DETERMINATION OF ABSOLUTE IONIC ENTROPIES FROM KINETIC DATA

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Starting from the fact that the overvoltage for passage from barrierless discharge to ordinary discharge is such as to equalize the ideal activation energies for these two processes, an equation has been derived which permits the calculation of the reversible heat of an electrode reaction (change in entropy for the reaction, temperature coefficient of the absolute reversible potential difference) from the actual activation energies and the overvoltage corresponding to the intersection of two polylogarithmic lines.

It is a well-known fact that neither the absolute potential difference at the interface between two phases, the chemical potentials of charged particles, or the temperature derivatives of such potentials can be obtained from the experimentally determined work or heat of reaction. This situation traces back to the observation that charged particle transfer through a phase interface is always accompanied by the delivery of chemical work (change in the chemical potential) and electrical work (passage from one potential to another). Thus a determination of the work delivered in a reaction gives only the sum of these two components, but not the value of either separately.

On the other hand, the impossibility of determining these quantities in this manner does not indicate that they are devoid of physical meaning and cannot be measured by some other method.

It will be shown in the present communication that kinetic data can be used to determine the reversible heat, q, of an electrode reaction, i.e., the change in entropy, ΔS, or, in other words, the temperature coefficient of the absolute potential difference. From a knowledge of the entropy change accompanying the reaction, one can find with essentially the same accuracy as ΔS the entropy of the individual ion, the entropy of the electron, the other charged particle participating in the reaction, being essentially equal to zero.*

As Temkin has shown [2], the true activation energy determined from the temperature dependence of the reaction rate at fixed overvoltage, η, differs from the ideal activation energy, W, corresponding to the potential difference at the electrode–solution interface† by an amount α q, where α is the transfer coefficient,

$$A = W - \alpha q. \tag{1}$$

Here q is the heat absorbed by the system in passing reversibly from initial to final states, for example, in the reaction:

$$H_3O^+_{sol} + e_{met} \rightleftharpoons {}^1\!/_2 H_2 + H_2O. \tag{2}$$

The difference between A and W arises from the fact that a fixed overvoltage corresponds to different values of the potential difference at different temperatures, with the result than an alteration of the temperature at fixed η changed the activation energy by an amount proportional to the temperature coefficient φ.

We have shown earlier that it is possible, in principle, to have electrode reactions for which α is equal to either 0 or 1 (activationless and barrierless reactions) [3, 4], and have given instances of actual barrierless processess [4-8]. In reactions of this last type, the activation energy is equal to the heat of reaction, which is to say, that the reaction path avoids the barrier on the energy profile. Passage from ordinary discharge to barrierless discharge occurs at rather low overvoltages. The activation energy for discharge increases as the overvoltage is diminished, but the activation energy for the reverse reaction of ionization falls at the same time, which is to say, that the barrier moves toward the final state energy level. This eventually reduces the barrier to zero, and the

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*Estimates give the entropy of the electron gas in the metal as about 0.05 eV (e.g., [1]), which is less than the possible experimental error.

†It is here a matter of a potential difference in the macroscopic sense of the word, i.e., a mean value obtained by averaging over the interfacial surface.

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reaction passes from ordinary discharge to barrierless discharge. For ordinary discharge, the activation energy falls as the overvoltage is increased according to the expression $\alpha\eta F$, with $\alpha = 1/2$; for barrierless discharge, the fall-off relation is the same but with $\alpha = 1$.

$$W_\eta^{(0)} = W_e^{(0)} - \alpha\eta F; \quad A_\eta^{(0)} = A_e^{(0)} - \alpha\eta F \tag{3}$$

$$W_\eta^{(b)} = W_e^{(b)} - \eta F: \quad A_\eta^{(b)} = A_e^{(b)} - \eta F. \tag{4}$$

Here the superscripts (0) and (b) designate ordinary and barrierless discharge, respectively, while the subscripts η and e indicate that the quantity in question refers either to overvoltage η or to the equilibrium potential.

The activation energy has a fixed value at passage from ordinary to barrierless discharge, regardless of whether the point of passage is considered to lie on line (3) or line (4). In the physical sense, it is clear that the ideal activation energies must be equal at this point, these being the parameters which determine the true form of the reaction energy profile. On the other hand, the true activation energies are not directly related to the form of the potential barrier. Thus A can be negative if the value of q is positive and large in magnitude, and this despite the existence of an energy barrier of considerable height. Thus at passage from barrierless discharge to ordinary discharge (the corresponding overvoltage will be designated by η') one has

$$W_{\eta'}^{(0)} = W_{\eta'}^{(b)}. \tag{5}$$

Ideal activation energies cannot be obtained by direct measurement, but true activation energies related to W through Eq. (1) can be determined. It should be emphasized that its very derivation shows Eq. (1) to be valid for any value of α, which is to say, that this equation can be applied to both ordinary and barrierless discharge. By using (1) to express $W_{\eta'}^{(0)}$ and $W_{\eta'}^{(b)}$ in terms of the corresponding true activation energies, one obtains

$$A_{\eta'}^{(0)} + aq = A_{\eta'}^{(b)} + q,$$

$$q = \frac{1}{1-\alpha}\left(A_{\eta'}^{(0)} - A_{\eta'}^{(b)}\right). \tag{6}$$

Thus one can find the reversible heat of the electrode reaction from the experimentally determined values of $A_{\eta'}^{(0)}$ and $A_{\eta'}^{(b)}$. Strictly speaking, one cannot obtain two values of the activation energy at one fixed overvoltage, but this is not required here, it being sufficient to determine the constants of Eqs. (3) and (4) for any values of the overvoltage and then extrapolate to η'. The value of η' is fixed by the point of intersection of the two linear segments in the Tafel plot, the one corresponding to $\alpha = 1/2$ and the other to $\alpha = 1$. Substitution of (3) and (4) into (6) gives

$$q = \frac{1}{1-\alpha}\left(A_e^{(0)} - A_e^{(b)}\right) + \eta' F. \tag{7}$$

Actually, departures from linearity in the η vs log i plot are observed as one approaches the point of transfer from one reaction type to the other, the reason being that Eqs. (3) and (4) are then no longer completely exact. These departures do not, however, generally range over more than 50 mV [5, 9], and since the interchange point undoubtedly lies in the middle of this interval, the error in fixing its location is probably no more than 10 mV.

One further remark should be made before passing to the treatment of the experimental data. The activation energies determined by the usual electrochemical measurements are apparent parameters, referring as they do to fixed reactant concentration in the body of the solution rather than on the electrode surface. They differ from the quantities appearing in the above equations by the adsorption energy of the particle undergoing discharge. This would, however, introduce a uniform correction for both ordinary and barrierless discharge, and Eq. (7) is therefore valid for the apparent activation energies determined by experimentation.

The adsorption energy for particles which do not have pronounced specific adsorbability is equal to $z\psi_1 F$, z being the valence and ψ_1 the potential relative to the solution in the plane of the centers of the discharging ions. Thus it might seem that one could not predict the effect of ψ_1 on the results of calculations based on Eq. (7). Actually, the corrections to the activation energies required for passage from apparent to true parameters will compensate, as pointed out above. It should, however, be remembered that the ψ_1 potential can vary markedly with the temperature, and thus make an appreciable contribution to the measured value of the activation energy for ordinary discharge.* It is a matter of considerable difficulty to find the necessary correction factor here,† and calculation based on Eq. (7) will be limited to solutions for which $\psi_1 \simeq 0$.

For barrierless discharge of hydrogen ions on a mercury cathode, we have found an activation energy of $A_e^{(b)} = 22.9 \pm 0.7$ kcal [11]. Here the overvoltage is independent of both the solution composition and the double-layer structure [3-5]. Iofa and Mikulin [12] have studied the temperature dependence of the rate of ordinary hydrogen discharge on mercury in a solution containing 0.25 g-eq/liter H_2SO_4 + 1.0 g-eq/liter Na_2SO_4. This solution was sufficiently concentrated so that one could consider ψ_1 equal to zero and neglect its temperature variation in a first approximation. Temkin [13] used the data of Iofa and Mikulin and the value of the heat of dissociation of HSO_4^- to calculate the activation energy for ordinary discharge, obtaining the value $A_e^{(0)} = 21.7$ kcal. Extrapolation of the polarization curves of [12] to intersection with the barrierless branch gave $\eta' = 177$ mV. These data substituted into Eq. (7) gave q = + 1.67 kcal, which is to say, $\Delta S = +5.6$ eu. This indicates that the absolute potential difference for the reversible hydrogen electrode becomes more positive as the temperature increases in this solution, $d\varphi_e/dT = +0.24$ mV/deg.

Having determined ΔS for Reaction (2), one can now obtain the absolute entropy of the hydrogen ion. Knowing the entropy of gaseous hydrogen and liquid water [14], the value of the partial molar entropy of the H_3O^+ ion in a solution of the above composition can be calculated, the value obtained being 26.8 eu. In view of the large excess of SO_4^{2-} ions, the dissociation equilibrium,

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-} \tag{8}$$

is markedly displaced to the left in this solution. From the known value of the dissociation constant for HSO_4^- (10^{-2} [15]), one can estimate the hydrogen ion concentration ($^2/_3 \cdot 10^{-2}$) and thus find the standard value $S^0_{H_3O^+} = 26.8 + R \ln {}^2/_3 \cdot 10^{-2} = 16.8$ eu.‡

Unfortunately, the accuracy of these values of ΔS, $S_{H_3O^+}$ and $S^0_{H_3O^+}$ cannot be more than several eu, since the activation energies were not determined with high precision (this is especially true of $A_e^{(0)}$ where proof must be given justifying the neglect of the temperature variation of the ψ_1 potential). With more precise data it would still be necessary to introduce a correction for solution ideality in passing from $S_{H_3O^+}$ to $S^0_{H_3O^+}$. These facts suggest the necessity of further experimental work.

A very rigorous test here would be the determination of the entropy of some other ion in the same manner, then the sum or difference of such absolute entropies could be compared with the corresponding sum or difference calculated with high accuracy from thermodynamic data. Work of this kind for the anodic evolution of chlorine on graphite saturated with a dilute solution of lead chloride is reported in [6] (data are also given there for the porous graphite electrode, but these are of considerably lower accuracy). The reported values are: $A_e^{(0)} = 7.9$ kcal, $A_e^{(b)} = 7.2$ kcal, and $\eta' = 80$ mV, from which it follows that: q = 3.2 kcal; $\Delta S = 10.8$ eu; $d\varphi_0/dT = 0.47$ mV/deg; $S_{Cl^-} = 15.8$ eu; and $S^0_{Cl^-} \simeq 18$ eu. It should be emphasized that these values undoubtedly contain errors tracing back to the temperature variation of the ψ_1 potential; these have not yet been estimated.

The sum is $S^0_{H_3O^+} + S_{Cl^-} \simeq 35$ eu, while the exact value of the same is 30.3 eu [14].** The concordance here must be considered satisfactory in view of the above remarks, especially those concerning S_{Cl^-}.

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*A correction of this type is not usually needed with barrierless discharge since the ψ_1 potential is then independent of the overvoltage [3-5].

†The usual calculation of the ψ_1 potential from equations borrowed from double-layer theory involves various assumptions which can markedly affect the value obtained for the temperature derivative. It is especially significant that the potential of interest here is to be measured over the region where the discharging ions are in direct contact with the electrode, i.e., in the part of the system where the noncoulombic effect neglected in the theory can become quite pronounced [10]. Evaluation of the ψ_1 potential from kinetic data requires measurements on solutions with $\psi_1 = 0$ and thus gives nothing new.

‡We have not introduced a correction for deviation of the solution from ideality, a matter of difficulty in principle, since it involves the problem of determining activity coefficients for the individual ions. In so far as one can judge from data on the activity coefficients of electrolytes, such correction would scarcely exceed some tenths of an eu, and would thus fall outside the limits of experimental error.

**The literature generally cites S^0_{HCl}, i.e., the value of $S^0_{H^+} + S^0_{Cl^-}$. The value of $S^0_{H^+}$ obtained in this manner differs from $S^0_{H_3O^+}$ by $S^0_{H_2O} = 16.76$ eu.

The literature frequently gives "absolute" ion entropies based on $S^0_{H_6O+} = 11.3$ eu ($S^0_{H^+} = -5.5$ eu, see, for example, [16, 17]). Highly arbitrary assumptions are, however, involved in the determination of these quantities. One such determination of $S^0_{H_3O^+}$ starts by assuming that the potential difference at the null-charge point is independent of the temperature. This assumption is clearly invalid, if for no other reason than that temperature affects the orientation of solvent molecules at the electrode–solution interface.* Still another method leading to the same results is based on thermoelectric forces. Strict analysis shows, however, that data of this kind lead only to transfer entropies ("moving ion entropies") and not to absolute ion entropies in the sense that the term is used in the analysis of the thermodynamic properties of solutions [17, 18]. Thus this method gives only an estimate, the limits of the validity of which are, in principle, unknown. It should be noted that these results are close to our own in order of magnitude.

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*In practice, this assumption has been applied to the data obtained with a one molar chloride solution; here the position of the null-charge point must be vitally affected by the specific anion adsorption, all other conditions being held constant.