METHODS OF DERIVING ELECTROCHEMICAL KINETIC EQUATIONS

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It was demonstrated by Frumkin in 1932 that the basic equation for the kinetics of electrode reactions – Tafel's equation – can be derived on the basis of a general-kinetic regularity: Brönsted's relationship which links the activation energy and the heat effect of the given stage of the reaction [1]. Brönsted's relationship is usually validated by the potential curve method in which variation in the distance between their minima should lead to variation in the activation energy [2].

Over the last few years, apart from Brönsted's relationship, there has been frequent use of another method of deriving electrochemical kinetic equations, based on the assumption of a fractional charge in the transition state (see, for example, [3]). Here a specific assumption only relating to the electrode reaction is introduced, i.e., it is taken that the dependence of the energy of the activated state on the potential is governed solely by the presence of a purely electrostatic term in this energy and that the term is associated with the charge of the activated complex.

It is clear, however, that no matter how the charge is distributed in the activated state, the effect of the relative arrangement of the potential curve minima, expressed by Brönsted's relationship on the activation energy should be retained to some degree or other. Brönsted's relationship (often called Polyani's rule as well) is general in nature; it is well observed in the case of the overwhelming majority of reactions both in gas as well as liquid phases [4], and on that account there are no grounds to doubt it's applicability, albeit qualitatively, to electrochemical reactions. Hence, to explain the dependence of the activation energy on the electrode potential solely by the presence of a charge in the transition state is out of the question, and we must take into account at the same time Brönsted's relationship in some other form.*

Furthermore, to obtain correct results when solving kinetic equations by the second method, it is necessary to assume that with neutralization of a fraction α of the charge, the energy of the activated state includes a term for a fraction α of the energy of the end state of the elementary act; for example, of adsorbed hydrogen. However, how much physical basis this assumption has remains unclear.

Both methods of derivation give us the same form of kinetic equation, but the equations are different in the physical sense of the quantity ψ_1 contained in them [3]. In the first case ψ_1 relates to the point of location of the center of the ion charge directly before its discharge, and in the second case to the point at which the (fractional) charge of the activated state is concentrated. The fact that when found from data for the hydrogen overvoltage in the presence of the adsorbed iodine ψ_1 is more negative than the ψ^0-potential in the plane of the cations is considered in [3] as an argument in favor of relating ψ_1 to the activated state.

There may, however, be doubt that the observed difference between ψ_1 and ψ^0 is high enough to allow the unequivocal choice of the second method of viewing the elementary act of discharge. Indeed, during generation of hydrogen the activated state may lie very close to the electrode surface – at a distance only slightly greater than the covalent radius of hydrogen, which is 0.3 A. Thus, assumption with regard to the fractional charge of the activated state requires, it would seem, that it should come closer to the electrode by a distance less than the distance between the charge centers of the adsorbed anions. Hence, from the model given we ought to expect ψ_1 to be not only more negative than ψ^0 but also considerably more negative than ψ^i. In actual fact, however, ψ_1 is somewhere between ψ^0 and ψ^i.

How can we explain the discrepancy between ψ_1 and ψ^0 if we remain within the bounds of Brönsted's relationship? It seems most likely that the discrepancy is due to the simplified model of the structure of the double layer used to calculate ψ^0.

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* These considerations also relate to the other version of the theory, which is restricted by a purely electrostatic effect – when the activated state charge is taken as equal to the charge of the initial state, but it is assumed that it is acted on solely by the portion α of the potential jump in the dense part of the double layer.

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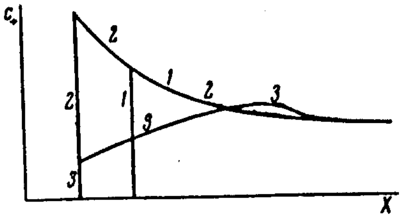

Indeed, the model assumes that the cations do not get nearer the electrode than the plane corresponding to ψ^0, and that their spatial distribution in the solution is conditioned by only coulomb forces and thermal motion (this is shown diagrammatically by curve 1 in the figure). Calculation from adsorption data based on this model gives us an ion-free layer thickness of the order of 3-4 A [5] (in the negative-charge region).

If this quantity is regarded as the true distance of maximum approach by the ions to the electrode, we will have to take it that the ions are discharged at great distances from the electrode without the possibility of forming an adsorbed product (for example, H) or becoming embedded in the electrode (for example during formation of amalgams). At the same time it is clear that in a number of cases the discharge generally only becomes possible by virtue of the gain in energy during adsorption or dissolution.

The model described by curve 1 is unrealistic for the following reason. The sharp jump in concentration ought to have resulted in the occurrence of very large (infinitely large at the limit) concentration gradient, i.e., a very large diffusion force that makes the ions move toward the electrode. To prevent this advancement we have to have a very strong repellent force. In all probability the only force of this kind would be the force arising when the electron shells of the ion and metal overlap, but it can only be appreciable at a distance from the electrode of the order of the ion crystal radius, but not at distances greater than 3 A. If, alongside the coulomb force, this force was the only one active, the concentration distribution would take the form of curve 2. But then the calculation of the type contained in [5] would give us an empty layer thickness of the order of 1.5 A.

In actual fact we have to keep in mind one more effect – variation in the structure of the solvent in layers directly adjoining the electrode, in particular dielectric saturation. This fact weakens interaction between the ion and the solvent, i.e., it creates a certain repellent force which attenuates at a certain distance from the electrode. This force reduces the ion concentration near the electrode as compared with the concentration for a homogeneous dielectric (curve 2), as shown schematically in curve 3.* Comparison of curves 1 and 3 shows that curve 1 is a kind of averaging of curve 3, and that the thickness of the ion-free layer calculated by means of this layer is only an effective quantity. Hence the potential in the plane of location of the discharging ions, i.e., ψ_1, proves more negative than the potential in an effective plane of maximum closeness of the cations, since the former plane is nearer to the electrode than the former plane. This difference seems to be small in a solution not containing surface-active anions, but becomes substantial when they are present.

This, in our opinion, provides a reasonable explanation for the difference between ψ_1 and ψ^0 observed experimentally. It cannot be regarded, however, as a weighty argument in favor of the hypothesis of a fractional activated state charge.

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* The slight rise in curve 3 above 1 at a little way from the electrode is caused by the action of image forces which are not manifested to the same degree at shorter distances because of the strong effect of the reduced dielectric constant. Qualitatively, this path by the curve results from [6] in which is considered a model of the diffusion double layer taking into account the low dielectric constant of the "layer" close to the electrode.