

Electrode Reactions and Equilibria.

By Dr. ERIC K. RIDEAL.

THE conditions of reversibility at electrodes as well as the cause of the phenomena to be noted at irreversible electrodes were discussed at a meeting of the Faraday Society on November 26.

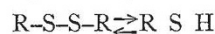
It has long been an accepted fact that the hypothesis of an electrolytic solution pressure as a characteristic property of a metal, originally suggested by Nernst, although convenient for purposes of arithmetical calculation, does not give any insight into the true mechanism of reversible electrodes. The alternative suggestion of a characteristic ionic solubility advanced by van Laar is certainly a more tenable hypothesis, although the enormous values to be attributed to the partition coefficients of the ions between electrode and solution when equilibrium is established somewhat strain the imagination. The hypothesis of Smits, based upon ionic and electronic solubility coefficients, does not appear to be an improvement on van Laar's view, and indeed the accuracy of Faraday's laws appears to offer a very direct proof of its untenability.

A cause for the difference in the electromotive behaviour of the elements is to be found in the nature of the atom itself. The work required to remove an electron from a metal, a value which may be determined from the investigations on thermionic emission by Richardson or from the data on photoelectric emission with the aid of Einstein's quantum relationship, varies from element to element in a manner very similar to the electrode potentials, and indeed it is possible to formulate an expression for the E.M.F. of a cell in reversible equilibrium with the aid of this conception. We are at present uncertain as to the nature of the ionic equilibrium at the surface of the electrode. Attempts have been made to investigate the conditions of a dynamic equilibrium between metal cations and anions being simultaneously discharged at a metal surface resulting in the formation of a definite potential difference and a definite ionic concentration in the solution; but the relationship (if any) of such potential differences to the electro-kinetic potentials due to adsorption and discharge at non-metallic surfaces is by no means clear.

A gap between "reversible" and "irreversible" electrode reactions is to be found in the so-called "inaccessible" electrode reactions. These are generally observed in oxidising or reducing solutions; thus, although a ferrous-ferric ion solution will affect a platinum electrode so as to create a definite reproducible potential difference between metal and solution, yet a solution of glucose or an arsenite-arsenate mixture will not. The inaccessibility of such a potential measurement is due apparently to the relative speeds at which equilibrium at the surface and within the electrode is attained. By suitable artifices, however, inaccessible electrode potentials may be accurately measured.

Certain oxidising and reducing agents, on the other hand, are completely and rapidly electromotively active; such is the quinhydrone electrode of Bijlman, which is now so widely employed for the accurate measurement of the P_H of solutions and the hydrolytic

constants of weak acids and bases. A number of similar organic oxidising and reducing agents are likewise electromotively active; the case of the system



which was investigated by Hopkins, appears to be transitional in that equilibrium potentials can only be obtained under very limited experimental conditions.

Truly irreversible electrode reactions embrace, *inter alia*, the phenomena of passivity and overpotential. Although passivity may be caused by films of multi-molecular thickness, yet in most cases a unimolecular film is sufficient for the purpose, and, in general, oxygen is the cause of passivity. In the case of the ordinary oxygen electrode consisting of platinum immersed in an electrolyte of definite oxygen pressure, there is little doubt that the oxygen penetrates into the interior of the solid metal. It is uncertain as yet whether definite oxides of platinum are formed, but it is more than probable that the oxygen atoms simply interpenetrate the space lattice of the metal and may take up positions of greatest stability when definite stoichiometric ratios obtain. The irreversible nature of this electrode, at least, must be attributed to the slow diffusion rate of the oxygen in the metal, a factor frequently complicated by a transfer resistance at the electrode boundary in those cases where the chemical reaction of oxidation or reduction is non-ionic and relatively slow.

The many and varied theories advanced to explain the phenomenon of hydrogen overpotential have not yet been reduced to a reasonable number, and it is still a matter of dispute whether the make-and-break or continuous-current method is not suitable for the determination of this value. The use of the positive ray oscillograph for the former and minute polarising currents for the latter appear to be the most promising methods for experimental comparison.

Supporters of the view that overpotential is caused by the formation of small bubbles at the electrode, a suggestion first advanced by Helmholtz, are apparently diminishing in numbers, and the consensus of opinion is gradually veering round in favour of the conception either of a hydrogen atom solid solution or adsorbed hydrogen film; there are, however, numerous difficulties associated with any conception hitherto advanced.

The simple capillary electrometer used almost universally in conjunction with zero potential determinations appears likewise to offer an interesting field for research. The existence of a Quincke electrostatic double layer at the surface of the mercury does not account for the parabolic form of curve obtained when the surface tension is plotted as a function of the applied electromotive force; there appears to be little doubt that the adsorption of ions producing an electro-kinetic potential difference at the interface and a concentration gradient in the electrolyte may give rise to a similar form of curve, and it remains a subject of further investigation whether any effect at all is to be attributed to an electrostatic action unaccompanied by a material or ionic transfer.