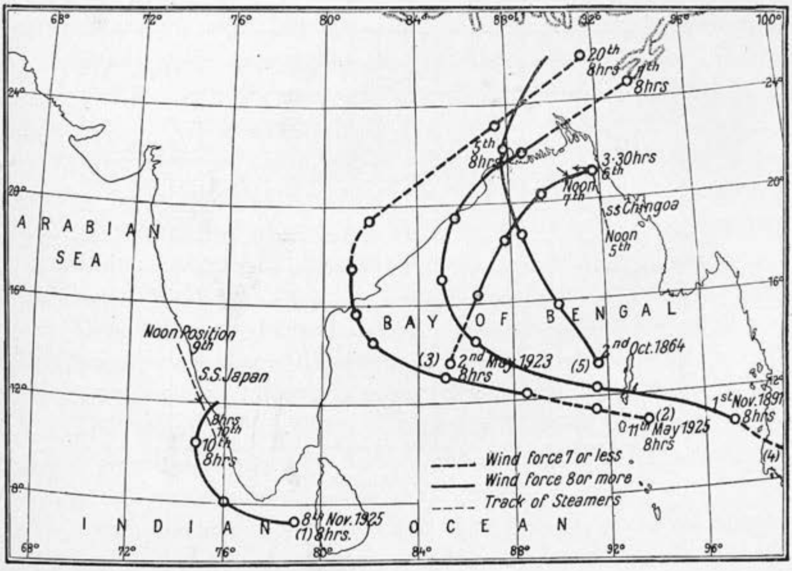

Fig. A.

This storm (1 in Fig. A) formed to the west of Colombo, moved first in a WNW-ly direction and later curved northeastwards through northwest and north. It filled up very rapidly after striking the north Malabar coast in the early hours of the 11th morning. The storm although of very great intensity was a concentrated one, the diameter of the area of stormy winds not exceeding 70 to 80 miles on the 10th morning.

In Fig. 1 are shown the four hourly observations of pressure, winds and weather remarks recorded on S. S. Japan, bound from Bombay to Colombo, which experienced the full force of the storm between 8 and 16 hours on the 10th. The course of the steamer is shown in broken line in Fig. A. Between 8 hrs. and 10 hrs. on the 10th, the pressure fell very rapidly from 29.60″ to 28.88″ and rose equally rapidly between 10 and 12 hours. With the steep fall of pressure between 8 and 10 hrs. the wind increased from light breeze (force 3) to storm force (force 11). On the other hand, between 10 and 12 hrs. when the pressure was rising rapidly, the wind was blowing with hurricane force which was maintained till about 16 hrs. After the shift in wind direction between 10 and 12 hrs. heavy rain and vigorous squalls were also recorded (at 12 hrs.) — a feature which is absent for the corresponding period of rapidly falling barometer. Between 12 and 16 hours although the rise of pressure was less rapid yet the wind continued to blow with hurricane force, while there was only light breeze at the corresponding period of the falling barometer between 4 and 8 hrs. on the 10th; also, the wind direction was constant at SSE for 6 hours, changed fairly suddenly

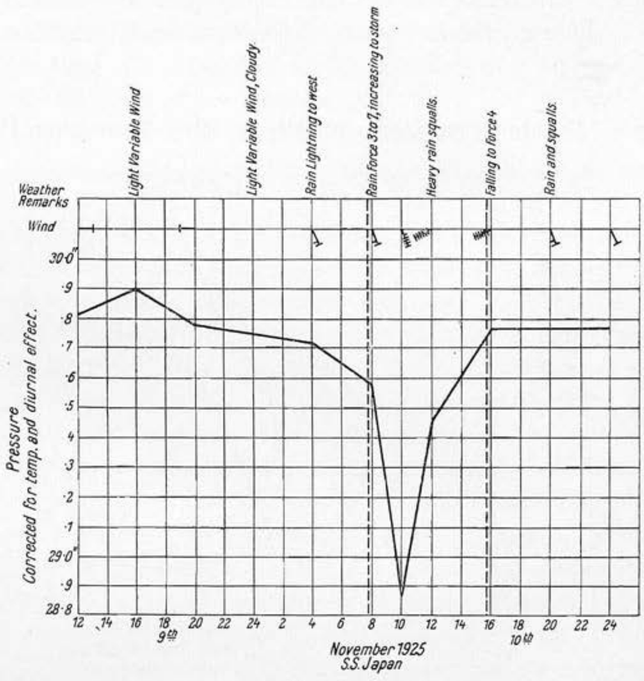

Fig. 1.

and then became constant for 6 hours at WSW. From the available reports it is not possible to say if there was a calm centre in this cyclone.

It is thus quite apparent that there was considerable difference between the wind force and weather experienced during the falling and rising periods of the barometer and that there were two persistent wind fields one SSE and the other WSW.

Case 2. Masulipatam Cyclone of 16th May 1925.

A depression, which formed in the South Andaman Sea on the 11th, moved westnorthwestwards and intensified into a severe storm (2 in Fig. A) on the 13th. Thereafter the cyclone took a more northerly course, crossed the coast a little to the north of Masulipatam on the 16th afternoon and weakened rapidly into a depression by the next morning; the diameter of the inner stormy area was about 100 miles on the 16th morning. The depression curved northeastwards and broke up in the Khasi hills in Assam on the 20th.

The observer at Masulipatam recorded a valuable set of hourly barometer readings and other observations on the 16th; these are given in Fig. 2. The rapid fall of pressure began at about 8 hours on the 16th and the lowest barometer was reached at about 13.45 hours. It is noticeable from the figure that the change in wind direction from NNE (force 6) to SW (force 8) between 8 hrs. and 9 hrs. on the 16th took place much earlier than the arrival of the calm centre with the barometric minimum at 13 hrs. 45 mins. After 13 hrs. 45 mins. there was a calm for about 10 minutes and then the wind again began to blow a whole gale from almost the same direction from which the wind was blowing before the arrival of the calm centre.

Thus the striking features in this case are (a) a wind shift much earlier than the arrival of the barometric minimum with calm centre and (b) wind from the same direction on the two sides of the barometric minimum and calm centre.

Case 3. Cyclone of 4th to 6th May, 1923, in the Bay of Bengal.

This cyclone (3 in Fig. A) originated in the central Bay of Bengal on the 3rd and moving at first in a NE-ly and then in an ENE-ly direction struck the coast to the south of Cox's Bazar on the 6th morning and broke up in the Arakan hills in the course of that day. Two steamers S. S. Okara and S. S. Chinkoa were involved in the central calm region, the first of which foundered while the latter survived; the observations recorded

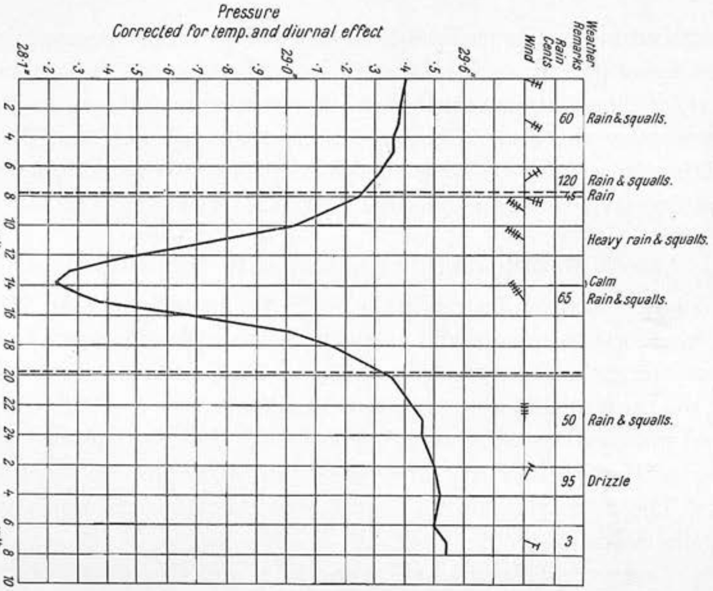

Fig. 2.

May 1925 Masulipatam

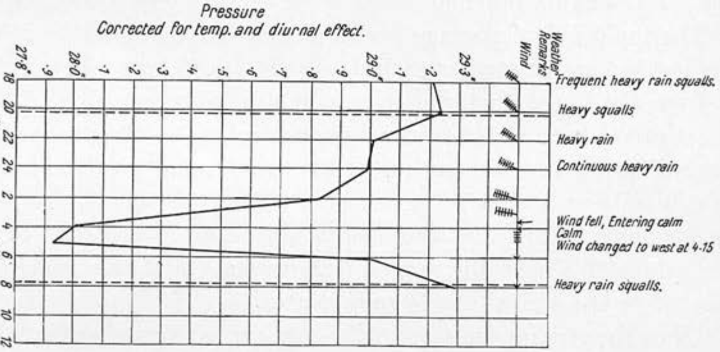

Fig. 3.

May 1923 S.S. Chinkoa

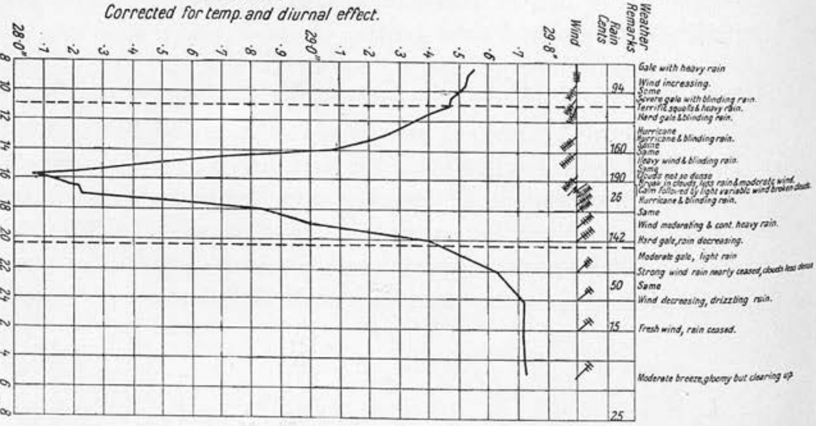

Fig. 4.

November 1891 False Point Light House

on this Steamer are shown in Fig. 3. The course of the S. S. Chinkoa is shown in broken line in Fig. A. It is to be noted that she changed her course to west after 3.30A. M. on the 6th as given in her log. The diameter of the central calm was about 7 miles and of inner stormy area more than 100 miles on the 6th morning.

At 20 hrs. on the 5th the wind experienced by S. S. Chinkoa increased to a southwesterly hurricane which, together with the commencement of the quick fall in pressure, marks the entry of the steamer into the inner stormy region. From 22 hrs. on the 5th to 2 hrs. on the 6th, the wind was slightly backing. After 2 hrs. the pressure began to fall very rapidly, the fall continuing upto 5 hrs. when the lowest pressure was recorded. Between 3 and 3.30 A. M., however, the direction of the wind had changed from south to north, and its strength had decreased showing that the steamer was entering the central calm area; between 3.30 and 4 A.M. she was within the calm centre. At 4 hrs. the wind was blowing from north, at 4.10 hrs. from northwest and five minutes later from west. At 5 hrs. the wind had again increased (force 10) and the pressure commenced to rise very rapidly. By 6 hrs. the pressure had risen from 27.93″ to 29.00″ and the wind had decreased in strength.

The points which should be noted are that (a) the wind shift between 3 and 3.30 A.M. occurred before the calm centre passed over the ship and that (b) the calm centre was encountered $1^1/_2$ hours before the time of the lowest barometric pressure.

Case 4. Port Blair Cyclone of 5th November 1891 (over False Point).

A storm (4 in Fig. A) entered the Bay from the Gulf of Siam on the 31st October 1891; it passed over Port Blair in the early hours of the 2nd November and continued to move in a NW-ly direction till the 3rd. It then curved to north and then northeastwards and passed over False Point on the afternonn of the 5th, near Saugor Island on the 6th and, rapidly weakening thereafter, filled up near Silchar in Assam on the 7th. On the 5th morning, the diameter of the central calm was about 5 miles and of inner stormy region about 90 miles. The central calm area passed over the False Point Light House between 4.05 and 4.45 P.M. on the 5th. The Port Office which was about 6 miles to the NNE of the Light House was just on the outer western edge of the calm centre. The comparative observations at the Port Office and the Light House at False Point are given in ELIOT's Cyclone Memoirs, Part IV, pp. 77—79.

The hourly values of pressure at the Light House and the direction and force of the wind, the weather remarks and the rainfall amount whereever available are given in Fig. 4.

By 11 A.M. the steep pressure fall of the inner storm area had started and the wind was blowing a SE-ly hurricane accompanied by heavy rain upto 15.30, at 14 hrs. 1.6″ of rain being recorded. At 15.45 the lowest pressure was reached and the clouds became less dense. At 16 hrs. rain decreased and there was a break in the clouds. The calm centre passed between 16.05 and 16.45 with variable winds following the calm. At 17 hrs. the wind had again reached hurricane force, but was NW-ly and was accompanied by heavy rain. A NW-ly hurricane continued to blow while pressure was rising rapidly and heavy rain occurring at the same time; 1.42″ were recorded between 5 and 8 P.M. After 20 hrs. the rise in pressure became less rapid and the wind decreased and moderated.

The noteworthy features in the inner region of this cyclone are (1) the wind shift from SE to NW did not occur immediately before and after the barometric minimum, but occurred during the rapid rise of pressure after about 30 minutes of the barometric minimum, so that the calm centre with the wind shifts on its two sides did not coincide with the occurrence of the lowest pressure and (2) greater intensity of rain between 11 and 16 hrs. (about $3^1/_2$″) than between 16 and 21 hrs. (about $1^3/_4$″).

Case 5. Calcutta Cyclone of 5th October 1864.

This cyclone (5 in Fig. A) formed in the neighbourhood and to the west of the Andaman Islands on the 2nd and moved in a NNW-ly direction upto the 4th. Thereafter, it curved to NNE through N, passed to the northwest of Calcutta on the 5th afternoon and broke up near the Khasi hills in Assam by the next day. The diameter of the calm centre was about 5 miles and of the inner stormy region about 80 miles on the 5th morning.

Although the calm centre did not pass over Calcutta yet that station experienced the full fury of the hurricane zone and was inundated by a huge storm wave. The hourly values of pressure and the autographic records of rainfall and wind obtained at the Surveyor-General's Office, Calcutta, as well as the wind directions and weather remarks for the period after the anemograph was blown off are taken (Fig. 5) from the report on the cyclone by Lt. Col. Gastrell and Mr. Blanford.

At 10 hrs. the wind suddenly veered to ESE, its pressure being about

8 lbs. per sq. foot (50 mph) and the rainfall ceased 10 minutes later. Hereafter a sharp fall of pressure began, the pressure reaching a minimum at about 14 hours 45 minutes. The wind continued to blow from an ESE-ly direction upto 12 hrs. when it veered to SE, its force rising rapidly at the same time. It was blowing a hurricane between 12 and 13 hrs. after which the vane of the anemometer was bent and broken

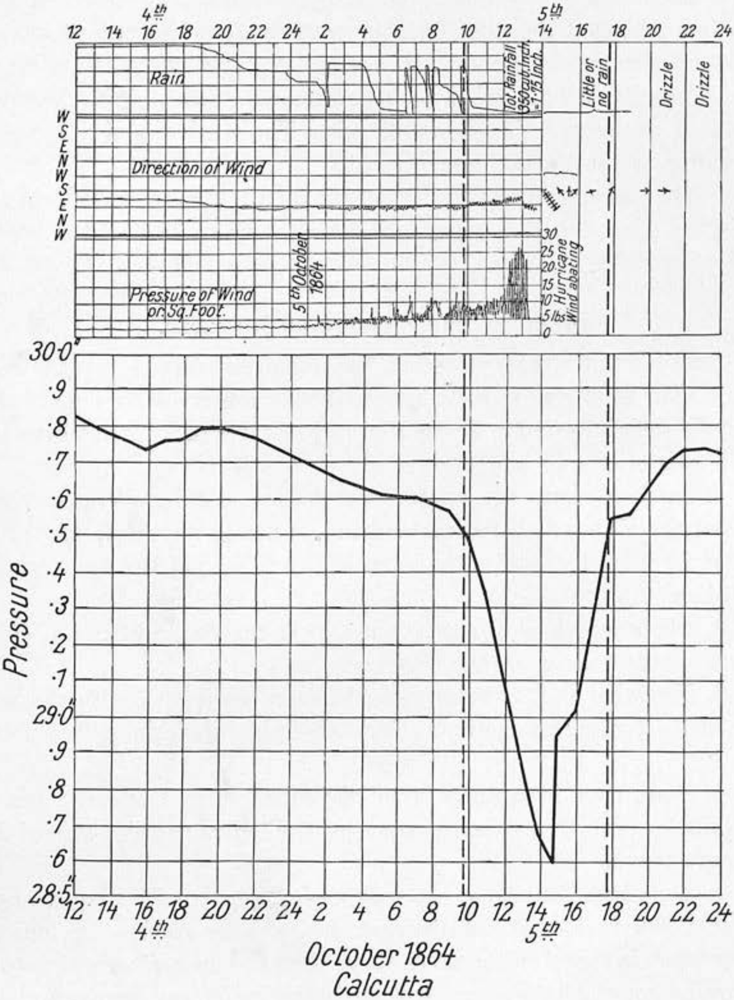

Fig. 5.

and its indications were untrue; at about 13.30 hrs. the whole of the apparatus in the roof and verandah of the observatory were blown away. According to the report, however, the maximum wind velocity was experienced at the time of the lowest barometer and was estimated at 90 miles or more per hour. After 14 hrs. 45 mins. the pressure began to rise rapidly and the wind velocity decreased although its direction remained unchanged till 15 hrs. 30 mins. The wind direction changed thereafter to southwest through south.

The important feature in this cyclone is that there was no change in the wind direction before and after the occurrence of the lowest barometer at 14.45 hrs.

Summary and Concluding Remarks.

Five cases of severe cyclones in the Indian seas have been examined with a view to study the distribution of the various meteorological elements in their inner storm areas. The chief features brought out from the study can briefly be summarised as:

1. In some cases, the rainfall distribution is different on the two sides of the V-shaped barogram and the nature of the precipitation, as well as its intensity, within the hurricane zone are not the same on the two sides.

2. The strength of winds is found to be markedly different before and after the passage of the centre.

3. The wind shift in some cases does not correspond with the passage of the barometric minimum, but takes place sometime after or before it.

4. Cases have been found when the calm centre does not coincide with the lowest pressure; it may occur on the falling or rising side of the pressure curve.

In a study of this kind, the only useful data are the frequent and detailed observations at the observatories near the track of cyclone or on steamers involved in the inner storm area and such observations are naturally scarce. All the severe cyclones in the Indian seas were examined from this point of view. In many of the cases however, detailed information about the nature and intensity of precipitation and the characteristics of weather were lacking, and therefore they could not be used to support the views presented in this paper. However, the five cases described above point out that the recorded observations are difficult to reconcile with the ideas of symmetrical distribution of meteorological elements within the inner storm area. It is proposed to discuss in a subsequent paper the structure of these cyclones with special reference to their inner storm areas.

We take this opportunity of expressing our sincere thanks to Dr. C. W. B. Normand for his very valuable suggestions and criticisms during the course of preparation of this paper.

Meteorological Office, Poona (India).

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VERTICAL STRUCTURE OF THE SURFACE OF DISCONTINUITY BETWEEN THE CONTINENTAL AND THE MONSOON AIR MASSES IN THE PRE-MONSOON PERIOD.

By

B. N. Desai and S. Mal
Poona

(With 4 figures)

In a previous paper (1) it has been shown that the characteristics of the fronts associated with the cyclones of the post-monsoon period are similar to those of the cyclones of middle latitudes. The present note describes the nature of the front between the continental and monsoon air masses in the pre-monsoon period.

Although the seasonal trough of low pressure was established over the Gangetic plain by the beginning of May, 1930, the "low" over the south Bay of Bengal associated with the northeast monsoon had not been pushed down below the latitude of Ceylon; signs of the development of a surface of discontinuity between the air of land origin (continental air) and of oceanic origin (monsoon air) in the neighbourhood of Lat. 6 °N and Long. 87 °E were noticeable on the 2nd. This surface of discontinuity moved westwards and with the strengthening of south-easterly to southerly winds, a depression formed by the 5th evening with centre in the neighbourhood of Lat. 6 °N and Long. 84 °E. The position of the surface of discontinuity on the 6th, 7th and 8th is given in Fig. 1.

The 8 hrs. temperatures at Mercara, Coonoor and Kodaikanal on the 7th and 8th which are given in the following Table give an idea about the thermal properties at different heights upto about 2.4 km. of the two air masses.

Table I.

Station	Height above M. S. L.	7th			8th		
		D. B.	W. B.	Specific Humidity	D. B.	W. B.	Specific Humidity
Mercara . .	1.15 km.	71° F	69° F	17.4 g/kg.	65° F	64° F	14.5 g/kg.
Coonoor . .	1.74 ,,	60 ,,	59 ,,	12.3 ,,	61 ,,	61 ,,	14.6 ,,
Kodaikanal .	2.34 ,,	52 ,,	52 ,,	11.0 ,,	58 ,,	57 ,,	13.4 ,,

The average lapse rates come to 15 to 17 degrees F. and 5 to 7 degrees F. at 8 hrs. on the 7th and 8th respectively. These lapse rates can therefore be taken to indicate that on the 7th morning there was continental air over these stations and this was replaced by the monsoon air (of oceanic origin) by the 8th morning. An examination of the source of air masses over these stations on the 7th and 8th also supports this conclusion. The values of specific humidity at Mercara might give one an idea that the continental air has higher moisture content than the monsoon air. This apparent inconsistency is due to the fact that in the lower levels the temperature of the continental air is higher than that of the monsoon air and it is quite likely that an air mass with higher dry bulb temperature, although it may be unsaturated, may show higher specific humidity than another air mass with lower dry bulb

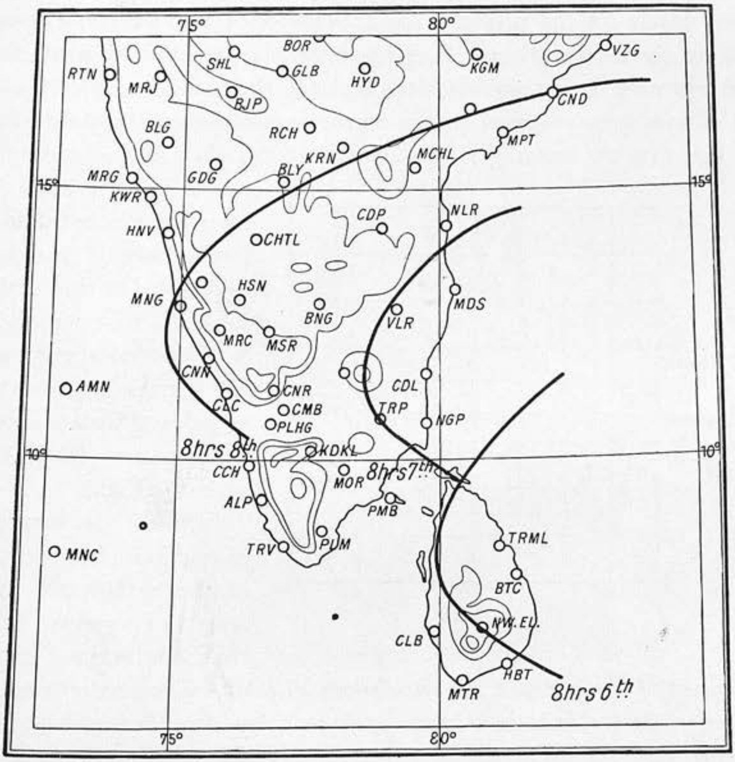


Fig. 1.

temperature but saturated at the same time; the moisture retaining capacity of the continental air below the reversal level due to its higher temperature will certainly be greater than the monsoon air. It is also likely that the monsoon air may be supersaturated although the dry bulb and wet bulb readings do not indicate it. It will also be seen from the Table that the monsoon air is colder than the continental air in the lower levels (in the present case at least upto the level of Coonoor) and up above it is warmer than the latter as indicated by Kodaikanal temperatures. It is therefore clear that the thermal relation of the two air masses gets reversed in the upper levels above a certain height in the present instance above about 1.75 km. (2). As the continental air is warmer than the monsoon air in the lower levels only it has been designated as the "surface heated" continental air. The vertical structure of the surface of separation as deduced from the above temperature changes is given in Fig. 2.

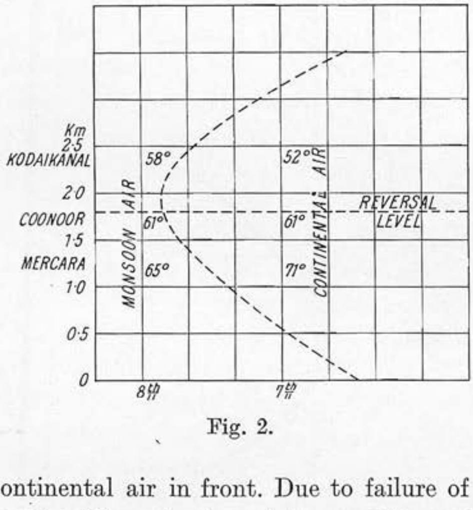
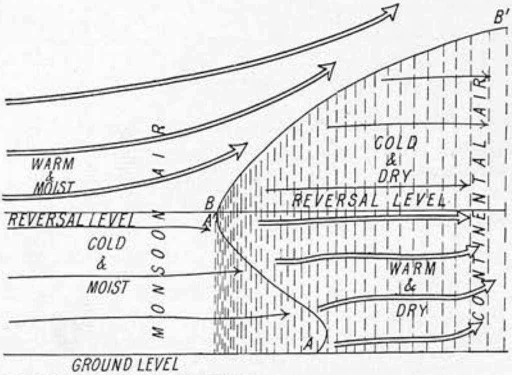


Fig. 2.

From the synoptic charts it is observed that at the surface the monsoon air moves faster than the surface heated continental air in front. Due to failure of pilot balloon ascents on account of low clouds and heavy rain on these days it is not possible to say how the wind speed varies with height near the front in the two air masses above a height of about 1 km. From the data available it can be said that upto about 1 km. the monsoon air moves faster than the surface heated continental air in front; also the wind speed in the surface heated continental air near the front increases with height, while that in the monsoon air shows a tendency for a decrease with height.

The monsoon air being specifically heavier and moving faster than the surface heated continental air in the lower levels will push underneath the latter. Above the reversal level the monsoon air being specifically lighter than the surface heated continental air will rise above it. Thus in spite of the fact that in the lower levels the surface of discontinuity acts like a cold front higher up it behaves as a warm front. The probable vertical structure of such a front will be as given in Fig. 3. It should be stated that it is generally found difficult to locate the position of this front at the surface as it is somewhat diffuse. It is likely that the mixing which takes place at the surface of separation is responsible for the diffuse nature of the front.

It will be quite apparent from Fig. 3 that the lifting up of the surface heated continental air over the monsoon air at AA' will not entail any condensation and hence no energy will be liberated. Higher up the thermal conditions however get reversed and therefore as the monsoon air ascends over the surface heated continental air at BB', condensation will occur and a considerable amount of energy will be liberated. It is therefore clear that the structure of the front above the reversal level is more important than that below it from a thermodynamic point of view.



VERTICAL STRUCTURE OF FRONT
EAST TO WEST MOVEMENT OF FRONT

Fig. 3.

From the vertical structure given above (Fig. 3) it will be clear that the rainfall associated with the front will actually begin at stations below A' and hence from the point of view of distribution of rainfall with reference to the position of front at the surface it will be found to be occurring on both the sides of the front in the monsoon air as well as in the surface heated continental air. The area over which the rainfall will occur towards the monsoon air side will depend on the slope of the surface of separation AA', for if it is steep the precipitation will not be found to be occurring over an extended area in the monsoon air although the intensity might be great in the monsoon air near the surface of separation. At stations above the reversal level the frontal rain will occur only on the surface heated continental air side as in the case of warm front in the post-monsoon storms and in the extra-tropical cyclones. How far this type of distribution of rainfall occurs actually will be seen from Fig. 4[1]) and Table II.

It will be seen from Fig. 4 that at Bangalore, the station below the reversal level, the frontal rain began at about 9 hrs. on the 7th and although the station actually got in the monsoon air between 12 and 16 hrs. as shown by temperature changes, it continued to have rain till the next morning. This record therefore shows that the theoretical consequences of a vertical structure of the type given in Fig. 3 were satisfied in the present instance. On the other hand at stations above the reversal level the distribution of rainfall in connection with the surface of separation was wholly on the surface heated continental air side as seen from Table II. Kodaikanal began to get warm front rain after 10 hrs. on the 6th, no rain having been recorded in the previous 24 hrs. The intensity of precipitation increased with the approach of the warm front to the station. The front seems to have passed over the station after the time of minimum temperature and before 8 hrs. on the 8th as indicated by a rise of temperature during that period; also at 8 hrs. the station was not having any rain thus showing that it was already well within the monsoon air. Between 8 hrs. on the 8th and 9th the station recorded only 56 cents of rain and this had probably fallen in connection with the showery weather in the monsoon air.

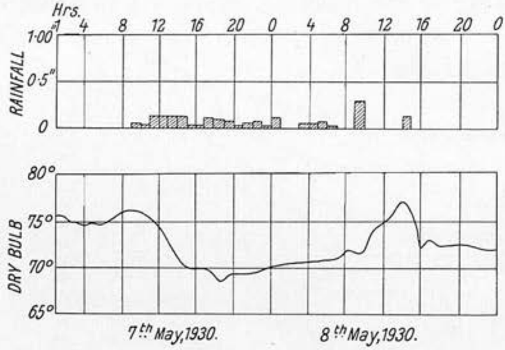


Fig. 4.

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[1]) The Bangalore records were kindly supplied by Mr. SESHACHAR, the Mysore State Meteorologist.

Table II.

Date	Hours	D. B.	Rainfall cents.
6th	16	53	11
7th	Minimum time	51	—
	8	52	110
	10	52	61
	16	53	289
8th	Minimum time	50	—
	8	58	113
	10	59	Nil
	16	59	7
9th	8	57	49

Summary and conclusions.

A study of the structure of a front between the continental and monsoon air masses in the pre-monsoon period during May 1930 reveals that although the continental air is warmer than the monsoon air in the lower levels the thermal relation gets reversed higher up and it is the structure of the front above the reversal level which is important from the point of view of condensation and liberation of energy; the structure of the front above the reversal level is similar to the structure of warm front in post-monsoon storms and extra-tropical cyclones. The actual distribution of precipitation at stations near the front above and below the reversal level agrees with that deduced from the structure discussed in the note.

The authors have very great pleasure in thanking Mr. S. Basu for some valuable suggestions during the preparation of this note.

Meteorological Office, Poona, India.

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A DISCUSSION ON THE STRUCTURE OF THE INNER ZONE OF SOME INDIAN CYCLONES.

By

S. Basu and **B. N. Desai,** Poona.

[With 5 figures*).]

Summary: Weather charts illustrating the cyclones discussed in a previous paper on this subject have been reproduced and explanations have been suggested for the apparently anomalous distribution of the meteorological elements in the inner storm area of the cyclones on the basis of fronts and air sectors within that region. In the absence of other adequate explanations of the apparent anomalies of wind, weather and rainfall distribution around the centre of the cyclones, it has been argued that a non-symmetrical frontal structure of the inner storm area may have to be recognised to reconcile most of the observed facts. A tentative suggestion has been put forth that the inner storm area of a tropical cyclone may have a frontal structure during certain phases of the existence of the cyclone, while during other phases viz., when in the occluded state (occlusions should be frequent in view of the very high wind velocities in the inner region), it may show, in effect, symmetrical distribution of weather, rainfall and wind round the "eye" of the storm.

In a previous paper1) it has been shown that the ideas about the symmetrical distribution of the various meteorological elements in the inner storm area of a cyclone are not supported by actual observations in the case of some of the most intense cyclones in the Indian seas. It is now proposed to examine the cases discussed in that paper and to attempt tentative explanations of the apparent non-symmetry in the meteorological changes over a place due to the passage of a cyclone.

The reasons that would readily suggest themselves as being responsible for introducing a non-symmetry in an otherwise symmetrical cyclone may be summed up as follows:

(1) The fact that the axes of cyclones treated as revolving air systems are considered generally to be inclined to the vertical due to differences in wind speeds at different levels may influence the distribution of pressure and, indirectly, of the other meteorological elements round the pressure centre.

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*) The figures of this paper are numbered beginning with No. 6, in continuation of the numbering of figures of the paper by B. N. Desai and S. Basu on "Evidence in favor of nonsymmetrical structure in the inner storm area of cyclones in the Indian Seas" in this J. **40** (1933) 1—11.

(2) The close proximity of land and sea (most of the cases dealt with in the previous paper are cyclones with centres very near the coast) may be distorting the symmetrical storm field and thereby causing apparently anomalous distribution of the various elements in the inner storm area.

(3) Different air masses enter into the structure of the cyclones even upto the inner storm area and the apparently anomalous distribution of wind, rainfall and other phenomena may be a direct outcome of the existence of different air-sectors and fronts within the inner zones.

Regarding (1) above, we may refer to the definiteness that Sir Napier Shaw has given to the general idea of the axis of a cyclone being inclined to the vertical when the cyclone is treated as a revolving air system[2]). He concludes that the possibility of a vertical column which preserves its attitude in spite of the differences in the motion of the air at different levels seems to be provided by a term in the general equation of motion which is proportional to the vertical velocity and the cosine of the latitude[3]). The term $2\,\omega w \cos \varnothing$ in the equation of acceleration in the direction of motion would appear as an acceleration opposed to the motion and might help to keep the columnar structure upright so long as the vertical velocity w is vigorous[4]), especially in lower latitudes. It seems therefore that a very greatly inclined axis may be ruled out. It may also be observed that an inclined axis can have well marked effects only if the whirl is supposed to extend upto great heights; if the height is small, extending not very much beyond the levels where the sustaining energy is supplied[5]), then, as this height is small in comparison to the horizontal extent of the storm area, the inclination of the axis cannot have any very marked effect[6]). It is obvious therefore that the non-symmetry of the inner storm area cannot be adequately explained by postulating merely the possibility of the axis of symmetrical cyclonic whirl to be inclined to the vertical.

With regard to (2), viz., the effect of the difference between land and sea, it is admitted that orographical features existing over the land as different from the conditions over the sea would modify, to varying degrees, the configuration of isobars and the distribution of the meteorological elements in an originally symmetrical vortex. Yet it is doubtful if the effect of orography, say when the cyclone is centred at the head of the Bay of Bengal, or near Masulipatam or near Calcutta (these are some of the positions for which observations are discussed in the previous paper), would be so great as to introduce in the otherwise symmetrical vortex a non-symmetry to such an extent that the resultant anomalous distribution of the elements round the centre could practically fit in with the existence of different air-sectors and fronts (as will be shown later). Orography would distort both an originally symmetrical or originally non-symmetrical system, and nothing precludes the distorted system from being originally non-symmetrical. The pre-existence of air-sectors and fronts is therefore by no means ruled out by the fact that what we ultimately see depicted is a system considerably modified from its original disposition by the orographical differences in different parts of the storm field.

The reason for the non-symmetry of structure in the inner areas of the cyclones may therefore be sought in the possibility of the existence of different air-sectors and fronts, that is, factor (3) above. For all regions in the field of a cyclone, except the inner storm area, it has now been recognised that air masses of different origin enter into the structure of the cyclones of the Indian seas giving rise to air sectors and fronts. In the following paragraphs an attempt has been made to picture the possible structure of the cyclones described in the previous paper on the basis of air masses, and by extending the frontal structures into the inner storm areas, to suggest at least tentative explanations for the apparently anomalous distribution of the meteorological elements immediately around the centre of the cyclones.

Note: In figures 6 to 10 are reproduced the weather charts relating to each of the five cyclones described in the previous paper giving whatever data are available. The following discussion on these weather maps should be read with particular reference to the respective figures 1 to 5 in the previous paper*) wherein the actual records of the meteorological elements immediately before and after the passage of the central region over the place have been exhibited graphically. In view of the free reference to figures 1 to 5 of the previous paper, the weather maps have been numbered 6 to 10 in this paper.

The following notations have been used in reproducing the weather maps:

▲▲▲▲▲▲▲▲▲ = Front at which the moist monsoon air gains over the air of land origin.

▼▼▼▼▼▼▼▼▼ = Front at which the air of land origin gains under the monsoon air. These fronts are analogous to the warm and cold fronts respectively at all heights in the case of the post-monsoon (October to December) storms. In the case of the pre-monsoon (April to June) storms they behave as warm and cold fronts only after a certain height[7]).

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*) See Gerl. Beitr. Geophys. **40** (1933) 1—11.

◎ = Medium or high clouds.
● = Low clouds.
The part of the circle shaded showing the amount of sky covered with cloud.
+ = Drizzle.
• = Rain.
⁝ = Heavy rain.
y = Squalls.
yy = Heavy squalls.
⌐ = Thunderstorm.
///// = Rain falling at the time of observation.

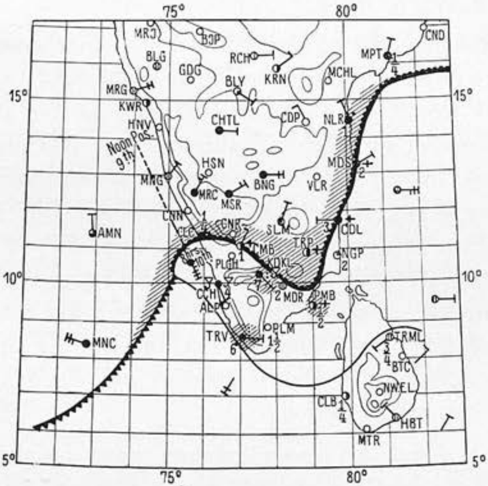

Fig. 6. Weather Chart for 8 hrs. on 10.11.1925.

Case 1. In fig. 6 is reproduced the weather chart for 8 hrs. for the 10th November 1925 illustrating the Arabian Sea storm of 9th to 10th November 1925, the centre of which passed very near the steamer S. S. Japan. The probable positions of the various fronts and sectors are also indicated on the chart*). The course of the steamer S. S. Japan, which experienced the full force of the storm, is indicated by a broken line in the figure. From fig. 6 it is seen that the steamer was approaching the front at which the monsoon air was rising over the continental air (warm front) during the night on the 9th; at 4 hrs. on the 10th she was experiencing a southeast wind [see fig. 1 in Gerl. Beitr. Geophys.

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*) It may be pointed out here that surface temperature data even in the few cases for which they are available are not in general found to be very useful in identifying air masses or in locating fronts. This is to be expected if one remembers that (1) the initial temperature contrast between the conflicting air masses in the tropics is much smaller than the temperature differences between the polar and equatorial air masses in the middle latitudes and (2) even the little temperature contrast that may be present initially will fail to show itself in the lower layers being very much affected by the intense precipitation over wide areas associated with fronts in tropical storms.

40 (1933) 3] and light rain, showing that at this time she had already entered the warm monsoon air sector. As no observations are available between midnight and 4 hrs. it is not possible to fix exactly the time when she crossed the front nor whether there existed any pre-frontal rain or drizzle. If there was a drizzle or rain belt in advance of the front, it must have been comparatively narrow since no rain or drizzle was recorded at midnight on the 9th which was at the most 4 hours earlier than the time of her entry into the warm sector. After 4 hours the wind in the southeast air sector continuously increased due to her approaching the inner stormy region of the cyclone as indicated by a rapid fall of pressure (fig. 1). Between 10 and 12 hours the wind changed from southeast to southwest and at 12 hrs. heavy rain squalls were being experienced. It is possible that between these hours the steamer actually crossed the other front between the southeasterly air on one side and southwesterly air on the other. The southeasterly air is probably a part of the easterly circulation over the south Bay of Bengal [cf. S. C. Roy and A. K. Roy[8])] while the southwesterly air may be the retreating southwest monsoon air brought temporarily northwards by the cyclone. This latter view is supported by heavy rain (6″) at Trivandrum and (4″) at Cochin as well as heavy rain squalls experienced by the steamer in the southwesterly air sector; also 2″ of rain recorded at Minicoy between 8 hrs. on the 9th and 8 hrs. on the 10th support the temporary excursion of the southwest monsoon air. The steamer continued to experience a southwesterly hurricane till 16 hrs. after which the wind abated rapidly with her increasing distance from the inner storm area.

Case 2. The weather chart for the morning of the 16th May for the Masulipatam cyclone of May 1925 is given in fig. 7 in which the probable air sectors and fronts have also been shown. According to the weather remarks given by the observer at Masulipatam, the station began to get rain for the first time at 14 hrs. on the 15th when the station was having an eastnortheast wind; thereafter throughout all the successive observations upto 8 hrs. on the 16th there was more or less continuous rain at the station [see fig. 2 in Gerl. Beitr. Geophys. **40** (1933) 6]. It is plausible to assume that this rain preceded the passage of the front over the station. By 23 hrs. on the 15th 0.53″ of rain had fallen; with the front advancing towards the station, the intensity of the rainfall increased and between 23 hrs. on the 15th and 8 hrs. on the 16th 2.16″ of rain was recorded. Most probably the front passed over Masulipatam between 8 and 9 hrs. as shown by a change in wind (from NNE force 6 at 8 hrs. to SW force 8 at 9 hrs.); so that from 9 hrs. onwards and upto 22 hrs. on the 16th the station remained in the monsoon air sector which is characterised by rain and squalls, and being in the same air sector throughout, although the calm centre passed over the station during this period, no wind shift was experienced on the two sides of the V-shaped barogram (fig. 2). The heavy rain in the monsoon air sector near the front is what is to be expected in the case of pre-monsoon storms [cf. Desai and Mal[7])]. This is because the continental air being warmer than the monsoon air in the lower levels will ascend over the latter; but higher up where the monsoon air becomes the warmer of the two air masses (due to a much smaller lapse rate), it ascends over the cold continental air mass. As a consequence of this structure the heavy warm front rain is mostly in the monsoon air sector itself. The heavy rain in the monsoon sector near the centre of the cyclone may also be partly due to (1) the air in the monsoon sector (warm sector aloft) ascending very rapidly (the ascending motion

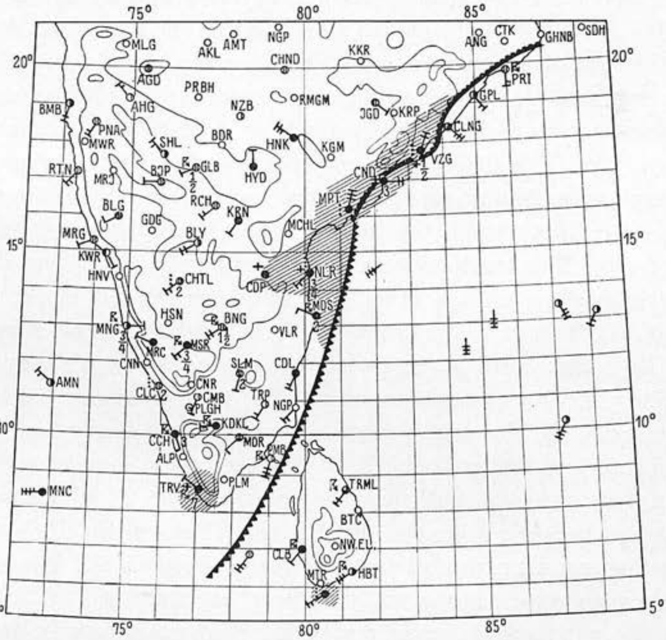

Fig. 7. Weather Chart for 8 hrs. on 16. 5. 1925.

in the part of the warm sector nearest the centre must undoubtedly be admitted in many cases) and (2) the rapid fall of pressure increasing the relative humidity of the already saturated air current simultaneously at all the levels and giving rise to thick cloud masses; in such a current even slight convergence—there is always some general convergence towards the centre—will give rain[9]).

Case 3. The weather chart (fig. 8) for 8 hrs. of the 5th May shows the positions of the fronts in the Bay of Bengal cyclone of 4th to 6th May 1923 in which the S. S. Okara foundered; the track of the S. S. Chinkoa, which was also involved in the central region, but survived, is shown in broken lines. From the log of the steamer it is found that from 4 hrs. on the 5th she was having southwesterly gales and frequent squalls or rain squalls, the characteristics of monsoon air. At 20 hrs. the wind increased to a hurricane, still from the southwest, and was accompanied with heavy squalls [see fig. 3 in Gerl. Beitr. Geophys. **40** (1933) 6]. From 22 hrs. to midnight she reported continuous heavy rain, the steamer still being in the monsoon air sector. The wind changed from southsouthwest to north only between 3 and 3.30 A. M. on the 6th when the steamer probably crossed the front and entered the continental air sector. The reason of heavy rain near the front in the monsoon air sector has already been given in case 2 above. After 3.30 A. M. the steamer changed her course to west (as given in her log) and was moving near the front but on the continental air side, passed the calm centre between 3.30 and 4 A. M. and was approaching the other front at 8 hrs. when she was again experiencing a westerly gale accompanied with heavy rain squalls. It is not very clear why the clam centre did not coincide with the barometric minimum (fig. 3).

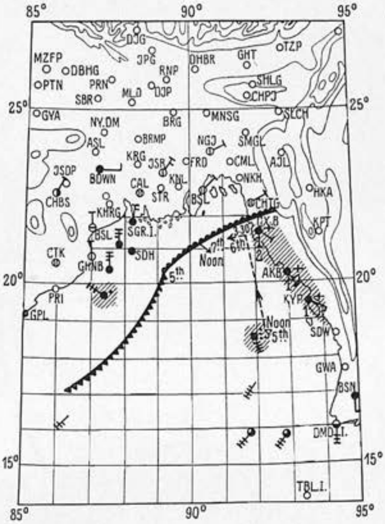

Fig. 8. Weather Chart for 8 hrs. on 5. 5. 1923.

Case 4. In fig. 9 is given the weather chart for the morning of 5th November 1891 to illustrate the Port Blair cyclone of November 1891 over False Point. The probable position of the fronts is also indicated on the chart. From 8 A. M. to 4 P. M. on the 4th there was, at the Light House, a northnortheast wind which changed to easterly by 8 hrs. on the 5th [see fig. 4 in Gerl. Beitr. Geophys. **40** (1933) 6]. Correspondingly the rainfall also increased; thus 20 cents fell in the 24 hours ending at 8 hrs. on the 4th, 93 cents between 8 and 16 hrs. and 2.91 inches between 16 hours on the 4th and 8 hrs. on the 5th. The warm front passed over the station between 8 and 10 hrs. with a veer of the wind to eastsoutheast, 94 cents of rain being recorded during this period. The station was in the warm sector upto about 16 hrs. and the calm centre, followed by variable winds, passed between 16.05 and 16.45 hours. The causes of the calm centre and the barometric minimum not occurring simultaneously are again not clear (fig. 4). Thereafter with the passage of the cold front the wind at the station backed to northwest and was of hurricane force at 17 hrs. and was accompanied by heavy rain which occurred upto 20 hrs. The heavy rain experienced in the monsoon air (warm) sector near the centre of this post-monsoon cyclone is not very clearly understood; but as already pointed out [J. Bjerknes[9]] convergence of the wind resulting from a very steep

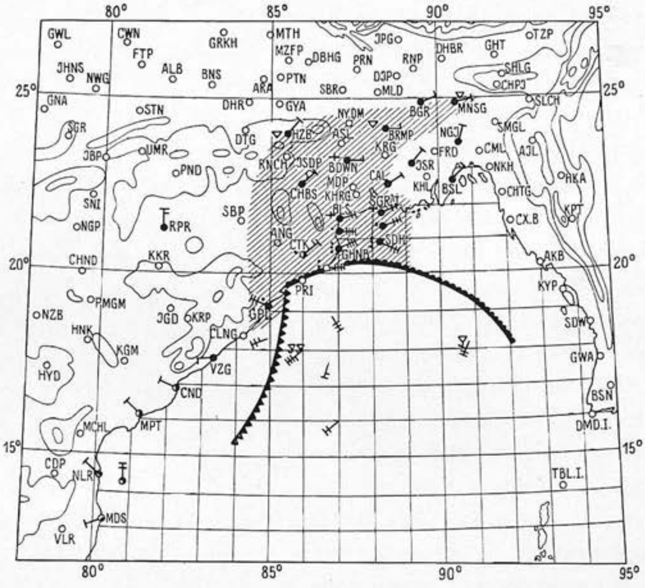

Fig. 9. Weather Chart for 8 hrs. on 5. 11. 1891.

fall of pressure (about 1.5″) may be suggested as one of the possible reasons, though this is not verifiable with the available data.

Case 5. The weather chart for the 5th October morning is given in fig. 10 which also shows the probable air sectors and fronts in the Calcutta cyclone of October 1864. The station began to get the warm front rain at 19 hrs. on the 4th [see fig. 5 in Gerl. Beitr. Geophys. **40** (1933) 6]. With the approach of the front towards the station the intensity of the rain increased (after 4 hrs.), the wind also increasing at the same time. The wind continued to blow from an eastnortheasterly to easterly direction and there was continuous heavy rain from 6.30 to 10 A. M. with a gradual increase in the wind velocity and intensity of squalls (fig. 5). At 10 hrs. the wind suddenly veered to eastsoutheast and the rainfall ceased ten minutes later indicating that the warm front passed over the station at that time. Between 10 hrs. 15 mins. and 20 hrs. practically no rain was recorded as would be ordinarily expected for a station in the warm sector. Between 19 and 20 hrs. the wind veered to west and was accompanied with showers; this marks the passage of the cold front over the station.

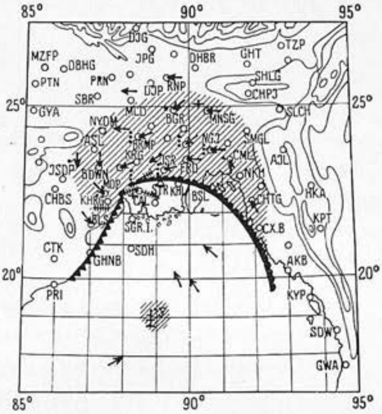

Fig. 10. Weather Chart for 8 hrs. on 5.10.1864.

Before passing on it may be stated here that the structures described above cannot in the absence of more detailed and frequent synoptic observations claim to be exact, but they merly represent rough pictures of the possible air sectors and fronts that could have been present at the time of the observations. Similarly, the explanations suggested, with reference to these fronts and air sectors, of the meteorological changes at the places of observation have no better claim than being merely tentative suggestions in the absence of any other and more certain explanations.

It will appear from the foregoing considerations that the distribution of the various meteorological elements in the cyclones discussed above—though anomalous from the point of view of symmetrical structure—fit in better if the existence of different air sectors and fronts is admitted even in the inner storm area of the cyclones.

ELIOT has made an extensive study of cyclones in the Indian seas[10]). In concluding Part III of his Cyclone Memoirs he has set forth the more important inferences with regard to the constitution and motion of the cyclonic storms. Some of his inferences are

(*a*) That the winds differ considerably in intensity in different quadrants and that this difference is mainly caused by the fact that the humid winds which maintain the vigorous circulation of the cyclone enter mainly in one quadrant.

(*b*) That the amount of ascensional movement or uptake differs very considerably in different quadrants and is usually most rapid and vigorous in the advancing quadrant at some little distance in front of the centre.

(*c*) In consequence of ascensional motion and rainfall taking place most vigorously in the advancing quadrant or in front of the cyclone, the isobars are oval in form and the longest diameter coincides approximately with the direction of the path of the centre. The centre of the cyclonic circulation and of the storm is not in the middle of this diameter but is at some distance behind. As a further consequence, the gradients are steepest in the rear of the storm centre.

(*d*) That a cyclonic circulation cannot be resolved into the translation of a rotating disc or mass of air. The fact that the main supply of the energy is applied in front of the cyclone suggests that it is perpetually renewed in front, and that its motion and transmission are rather to be explained by some process analogous to the transmission of a wave.

Speaking generally of the structure of Indian Cyclones, ELIOT's inferences quoted above can only be accounted for on the basis of non-symmetric structure of these storms. Thus the cyclone having formed as a result of the conflict of different air masses one would naturally expect differences in the strength of winds in different quadrants; the humid winds also would enter the cyclone area through only one quadrant i. e., through the warm (moist) air sector. If a warm front is assumed to be present within the cyclone, then the most vigorous ascension and rainfall in the advancing quadrant in front of the cyclone is what should be a very natural result; the fact that in advance of the warm front heavy continuous rain is met with has been pointed out while discussing the individual cases. The isobars drawn within a storm field, when due regard is paid to the air sectors and the probable location of fronts, are hardly ever symmetrical circles. In this connection it is interesting to note that from a study of the Cyclones of the far East, ALGUÈ believed that the facts sufficiently corroborated the "theory of convergent winds" and completely destroyed the "much talked of theory of circular winds"[11]). Particularly with regard to the cyclonic vortex, ELIOT's inference that a cyclonic circulation cannot be resolved into the translation of a rotating disc or mass of air and the suggestion that the cyclone is perpetually renewed and that its transmission is a process analogous to the transmission of a wave may be regarded as being in agreement with the comparatively recent ideas of the origin, development and movement of cyclones formed at a surface of discontinuity. It seems therefore that ELIOT's inferences, based on a very systematic and searching study of storms, can be regarded as more in favour of a non-symmetrical structure throughout the storm field rather than unaccounted for facts in symmetrical cyclones.

Conclusion.

Having thus shown the possibility of the existence of air sectors and fronts in the inner storm area of the cyclones, one essential feature of tropical cyclones should be considered, viz., the effect of the very high wind velocities that are met with round the centre owing to the very steep pressure gradient. It is to be realised that such strong winds should be working continuously towards weakening and even obliterating the well-marked fronts by processes which may be compared with rapid occlusion (or seclusion) or rapid disintegration of the fronts, and it is plausible to assume that during certain phases of the existence of the cyclone, e. g., immediately after an occlusion, the inner storm area may for the time being exhibit, at the surface level, characteristics of one air mass structure and practically symmetrical distribution of weather and rainfall around the centre. Obviously, this in itself would not be against the idea that during some earlier phase, the inner storm area could have exhibited air sectors and fronts with non-symmetrical distribution of the meteorological elements around the centre of the cyclone, nor would a regeneration of fronts in the inner zone be precluded at a subsequent stage. It is suggested therefore that it may be more correct to picture a continuous process of disintegration and regeneration of fronts and rapid occlusions with subsequent reappearance of air sectors to be going on throughout the life history of an intense cyclone within the inner storm area where very high winds prevail. The passage of the inner storm area of a cyclone over a place may therefore be attended either with regular changes of wind, weather and rainfall before and after the passage of the centre or with anomalous changes in these elements, as shown in the cases discussed in this paper, dependent upon whether the core of the cyclone passes over the place in an occluded state or in a state with the fronts and sectors still intact. Thus we may look upon the inner storm area of a cyclone to be non-symmetrical at certain phases of the life history of the cyclone and symmetrical (occluded state) during other phases. Naturally no more definiteness can be given to this idea in the present state of our knowledge of the inner areas of the cyclones. It is only when more detailed, precise and adequate data of continuous observations within the core of cyclones are available for individual cyclones throughout their life history that more detailed examination will be possible. Till then the above very tentative suggestion has been made for whatever it may be worth to be further developed or modified or rejected to give place to more exact ideas which may fit in with more observed facts in the light of further investigations.

In the end, we wish to record our thanks to Dr. C. W. B. Normand and Dr. S. K. Banerji for their very valuable criticisms on various points during the course of preparation of this paper.

Meteorological Office, Poona 5.
April 1934.

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COLLOIDS IN THE ATMOSPHERE*

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Summary. In this article an attempt has been made to summarise the present position of the subject of "Colloids in the Atmosphere". As far as possible references to all important papers on the subject have been included. The article contains a detailed account of important properties of colloidal particles in the atmosphere with reference to some meteorological factors. Difficulties in the way of applying the ideas of coagulation of colloidal solutions to colloids in the atmosphere have also been pointed out.

GENERAL

A systematic study of disperse systems started with Graham. In a disperse system the dispersion medium may be a solid, liquid or gas; the disperse phase can exist in one or more of the conditions—solid, liquid or gaseous. Most of the investigations of colloid chemists have been directed to systems in which the dispersion medium is either liquid or solid.

Ordinarily the atmosphere at least in the troposphere can hardly be taken as only a molecular dispersion system. The atmosphere is a colloid dispersion system in which the dispersion medium is in a gaseous condition and the disperse phase in solid and liquid conditions. On the analogy of calling a system in which water is the dispersion medium a hydrosol, a system in which air acts as dispersion medium is called an aerosol. The nature and size of the particles of the disperse phase in the atmosphere vary considerably.

The disperse phase in the atmosphere plays a very important part in various meteorological phenomena. A systematic study of colloids in the atmosphere can be said to have started with John Aitken (Collected Scientific Papers of John Aitken, Cambridge University Press, 1923).

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*In preparing this article free use has been made of "Atmosphäre als Kolloid" by Schmauss and Wigand, "Clouds and Smokes" by Gibbs and of other scientific papers and books mentioned in the body of the text.

SMALL IONS

The classification of the disperse phase in the atmosphere is generally based on the size of the particles of the dispersed component.

When air is exposed to ionising agents such as radiations from radio-active substances, ultra-violet rays from the sun and cosmical penetrating radiation, the molecules of the atmosphere get ionised. These ionised molecules collect round other molecules of air, water vapour or carbon dioxide and become molecular aggregates which are usually designated as small ions. These small ions may be charged either positively or negatively.

The size of the small ions has been calculated by various investigators by their movement in an electrical field as well as from the condensation effect. In an atmosphere of normal humidity they move with a speed of 1 to 2 cms. per second in a field of one volt per centimetre and this speed generally decreases with an increase of humidity. Also the negative ions generally move faster than the positive ions. The radius of the small ion is 3 to 4×10^{-8} cm. according to calculations of J. J. Thomson (see Applications of Dynamics to Physics and Chemistry) and Chauveau (Le Radium, 9, 161, 1912). According to Loeb (Ann. d. Phys., 84, 689, 1927) the number of molecules in a normal small ion does not exceed 6 while according to Lenard (ibid., 41, 91, 1913) it is more than 9 of the magnitude O_2 molecules. As more and more new small ions are formed some of the old ions are removed by reunion and therefore their number cannot go on increasing indefinitely. Nolan (Proc. Roy. Irish. Acad., 41, 61, 1933) has observed that at high concentrations the rate of disappearance of small ions is proportional to the concentration; he further argues on this basis that the former is a result of coagulation while the latter of diffusion. According to Hess (Wien. Ber. [2 a] 136, 603, 1927; Phys. Zeit., 28, 882, 1927) the average life of small ions is about 30 seconds.

On an average the number of small ions of one sign comes out to be about 700 per c.c. Mathias (Gerlands Beitr. z. Geophys. 27, 360, 1930) has determined the small ion content of the atmosphere at Heligoland and found that the relative humidity shows correlation with the ratio of the number of small positive ions to the number of small negative ions. He has also found a remarkable relation between the number of small ions on the one hand and the direction of wind, transparency, sunshine etc. on the other. J. J. Nolan and P. J. Nolan (Gerlands Beitr. z. Geophys., 25, 414, 1930) have observed that the ratio of positive to negative small ions is about 1·45, there being thus an excess of positive small ions.

The vapour pressure over a convex surface (presuming that spherical drops are formed) being greater than over a plane surface (the smaller the radius of curvature the greater the vapour pressure) one may be inclined to think that condensation may not take place on these small ions, for the very fine drops may evaporate no sooner they are formed. However, as stated before, these small ions are electrically charged—every ion probably carries at least an elementary charge $e = 4{\cdot}77 \times 10^{-10}$ E.S.U.—and the presence of the electric charge diminishes the vapour pressure to an extent that is proportional to the fourth power of the radius of the drop. On the basis of this relation it is found that the vapour pressure over the charged drop when compared with that over a plane surface increases with the increase in the size of the drop till r becomes $0{\cdot}63\mu\mu$; if the drop increases further in size the vapour pressure however begins to decrease. It will thus be seen that charged droplets whose radius is greater than $0{\cdot}63\mu\mu$ can act as nuclei for condensation. As stated before, the radius of the small ions is of about this order and hence, as a result of the electric charge which they carry, the effect of curvature will not be felt and they will be able to act as condensation nuclei. Thus the electric charge plays the role of hygroscopic agent inasmuch as it can lower the vapour pressure and facilitate condensation of water vapour even when there is low degree of supersaturation. The fact that condensation takes place on such charged ions has been conclusively proved by the classical experiments of C. T. R. Wilson (Phil. Trans., 189, 265, 1897 ; 192, 403, 1899).

In view of the greater size of positive ions than that of negative ones one would expect that condensation should take place at lower values of supersaturations in the former case than in the latter. Wilson's (loc. cit.) experiments have, however, conclusively shown that condensation takes place on negative ions at supersaturation value $S=4$ and on positive ions at $S=6$.* Schmauss and Wigand (Atmosphäre als Kolloid, 1929, S. 3) think that the cause of this peculiar behaviour might lie in the different magnitudes of the electric forces which work between negative and positive ions on the one side and water molecules on the other side ; water vapour possesses polar properties on account of its constitution and condensation takes place more easily on negative than on

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*$S=C_1/C_2$, where C_2 is the concentration of the water vapour in the air after adiabatic expansion to volume V_2 and temperature T_2 and C_1 is the concentration of water vapour in the air immediately before expansion when volume is V_1 and temperature is T_1 ; V_2/V_1 is the expansion ratio or expansion.

positive ions. Sir J. J. Thomson (Conduction of electricity through gases, Vol. I, 1928, p. 332 et seq.) considers that at the surface of a water drop there is a double layer of electrification, *i.e.* a layer of one sign at the surface of the drop and a layer of opposite sign in the gas, the distance between the two layers being very small. He has further shown mathematically that if a layer of this kind existed, it would produce a difference between the condensing powers of positive and negative ions. According to this the layer will make an ion of the sign which produces at the surface of the drops an electric field in the same direction as that due to the double layer, more effective as a condenser than an ion of the opposite sign. Thus if the double layer in the case of water had the negative coating inside, a negative ion would be more effective in producing condensation than a positive one. When a fresh surface of water is exposed to air the latter gets negatively electrified and equal quantity of positive electricity goes to the water surface to form the outer coating of the double layer, so that double layer has the negative side next the water, the positive side next the air.

Wilson (loc. cit.) has also found that, at values of supersaturation 8 or more, the condensation can take place in the absence of any Aitken or charged nuclei, the size of drops decreasing upto value of $S=12$ after which the drops again become coarser. If the size of drops decreases with an increase in the number of drops, there being available the same amount of vapour for condensation, it can be taken to mean that the number of drops produced at $S=12$ is a maximum, it being less for higher or lower values of S. At values of $S=8$ or more the molecules of water vapour themselves act as condensation nuclei. This behaviour of water vapour is similar to the behaviour of supercooled melts and supersaturated solutions (also see Freundlich, Colloid and Capillary Chemistry, Eng. Trans. 1926, p. 769); it has been shown that the velocity of formation of nuclei passes through a maximum in this way as the temperature falls and the supercooling or supersaturation increases.

Usually the atmosphere does not contain the amount of water vapour sufficient to saturate it. However under favourable conditions it gets saturated with water vapour. From the efficiency of small ions as nuclei for condensation of water vapour, which has been discussed above, it will appear that under ordinary conditions they may not serve as condensation nuclei. Kopp (Beiträge z. Physik der frein Atmosphäre, 14, 169, 1930) has adduced evidence to show that a relative humidity of even 300 to 600% is sometimes met with in clouds and under such circumstances the small ions may be able to serve as condensation nuclei. Numerous humidity measurements by Conrad and Wagner (Monthly Weather Review, 11, 436, 1928) on Sonblick in the most dense clouds have shown average values of 102·5%, with an absolute maximum of 107% (also see L. H. G. Dines, Nature, 132, 938, 1933). Evidence of supersaturation sufficient for condensation to take place on small ions has also been brought forward by A. Wigand (Ann. d. Phys. 59, 721, 1919). During his flights at heights of about 9000 metres he noticed that dense clouds formed when air was breathed out and this is due to the fact that the exhaled air at the temperature of the human body is suddenly cooled to about — 40°C., thus giving rise to supersaturation sufficient for condensation on small ions; if supersaturation is, however, more than eightfold, condensation may take place on water vapour molecules themselves. Whether the drops formed as a result of supersaturation will remain in liquid condition or solidify will depend on the temperature. The exhaled air itself does not contain any condensation nuclei as has been shown by A. Wigand (Meteorol. Zeit., S. 10, 1913).

LARGE IONS

Langevin (Compt. rend. 140, 232, 1905) in the course of his study of the nuclei in the atmosphere came across charged ions which were larger and also moved much slower than the small ions ; these are known as large or heavy ions and also as Langevin ions. They are formed generally as a result of adsorption of small ions and electrons by the small neutral liquid or solid particles in the atmosphere. They can also be produced as a result of photochemical action which takes place in the atmosphere due to ultra-violet light from the sun; the light as it passes through air ionises the constituent gases and at the same time produces traces of such hygroscopic compounds as NH_3, H_2O_2, NO_2, etc. These large ions are generally found in considerable amount in the atmosphere over towns or industrial centres. This is partly due to the fact that the smoke from the chimneys sometimes contains some fine particles of sublimation products as well as SO_3 ; the latter specially is very hygroscopic and can form nuclei for condensation even in unsaturated air, the drops being stable as a result of lowered vapour pressure. Similarly the salt particles left in the air as a result of the evaporation of sea spray also act as very good condensation nuclei due to their hygroscopic nature. Owens (Proc. Roy. Soc., 110, 738, 1926) has observed that in various sea fogs the nuclei began to gather moisture to themselves at relative humidity of about 74 per cent. Pick (Q. J. Roy. Met. Soc., 58, 165, 1932) has shown that not only do fogs occur in unsaturated air but that saturated air is not necessarily accompanied with fog. These fine liquid drops though originally uncharged can get charged as a result of adsorption of small ions or electrons at their surface. From their movement in electrical field as well as the condensation effect their radius is estimated to be of the order of 10^{-6} cm. (Lenard, Ann. d. Phys., 1, 486, 1900; 3, 289, 1900; Meteorol. Zeit., S. 150, 1912; Chauveau, loc. cit. and Booth, J. and Proc. R. Soc. New South Wales, 57, 173, 1923; Meteorol. Zeit., S. 251, 1925). Light scattering experiments give the value of r to be about $5{\cdot}5 \times 10^{-6}$ cm. (Maclaughlin, Compt. rend. 184, 1183, 1571, 1927). They move with a speed of about 0·0005 cm./sec. in a field of one volt per centimetre.

Nolan and De Sachy (Proc. R. Irish Acad., 37, 71, 1927), Pollock (Le Radium, 6, 129, 1909; Phil. Mag., 29, 514, 636, 1915) and Gockel (Neue Denksch. d. Schweiz. Natur f. Ges., 54, Abh. 1, 1917) have discovered in the atmosphere ions which are of an intermediate size greater than small ions and smaller than big ions. They move with a speed of about 0·01 to 0·05 cm./sec. and have radius about 4×10^{-7} cm. In their property they very much resemble large ions. Hogg (Gerlands Beiträge zur Geophysik, 41, 1, 1934) has also detected presence of intermediate ions in Australia; they have been found to carry only an elementary charge. The ratio of the number of intermediate and large ions varied with the meteorological conditions.

The large ion content of the atmosphere varies with locality. In very recent measurements Isräil (Gerlands Beitr. z. Geophys., 23, 144, 1929; 26, 283, 1930) has determined the ratio of large ions to small ions and found it to be about 6-7. Thus about 15% of nuclei were found to be charged. The number of large ions was found to decrease with improved visibility and decreased humidity. He also analysed the results with reference to air masses and found that polar air shows fewer large ions than tropical air, the number being least for old polar air and low humidity and most for mixed air at surfaces of discontinuity. The dust nuclei variation was similar to the large ions. He also observed that the number of large ions (also dust nuclei) was maximum in winter and minimum in summer, the variation of small ions being in a reverse direction. The changes were found to be maximum at 4 and 14 hrs. and minimum at 8 and 13 hrs.

The investigations of Nolan, Boylan and De Sachy (Proc. R. Irish Acad., 37, 1, 1925) and of Arendt and Kallmann (Zeit. f. Phys., 35, 421, 1926) on fog particles have shown that the big ions carry only an elementary charge. Thus in the case of these big ions in consideration of their magnitude, the charge which they carry does not appreciably affect condensation. Those of the big ions which do not contain hygroscopic substances require a supersaturation of a few per cent. in order to act as nuclei to produce visible fog particles (Gockel, loc. cit.; Booth, loc. cit.). It has been observed by Pollock (loc. cit.) that the size as well as rate of movement of the big ions changes with a change in humidity. Torrenson and Wait (Terr. Mag. and Atmos. Electricity, 39, 47, 1934) have determined the number of large ions and uncharged ions for Washington and found that the ratio of the latter to the former comes to about 6; most of the large ions were found to carry only an elementary charge but some of them had also double charge.

The big ions move very slowly under gravity. Ions of radius 10^{-6} to 10^{-7} cm. fall according to Stokes-Kirchoff formula only at a rate of 2×10^{-5} cm./sec. or less than 1 mm./hr. The small ions which are of a still smaller magnitude will move much slower than the big ions. Both these air ions, however, move at an appreciable rate in the electrostatic field of the earth. The big ions in a normal vertically directed field of 1 volt/cm. travel at a rate of 5×10^{-4} cm./sec.; but during a thunderstorm when a vertical field strength of 1 kilovolt/ cm. is not at all unlikely, they move at a rate of 0·5 cm./sec., or during a lightning discharge when the field may be 100 times greater they move even at a rate of 5 cms./sec. The small ions move in ordinary earth's field at a rate of 1 cm./sec., but in a thunderstorm field or when a lightning discharge takes place they can move as fast as 10 metres/sec. and 100 metres/sec. respectively.

DUST

The atmosphere also contains dust particles of varying sizes. In this we can include cosmic dust, *i.e.* the particles which come from meteors. A regular and a large supply of dust particles in the atmosphere comes, however, from the surface of the earth as a result of wind which loosens the particles from the liquid or solid crust and carries them into higher levels of the atmosphere. These particles if uncharged will gradually settle down according to Stoke's law. During the day when the earth's surface gets heated convection currents are set up and they help to keep the dust particles in suspension. Also during volcanic eruptions a considerable amount of impurity is added to the atmosphere. These products of volcanic eruption are sometimes carried to very great heights and travel round the earth several times and also produce brilliant colours at sunrise and sunset. One such very famous eruption of Krakatoa occurred in the year 1883.

Some of these dust particles in the atmosphere also carry electric charge and this charge is considerably greater than the charge carried by the small and big ions. The charge might have been acquired as a result of adsorption of gaseous ions at the surface of the particles or due to friction. Rudge (Phil. Mag., 23, 852, 1912; 25, 481, 1913) has shown that the nature of the charge on dust particles when they are blown about in the air depends on the chemical composition of the dust. Generally speaking non-metallic dust and dust of acid forming oxides becomes positively charged, metallic dust and dust of basic-forming oxides becomes negatively charged and in the case of salts the charge depends upon relative strength of the acid and basic ions. The electric charge carried by the dust particles produces considerable changes in the atmospheric potential gradient. The mineral dust particles are considerably larger than the big ions.

The atmosphere also contains fine particles of carbon as a result of smoke from the fires. The number of carbon particles is generally largest in the air of industrial towns and of forests where fires are very active.

Regarding the condensation effect it may be stated that only those dust particles which are chemically or physically hygroscopic act as effective condensation nuclei (Wigand, Meteorol. Zeit., S. 10, 1913; also Ann. d. Phys., 59, 693, 1919). Measurements of H. Koppe carried out in Öilberg in Jerusalem in 1916-1917 have shown that the east wind which appears there as dry sirocco brings with it very large amount of dust from the desert and reduces visibility considerably; in this air mass the condensation nuclei per c.c. were found to be very few. On the other hand, in the west wind which blows from sea the number of nuclei was about 2000 per c.c. C. Braak (Verb. Konk. Magn. en Met. Obs. Batavia, No. 10, S. 14, 1922) has also found that the usual dust clouds are poor in nuclei. Wigand (loc. cit.) and Boylan (Proc. Roy. Irish Acad., 37, 58, 1926) have observed that non-hygroscopic dust particles do not act as nuclei even in supersaturated atmosphere.

HYDROMETEORS

Besides the small and big ions and dust particles mentioned before, the atmosphere also contains solid or liquid particles produced as a result of the condensation of water vapour contained in it. These solid or liquid particles separate out as a result of supersaturation and are commonly known as hydrometeors in order to distinguish them from the real precipitation. The action of gravity on the hydrometeors is not appreciable. Their horizontal movement depends upon the wind velocity at their own level. The magnitude of the hydrometeors varies considerably. The diameter of the haze particles which are visible has been estimated to be below $2{\cdot}5 \times 10^{-5}$ cm. by A. Wegener (Thermodynamik der Atmosphäre, Leipzig, 1911, S. 251). The haze particles which are larger are termed fog particles, the lower drop magnitude of which lies near 4×10^{-4} cm. and the upper limit near 3×10^{-3} cm. In country fogs in England the number of fog droplets is sometimes as great as 1500 per c.c. The drops in the clouds are generally bigger than fog particles and the radius may be even of the order of 1×10^{-2} cm. The radius of the rain drops may range from 1×10^{-3} to nearly 0·2 cm. These liquid or solid particles may be charged if condensation has taken place on ions or may get charged by adsorption of ions on the surface. If the temperature is sufficiently low the water vapour condenses to fine ice needles. The words fog and cloud are generally used loosely. As mentioned by Humphreys (Physics of the Air, 1929 Edition, p. 273) "fog is a cloud on the earth ; cloud is a fog in the sky".

NUMBER OF CONDENSATION NUCLEI

Numerous investigations have been carried out for determining the number of nuclei on which condensation can take place on small adiabatic expansions of air in different localities and under different weather situations. The number of nuclei per c.c. under different conditions comes to be

1000 — 10,000	Cyclonic (barometric depression) weather.
10,000 — 100,000	Anticyclonic (barometric high) weather.
> 100,000	Big town and industrial centres.
100	Pure land air and in hills.

Wigand (Ann. d. Phys., 59, 693, 1919) has determined the number of nuclei at different heights in an anticyclonic weather situation and obtained the following results:—

Height in Metres.	Number per c.c.	Cloud stage.
100	44,000	
500	13,000	Stratus and Cumulus.
1,000	5,000	
2,000	550	
3,000	200	Alto-Stratus and Alto-Cumulus.
5,000	50	
8,500	5	Cirrus.

Rain, high wind and especially Föhn wind caused marked decreases in the number of nuclei (Hess, Gerlands Beitr. z. Geophys. 28, 129, 1930). Intensity of sunshine or transparency of the atmosphere was found to be ineffective in controlling the number of condensation nuclei. Nuclei were fewest with medium humidity and cloudiness was found to have no influence except when it was raining. Highest numbers coincided with high and steady barometer and lowest with falling one. There was also some indication of low numbers preceding by some 12 hrs. change in the weather, pointing to a possibility of local forecasting. Wright (Met. Office, London, Geophy. Mem. No. 57, 1932) has also observed that number of condensation nuclei at Kew is affected by wind and humidity but not by cloud.

On plotting log K (number of nuclei per c.c.) against height, Wigand found that the curve was not uniform but consisted of three straight line pieces with kinks at 1750 and 3000 metres height. According to him this indicates a stagewise layering corresponding to the most frequent heights at which different types of clouds form, *e.g.* in this case stratus and cumulus and alto-stratus and alto-cumulus respectively. Wigand has expressed the variation of nuclei (K) with height (h) in each stage by the formula :

$$h_2 - h_1 = x \ (\log K_1 - \log K_2)$$

In every stage the factor 'x' has a different value. This expression fitted well with his results. Hess (loc. cit.), however, found that Wigand's formulæ did not hold for his results.

CHEMICAL COMPOSITION OF THE CONDENSATION NUCLEI AND SIZE OF WATER DROPS IN CLOUD AND FOG

It has been stated before that considerable supersaturation is necessary for the small ions in the atmosphere to act as nuclei. In view of this it may be taken that in the lower levels of the atmosphere (below the cirrus level) they may not usually act as condensation nuclei. The big ions, however, require proportionately much less degree of supersaturation and may act as condensation nuclei even in lower levels. H. Bongards (Monthly Weather Review, 11, 437, 1928) has tried to show a statistical relation between density of big ions and fog formation and come to the conclusion that presence or absence of big ions as nuclei was the cause of greater or lesser fog frequency at Lindenberg.

Aitken (loc. cit.) on the basis of a series of interesting experiments came to the conclusion that it is mostly the hygroscopic nuclei (See section on "Large Ions") which effect condensation under ordinary circumstances because in such cases condensation can take place even in unsaturated air. In industrial centres one finds presence of SO_3, tar and other insoluble matters. Köhler (Series of papers in Geofysiske Publikationer of Oslo and in Met. Zeit.) has made observations at Partetjakko in Sweden and at Haldde Observatory in North Norway and come to the same conclusion as Aitken about the effectiveness of hygroscopic nuclei in condensation. Of about 4000 humidity measurements taken in Sweden and Norway he found only four or five showing supersaturation. His observations apparently do not support Kopp's results about supersaturation.

Köhler's measurements (this is taken from Willett's article in Monthly Weather Review, 56, 435, 1928) were taken for the greater part at temperatures below 0°C., the lowest being −28°C. He made the following principal observations, chiefly at Haldde (900 metre elevation) but to a lesser extent also at Partetjakko (1850 metres elevation):—

(1) Relative humidity with respect to water rarely exceeded 100%, never by more than one half per cent; relative humidity with respect to ice, however, was frequently greater than 100%.

(2) Fog-frost deposits at whatever temperature laid down showed clearly under the microscope that they were formed by the deposition and freezing of supercooled droplets, not by sublimation in crystalline form. Furthermore the microscopic examination showed that precipitation in the solid form apart from hail, had three forms: (*a*) fine snow crystals the product of sublimation, (*b*) snow crystals more or less covered and melted by the deposition and congealing of supercooled droplets, and (*c*) ice clumps produced by the meeting and congealing of two or more supercooled droplets.

(3) On the average 13 out of 20 fog droplets belonged to a series whose sizes increase as 1, 2, 4, 8, 16, 32; the most frequent size of drops of this series being 0·07 mm., he called the series the "7 series". He also found traces of an "8 series". From certain coronal characteristics in such clouds, which he detected also in coronas produced in alto-stratus and cirrus clouds, he concluded that the same series exist among supercooled droplets in the highest cloud levels.

(4) Numerous tests applied to fog-frost deposits showed an almost constant chlorine amount, 3·59 mgm. per litre, just 1/10,000 the concentration in sea water. Quantitative tests for magnesium showed the same ratio to chlorine amount as exists in sea water, and the presence of calcium was proved qualitatively. Köhler tried, by choosing the fogs whose deposits he had tested according to the size of the prevailing droplets, to test the sea salt content of each droplet series, and he came to the conclusion that only the "7 series" contributed actively to these deposits; for the "8 series" he considers that the nuclei are derived from the plant world or from the nitrogen compounds which are present in the atmosphere. He found that pure

snow flakes had no chlorine content, those with frozen droplets attached showed chlorine amounts increasing with the number of droplets, while the ice clumps showed the same chlorine amounts as the fog-frost deposits.

Köhler's results seem to be supported by observations of Kinch (at Cirencester, England, 1885-86) in which he found that winter rain water contained 3·58 mgm. of chlorine per litre, approximately Köhler's value; A. Defant (Meteorol. Zeit., S. 321, 1905 ; also see Schmidt, ibid., S. 496, 1908 ; F. Albrecht, Sonnblick—vereins—bericht, S. 11, 1924) found for Vienna, an inland station, a chlorine quantity only two-thirds of the value of Köhler. The results of Defant (loc. cit.) and Niederdorfer (Met. Zeit., 49, 1, 1932) also show existence of drop series.

According to Köhler's results one has to assume that salt particles or droplets of only one particular size are driven from the sea. One will expect that the size of droplets driven from the sea surface will depend on the strength of the wind blowing over sea and as such droplets of different sizes may be driven from the sea. Köhler's work also shows that there is a greater attraction between drops of the same magnitude than between those of different magnitudes, a fact which has not been observed in other colloidal phenomena. On the contrary it is a common experience to find that there is always a tendency for smaller particles to unite with the relatively larger particles or as is popularly called the larger particles grow at the expense of smaller ones. Also it is not clear why the "7 series" drops should invariably contain ingredients of sea salt, while the "8 series" drops contain nitrogen compounds mostly.

Besides the fact that rain drops contain salt particles derived from the spray of sea water it has also been noticed that rain water brings down with it appreciable quantities of nitrites and nitrates. Recently Dhar and Atma Ram (J. Indian Chem. Soc. 10, 125, 1933) have estimated the amount of nitric nitrogen and ammoniacal nitrogen in Allahabad and Dehra Dun and found that appreciable amounts of these substances are brought down during rain ; the ratio of nitric to ammoniacal nitrogen was found to be greater than unity. In their paper they have also given a summary of the results of similar estimations carried out in other parts of the world. Their results are summarised below:—

(1) At Allahabad the average amount of ammoniacal nitrogen is 0·31 part in million parts of water and of nitric nitrogen 0·9 part in the same volume of rain water, the ratio of nitric to ammoniacal nitrogen being 2·9.

(2) From the summary of the analysis of rain water carried

out in various countries, it appears that the ratio of nitric to ammoniacal nitrogen is greater in tropical than in temperate countries.

Owens (Q. J. Roy. Met. Soc., 58, 282, 1932) has found presence of crystals, pollen and amorphous dust in country air, the crystals being those of sulphates, chlorides and nitrates of some alkalies and alkaline earths.

EFFECT OF SUSPENDED PARTICLES ON THE TRANSPARENCY OF THE ATMOSPHERE

As soon as condensation of water vapour takes place on the nuclei, a change in the visibility (distance upto which objects can be seen) of the atmosphere takes place. A quantitative idea of these changes can be had by means of visibility finder designed by Wigand (Meteorol. Zeit., S. 342, 1919 ; S. 216, 1924) or by the measurement of sun's radiation as done by Linke (Beitr. z. Physik. der frein Atmosphäre, 10, 91, 1922). W. Milch (Meteorol. Zeit., S. 109, 1924) has shown that the transparency of the atmosphere varies according to the origin of the air mass. In fact this transmission coefficient is now also utilised by the Norwegian Meteorologists for identifying air masses.

ELECTRIC CHARGE ON RAIN DROPS AND ITS CAUSES

The fog and cloud droplets carry charge and the efforts to dissipate fog or produce rain are wholly based on this property of fog and cloud. Wigand and Wittenbecher (Phys. Zeit., 27, 803, 1926) have measured the charge on fog drops and found high values of 350 to 2000 elementary charges per drop for anticyclonic radiation fog and 60 to 400 for cyclonic fog. The presence of both positive and negative charge was detected, the proportion of positively and negatively charged drops varying under different situations.

About the charge on rain drops and snow particles a reference may be made to classical experiments of Simpson (Mem. Indian Meteorol. Dept., 20, part 8, 1910) which were carried out in Simla during 1908 to 1909. Some of his results are given below:—

(1) The total quantity of positive electricity brought down by the rain was 3·2 times greater than the total quantity of negative electricity.

(2) Treating charged rain as equivalent to a vertical current of electricity, the current densities were, generally, smaller than 4×10^{-15} amperes per cm^2 ; but on a few occasions, greater current densities, both positive and negative were recorded.

(3) The charge carried by the rain was, generally, less than 6 E.S.U. per c.c. of water, but larger charges were occasionally

recorded ; in one exceptional thunderstorm of 13th May, 1908, the negative charge exceeded 19 E.S.U. per c.c.

(4) With all rates of rainfall positively charged rain occurred more frequently than negatively charged rain and the relative frequency of positively charged rain increased rapidly with increased rate of rainfall. With rainfall of less than about 1 millimetre in 2 minutes, positively charged rain occurred twice as often as negatively charged rain, while with greater intensities it occurred fourteen times as often.

(5) When the rain was falling at a less rate than about 0·6 millimetre in 2 minutes, the charge per c.c. of water decreased as the intensity of rain increased. With rainfall of greater intensity than about 0·6 millimetre in 2 minutes the positive charge carried per c.c. of water was independent of the rate of rainfall, while the negative charge carried decreased as the rate of rainfall increased.

(6) The data do not suggest that the negative electricity occurs more frequently during any particular period of a storm than during any other.

(7) More positive than negative electricity is brought down by snow in the proportion of about 3·6 to 1.

Thora C. Marwick (J. Roy. Met. Soc., 56, 39, 1930) has measured the electric charge on drops in different types of rain at Otago in New Zealand and observed that there is 94·6% positive charge in thunderstorm rain, 79·5% positive charge in ordinary rain, 100% positive charge in drizzle, and 39·4% positive charge in hail and rain. For snow equal amounts of positive and negative electricity were found, but charge per c.c. was found to be much greater for positive samples. For thunderstorms the greatest changes of potential gradient and highest charges occurred at the beginning of the storm.

Scrase (Met. Office, Geophys. Mem. No. 58, 1933) has found that 70% of dense fogs contain drops carrying negative charges of the order of 35 E.S.U.

Dauzére (Comptes Rendus, 189, 1092, 1929) has suggested that ice crystals in cirrus are positively charged due to action of ultraviolet light.

The causes responsible for the electrification of water droplets may be:—

(1) Adsorption of ions from the atmosphere.

(2) Breaking up of large drops by the resistance of the air through which they are falling at high velocity.

(3) Action of ultra-violet light in the upper air.

(4) Friction between water drops and ice crystals or dust particles.

(5) Collision between large and small drops.

We shall consider here the influence of the first two factors somewhat in detail as they have a direct bearing on the two rival theories of electricity in thunderclouds.

In Wilson's (J. Franklin Inst., 208, 1, 1929 in which a review of the theory is given) induction theory, which was originally suggested in another form by Elster and Geitel (Wied. Ann. 25, 116, 1883), each drop acquires by induction a negative charge above and a positive below, the normal electric field in the air being downward. As it falls through the air, or as the air blows past it, negative ions in the air will be attracted towards the lower parts of the drops and some will strike them and coalesce with them. The mobility of the positive ions in the air is considered to be too small for them to catch up the falling drops. Thus the drop will become negatively charged and the air will be left with a resultant positive charge. On this view the top of thundercloud should be positive and the bottom negative. This theory has been supported by observations on polarity of clouds by Wilson himself (Proc. Roy. Soc., 92, 555, 1916; Phil. Trans., 221, 73, 1921) and by Schonland (Proc. Roy. Soc., 114, 229, 1927; 118, 233, 252, 1928; also see Appleton, Watt and Herd, ibid., 111, 615, 1926; Wormell, ibid., 127, 567, 1930; Halliday, ibid., 138, 205, 1932; Gott, ibid., 142, 248, 1933).

Kähler (Gerlands Beitr. z. Geophysik, 27, 226, 1930) has counted at Potsdam Observatory the number of ions of various kinds, from the very mobile ions to the large slow ions, during light rain, heavy rain, squalls and thunderstorms and found that the results support Wilson's theory. Deppermann (Terr. Mag, 37, 179, 1932) and Sil (ibid., 38, 66, 1933) observed that the overhead false cirrus increased the intensity of normal electric field to a considerable extent and this also agrees well with the disruption theory of Wilson (Phil. Trans., 221, 105, 1921), false cirrus being a part of the upper part of cumulo-nimbus which may be positively charged.

From a study of the behaviour of a water drop in an intense electric field such as exists in a thunderstorm, J. J. Nolan (Nature, 132, 938, 1933) has come to the conclusion that the low mobility ions required by Wilson's theory of thunderstorm electrification are not directly produced by discharge from rain drops. The condensation nuclei of the ordinary type are also not produced by a discharge in an intense electric field (Nolan and Ryan, Ger. Beiträge zur Geophysik, 41, 185, 1934). If therefore the small ions produced copiously by the discharge are to be loaded up so that they may be carried by an air current against an adverse field, the loading must be accomplished by attachment to some kind of body other than nuclei produced by the discharge itself.

Lenard (Wied. Ann., 44, 584, 1892) found that when a drop of pure water splashes against a plate the drop gets positively charged and the surrounding air is negatively electrified. Simpson's (Phil. Trans., 209, 374, 1909 ; Proc. Roy. Soc., 114, 376, 1927) theory is based on this Lenard effect. According to him thunderstorms are caused by the splitting of rain drops in an ascending current of air when they grow to more than a certain size. Electrification by splashing occurs and the negative electricity is carried upwards by the air of fine spray while the positive charge remains on the drop which is supported by the up-current. Thus the upper part of the cloud is negatively charged and the lower part positively, though Simpson considers that the negative electricity may be carried down again at the back of the cloud. This theory is completely supported by Simpson's observations on charge on raindrops at Simla (loc. cit.).

The measurements of Banerji (J. Roy. Met. Soc., 56, 305, 1930 ; Phil. Trans., 231, 1, 1932) about polarity of thunderclouds at Bombay have shown that the front part of thundercloud is negatively charged, the centre positively charged and the rear negatively charged. The results support Simpson's breaking-drop theory.

Observations of positive polarity of thunderclouds (positive above and negative down) recorded by Wilson and others (loc. cit.) fit in with breaking-drop theory, as shown by Simpson (Proc. Roy. Soc., 114, 376, 1927), if it is realised that a lightning discharge may start downwards from the lower, or positive, pole without reaching the ground.

Regarding production of electricity by spraying, Lord Kelvin (Proc. Roy. Soc., 57, 335, 1894 ; Phil. Trans., 191, 187, 1898) has shown that air bubbled through pure water carried with it a negative charge, but on the addition of salts of acids to water not only the charge diminishes but in some cases the sign of electrification may also reverse (also see Lenard, Wied. Ann. 46, 584, 1892). It has been shown before that the analysis of rain water reveals that it contains NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$ as well as nitrites and nitrates of ammonia. If this be the case it is possible that breaking of rain drops containing salt in solution will give negative charge to drops and positive charge to atmosphere. Under such circumstances the lower part of thundercloud may be negatively charged and the upper part positively charged—the same type of polarity as may be expected according to Wilson's theory. D. Nukiyama and H. Noto (Japanese J. of Astro. and Geophys., 6, 71, 1928) from a study of charges on thunderclouds have concluded that the thunderclouds generated in the inland parts of Japan are of the Simpson type, while those generated near the coast are of the Wilson type. It is quite possible that near the coast there will be a considerable amount of salt nuclei available for condensation and as stated above, the breaking of such rain drops may give negative charge to the lower portion of the thundercloud and positive charge to the upper portion. Before, however, anything can be said definitely on this point, it is necessary that in such cases of polarity of thunderclouds, an analysis of rain drops is made to find out the salt concentration per drop in order to see whether it agrees with laboratory experiments.

INFLUENCE OF SUSPENDED PARTICLES IN THE ATMOSPHERE ON ITS ELECTRICAL CONDUCTIVITY AND ON THE VERTICAL POTENTIAL GRADIENT

Normally the surface of the earth is negatively charged and the air positively charged and the value of the vertical potential gradient is about 100 volts per metre. As a result of this vertical electrical field, positively charged ions, dust particles and water droplets move down while negatively charged particles move upwards. The electrical conductivity of the air at any point will thus depend upon the number of such charged particles present, the rate at which they move under the existing vertical field and the charge that is carried by each of them. As stated before, the small ions move fastest while the large ions consisting of dust particles, water droplets, etc., to which a small ion might have become attached move with only about one-threethousandth of the velocity of the small ions. Most of the current will thus be carried by the small ions as a result of their speed, although their number may be smaller than that of big ions. The number of small ions in the atmosphere may decrease considerably by combination with dust particles and water droplets and the conductivity may thus appreciably decrease. Light clouds, fog and mist diminish the conductivity of the air as a result of the adsorption of the ions ; the vertical potential gradient within the cloud may increase much and that in the air above and below the cloud diminish. A very thick cloud layer may reduce the vertical current, and hence the potential gradient at the ground almost to zero. Cumulus clouds as well as cirrus and other high clouds do not appreciably affect the potential gradient at the ground level. During rain or when a thundercloud passes overhead the potential gradient may considerably increase and it may even be reversed sometimes.

Very low or negative values of potential gradient in fine weather are generally associated with great dustiness of the air, sometimes the normal field may even increase due to dust if the particles are negatively charged, thus increasing the positive charge of the air. The potential gradient in higher levels (at a height of a few Kms.) is considerably reduced due to absence of dust particles.

Simultaneous measurements of electrical potential gradient of the atmosphere and different meteorological elements under different types of weather situations are very few. Recently Sil (J. Roy. Met. Soc., 59, 23, 1933) has studied variations in potential gradient at Poona caused by some meteorological phenomena and obtained very interesting results. In order to interpret such data it is, however, necessary that simultaneous measurements are also made of conductivity, the small and big ions and the dust and other particles as well along with potential gradient measurements ; it is also necessary to determine the chemical composition of dust and other particles. A summary of his results is given below :—

(1) During strong insolation the earth's field is weakened.

(2) On a dry hot day strong and gusty winds reduce the field to zero or even to negative values.

(3) The sea breeze reverses the normal field.

(4) During a dust-storm the earth's field is quickly reversed and a strong negative potential gradient established.

(5) During haze and fog the earth's field is increased, the effect being more marked with haze than with fog. When the fog begins to be lifted the potential suddenly decreases and sometimes is even reversed.

(6) When alto-cumulus and cumulus clouds formed overhead the potential gradient increased considerably.

Potential gradient variation over land is largely governed by variation of dust and nuclei ; generally the less the atmospheric pollution, the lower the potential gradient (Whipple, Q. J. Roy. Met. Soc., 55, 351, 1929). Chree (Proc. Roy. Soc., 95, 210, 1918) showed that good visibility went with low potential gradient and poor visibility with high potential gradient. Chree and Watson (ibid., 105, 311, 1924) have observed a close parallelism between daily variation of potential gradient and of pollution. The potential gradient variation curve shows two minima and two maxima in 24 hours. Hogg (Gerl. Beiträge zur Geophysik, 41, 1, 1934) has come to the conclusion that changes of the rate of ionisation and nucleus concentration determine the daily march of the conductivity of air.

STABILITY AND SETTLING OF CLOUD AND FOG AND FORMATION OF PRECIPITATION

The causes for the floating of cloud become clear if one considers the magnitude of drops in the cloud. W. Schmidt (Meteorol. Zeit. S. 183, 1909) has worked out the rate of fall of drops of various magnitudes and found that when $r = 0{\cdot}02$ cm. the descending velocity v is 1·8 cm./sec.; the expression changes over to Stokes-Kirchoff law for drops of smaller magnitude, when $r=5\times10^{-5}$, $v=3\times10^{-3}$ cm./sec. Thus it becomes clear that with the ordinary movements which take place in the atmosphere there will not be any difficulty in keeping the water drops in clouds suspended in the air. Also the drops being very fine the surface area is extremely large and hence adsorption can take place to a very appreciable extent ; the surface coatings so formed may increase the stability of drops.

If there was no horizontal or upward movement in the atmosphere the suspended particles would slowly settle due to action of gravity, the largest ones being in the lowest levels. Such conditions, however, do not persist and therefore the self-purification process of the atmosphere cannot take place to any appreciable extent except in the case of very large particles which are raised up during sand or dust-storms.

Fog and smoke particles in the atmosphere settle quicker under the action of gravity than particles of the same size and under the same density difference suspended in water. Fog drops consisting of water and of radius $400\mu\mu$ reach a falling velocity of 0·03 cm./sec. (H. Freundlich, Kapillarchemie, 1922, S. 1083).

Smoke particles have a greater amplitude of Brownian movement than particles in liquid sols and thus the smoke particles will be prevented from settling rapidly. Cloud and fog particles, however, do not show any Brownian movement and therefore they will settle in air unless vertical convection currents prevent their fall.

If the particles of an aerosol diffuse the chances of collision increase and this may lead to flocculation of the particles. Diffusion as a result of Brownian movement is most pronounced with very fine particles and becomes less and less marked as the particles increase in size. The particles of a freshly formed smoke whose diameter is of the order of 10^{-7} cm. show a vigorous Brownian movement and the small as well as big ions which are also of this magnitude show a pronounced Brownian movement and diffusion. The work of Whytlaw-Gray and collaborators (Proc. Roy. Soc., 102, 600, 615, 1923) on smokes has shown that there are three distinct periods in the life history of such systems, *viz.*,

(1) An unstable period, lasting for five hours or more, in which the decrease in the number of particles with time is very rapid. This is due to aggregation of primary particles.

(2) A stable period in which the number of particles decreases very slowly, chiefly as a result of sedimentation. This stage may last for 24 hours or more.

(3) Stages (1) and (2) overlap to produce intermediate stage in which both aggregation and settling take place.

As the particles decrease, the frequency of collision will also decrease and when the particles reach a radius of the order of about 10^{-5} cm. or more the Brownian movement is found to be almost absent ; the particles under such circumstances settle under the action of gravity, flocculation being absent. The photographs of zinc oxide taken by Whytlaw-Gray, (loc. cit.) also show that there is a tendency for larger particles to grow at the expense of smaller particles instead of particles of the same size combining with each other.

Although clouds and fog may not flocculate as a result of diffusion, it being small or negligible, they may do so as a result of neutralisation of their electric charge or by the removal of the film of absorbed gas which may surround the drops. The latter can be removed by charging the drops, the effect of charge being to oppose the effect of surface tension (Burton and Wiegand, Phil. Mag., 23, 150, 1912). It is found that water drops colliding in air rebound from each other as a result of the surrounding film of gas but if the air in the immediate vicinity is charged, the drops become charged due to adsorption of ions and then coalesce when they collide with each other (Rayleigh, Proc. Roy. Soc., 28, 406, 1879 ; 29, 71, 1879 ; 34, 130, 1882). Even if some particles in an aerosol are neutral, flocculation can take place between charged particles and neutral particles, as a charge opposite to that on charged particles will be induced on neutral particles. In a cloud or fog generally some particles may be negatively charged while others may be positively charged and therefore flocculation is quite possible. The diffusion in such a system is small but there being always some turbulence in the atmosphere, the particles can come in contact with each other for allowing coalescence to take place. When the particles are all neutral a breeze may bring them together and larger aggregates may be formed. The particles in a fog or cloud can also grow as a result of evaporation of relatively smaller particles, or as a result of further condensation from vapour phase as a result of cooling of the system.

In the case of condensation of zinc vapour in various gases Kohlschütter (Kolloid Zeit., 42, 209, 1927 ; also Schmauss, Meteorol. Zeit. S. 473, 1927) has also shown that under the same conditions of pressure and temperature the size of the particles increases and their number decreases with a decrease in the density of the gas ; with the same gas an increase of pressure increases the degree of dispersion as well as the number of particles. Schmauss and Wigand (loc. cit. S. 16) consider that such an effect is produced in the atmosphere when a cloud is lifted up ; decrease of pressure may probably explain the decrease in the degree of dispersion. Kopp's observations (loc. cit.) also show that in a thundercloud the drops at the bottom are finer while those higher up are bigger and fewer in number. Kopp's observations can, however, be also explained on the view that the number of nuclei in higher levels being small relatively large drops will be formed.

If the cloud or fog contains particles of unequal size it may become unstable due to growth of relative larger particles at the expense of smaller ones as a result of isothermal distillation. If all the particles are however of the same size the stability will not be affected as a result of this evaporation effect.

In the case of a town fog the stability of which is sometimes very great, there are other factors to be considered. The evaporation of the fog particles might be prevented as a result of the absorbed layer of organic gases as well as oil at the surface.

Recently A. Wigand and E. Frankenberger (Phys. Zeit., 31, 204, 1930) have given a theoretical treatment of the question of persistence and coagulation of fog and cloud by considering the effect of the electric double layer and the application of v. Smoluchowski's theory of kinetics of coagulation of hydrosols. It must be stated here that even at present our understanding of the property of the double layer round the particles in a hydrosol is not quite clear and complete, and we are not at all sure of the existence of double layer in the case of charged particles in fogs and clouds. Even granting the existence of double layer round the particles in clouds and fogs, we are not aware, if in the case of clouds and fogs also as in the case of hydrosols, the charge on the particles has to be reduced to a particular value before coagulation of clouds and fogs can take place. It is known that rain drops carry electric charge; if it is so, the case is somewhat different from that of hydrosols unless one assumes that the rain drops have got re-electrified after leaving the cloud as a result of adsorption of ions ; there is however no conclusive experimental evidence for or against this assumption. Also it is doubtful if the coagulation process is such a simple reaction as postulated by v. Smoluchowski ; in the case of hydrosols there is definite evidence that the coagulation reaction has an auto-catalytic character. During the first period after the addition of electrolyte the alteration in the sol is slight ; then after some time, the amount flocculated increases rapidly and finally it slowly approaches the end state. There is no experimental evidence to show whether in the case of clouds and fogs the aggregation is of the simple type as postulated by v. Smoluchowski or has an auto-catalytic character. It is doubtful whether the results of Defant and Köhler about the drop series of the order of 1, 2, 4, 8, etc., can be taken to indicate coagulation of droplets in a cloud or fog similar to that in the case of hydrosols. The theoretical treatment given to the question of coagulation in clouds and fogs by Wigand and Frankenberger should therefore be taken with reservations.

On examining critically various theories which hold for the coagulation of suspended matter in hydrosols, it is found that these fail to explain satisfactorily the precipitation of rain from clouds. Almost all the rainfall over the world occurs in connection with the movements of "lows" and "heat thunderstorms". In these cases warm and moist air is made to rise higher up. In the case of warm front rain the warm moist air rises over relatively cold dry air. The cold front rain is as a result of the lifting of warm moist air by cold dry air. In the case of heat thunderstorms warm moist air is made to rise as a result of strong convection set up due to insolation. Thus rain always forms in an ascending air current. Its mechanism can therefore be pictured as follows :—

As the warm moist air rises up, its temperature begins to fall and when the dew point is reached condensation begins to take place on nuclei which are always present in large numbers ; condensation may begin even before dew point is reached if the nuclei are very hygroscopic. Now as the air continues to rise further, the cloud particles already formed may lag behind and the air is thus made gradually poorer and poorer in nuclei. Therefore a higher degree of supersaturation will be necessary before condensation can take place ; the number of nuclei left in the rising air mass being comparatively very few, the drops formed as a result of further condensation will be sufficiently large and fall to give rain. It is possible that these drops may further grow during their fall through ascending air current as a result of more moisture condensing upon them because of their lower temperature than the surrounding air or due to coalescence on account of collision with droplets that may be oppositely charged or similarly charged but having a different density of charge. The nature of precipitation—drizzle, heavy rain, etc.,—will depend upon the amount of moisture available as well as the conditions of condensation.

About the nature of precipitation Schmauss (Meteorol. Zeit., S. 339, 1927) has mentioned that the centre of Munich gets excess of weaker rain than the adjoining suburbs (smaller drops in the middle of the town than in the surrounding area). This he considers due to the fact that in the heart of the town a considerably large number of nuclei are present due to working of factories, and therefore relatively smaller drops are formed, the amount of water vapour available for condensation being the same in the two cases. Of course it is a common observation that the frequency of the low clouds and fogs is greater over an industrial area than over the adjoining countryside. This is due to a considerable number of nuclei that are made available from the chimney smoke, some of the nuclei being very hygroscopic. Condensation can therefore occur even if air is unsaturated. Moreover with the chimney smoke, some water vapour also escapes—in fact this is the result in almost every combustion process—and thus the amount of water vapour available for condensation is also relatively great. The same causes may also be responsible for cloud formation over the mouths of active volcanoes.

In this connection mention may also be made about a recent paper by Ashworth (J. Roy. Met. Soc., 55, 341, 1929 ; also see Nature, 132, 443, 1933) in which the influence of smoke and hot gases on the rainfall is considered. He has analysed the records of a number of years of Rochdale, an industrial town in England, and shown that (1) a smaller average total rainfall occurs on Sundays than on other days, (2) during working hours 7 A.M. to 6 P.M., the duration of rainfall was greater than for other part of the day and (3) there was a close agreement between the amount of impurity and rainfall. He ascribes this effect to the smaller number of nuclei in the atmosphere on Sundays due to factories being closed, and the larger number of condensation nuclei available in smoke and hot chimney gases during working hours. It may be pointed out here that such an analysis by Mr. U. N. Ghosh for Ahmedabad, a large industrial town in Gujarat, did not show relation of the type observed by Ashworth in the case of Rochdale ; analysis showed that the average total rainfall on Sundays was larger than on other days, the ratio of the total rainfall on all Sundays during last 31 years×7 to that of the total of all the days being 1·09. On the other hand, for Asansol, in the middle of a coal district in Bengal, the value of the ratio is 0·93 (average of 31 years), and for Cawnpore, another industrial town in the East United Provinces, the value of the ratio is 0·87 (average of 31 years). The results for Asansol and Cawnpore apparently support Ashworth's analysis for Rochdale, Halifax and Llanfairfechan, the values of the ratio at the last three stations being 0·94, 0·98 and 0·93 respectively (Ashworth, Nature, loc. cit.). It will be also interesting to mention here the results of similar analysis for Deesa, a city in Gujarat in the Palanpur State, in which there is hardly any factory ; the value of the ratio comes to 0·93 (average of 31 years). It is difficult to understand the reason for less average rainfall on Sundays than on other days at Deesa ; one might incline to the view that condensation nuclei are not the deciding factors for these differences of rainfall on Sundays and other days.

In the end I wish to thank Dr. S. Mal for the help in preparing this article and Dr. K. R. Ramanathan for some valuable suggestions.