SOME GENERAL QUESTIONS OF ELECTROCHEMICAL KINETICS AND THE THEORY OF IONIC REACTIONS

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In the evolution of modern electrochemistry we can distinguish three stages, each of which has exerted and still continues to exert an influence on chemistry as a whole. I shall refer only briefly to the first two, since their significance is generally known. The experimental investigation of the laws underlying the conductivity of salts and acids led to the inference of the existence of free ions in solutions, and this view was then developed in a brilliant manner as a result of x-ray investigation of the structure of salt crystals. Establishment of the relation between the free energy of formation of chemical compounds and the emf of reversible cells resulted in the development of a very effective method of investigating the state of solutions with the aid of measurements of equilibrium potentials, and the application of this method is constantly expanding.

The third stage in the history of electrochemistry, which began about a quarter of a century ago, is characterized by the development of electrochemical kinetics. As a prerequisite to this development it was necessary to make a more profound study of the structure of the metal-electrolyte interface by the use of several new physical methods of investigation. In this paper I should like to show with the aid of some examples with which I have been closely concerned that the development of this side of electrochemistry again enables us to establish some close relations with adjacent fields of physical chemistry. The results obtained up to now are still modest in significance and cannot be compared with those referred to above, but I consider that they are of definite scientific interest.

1. Adsorption of Gases on the Surface of Solid Metals

Calculation of the rate of a heterogeneous chemical process as a function of the pressures of the gases taking part in the reaction requires a knowledge of their adsorption isotherms with respect to the catalyst surface. In the early stages of the evolution of the theory of heterogeneous catalysis, the Langmuir isotherm was generally used for this purpose. The determination of charging curves, i.e., the measurement of the relation between the potential of an electrode and the amount of electricity passed under conditions such that this electricity is used entirely for the removal of adsorbed particles from, or the deposition of particles on, the surface, is equivalent to the determination of the relation between the amount adsorbed and pressure. In this determination the current density must be so small that the potential of the electrode can be regarded as having its equilibrium value. Such measurements, first made by Shlygin, Ershler, and the author [1-3], led to the unexpected conclusion that the amount of hydrogen absorbed on platinum is, to a first approximation, a linear function of the logarithm of the pressure over a wide range of pressures (e.g., variation in pressure by a factor of about 10^{10}). These results have recently been confirmed by the measurements of Knorr and co-workers [4]. The theory of the logarithmic isotherm has been given by Temkin [5], who showed that the observed relation is to be expected when the adsorption energy falls linearly as the surface becomes covered with adsorbed particles. The cause of this fall could be both the repulsive forces between the adsorbed particles and the heterogeneity of the surface.* Later,

*If we consider the surface to be homogeneous, then the logarithmic isotherm can be explained if we assume that electrons binding adsorbed atoms to the surface are not localized, but are in orbitals that embrace the whole surface. In this case, every extra electron must take up a higher energy level, so that the adsorption energy will fall as the surface coverage increases [6].

by the use of alternating currents of various frequencies, we succeeded in measuring not only the relation of the equilibrium amount of adsorbed hydrogen to the potential, but also the rate at which this equilibrium is disturbed as the potential is displaced owing to the passage of electricity; over a certain range of potentials this rate was found to be approximately independent of potential [7]. In order to explain this it is necessary to assume that, like adsorption energy, the activation energy for the ionization of adsorbed hydrogen at constant potential falls linearly with increase in the coverage of the surface with adsorbed hydrogen and to an extent which is a fractional part of the change in adsorption energy. Electrochemical investigation, therefore, has led to the conclusion that adsorption layers exist in which adsorption energy and activation energy bear a definite relation to surface coverage. This concept was widely applied by Temkin and co-workers in the interpretation of the phenomena of heterogeneous catalysis. On the assumption that the adsorption layers of nitrogen on iron have such properties and that the stage determining the rate of the process as a whole is the stage of chemisorption of N_2 molecules, Temkin [8] succeeded in deriving the following equation for the rate of ammonia synthesis:

$$w = k_1 p_{N_2} \left(\frac{p_{H_2}^3}{p_{NH_3}^2} \right)^{\alpha} - k_2 \left(\frac{p_{NH_3}^2}{p_{H_2}^3} \right)^{1-\alpha},$$

in which $0 < \alpha < 1$. Of all equations yet proposed, this gives the most satisfactory agreement with the experimental data on this important reaction. The same approach was used by Temkin and co-workers in the determination of the mechanism of transformations of CO and of other heterogeneous processes [9].

Temkin and co-workers later developed a method of studying surface layers which is to a certain extent analogous to the method of charging curves [10]. This method is based on the study of equilibria established as a result of reversible chemical interaction between adsorbed particles and components of the gas phase (for such equilibria the term "adsorptional-chemical equilibrium" has been proposed). Thus, equilibrium between nitrogen adsorbed on an iron catalyst for ammonia synthesis and gaseous hydrogen and ammonia were observed directly:

$$N(ads) + \tfrac{3}{2} H_2(gas) \rightleftharpoons NH_3(gas).$$

As the coverage of the surface with nitrogen increases, the ratio p_{NH_3}/p_{H_2} increases. By combining these results with known values of equilibrium constants for

$$\tfrac{1}{2} N_2(gas) + \tfrac{3}{2} H_2(gas) \rightleftharpoons NH_3(gas),$$

we obtain the adsorption isotherm for nitrogen. In a similar way, by use of the equilibrium

$$O(ads) + H_2(gas) \rightleftharpoons H_2O(gas)$$

the properties of the surface oxygen of oxides (Fe_3O_4, etc.) were studied.

Like the determination of charging curves, this method can cover a wide range of variation of equilibrium pressures of adsorbed gas, including values inaccessible to direct measurement. The experimental data, both for nitrogen on iron and for surface oxides correspond to the logarithmic adsorption isotherm.

2. Electrocapillary Phenomena and Anomalous Properties of Thin Layers of Liquids

Until recently, two main cases of transition from an adsorbed layer to a new phase were distinguished. In the condensation of vapor on any surface it was assumed that, in the case of complete wetting, as the pressure of the vapor approaches the saturation value, gradual and unlimited increase in the thickness of the adsorbed layer occurs, i.e., the transition from the adsorbed layer to the new phase is continuous. On the other hand, with incomplete wetting the adsorbed layer that is in equilibrium with saturated vapor is substantially different from the bulk phase and is unimolecular or is only a few molecules thick. If a hydrogen or nitrogen bubble is placed at the interface between mercury and electrolyte solution, it has a contact angle which, in the case of an uncharged mercury surface, is about 100° (poor wettability of mercury). From the value of this angle, which depends on the potential of the electrode, we may calculate the interfacial tension at the mercury-bubble interface, on which there is an adsorption layer that is in equilibrium with saturated water vapor [11]. It was found that this inter-

facial tension is also dependent on the potential and follows a certain electrocapillary curve. It follows that this layer contains not only solvent molecules, but also electrolyte ions; it must therefore have a considerable thickness: in a layer that is only 1-2 molecules thick the solvation energy of the ions would be so much reduced that their concentration in equilibrium with the solution would become infinitesimally low. In equilibrium with saturated vapor, therefore, relatively thick layers will be found: they may be dozens of molecules in thickness and yet cannot show a continuous transition into the bulk phase.

These measurements were later repeated with water-alcohol mixtures [12]. Addition of alcohol, which wets the mercury better than water does, results in a further increase in the thickness of the equilibrium layer. In 90% alcohol, the layers obtained give electrocapillary curves that scarcely differ from the usual electrocapillary curve, although the surface tension of mercury in presence of these layers differs by quite an appreciable amount (of the order of one-tenth of an absolute unit) from the tension in presence of liquid in the form of a bulk phase.* I refer to these results because Deryagin and co-workers recently succeeded in showing by optical measurements that as we approach the saturation point the thickness of the adsorbed layer of a polar liquid, e.g., water or an alcohol, on a smooth glass surface does in fact attain a value equivalent to dozens of molecules (up to 100 A), and there is nevertheless a tendency to move to a final limit, i.e., not to grow continuously with transition into the bulk phase; the appearance of the bulk phase is a sudden one [13]. Such anomalies of thin, but not molecularly thin, layers, which were discovered and investigated by Deryagin and co-workers by various other and independent original methods, undoubtedly form a remarkable peculiarity of the liquid state, and we cannot yet give a complete explanation for it.

These examples can be greatly multiplied. Here I will mention only Rebinder's discovery of the electrocapillary effect of change of hardness with polarization and the preparation by Balashova and Bakh of positively charged platinum sols, which became possible when the relation of the sign of the surface charge of platinum to potential was determined by adsorptional-electrochemical methods.

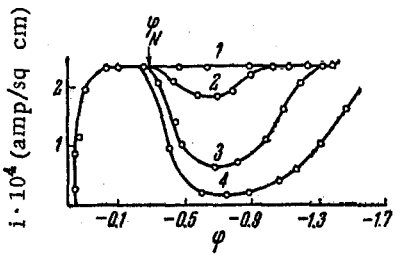

Fig. 1. Relation of current density to potential in 10^{-3} $K_2S_2O_8$ in presence of Na_2SO_4 determined with the aid of rotating amalgamated disc electrode. Potentials referred to the normal hydrogen electrode. φ_N is zero-charge potential. Na_2SO_4 concentration: 1) 1 N; 2) 0.1 N; 3) 0.008 N; 4) 0.

I wish to discuss in greater detail the relationships that I regard as particularly important and the most promising for study at the present time, namely the relationships between electrode processes and ionic reactions in solutions. I shall try to show that comparison of electrochemical data with the results of the investigation of ionic reactions can greatly help in the analysis of reaction mechanisms. In this comparison, however, it must be remembered that the rate of an electrode process is determined by the concentration of particles near the electrode surface, and this may be substantially different from the bulk concentration. This fact can be best illustrated by the behavior of various anions, e.g., persulfate $S_2O_8^{2-}$, in electroreduction at the surface of a mercury or other electrode [14]. The persulfate anion is readily reduced at mercury even with weak cathodic polarization (Figure 1). However, if we pass to more negative potentials at which the mercury surface acquires a negative charge, the rate of reduction falls off sharply and may approach zero at a sufficiently low concentration of supporting electrolyte. This fall in reaction rate is due to lowering of the concentration of the anion in the surface layer resulting from its electrostatic repulsion by the negatively charged surface. The repulsion is eliminated, or at least reduced, by raising the concentration of supporting electrolyte and so screening the electric field of the surface charges and reducing the range of the Coulomb forces. The difference in concentration between the surface layer and the bulk of the solution can be allowed for quantitatively in the case of small ions by introducing the concept of a localized potential (ψ_1-potential) at the center of charge of the reacting particle [15]. In the case of large organic ions and, particularly, neutral molecules, great importance is acquired by effects that depend on the square of the field and are well known from the theory of salting-out of solutes by strong electrolytes [16].

While keeping these differences between bulk and effective concentrations of particles in electrode process

*More accurately, comparison is between the sums of tensions at the mercury-solution and solution-gas boundaries for the cases in which the solution is in the form of a polymolecular layer and in the form of the bulk phase.

in mind, we will examine the catalytic effect of ions on electrode processes. As Iofa, Kabanov, and co-workers have shown [17], hydrogen overvoltage at a mercury cathode falls sharply in presence of adsorbed anions such as bromide and iodide; that is to say, these anions accelerate the electroreduction of a hydrogen ion. This phenomenon, which is the main cause of the relatively low overvoltage in concentrated hydrohalic acids and therefore of their enhanced corrosive action on metals (as shown by, e.g., Heyrovsky [18], Randles [19], and Piontelli [20]), is not confined to the case of the hydrogen ion, but is characteristic for many cases of the electroreduction of cations. Thus, the presence of an adsorbed layer of pentyl alcohol greatly retards the electroreduction of Cd^{2+} and Cu^{2+} ions. However, according to Martirosyan and Kryukova, chloride and bromide ions accelerate this process to such an extent that the inhibiting effect of pentyl alcohol ceases to be noticeable [21].

Antropov [22] made the suggestion, which probably goes too far, that the main cause of the high values of exchange currents for certain metals is their ability to adsorb anions. The catalytic effect of anions disappears or becomes weaker at highly negative potentials, at which the anions cease to be adsorbed. The most elementary explanation of the action of anions that is referred to in Iofa and Kabanov's paper is that the adsorption of an anion causes displacement of the potential in the double layer (ψ-potential) in the negative direction, so that the surface concentration of reacting cations and the rate of reduction are increased. It is possible, however, that anions can participate directly in the electrode process, acting as a carrier of an electron from the electrode to the cation being reduced, a suggestion first made by Heyrovsky.

However we may represent the participation of adsorbed anions in the elementary act, there can be no doubt that they form bridges between the electrode surface and the cation being reduced. Later, the concept of the formation of anion bridges was arrived at by foreign investigators who studied the mechanism of oxidation-reduction processes and isotope exchange in the bulk of a solution with the aid of labeled atoms [23]. Anions, e.g., F^-, Cl^- and OH^-, greatly accelerate processes occurring between cations in solution. The actual mechanism of the action of anions can be represented in various ways. In the case of the oxidation of Cr^{2+} ions with $Co(NH_3)_5Cl^{2+}$, it was shown by the use of labeled chlorine that reaction proceeds with intermediate formation of the activated complex $[Cr-Cl-Co(NH_3)_5]^{2+}$ with transfer of a chlorine atom from cobalt to chromium. It may be supposed that in other cases the role of the anion is to facilitate mutual approach of cations and reaction proceeds by a direct electron transition.

The significance of the formation of anion bridges in reactions with participation of cations is beyond doubt. The question arises of the possibility of the formation of analogous cation bridges in reactions in which anions take part. By the use of labeled atoms it may be shown that a rapid exchange of charges occurs between highly charged anions such as $FeCy_6^{4-}$ and $FeCy_6^{3-}$ or $MoCy_8^{4-}$ and $MoCy_8^{3-}$ [24]. This occurs in spite of the high charges of these anions which, being of the same sign, must create a considerable resistance to the mutual approach of the ions. In explanation of the mechanism of this reaction it was suggested that it proceeds by a tunnel transition of electrons from one reacting particle to another without any direct mutual approach [25]. Some sort of answer to our question may be given by an investigation of the mechanism of the electroreduction of anions at the surface of a negatively charged electrode, which is in many ways analogous to the reaction just mentioned. The more gradual fading off of the electric field at the flat surface of an electrode, as compared with the field around an ion, has the result that the electrostatic repulsive effects must be much more strongly marked in the case of electrode processes. Correspondingly, as I have already mentioned, in the investigation of the electroreduction of anions,considerable retardation of the process is observed when we pass to potentials corresponding to a negatively charged surface. However, at still more negative potentials, in spite of further increase in the negative charge of the surface and therefore in the repulsion of anions, the reaction again acquires a considerable speed (Figure 1). Several arguments can be advanced in support of the view that under these conditions reaction proceeds by tunnel transitions of electrons over distances comparable to the thickness of the double electrical layer. At one time we regarded this suggestion as sound [26], and it is possible that there is some truth in the view. As we shall see below, however, there can be no doubt that the formation of cation bridges plays an important part in the electroreduction of anions. It has already been stated above that the rate of reduction of the persulfate anion increases with increase in the concentration of the supporting electrolyte, i.e., with increase in the concentration of cations in the solution. This effect is all the more notable, the higher the charge of the cation, but I do not wish to discuss this further here because the conclusions that I wish to examine are based on a study of the effect of other factors, namely adsorbability and cation radii.

The data given below are borrowed from the results of Nikolaeva-Fedorovich and co-workers obtained in the Electrochemistry Department of Moscow University. The reduction of persulfate is greatly accelerated if a

surface-active cation, such as the tetrabutylammonium ion, is introduced into the solution [27]. As will be seen from Figure 2, at a concentration of only 10^{-5} N, tetrabutylammonium completely eliminates the anomaly from the polarization curve. Other adsorbable cations behave similarly. However, at sufficiently high negative potentials the effect of tetrabutylammonium disappears and the repulsive effect of the surface on the anion operates in the same way as in the absence of this cation. The key to the understanding of this effect is given by measurements of the capacity of the electrode made with alternating current (lower curve on Figure 2). At the potential at which the action of the organic cation ceases there is a sharp maximum on the capacity curve; this is a desorption peak, indicating that this is the potential marking the limit of the range in which adsorption of the tetrabutylammonium ion occurs. Hence, the tetrabutylammonium ion acts only when it is adsorbed on the electrode surface. The view that the effect of any component of a system on a heterogeneous process e.g., heterogeneous catalysis, can appear only when it is adsorbed at a suitable interface lies at the basis of all the theory of these phenomena, but it is doubtful whether any other methods could give such an unequivocal proof of its correctness. Similar results were obtained for the reduction of the ferricyanide [28] and $HgCy_4^{2-}$ [29] ions.

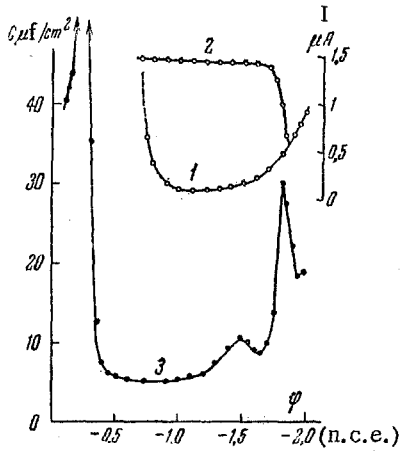

Fig. 2. Relation of current to potential in the electroreduction of the $S_2O_8^{2-}$ anion at a dropping mercury electrode: 1) 10^{-3} N $K_2S_2O_8$; 2) 10^{-3} N $K_2S_2O_8$ + 10^{-5} N $[N(C_4H_9)_4]SO_4$; 3) differential capacity of mercury in 10^{-2} N Na_2SO_4 + 10^{-5} N $[N(C_4H_9)_4]SO_4$.

In the solution of the question raised in this paper, namely the part played by the formation of cation bridges, data on the relation of the effectiveness of cations to their radii are of the greatest importance. Figure 3 shows polarization curves for the electroreduction of 10^{-3} N $K_2S_2O_8$ in presence of 10^{-2} N alkali-metal chlorides (Li^+, Na^+, K^+, Rb^+, and Cs^+ from bottom to top) according to Nikolaeva and Damaskin [27, 30]. These curves were obtained with the aid of a dropping electrode; only parts of the curves corresponding to a negatively charged surface are given in Figure 3, since at positive charges the curve is distorted by a polarographic maximum of the first kind. As will be seen, reaction rate varies greatly with change in the radius of the cation. When a correction is applied to the observed values of the current to take account of changes in concentration due to passage of current, it is found that the rate in presence of 10^{-2} N Cs^+ is about 40 times as great as in presence of Li^+ at the same concentration. A similar relation between the rate of the process and the radius of the cation was found by Zezula for the reduction of the $S_4O_6^{2-}$ anion [31]. As Nikolaeva-Fedorovich showed, a similar relation is observed also in the reduction of the $PtCl_4^{2-}$ anion, which probably proceeds by a somewhat different mechanism.

The dependence of the rate of electrode processes in presence of alkali-metal cations on the radius of the cation was observed earlier (Herasymenko and Slendyk [32] for the electroreduction of hydrogen ions, Izgaryshev and Ravikovich [33], and Vasenin and Gorbachev [34] for the electroreduction of some metal cations). The sign of these effects is opposite to that for the discharge of anions, i.e., the rate of discharge of H^+ ions diminishes as the cation radius increases. In absolute value these effects are relatively small: they are much smaller than the effects observed in the electroreduction of anions. Measurements of electrocapillary curves [35] and particularly the precise measurements of capacity carried out by Grahame [36] have shown that the charge of a negatively charged mercury surface is somewhat dependent on the radius of the cation, and this must lead to differences in the value of the ψ_1-potential and therefore in the kinetics of the processes occurring at the surface. These differences in the rates of reactions in which cations take part may explain the variations in the mean values of the ψ_1-potential, but in the case of the electroreduction of anions the differences in rate are too high to be explained completely without recourse to the concept of a closer interaction between the reacting anion and the cation of the supporting electrolyte, i.e., to the idea of cation bridges. The more readily adsorbed and less highly hydrated Cs^+ ions are found to be more effective than Li^+ ions.

This conclusion is confirmed by measurements of the temperature coefficient of the electroreduction of persulfate [30, 37]. It was found that the temperature coefficient of the rate of this reaction, referred to constant concentration of reactant, falls as we replace the cation of the supporting electrolyte Na^+ by K^+ and particularly

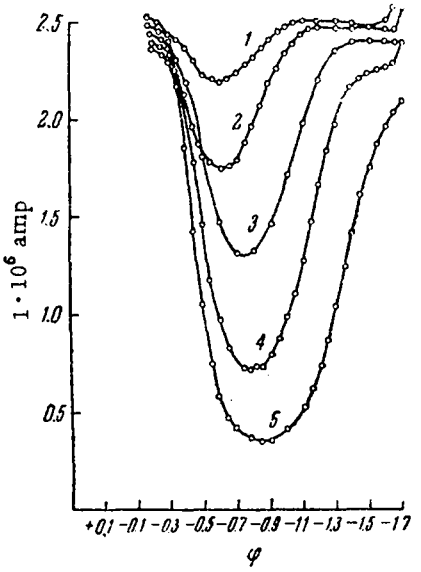

Fig. 3. Relation of current at dropping electrode to potential in 10^{-3} N $K_2S_2O_8$ in presence of 10^{-2} alkali-metal chloride: 1) CsCl; 2) RbCl; 3) KCl; 4) NaCl; 5) LiCl.

by Cs^+, which indicates increase in the strength of the bond formed with the anion in this order. In the case of a Cs^+ supporting electrolyte, the temperature coefficient of the reaction becomes negative. Analogous conclusions are reached by a comparison of the rates of electroreduction of the BrO_3^- anion in supporting electrolytes containing various cations [38]. The formation of cation bridges has been recently confirmed by a comparison of differential capacities of the electrode in presence of the chlorides and iodides of sodium and cesium [39].

In a paper read in 1955 at a conference on chemical kinetics, I expressed regret at the absence of data on salt effects in bulk reactions between anions which could throw light on why electrostatic repulsion does not prevent rapid reaction in these cases [40]. In 1957 there appeared a paper by the American authors Sheppard and Wahl [41], who investigated the kinetics of exchange between MnO_4^{2-} and MnO_4^- and showed that the rate of this process is greatly dependent on the nature of the cation, which led them to suggest that a cation bridge of the type $[MnO_4-K-MnO_4]^{2-}$ plays a part in the reaction, a suggestion analogous to that made by us on the basis of electrochemical data.*

The effectiveness of cations in the formation of cation bridges is not determined entirely by their adsorbability and hydration energy, but probably depends also on relations between the dimensions of the cation and the distance at which the center of the activated complex will be found in the transition of an electron from the electrode surface to the anion being reduced. Large organic cations such as $N(C_4H_9)_4^+$, which accelerate the reduction of the anions $S_2O_8^{2-}$, $FeCy_6^{3-}$, and $HgCy_4^{2-}$ to an extremely high degree at potentials corresponding to the minimum of the polarization curve, do not accelerate, but even retard, the reduction of $PtCl_4^{2-}$ [28]. It is possible that, owing to the planar configuration and, probably, high adsorbability of this anion, the transition of an electron in the reduction proceeds at a much shorter distance from the electrode surface than in the reduction of the anions already discussed, and the positive charge of the cation, which is at a relatively great distance from the electrode surface, is ineffective. Only at higher negative potentials, at which, judging from measurements of differential capacity, there appears to occur some flattening of the tetrabutylammonium cation at the electrode surface, is some acceleration of the process observed, and this disappears at still more highly negative potentials owing to the desorption of the cation from the surface.

I have tried to illustrate the relation between electrochemical kinetics and the kinetics of ionic reactions in the bulk of a solution with the aid of examples of processes proceeding with the participation of anions. Of no less interest would be a comparison of phenomena of acid-base catalysis with discharge of hydroxonium ions and other proton donors at electrode surfaces, but this is outside the scope of the present paper.

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