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## STUDIES IN HETEROGENEOUS EQUILIBRIA.

### PART II.<sup>1</sup>—THE KINETIC INTERPRETATION OF THE NERNST THEORY OF ELECTROMOTIVE FORCE.

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According to the classical theory of Nernst the potential difference at the surface of a metal dipping into a solution containing its ions is determined by two factors (1) the tendency of the metal ions to pass into solution, the so-called electrolytic solution pressure, (2) the osmotic pressure of the metal ions in the solution. In order to obtain the logarithmic relation between the potential difference and the concentration of metal ions in the solution Nernst was obliged to resort to a purely formal analogy with dilution. Regarding the process as a dilution from the electrolytic solution pressure  $P$  to the osmotic pressure of ions in the solution  $p$ , he obtained by a simple thermodynamical cycle the well-known expression :

$$E = - \frac{RT}{nF} \log \frac{P}{p} \quad . \quad . \quad . \quad . \quad (1)$$

However, as Leffeldt<sup>2</sup> pointed out the values of  $P$  calculated from the observed potentials range from the enormously great (e.g.  $9.9 \times 10^{18}$  atmospheres for zinc) to the infinitely small ( $1.5 \times 10^{-36}$  atmospheres for palladium) quantities to which it is difficult to ascribe a real physical significance. This difficulty has thrown discredit on the Nernst theory, which has come to be regarded as a convenient fiction, useful for the academical deduction of the logarithmic relationship and the latter is commonly written in the more empirical form

$$E = E_0 + \frac{RT}{nF} \log C \quad . \quad . \quad . \quad . \quad (2)$$

where  $E_0$  is the normal potential.

The normal potential  $E_0$  is a quantity of outstanding importance in determining the chemical behaviour of the metals, and in recent years several

<sup>1</sup> For Part I. see p. 659.

<sup>2</sup> *Phil. Mag.* [V], 1899, 48, p. 430.

attempts have been made to elucidate the factors determining it, mostly by means of thermodynamical arguments.<sup>1</sup>

The adequacy of the Nernst conception has been disputed in some recent discussions. According to Smits it is necessary to assume "that when a metal is brought into contact with an electrolyte, not only metallic ions, but electrons also may pass into solution and that consequently the laws of dilute solution hold good for the electrons in the electrolyte."<sup>2</sup> Further he states, "these considerations differ from the well-known views of Nernst in that the assumption has here been made that the ions and electrons of the metal are in heterogeneous equilibrium with the ions and electrons of the electrolyte, whilst formerly only the atoms of the metal and the ions of the electrolyte were taken into account in the deduction of the potential difference."<sup>3</sup> Kleeman<sup>4</sup> also regards the Nernst theory as insufficient and has proposed a "transition layer" theory of the voltaic cell according to which the potential difference between metal and solution is due to the segregation of ions in a "transition layer" at the surface of the metal owing to the difference in the diffusion velocities of the positive and negative ions. According to this theory the tendency of the metal to go into solution is "a purely secondary effect as far as the production of an e.m.f. is concerned."

We shall apply the methods of the previous paper to the case of a metal dipping into a solution containing its ions, and we shall show that on kinetic grounds the Nernst conception is capable of accounting for the potential differences exhibited by metals in their salt solutions. We shall confine ourselves to metals giving rise to only one kind of ion in solution.

The process giving rise to the potential difference at the surface of the metal is regarded as essentially a solubility phenomenon. In the solution of a salt crystal made up of positive and negative ions, both kinds go into solution. In the case of a metal only the positive ion can do so. The insolubility of the metals as such in ordinary solvents indicates that the latter exert but little attraction on neutral metal atoms, but under appropriate conditions the solution and deposition of metal ions readily occur.

It is generally agreed among physicists that metals are largely ionised into positive ions and free electrons. Indeed attempts<sup>5</sup> have been made to account for the physical properties of the metals on the assumption that ionisation is complete, the metal ions and electrons being arranged in independent space lattices like the positive and negative ions of a salt. In any case we may safely assume that the surface layer of a metal is largely composed of metal ions. The electromotive process is concerned with the metal ions in the surface layer and those in the solution. Equilibrium is attained when equal numbers of ions are dissolved and deposited at the surface in any interval of time.

If the concentration of metal ions in the solution is less than corresponds to equilibrium, that is if the rate of deposition is less than the rate of solution, metal ions will leave the surface of the metal and pass into solution, thereby leaving the surface of the metal with an excess of negative electrons.

<sup>1</sup> Herzfeld, *Annalen d. Physik.* [4], 1918, 56, p. 133; Smits, "Theory of Allotropy," London, 1922, Chapter VII; Reichenstein, *Zeit. phys. Chem.*, 1920, 95, p. 472; Heyrovsky, *Proc. Roy. Soc. [A]*, 1923, 102, p. 638.

<sup>2</sup> *loc. cit.*, p. 116.

<sup>3</sup> *loc. cit.*, p. 118.

<sup>4</sup> *Phys. Review*, 1922, 20, p. 174.

<sup>5</sup> Sir J. J. Thomson, *Phil. Mag.* [VI], 1922, 43, p. 721.

The effect of this negative charge is to retard the passage of positive ions away from the surface and to assist their deposition from solution. The rate of deposition will be increased and the rate of solution decreased; consequently the charge will accumulate until the two processes occur at equal rates.

The conditions will of course be reversed if the concentration of metal ions in the solution is greater than corresponds to equilibrium. In this case deposition will occur and a positive charge will accumulate until the rates of solution and deposition are equalised.

So far we have only stated the Nernst conception in terms of the more precise physical conceptions of to-day. Let us now apply the kinetic considerations of the previous paper to define the conditions of equilibrium.

The state of affairs near the surface is represented in Fig. 1. As in the general case of a crystalline solid, we suppose that the metal exerts a force of attraction on metal ions in the vicinity of the surface, and since the metal ions are fixed in definite positions so as to continue the crystal lattice, the force of attraction is highly localised, that is, it falls off rapidly with the

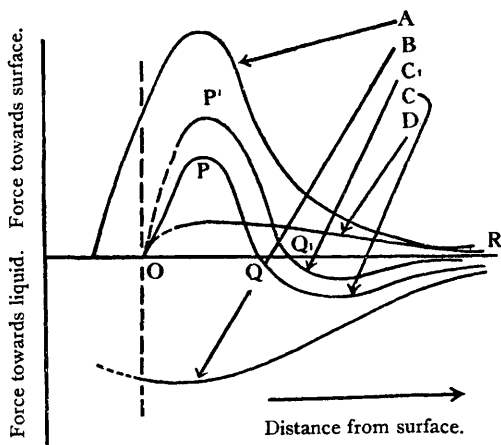


FIG. 1.

distance (A). Secondly we have to take into account the attraction of the liquid on metal ions. This is greatest at the surface and falls off on entering the liquid (B). The resultant of these opposing forces is given by C with a balance point in the general case Q.

It is necessary to consider how this disposition of forces will be modified by the existence of a potential difference at the surface. In the first place let us enquire how the electric charge is distributed near the surface.

There is no reason for supposing that the positive ions that have passed into solution and the negative electrons left in the metal constitute a rigid electrical double layer. Undoubtedly the positive ions in the solution will tend to arrange themselves as near as possible to the negatively charged surface, but the amount of metal ion passing into solution in the attainment of the equilibrium potential is so small that the concentration of metal ions even in the vicinity of the surface will not be appreciably affected. The lines of force emanating from the excess electrons in the surface may anchor themselves on any positive ions near the surface and owing to thermal agitation these will be at varying distances. Therefore the electrical at-

traction on a positive ion will be greatest at the surface and will gradually fall off as we penetrate into the zone of excess positive ions in the solution. This attraction is represented by D and the result of the superposition of this term on the others is given by the curve  $C_1$  with balance point  $Q_1$ .

Now, if the total potential difference between the surface of the metal and the interior of the solution be  $E$ ,<sup>1</sup> the work done by a positive ion in passing from the surface into the interior of the solution is  $nEF$  per gram ion, which is also equal to the area between the curve D and the two axes.

In order that an ion from the surface may reach the balance point it must do an amount of work represented by the area  $P_1OQ_1$ . This is made up of two parts  $W'_1$  the work done against the combined attractive process of the surface and the liquid in reaching  $Q_1$ , and  $-NE'F$  the work done against the electric field,  $E'$  being the potential difference between the surface and the balance point. The total work done in reaching the balance point is therefore  $W'_1 - nE'F$  and the number of ions reaching it in unit time is given by

$$\theta_1 = N_1 \sqrt{TA'} e^{-\frac{W'_1 - nE'F}{RT}} \quad . \quad . \quad . \quad (3)$$

where  $N_1$  = number of metal ions per square cm. in surface layer of metal.

Similarly in reaching  $Q_1$  from the interior of the liquid an ion does work represented by the area  $Q_1C_1R$ , and this again is made up of two parts

$$Q_1C_1R = QCR - Q_1C_1RC = W'_2 - nE''F.$$

where  $E''$  is the potential difference between  $Q_1$  and the interior of the solution. The number of ions reaching the balance point from the solution per second is then

$$\theta_2 = N_s A \sqrt{T} e^{-\frac{W'_2 - nE''F}{RT}} \quad . \quad . \quad . \quad (4)$$

For equilibrium  $\theta_1 = \theta_2$ . Equating we find

$$\frac{W'_2 - W'_1}{RT} + \frac{nF(E' + E'')}{RT} = \log \frac{N_s A}{N_1 A'}$$

Now  $W'_2 - W'_1 = W_2 - W_1 = U$  the heat absorbed in the passage of one gram ion of the metal into solution, and  $E' + E'' = E$ . Therefore we have

$$E = \frac{U}{nF} + \frac{RT}{nF} \log_e \frac{AN_0}{1000A'N_1} + \frac{RT}{nF} \log_e C \quad . \quad . \quad (5)$$

Comparing this with the empirical formula (2) we see that the normal potential  $E_0$  is given by the terms

$$E_0 = \frac{U}{nF} + \frac{RT}{nF} \log_e \frac{AN_0}{1000A'N_1} \quad . \quad . \quad . \quad (6)$$

and this quantity may be regarded as equivalent to  $-\frac{RT}{nF} \log P$  in the Nernst formula (1).

We have thus arrived at a deduction of the Nernst equation by the use of a kinetic mechanism which is physically acceptable in place of the

<sup>1</sup>Convention as to sign: we shall write  $E$  positive when the surface of the metal is positively charged with respect to the solution.

formal thermodynamical process of Nernst. The normal potential  $E_0$  is seen to be a composite term depending on the heat absorbed in the passage of the metal ions into solution and on quantities defining the statistical conditions. The equation (6) cannot be expected to give exact values of the normal potentials. As was pointed out in connection with solubility the last term can only be regarded as a first approximation; further two of the quantities involved in the term  $A'$ , *viz.*  $\nu$  and  $W_1'$ , are unknown. It is interesting to attempt a rough calculation using the values for these quantities employed in the previous paper, namely, for  $\nu$  the characteristic vibration frequency of the metal (reststrahlen) and for  $W_1'$  the latent heat of fusion of the metal. The essential data is given in Table I. The values of  $\frac{U}{nF}$  are taken from a table by Herzfeld<sup>1</sup> and refer to the total energy charge of a complete cell consisting of the metal electrode combined with the normal hydrogen electrode. The values of the heat effects at single electrodes are scarcely known but it has been stated that the heat absorbed at the hydrogen electrode is almost zero.<sup>2</sup> It is satisfactory to note that the calculated values in the last column are at any rate of the right order of magnitude.

TABLE I.

$$A = \sqrt{R/2\pi M} : A' = \nu \sqrt{R/W_1' \pi}$$

Process.	$E_0$ .	$U/nF$ .	$\nu \times 10^{-12}$ .	$W_1'$ Cals. <sup>3</sup>	$E_0 - U/nF$ .	$\frac{RT/nF \log e}{1000A'N_1}$
Ag $\rightarrow$ Ag $\cdot$	+ .799	1.097	4.5	2280	- .298	- .12
Zn $\rightarrow$ Zn $\cdot\cdot$	- .758	- .760	4.8	1840	+ .002	- .08
Cu $\rightarrow$ Cu $\cdot\cdot$	+ .345	.347	6.6	2740	- .002	- .08
Na $\rightarrow$ Na $\cdot$	- 2.71	- 2.486	4.0	730	+ .22	- .14
Fe $\rightarrow$ Fe $\cdot\cdot$	- .441	- .481	8.3	3860	- .04	- .09

### Summary.

The Nernst theory of the electrolytic P.D. of metals is developed on kinetic grounds and a kinetic deduction of the Nernst equation is given. Values of the electrode potentials calculated in accordance with the equations are at least of the right order of magnitude. The Nernst conception therefore gives an adequate and physically acceptable explanation of the facts.

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<sup>1</sup> *Annalen d. Physik.* [4], 1918, **61**, p. 133.

<sup>2</sup> Partington, "Thermodynamics," p. 477.

<sup>3</sup> Landolt-Bornstein.