The following contribution to this Section was received from **Professor Dr. H. Freundlich** (Berlin-Dahlem), in response to an invitation :—

THE EFFECTIVE POTENTIAL DIFFERENCE OF ELECTRO-OSMOSIS AND ALLIED PHENOMENA

BY

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The nature of the potential difference at work in electro-osmosis, kataphoresis and allied phenomena—which I group as electrokinetic —is not as yet fully understood. On the theory of *Helmholtz*[1] of the electron double layer we can satisfactorily represent the physical aspect of the processes. But the relation between this electrokinetic potential difference ζ and the ordinary *Nernst* potential difference ϵ, with which we deal so successfully in the theory of galvanic couples, is not by any means clear yet. We might best solve this problem by measuring simultaneously, at the same wall, both the potential differences ζ and ϵ. In the case of metals, for which ϵ is so well known, unobjectionable measurements of ζ are not easily obtained. The kataphoresis of metal sols is objectionable because we are doubtful as to the state of the surface of the metal (its oxidation, &c.). It would therefore appear preferable to measure ζ at the interface glass-aqueous solution. ζ may reliably be determined by the aid of electro-osmosis, or of stream potentials in glass capillaries. But *Haber* and *Klemensiewicz*[2] have demonstrated that there is also a Nernst p.d. at their "glass electrodes." In conjunction with *Rona* I have, therefore, determined, in the first instance, the stream potentials in glass capillaries, and in the second instance the Nernst p.d. at a glass electrode (made, so far as possible, of the same glass) after *Haber* and *Klemensiewicz*.

In measuring the stream potentials we made use of a capillary of an easily-fusible Thüringian glass, 10 cm. long, about ⅓ mm. in diameter, through which the aqueous solution was forced by the pressure of the nitrogen in a cylinder. The experiments are conveniently and smoothly performed, provided the electrodes be as reversible as possible. Our electrodes were $0 \cdot 1$ N. calomel electrodes ; they were joined to the ends of the capillary through tubes charged with a 3 per cent. agar jelly prepared from $0 \cdot 1$ N. solution of KCl. A binant electrometer served for the measurements.

In complete agreement with previous experiences[3] we found the concentration of the electrolytes to be of decisive importance. In concentrations exceeding about 1,000 micromols (millionth parts of a mol) stream potential could no longer be observed ; generally concentrations of from 10 to 100 micromols suffice to reduce the ζ of pure water to very small values.

The effect depends essentially upon the kations, their valency and other properties, which we may connect with their adsorbability. Salts with univalent kations such as NaCl, KCl and others are the least effective ; salts with bivalent kations, and further also acids, are considerably more effective. With none of these it was, however, possible to reverse the negative charge of the glass into a positive

charge. But this reversal is produced by aluminium chloride already at a concentration of 1 or 2 micromols (*i.e.*, about 0·15 mg. per litre), further by crystal violet at about 50 micromols. The reversal with aluminium chloride was also observed when there were present in the solution 150 micromols of KCl in addition to 6 micromols of AlCl₃.

The measurements at glass electrodes were carried out exactly as previously by H. and K. A globe of very thin-walled glass dipped into a beaker filled with the electrolyte solution, these solutions being the same as those used for the stream potentials. The glass globe contained 0·1 N. solution of KCl and in it a platinum electrode joined to the binant electrometer. In the beaker was the earthed 0·1 N calomel electrode. Before each series of measurements we repeated the H. and K. sequence of experiments with solutions of H⁺ and OH′ ions of various concentrations to make sure of the applicability of the method.

It resulted that we did not find anything, in the experiments after H. and K., of the peculiar effects observed with stream potentials. When the electrolyte solution contained, *e.g.*, 100 micromols of KCl, and we added hydrochloric acid in concentrations increasing from 5 up to 50 micromols, we observed electrometer deflections up to about 50 millivolts, in the sense of increasing acidity. When we took aluminium chloride of the same molar concentration, in the place of HCl, we observed deflections in the same sense attaining 40 millivolts, whilst crystal violet yielded only a small deflection of about 15 milli-volts even at a concentration of 200 micromols.

The glass electrode after H. and K. behaves altogether like an H⁺ electrode. Since the H⁺ ion concentration is badly defined in solutions so poor in electrolytes, one cannot well expect to obtain exactly reproducible results. For this reason the same experiments were repeated with buffer mixtures (of sodium acetate and acetic
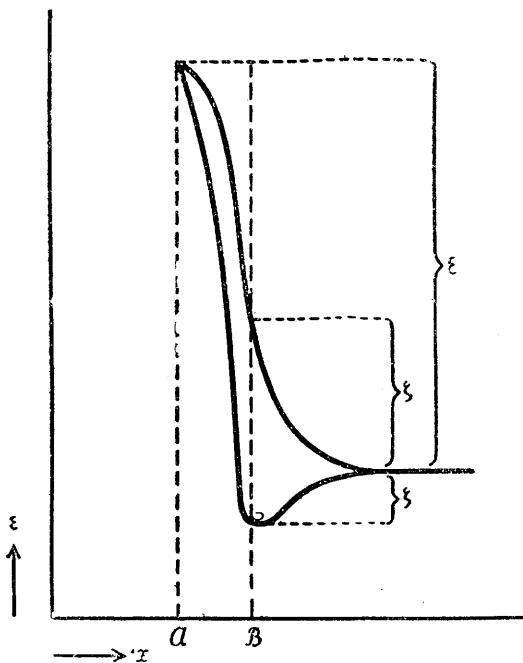
acid). The electrometer deflection, observed with a buffer-mixture of a definite H· ion concentration, was not in the slightest way changed by the addition of aluminium chloride and of crystal violet in concentrations up to 100 micromols. It follows from these experiments that ζ and ϵ are certainly not identical. We must, on the contrary, assume that there is a space charge at the solid interface, a diffuse double layer (after *Gouy*[4]) which projects rather deeply into the liquid. ζ represents the part of the double layer which lies entirely in the liquid, that is to say, the p.d. between the liquid film adhering to the wall and the movable liquid. On the other hand, ϵ is the p.d. between the acid wall itself and the interior of the liquid. The annexed diagram illustrates the relation. The ordinates represent the potentials, the abscissæ the distances from the solid wall, measured in the liquid. The fixed wall is on the left of A; between A and B is the film of liquid adhering to the wall; to the right of B the movable liquid. The diagram shows that with the possible variations of the potential curve, ζ may even differ from ϵ in sign.

Since ζ lies entirely within the liquid we have according to *Pellat* and *Perrin*[5], and in distinction from *Helmholtz*, to take the dielectric constant into consideration. When we then calculate the p.d. ζ after the formula of *Helmholtz*, $\zeta = 4 \ \pi\eta\lambda \ E/p.D.$[6], we find values up to about 100 millivolts, smaller therefore than the ϵ values, as we should indeed expect on our assumption. The potential ϵ being, in the experiments of H. and K., quite independent of ions such as those of aluminium and crystal violet, we understand why nobody, in taking p.d. measurements after Nernst at metallic electrodes has ever noticed any influence of the valency and adsorbability of such foreign ions, whilst that influence completely dominates the phenomena of electro-kinetic processes.

When we attempt to explain the influence of electrolytes upon the p.d. ζ, we have to bear in mind that according to *Gouy*[7] the thickness of the film projecting into the liquid decreases strongly as the concentration of the electrolyte increases. With higher concentrations the film soon becomes so thin and penetrates to so small a depth into the liquid that we can, in electrokinetic experiments, no longer separate the two coatings from one another. This point and the increasing conductivity of the solution account for the vanishing of the electrokinetic effect at higher electrolytic concentrations. With respect to the influence of the nature of the ions we seem to be constrained to ascribe importance to the adsorbability and to the valency essentially in connection with the adsorbability.[8] It is noteworthy that we meet with this striking effect of the aluminium ion and of other ions of high valency not only in electrokinetic experiments at glass walls, but also at phase boundaries of entirely different nature. We find it, to quote a few examples, in the kataphoresis of little droplets of hydrocarbons[9] and of air bubbles,[10] further in the coagulation—which, we know, is intimately connected with electrokinetic processes—of arsenic trisulphide,[11] and of gold[12] and silver sols,[13] &c. The facts suggest that we have in all these cases to deal with a distribution of the ions, depending upon the nature of the ions, in the layers of water directly adhering to the different phases.

There are, moreover, also electrochemical phenomena in which both ϵ and ζ come into play. Such are the capillary-electric phenomena at the interface mercury-aqueous solutions. The limiting surface tension of mercury is certainly not merely to be interpreted as a function of the potential difference and thus of the mercuric ions

which determine the p.d.   The distribution of the ions in the water-film adjacent to the mercury surface will certainly influence the surface tension.[14] When now we have ions present of pronounced adsorbability and consequently deal with a characteristic ζ, the maximum surface tension will not be attained at the same potential as in the presence of capillarily-active electrolytes; we thus find a displacement of the maximum of surface tension.   It is in accord with this view that the maximum of capillarily-active ions of opposite charges is displaced also in the opposite direction.[15]   Experiments made by myself and Miss *Wreschner*, Ph.D., show that basic and acid dyes which are so effective in electrokinetic phenomena, are prominent also in this respect.   Kations of basic colouring matters, like other kations which are capillarily-active, displace the maximum towards the ascending positive branch of the curve of electrocapillarity; anions of acid dyes, like other capillarily-active anions, shift the maximum over to the descending negative branch.   This displacement will also be noticeable at higher electrolytic concentrations, at which ζ has only small values; for the effect of the potential gradient lying in the liquid may still be very marked, although we measure only small potential differences in electrokinetic experiments owing to the high conductivity concerned.   That the maximum of such capillarily-active ions is not only displaced, but actually lowered, accords with the fact that capillarily-active substances may lower any interfacial tension.[16] In electrolytes, the anions and kations of which are both particularly inactive as regards capillarity, the p.d. is zero for the maximum of surface tension.   This condition occurs for mercury in a solution of KNO_3; in this instance the electrocapillary curve deviates merely by a few tenths of one per cent. from the parabolic shape—in accordance with the *Lippmann-Helmholtz* theory.[17]

Looking back, we may answer the question raised in the introduction in the sense that the *Nernst* potential difference ϵ is by no means identical with the electrokinetic p.d. ζ.   The *Nernst* potential ϵ represents the total difference between the interior of the first phase and that of the second phase; the electrokinetic potential ζ represents that portion of the difference which falls within the displaceable liquid layers.

[1] *Gesammelte Abhandl.*, I., p. 855.
[2] *Zeitschr. Physik. Chem.*, **67**, 385 (1909).
[3] Kruyt, *Kolloid Zeitschr.*, **22**, 81 (1918); also v. Elissafoff, *Zeitschr. Physik. Chem.*, **79**, 385 (1912), "Electro-osmosis in Glass Capillaries."
[4] *Journ. de Phys.*, **9**, 457 (1910).
[5] *Journ. de Chim. Phys.*, **2**, 601 (1904)
[6] p = excess pressure forcing the liquid through a capillary in a Poiseuille stream; E = p.d. between the electrodes; η = viscosity of the liquid; D = dielectric constant; λ = specific conductivity.
[7] *Loc. cit.*, p. 5.
[8] Freundlich, *Kapillarchemie*, pp. 243, &c. (1909).
[9] Powis, *Zeitschr. Physik. Chem.*, **89**, 91 (1915).
[10] McTaggart, *Phil. Mag.*, [6], **27**, 297 (1914).
[11] Freundlich, *Zeitschr. Physik. Chem.*, **44**, 129 (1903).
[12] v. Elissafoff, *loc. cit.*, p. 2.
[13] Burton, *Phil. Mag.*, [6], **12**, 472 (1906).
[14] Gouy, *Ann. d. Chim. et d Phys.* [7], **29**, 145 (1903); [8], 8, 291 (1906); [8], 9, 75 (1906).   Freundlich, *Kapillarchemie*, pp. 187, &c. (1909).
[15] Gouy, *loc. cit.*,, note 6, p. 8.
[16] Freundlich, *Kapillarchemie*, pp. 187, &c. (1909).
[17] Krüger, *Zeitschr. Elektrochem.*, **19**, 617 (1913).