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LI. A contribution to the theory of electrocapillarity

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appears in the spectrum of the capillary, in the capillary discharge, only very faintly if at all, but in the discharge in dilute sulphuric acid it is the most important part of the spectrum of the bubble which forms at each end of the capillary.

The lines of the metal of the dissolved salt appear in the brush. In the case of lithium their relative intensity varies with the salt used and also with the current. In weak solutions the metal lines are destroyed by the heavier condensed discharges. The metal lines appear very feebly in a capillary, and they are produced strongly only in the immediate neighbourhood of a metal electrode.

The spark-lines of platinum appear with the condensed discharges when a spark-gap is used.

In conclusion I wish to thank Professor H. Stroud, of Armstrong College, for the kind interest shown in this investigation. My thanks also are due to Mr. H. Morris-Airey, who suggested to me this problem for research and who was at all times willing to offer criticism and advice.

LI. *A Contribution to the Theory of Electrocapillarity.*
By DAVID LEONARD CHAPMAN [*].

FOR any substance which satisfies the laws of a perfect gas we obtain by equating to zero the variation of the sum of the potential and free energy the equation

$$P_1 - P_2 + Rt \log_e p_1 - Rt \log_e p_2 = 0,$$

P_1 and P_2 being the potential energies at the points 1 and 2 of a gram molecule of the substance, and p_1 and p_2 the respective hydrostatic pressures.

If the potential energy is electrical the above equation becomes

$$(V_1 - V_2)q + Rt \log_e p_1 - Rt \log_e p_2 = 0,$$

in which V is the line integral of electromotive intensity, and q the charge on a gram molecule of the substance.

The potential [†] of a monovalent metal in contact with a solution of one of its salts is therefore, according to Nernst's

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[*] Communicated by the Author.

[†] Although it sometimes leads to confusion, we shall for brevity adopt the usual convention of calling the line integral of electromotive intensity potential. Throughout the electrostatic system of units will be used.

double-layer theory, given by the equation

$$V_s - V_m + \frac{Rt}{\epsilon}\log_e \frac{p_s}{p_m} = 0^*,$$

in which ϵ is the charge on a gram ion of the metal, and s and m refer to points at some distance within the solution and on the surface of the metal respectively.

The above equation only holds if it is assumed that the charge on the metal is much closer to the surface than the charge in the solution—an assumption which can be shown to be in complete accord with Schuster's estimate of the concentration of the free negative electrons in conductors.

Assuming provisionally that the charge on the metal resides entirely on its surface, and that there is accordingly no difference of potential between the surface of the metal and its interior, we propose to investigate the distribution of potential and electric density within the solution, and thence to deduce the capacity of the condenser which the double layer forms.

Consider a plane surface of the metal, and let x be the perpendicular distance of a point in the solution from the surface of the metal. Let the potential at any point x be represented by V_x, and the pressure of the metal ion at the same point by p_x. Then

$$V_x - V_\infty = \frac{Rt}{\epsilon}\log_e \frac{p_\infty}{p_x}. \quad \ldots \quad \text{(A)}$$

Indicating by the affix $'$ that the symbol for a dimensional magnitude refers to the negative ion we obtain similarly for the anion

$$V_x - V_\infty = \frac{Rt}{\epsilon}\log_e \frac{p_x{}'}{p_\infty{}'}. \quad \ldots \quad \text{(A')}$$

From (A) and (A')

$$p_x{}' = \frac{p_\infty{}^2}{p_x}. \quad \ldots \quad \ldots \quad \text{(i.)}$$

since $p_\infty = p_\infty{}'$.

If by ρ_x we indicate the electric density of the positive charge on the metal ion

$$\rho_x = \frac{\epsilon p_x}{Rt},$$

whilst

$$\rho_x{}' = -\frac{\epsilon p_x{}'}{Rt}.$$

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* We shall leave out of consideration the effect of potential energy arising from non-electrical forces at the surface.

Whence
$$\rho_x + \rho_x' = \frac{\epsilon}{\mathrm{R}t}\left(p_x - p_x'\right)$$

$$= \frac{\epsilon}{\mathrm{R}t}\left(p_x - \frac{p_\infty^2}{p_x}\right) \quad \text{(from (i.))}$$

We shall now show that, with the assistance of Poisson's equation,

$$\nabla^2 \mathrm{V} = -\frac{4\pi\rho}{\mathrm{K}},$$

the electric state of any point in the field can be found, and the charge on the double layer condenser expressed as a function of the difference of potential between the solution and the metal.

In the special case under investigation Poisson's equation becomes

$$-\frac{d^2\mathrm{V}_x}{dx^2} = \frac{4\pi}{\mathrm{K}}\frac{\epsilon}{\mathrm{R}t}\left(p_x - \frac{p_\infty^2}{p_x}\right). \quad . \quad . \quad . \quad \text{(B)}$$

On substituting the value of $\frac{d^2\mathrm{V}}{dx^2}$, which can be obtained from (A), this reduces to

$$\frac{\mathrm{R}^2 t^2}{\epsilon^2}\frac{\mathrm{K}}{4\pi}\frac{d^2}{dx^2}\log_e p_x = p_x - \frac{p_\infty^2}{p_x}.$$

The above differential equation admits of solution in a simple form. Multiplying both sides of the equation by $d\log_e p_x$, and integrating between $x = x$ and $x = \infty$, we obtain

$$\frac{\mathrm{R}^2 t^2}{\epsilon^2}\frac{\mathrm{K}}{8\pi}\left[\left(\frac{d}{dx}\log_e p_\infty\right)^2 - \left(\frac{d}{dx}\log_e p_x\right)^2\right] = -p_x + 2p_\infty - \frac{p_\infty^2}{p_x};$$

but since $\frac{d}{dx}\log_e p_\infty$ is zero, this reduces to

$$\frac{\mathrm{R}t}{\epsilon}\sqrt{\frac{\mathrm{K}}{8\pi}}\frac{d}{dx}\log_e p_x = \pm\left(\sqrt{p_x} - \frac{p_\infty}{\sqrt{p_x}}\right).$$

It is obvious that the negative sign must be taken on the right-hand side of the equation; so that we obtain finally as the first integral of the differential equation

$$\frac{\mathrm{R}t}{\epsilon}\sqrt{\frac{\mathrm{K}}{8\pi}}\frac{d}{dx}\log_e p_x = \frac{p_\infty}{\sqrt{p_x}} - \sqrt{p_x}, \quad . \quad . \quad \text{(C)}$$

or
$$\frac{\mathrm{R}t}{\epsilon}\sqrt{\frac{\mathrm{K}}{8\pi}}\frac{dp_x}{dx} = \sqrt{p_x}(p_\infty - p_x). \quad . \quad . \quad \text{(C')}$$

The solution of (C') is

$$\frac{Rt}{\epsilon}\sqrt{\frac{K}{8\pi p_\infty}}\cdot\log_e\frac{\sqrt{p_x}+\sqrt{p_\infty}}{\sqrt{p_x}-\sqrt{p_\infty}}\cdot\frac{\sqrt{p_0}-\sqrt{p_\infty}}{\sqrt{p_0}+\sqrt{p_\infty}}=x.$$

The last equation is not at present of much practical importance.

What we require to know in order that we may be able to test the theory of electrocapillarity by a direct comparison of the experimental values of surface tension with those calculated from the theory, is the magnitude of the charge on the double-layer condenser for a given difference of potential between the solution and the metal.

By integrating Poisson's equation between 0 and ∞ we obtain

$$\frac{dV_0}{dx}=\frac{4\pi}{K}Q,$$

in which Q is the charge on unit surface of the solution. But

$$\frac{dV_0}{dx}=-\frac{d}{dx}\frac{Rt}{\epsilon}\log_e p_0.$$

Substituting in this equation the value of $\frac{d}{dx}\log_e p_0$ obtainable from (C), we deduce that

$$Q=\sqrt{\frac{K p_\infty}{2\pi}}\left(\sqrt{\frac{p_0}{p_\infty}}-\sqrt{\frac{p_\infty}{p_0}}\right).$$

A more convenient form of the above equation is

$$Q=\sqrt{\frac{K p_\infty}{2\pi}}\left(e^{\frac{\epsilon V}{2Rt}}-e^{-\frac{\epsilon V}{2Rt}}\right),\quad\ldots\ldots\quad(D)$$

where V is the difference of potential between the solution and the mercury.

Calculation of the Surface Energy of Mercury in contact with an Electrolyte.

The surface energy of the mercury in a capillary electromometer can be deduced in the following way.

Suppose that a layer of mercury A is in contact with a solution of potassium chloride which also contains mercurous chloride at a very low concentration. Assume also that the means exist for increasing and diminishing the surface of the mercury in contact with the potassium chloride. In the

solution of potassium chloride are immersed alloys of the elements potassium and chlorine with substances that are insoluble in water. The ionic solution pressures of the alloys are equal to the osmotic pressure of the potassium
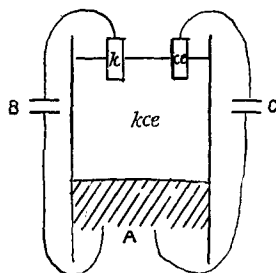
and chlorine ions in the solution. The alloys are in electrical contact with the mercury, and electromotive forces can be inserted in the circuits thus formed at B and C. The potential difference between the solution and the mercury can be increased by removing from the solution small amounts of ionic mercury and chlorine by means of the circuit C.

With this engine we perform the following reversible cycle of operations, keeping the concentration of the potassium chloride constant.

I. We start with a negligible amount of mercury surface in contact with the solution, the osmotic pressure of the mercury ions being equal to the solution pressure of the mercury. Mercurous chloride is withdrawn from the solution until the difference of potential between the solution and the mercury has risen to V. The work performed in this operation is in any case negligibly small, and is, moreover, almost completely recovered in a subsequent operation. After this operation there will be a negative charge on the metal and a positive charge in the solution.

II. The mercury surface is increased by unity. Now the positive charge in the solution close to the surface of the metal exists by reason of there being in that region a large excess of potassium ions, a large deficiency of chlorine ions, and a small excess of mercury ions. Therefore, if the concentration of the solution is kept constant as the surface increases, potassium and mercury ions must be introduced into the solution, and chlorine ions removed with the assistance of the circuits B and C. As the potassium ions with their positive charges enter the solution an equal amount of negative electricity passes from K to A. Let the quantity

of electricity which passes from K to A during the formation of unit surface be $-q$. It changes in potential by an amount $-V$, and therefore the work performed is qV. Let the negative charge on the chlorine ions removed from the solution during the formation of unit surface be $-q'$. This charge also passes to the mercury surface, and an amount of work $q'V$ is performed. The electrical energy required to introduce the small excess of mercury ions can be neglected. The total electrical work performed is $(q+q')V$ or QV, Q being the charge on unit surface of the mercury. An amount of work equal to T_v, the surface tension corresponding to a difference of potential V, is also performed.

III. Mercurous chloride is introduced into the solution until the difference of potential between the mercury and the solution is zero. This work is opposite in sign and almost equal to that performed in operation I. During the destruction of the double layer the excess of potassium ions re-enter the potassium alloy, whilst the deficiency of chlorine ions is supplied by the chlorine which entered the chlorine alloy during the formation of the surface. It is easy to see that the electrical work performed by the engine in order to effect this change will be

$$\int_0^V V.\, dQ.$$

IV. The surface is reduced by unity, and the work performed by the engine is T_0, the maximum surface tension.

If we sum the work performed on the engine in the cycle of operations and equate it to zero we obtain

$$T_0 - T_v = QV - \int_0^V V dQ = \int_0^V Q dV.$$

Now it has generally been assumed that the capacity of the condenser formed by the double layer is constant. This assumption would obviously make $T_0 - T_v$ proportional to V^2; but the first part of this investigation shows that the assumption is not justified.

Substituting in the above equation the value of Q from equation (D), we find that

$$T_0 - T_v = \int_0^V \sqrt{\frac{Kp_\infty}{2\pi}} \left(e^{\frac{\epsilon V}{2Rt}} - e^{-\frac{\epsilon V}{2Rt}} \right) dV$$

$$= \frac{2R}{\epsilon} \sqrt{\frac{Kp_\infty}{2\pi}} \left(e^{\frac{\epsilon V}{4Rt}} - e^{-\frac{\epsilon V}{4Rt}} \right)^2.$$

This equation can of course only be true so long as the ions behave as perfect gases. The increase in osmotic pressure of an ion for a change in potential of 0·1 volt is about 80 fold. So that if the solution were decinormal potassium chloride it would scarcely be legitimate to use the formula for a greater value of V than 0·1 volt. Unfortunately, the change in surface tension for an alteration in the applied electromotive force of 0·1 volt when the surface tension is at its maximum is so small that it cannot be accurately measured. I estimate from S. W. J. Smith's* electrocapillary curves and Quincke's value for the surface tension of mercury in contact with hydrochloric acid (assuming that the surface tension of mercury in contact with hydrochloric acid is the same as that of mercury in contact with a solution of potassium chloride), that the fall in surface tension when V is 0·1 volt lies between 3·5 and 4 c.g.s. units when the mercury

is in contact with $\dfrac{N}{10}$ KCl. The fall in surface tension

calculated from the above formula for the same change in the applied electromotive force is 4·8 c.g.s. units. It is therefore very probable that the observed change in surface tension can, as Helmholtz postulated, be largely accounted for by the electric charges in the double layer.

It is obvious that what is most needed to elucidate the mechanism of the capillary electrometer is a very thorough examination of the electrocapillary curve in the region of maximum capillarity, preferably with solutions which give no electromotive force in contact with mercury, such as those used by Palmaer† to investigate the electromotive force of the calomel electrode.

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LII. *On the Electrification associated with Dust-Clouds.* By
W. A. DOUGLAS RUDGE, *Professor of Physics, University
College, Bloemfontein* ‡.

[Plates VI. & VII.]

THE author has shown § that a considerable amount of electrification is imparted to the atmosphere by clouds of dust raised by the wind, and it seemed of interest to investigate the electrification developed by raising clouds

* *Zeit. f. Phys. Ch.* xxxii. p. 467 (1900).
† *Zeit. Elektrochemie,* ix. p. 754 (1903).
‡ Communicated by the Author.
§ Phil. Mag. June 1912 ; Proc. Roy. Soc. South Africa, 1912 ; South African Journ. Sci. 1912.