

This somewhat cumbersome method of expressing the strength of insulin is necessary if comparable results are to be obtained in different tests with animals of varying weight. A further complication has been found, in that some samples of insulin seem to contain a substance which may be described as an anti-insulin. de Jongh (*Biochem. Jour.*, 1924, vol. 18, p. 833) gives an account of its properties: its presence is only revealed when small doses of insulin

are injected, as in rabbits, but in man its influence appears to be small. It is apparently of a protein nature, and as the purification of insulin in the process of manufacture has been made more complete, the samples on the market at present appear to be free from it. In any case it is an illustration of the difficulties encountered by those who have to measure the strength of substances of unknown composition and isolated only in an impure condition.

Heterogeneous Equilibria.

THREE papers by Mr. J. A. V. Butler, in the Transactions of the Faraday Society, February 1924, and two in the *Phil. Mag.*, October and November, deal with problems of equilibrium at the boundaries between solids and liquids, and between two solids. The methods of statistical mechanics are applied in each case, and the first paper, "Conditions at the Boundary Surface of Crystalline Solids and Liquids," well illustrates the way in which other problems are dealt with.

A diagram shows how the attractions of the solid and of the liquid on a molecule of the solute and their resultant are assumed to vary with distance from the surface, with a balance point at which the two opposing forces are equal. A molecule from the surface will escape if, owing to thermal agitation, it has sufficient kinetic energy to carry it past the balance point. Molecules which reach the balance point from the interior of the liquid are attracted to the surface. An equation is deduced, similar to that of Langmuir, for the number of molecules reaching the boundary surface of a gas with kinetic energy greater than a certain quantity λ . This equation, which contains the mean collision frequency, applies to the molecules moving in the liquid towards the surface, but not directly to the molecules in the surface, the only motion of which is a vibration about an equilibrium position. The mean collision frequency is replaced in the equation for these molecules by a vibration frequency ν .

An expression for the solubility is thus obtained which leads to the le Chatelier-van 't Hoff equation for change of solubility with temperature, one of the terms of which is the heat of saturated solution. Assuming that ν is the characteristic vibration frequency of the solid, as determined by *rest strahlen*, and that the work done by the molecules from the surface layer, per gram molecule, in reaching the balance point is equal to the total heat absorbed in solution, unless this is less than the latent heat of fusion, when the latter is used, the author applies his equation to the alkaline chlorides. In this way he obtains results which are of the right order of magnitude.

Similar methods are employed in a discussion of the E.M.F. produced when a metal is dipped into a solution containing its ions. The process is regarded as essentially a solubility phenomenon. In the solution of a salt crystal, made up of positive and negative ions, both kinds are dissolved; but it is assumed that in the case of a metal, only the positive ions pass into solution, while the electrons which go to build up the crystal lattice are left behind. Equilibrium is attained when equal numbers of positive ions are dissolved from and deposited at the surface in unit time. The negative charge due to the free electrons left on the metal retards the solution and assists the deposition, and to this extent the phenomena of salt solution are modified. This is taken into account in the mathematical treatment of this case, with the result that a formula is obtained

for the potential which, in form, resembles that of Nernst. Instead of being based on osmotic pressure, however, it depends on the heat absorbed in the passage of the metal ions into solution, and on quantities defining the statistical conditions. The values calculated from the formula are again of the right order of magnitude.

In a third paper Mr. Butler proposes a kinetic theory of reversible oxidation potentials at inert electrodes dipped into a solution containing two substances related by a simple oxidation reduction process. An expression is obtained for the numbers of each of the two ions, M' and M'' , contained in the solution adsorbed by each square centimetre of the electrode, using a mathematical method similar to that applied above. The reaction between each of these ions and the electrode is considered, one of them tending to gain an electron and the other to lose one, and an expression for the oxidation potential is obtained. This is determined by the ionisation potential corresponding to the loss of an electron by the reduced molecule, the difference in the energies of hydration of the two substances, the thermionic work function of the metal and two statistical constants.

Mr. Butler deals with metal contact potentials in a paper in the *Philosophical Magazine* for October. He obtains an expression for the potential difference at the surface of a single metal in a closed space containing an electron atmosphere, the loss of electrons from the surface of the metal being balanced by the gain of electrons from the atmosphere. He then considers the case of two metals in the electron atmosphere, but not in contact, and finds that though the surface P.D. of each metal depends on the electron atmosphere concentration, the difference for any two metals is characteristic of them. If the metals are brought into contact, the conditions at the surfaces not in contact are unaltered, and if there is to be no continuous flow across the junction, there must be a P.D. at the junction equal to the intrinsic P.D. of the metals. The Peltier heat effect at the junction is explained, and the various equations of the thermionic effect are co-ordinated. On certain assumptions they lead to the conclusion that the Thomson P.D. is the same for the same difference of temperature in all conductors.

Finally, in a paper on the seat of the electromotive force of the galvanic cell (*Phil. Mag.*, Nov.) Mr. Butler co-ordinates the results of his previous papers, and derives a statistical theory of the galvanic cell. The existence of large metal contact P.D.'s is not inconsistent with the correspondence between the E.M.F. of the cell and the energy of the chemical reaction. The metal contact P.D. theory, the chemical theory, the Nernst theory of metal electrode potential differences and the relation between E.M.F. and total energy change expressed by the Gibbs-Helmholtz equation are included in the new theory as different aspects of the whole truth.