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STUDIES IN HETEROGENEOUS EQUILIBRIA.

PART III. A KINETIC THEORY OF REVERSIBLE OXIDATION POTENTIALS AT INERT ELECTRODES.

BY J. A. V. BUTLER, M.SC.

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When an inert electrode is dipped into a solution containing two substances related by a simple oxidation-reduction process, it usually acquires a perfectly definite and reversible electrode potential. Thermodynamically the electrical work done against this potential difference in the oxidation of one equivalent of the reduced substance at the electrode is a measure of the free energy of the process. Kinetically it may be supposed that the potential has its origin in the tendency of the more highly oxidised substance to take up electrons and that of the less highly oxidised substance to lose electrons, a transfer that occurs through the agency of the inert electrode.

The thermodynamical theory of these potentials was given by Peters,[1] who deduced thereby the well-known logarithmic relation between the P.D. and the concentrations of the substances taking part. So far as the writer is aware no explanation has previously been given of the mechanism whereby the transfer of electrons might occur and give rise to a reversible P.D. corresponding to the free energy of the process.

Consider the case of two "isomeric" ions M_I and M_{II} differing only in their state of oxidation and carrying n_I and n_{II} positive charges respectively. For simplicity we shall suppose that n_I and n_{II} differ by one. The extension to other cases will be obvious.

The process may be represented by the equation $M_I + \epsilon \rightleftharpoons M_{II}$ where ϵ represents an electron. When an inert electrode is dipped into the solution the ions in the immediate vicinity of the surface must come into contact with it from time to time and if there exists any residual affinity between the metal surface and the ions they may be absorbed to some extent. The electrodes that give the best defined potentials are those whose surfaces possess good adsorptive properties, as for instance platinised platinum, and though this may be due largely to the greater surface area and capacity of the platinised surface, it seems probable that the ions concerned are adsorbed at any rate to some extent. The difference between slight adsorption and simple collision is one of degree. If the surface does not exert any specific attraction on the solute molecules, those which come in contact with the

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[1] *Zeits. Physikal. Chemie.*, 1895, **26**, p. 193.

surface are not held and can pass again into solution without performing any work against surface attractive forces. But if the surface does exert a specific attraction on the solute molecules, those which reach the surface cannot escape until they have acquired sufficient kinetic energy to overcome the surface attractive forces. The first case is equivalent to simple "collision," the second to adsorption; the difference between them lies in the length of time a molecule remains at the surface.

We shall assume that if adsorption occurs, the adsorbed molecules do not cover the whole of the surface. On the assumption an expression for the adsorption of neutral molecules may be deduced, in a similar manner to the deduction of the solubility equation (Part I.). The only difference is that in the case of solubility the surface exerts an attraction on molecules of the same kind as those composing it, in this case the surface exerts a specific attraction on another species of molecules. In this way we obtain:[1]

$$xA'\sqrt{T}e^{-\frac{W_1}{RT}} = AN_s\sqrt{T}e^{-\frac{W_2}{RT}}(s-x) \quad . \quad . \quad . \quad (1)$$

where x = number of adsorbed molecules per sq. cm.
s = total number of molecules per sq. cm. for surface entirely covered with adsorbed molecules.
W = work done in reaching the balance point from the surface.
W = work done in reaching the balance point from the interior.

The adsorption of *ions* at a surface will give it an electric charge which will tend to retard the further adsorption of ions of the same sign. An ion coming up to the surface will perform work against this electric force, which is equivalent to the existence of a P.D. E between the adsorbed layer and the interior of the liquid. In the case of an ion carrying n positive charges we deduce the following expression for equilibrium:—

$$xA'\sqrt{T}e^{-\frac{W_1-nE'F}{RT}} = (s-x)A\,.\,N\sqrt{T}e^{-\frac{W_2+nE''F}{RT}} \quad . \quad (2)$$

where $E' + E'' = E$.

Now consider the simultaneous adsorption of two ions M′ and M″. Let the numbers of these molecules per cubic cm. of solution be N_s' and N_s'' respectively and the numbers adsorbed per sq. cm. surface x and y. For equilibrium two equations must be satisfied:—

$$\begin{cases} xA'\sqrt{T}e^{-\frac{W_1'-n'E_I'F}{RT}} = (s-x-y)AN_s'\sqrt{T}e^{-\frac{W_2'+n'E_I''F}{RT}} \\ yA'\sqrt{T}\,e^{-\frac{W_3'-n''E_{II}'F}{RT}} = (s-x-y)AN_s''\sqrt{T}e^{-\frac{W_4'+n''E''F}{RT}} \end{cases} \quad . \quad (3)$$

where $E_I' + E_I'' = E_{II} + E_{II}'' = E$.

From this we find that if the concentrations of the ions in the solution be c_1 and c_2 (gram molecules per litre)

$$\frac{x}{y} = \frac{c_1}{c_2}\,\frac{e^{\frac{W_1'-W_2'}{RT}}}{e^{\frac{W_3'-W_4'}{RT}}}\,\epsilon^{\frac{(n_2-n_1)E_IF}{RT}} \quad . \quad . \quad . \quad . \quad (4)$$

which gives the relation between the ratio of ions adsorbed and in solution.

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[1] A somewhat similar expression has been obtained by Henry, *Phil. Mag.* (VI.), 1922, **44**, p. 689 for the adsorption of gases. The kinetic treatment of adsorption of Mukergee, "The Physics and Chemistry of Colloids," Report of a general discussion by the Faraday Society and the Physical Society, 1921, p. 103, differs radically in its treatment of the forces concerned.

Now consider the reaction between $\mathrm{M_I}$ and $\mathrm{M_{II}}$ and the electrode surface. $\mathrm{M_{II}}$ will tend to lose its extra electron, while $\mathrm{M_I}$ will tend to gain an electron according to the equation $\mathrm{M_I} + \epsilon \rightleftharpoons \mathrm{M_{II}}$. This transfer may occur through the agency of the free electrons of the metal electrode. If the rate at which $\mathrm{M_I}$ takes electrons from the metal be greater than the rate at which $\mathrm{M_{II}}$ gives up electrons, the metal surface will be left with a deficiency of electrons, that is a positive charge. This process will alter the amounts of $\mathrm{M_I}$ and $\mathrm{M_{II}}$ at the electrode, but equilibrium with the ions in solution will be re-established in accordance with (4). Consequently the charge at the electrode will accumulate until the processes (*a*) $\mathrm{M_{II}} = \mathrm{M_I} + \epsilon$ and (*b*) $\mathrm{M_I} + \epsilon = \mathrm{M_{II}}$ occur at equal rates in the adsorbed layer, $\mathrm{M_I}$ and $\mathrm{M_{II}}$ being present in the equilibrium ratio given by (4).

Let us now consider the forces acting on an electron in the region between the adsorbed layer and the metal. It is well known that in escaping from a metal an electron has to perform work (expressed by the thermionic work function) against surface attractive forces. Further, since the ion $\mathrm{M_{II}}$ (*i.e.* $\mathrm{M_I}\,\epsilon$) is capable of independent existence and work must be done in removing the electron ϵ from its stable position or orbit, the residue $\mathrm{M_I}$ must exert an attraction on electrons in its vicinity. An electron in the region between $\mathrm{M_I}$ and the metal is therefore under the influence of two opposing attractions, and we may suppose that in the vicinity of the metal surface the resultant force is towards the metal, whereas in the vicinity of the ion $\mathrm{M_I}$ its attraction is predominant. In general there will be some point between the ion and the surface at which the forces of attraction balance. An electron from an $\mathrm{M_{II}}$ ion which reaches this point comes into the region of attraction of the metal and passes on. An electron from the metal which reaches the same point will pass on and becoming attached to the $\mathrm{M_I}$ ion will form $\mathrm{M_{II}}$.

Let the work done by an electron in reaching the "balance point" against the surface attractive forces of the metal be ϕ_1. If the metal surface is charged, an electron must perform electrical work in addition in escaping, corresponding to the existence of a P.D. at the surface. Let this P.D. be $\mathrm{E_s}$, then the total work done by an electron in reaching the "balance point" is $\phi_1 + \mathrm{E_sF}$. The number of electrons leaving the surface per sq. cm. per second with kinetic energy greater than $\phi_1 + \mathrm{E_sF}$ is given by the equation :—

$$\theta = ke^{-\frac{\phi_1 + \mathrm{E_sF}}{\mathrm{RT}}}\text{*} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $k = \mathrm{A}\sqrt{\mathrm{RT}/2\pi m}$; A being a constant, independent of the temperature and m the mass of the electron.

Of these, only that part which actually reaches the region of attraction of an $\mathrm{M_I}$ ion can be taken up, consequently the rate at which the metal loses electrons to $\mathrm{M_I}$ is also proportional to the number of the latter, x. The rate at which the process $\mathrm{M} + \epsilon = \mathrm{M_{II}}$ occurs is therefore :—

$$\theta_1 = k_1xe^{-\frac{\phi_1 + \mathrm{E\ F}}{\mathrm{RT}}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Similarly, let the work done by an electron in reaching the balance point from its stable position or orbit in $\mathrm{M_{II}}$ be ϕ_2. We require a relation between ϕ_2 and the number of electrons attaining this state per second. The statistical theory of the chance of an electron possessing more than a given quota of energy has not yet been worked out. But according to the

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* Richardson, "Emission of electricity from hot bodies," 1916, p. 29.

laws of chance we may assume that the relation is an exponential one. We may therefore write for the rate of loss of electrons by M_{II} ions :—

$$\theta_2 = k_2 y e^{-\frac{\phi_2}{RT}} \quad . \quad . \quad . \quad . \quad (7)$$

in which the value and form of k_2 are unknown.

For equilibrium $\theta_1 = \theta_2$; that is

$$E_s = \frac{\phi_2 - \phi_1}{F} + \frac{RT}{F}\log_e\frac{k_1}{k_2} + \frac{RT}{F}\log_e\frac{x}{y} \quad . \quad . \quad (8)$$

Substituting the value of x/y given in (4) we obtain

$$E_s + E_L = \frac{\phi_2 - \phi_1}{F} + \frac{RT}{F}\log_e\frac{k_1}{k_2} + \frac{W'_1 - W'_2 - W'_3 + W'_4}{F} + \frac{RT}{F}\log_e\frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad (9)$$

and $E_s + E_L = E$ the total P.D. between the interior of the metal and the interior of the solution.

Now $W'_1 - W'_2$, the heat evolved in the adsorption of M_I may be expressed as the difference of two work terms, W_1 the work done by the attractive forces of the metal and W_2 the work done against the attractive forces of the solution, in the passage of one gram ion from the solution into the adsorbed layer. Similarly, $W'_3 - W'_4$ may be expressed as the difference of two analogous quantities W_3 and W_4.

The terms W_2 and W_4 depend solely on the solution and are independent of the nature of the electrode, and the difference $W_2 - W_4$ is equal to the difference between the energies of hydration of the ions M_I and M_{II}, that is

$$W_2 - W_4 = H_{M_{II}} - H_{M_I}.$$

Further, the experimental fact that among the noble metals at any rate, the potentials are independent of the nature of the metal indicates that the difference between W_1 and W_3, the two factors depending on the metal, is negligible. This implies either that the two ions are adsorbed to practically the equal extents at all these electrodes or that the adsorptive forces are negligible in comparison with the other terms.

Our final expression for the oxidation potential is then :—

$$E = \frac{\phi_2 - \phi_1}{F} + \frac{RT}{F}\log_e\frac{k_1}{k_2} - \frac{H_{M_I} - H_{M_{II}}}{F} + \frac{RT}{F}\log_e\frac{c_1}{c_2} \quad . \quad (10)$$

Comparing this with the well-known thermodynamic equations of Peters,

$$E = E_o + \frac{RT}{nF}\log_e\frac{c_1}{c_2},$$

we see that on this theory, the normal potential is given by the terms

$$E_o = \frac{\phi_2 - \phi_1}{F} + \frac{RT}{F}\log_e\frac{k_1}{k_2} - \frac{H_{M_I} - H_{M_{II}}}{F} \quad . \quad . \quad (11)$$

Now since $\phi_2 = \phi_1$, the work done in the transfer of an electron from M_{II} to the metal, is equal to the difference between the work of removing an electron from M_{II} and that of removing an electron from the metal, we may write :—

$$\phi_2 - \phi_1 = (V - \phi_o)F$$

where V is the ionisation potential corresponding to the removal of an electron from M_{II} in solution (strictly in the adsorbed layer) and ϕ_o the thermionic work function of the metal. It is to be noted that V is not necessarily the same as the ionisation potential of M_{II} as vapour. In fact, the relation between the environment of a reducing molecule, such as M_{II}, and the ionisation potential is a matter of considerable interest.

The oxidation potential is thus determined by (1) the ionisation potential corresponding to the loss of an electron by the reduced molecule, (2) the difference in the energies of hydration of the two substances concerned, (3) the thermionic work function of the metal, and (4) the "statistical constants" k_1 and k_2.

In a complete cell in which both electrodes are of the same metal it will be seen that the "thermionic" work terms cancel out.

The quantities (1) and (2) are not even approximately known for any two substances connected by a simple reversible oxidation process of the type considered. A direct comparison between observed and calculated values is therefore not possible at present.

It is evident that the process at gas electrodes is similar to that described, but another factor is involved, the dissociation of the diatomic gas into atoms.

These conceptions also throw some light on another case of some interest, the P.D. of a metal dipping into a solution containing its ions in different stages of oxidation which will now be considered.

The P.D. of a Metal Ionising in More than One Stage.

Consider the case of a metal M in a solution containing the ions M_1 and M_2 carrying n_1 and n_2 unit positive charges respectively. Three distinct electromotive processes can occur at the surface of the metal :—

$$(a)\ M \rightarrow M_I + n_1\epsilon.$$
$$(b)\ M \rightarrow M_{II} + n_2\epsilon.$$
$$(c)\ M_I \rightarrow M_{II} + (n_2 - n_1)\epsilon.$$

(*a*) and (*b*) correspond to the solution of the metal as M_I and M_{II} respectively, (*c*) to the oxidation process between the two ions, the metal functioning as inert electrode. Each of these processes may be supposed to have its own equilibrium potential, that is, the potential which the metal would acquire under the same conditions except if the other two processes were not operative. Equilibrium with respect to all three processes is only possible when the concentrations of the two ions are such that the three equilibrium potentials are the same. For if the concentrations are such that the potential of the process (*c*) is greater than that of process (*a*) the former will proceed from right to left and the latter from left to right, with the result that the reaction

$$n_1M_{II} + (n_2 - n_1)M = n_2M_I$$

will go on until equilibrium is attained, which can only be the case when the potentials of the three processes are equal.

It has been shown thermodynamically[1] that if the potentials corre-

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[1] Luther and Wilson, *Z. Phys. Chem.*, 1900, **34**, p. 488; Luther, *ibid.*, 1901, **36**, p. 385.

sponding to the three processes (*a*), (*b*), and (*c*) in any solution be E_1, E_2, and E_3 respectively, then

$$n_1E_1 + (n_2 - n_1)E_3 - n_2E_2 = 0.$$

Therefore when two of these potentials are equal the third must have the same value.

How are these relations to be interpreted on the kinetic theory of this paper?

A metal which ionizes in two stages will contain in the solid form atoms that have lost electrons corresponding to both states. There will be a definite equilibrium between the two kinds of ions and electrons. The three processes occurring at the surface can only give rise to the same P.D. if the relative proportions of ions in the adsorbed layer are the same as in the interior of the metal. The solution which is in equilibrium with the metal is that which gives an adsorbed layer of ions in this proportion. The adsorbed layer is now identical in composition with the interior and there is no P.D. (E) between the two. That is, the whole P.D. is between the adsorbed layer and the solution and this is now the electrode potential for all three processes concerned.

SUMMARY.

A kinetic theory of reversible oxidation potentials at inert electrodes is developed. A general expression is deduced which is in accordance with the thermodynamic equation and which distinguishes the factors determining the normal potential. The relation between the (Nernst) metal potential and the oxidation potential for a metal in a solution containing its ions in different stages of oxidation, is discussed.

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Chemistry Department,
University College of Swansea.