KINETICS:

DISCUSSION

Some Results of Developments in the Study of Electrochemical Reaction Mechanisms in the Last Five Years by A. N. Frumkin

N. S. Hush. Several years ago A. N. Frumkin noted that since the original work of Horiuti and Polanyi in 1935 there has been no appreciable progress in the interpretation of the "transfer coefficient" (constant α) of electrode reactions. I wish to present briefly a new interpretation of the transfer coefficient and the nature of the activation barrier in the transfer of an electron.

The transfer of an electron between a metallic electrode and some particle on the solution side of the interphase caused by thermal motion is, generally speaking, an adiabatic process in which the motion of the electrons can be reconstructed in accordance with the configuration of the nuclei at all stages of the reaction. In work on the theory of electrode processes it is sometimes assumed that there is uncertainty in these processes. For example, the Franck-Condon principle is frequently used in an examination of the potential barrier while in actual fact only the Born-Oppenheimer adiabatic approximation is required. In the next approach we should examine the course of the reaction leading to the formation of the transition state in which the distribution of electron density is characterized by the wave function of the system and in which explicit allowance is made for the field of the dielectric, created by the given charge distribution and reacting against the charge.

Let us examine a one-electron transfer:

$$Me^{z+} + e \rightleftarrows Me^{(z-1)+}, \tag{1}$$

in which neither of the ions is specifically adsorbed by the surface. The reaction may be regarded as the exchange of an electron between an orbital metal x_1 and the lowest unoccupied orbital x_2 of the ion Me^{Z+}. In the case of ions of the first transition group x_2 will be the $3d\epsilon$ or $3d\gamma$ orbital. The energy of the electron bond and the energy of the interaction of the ion with its environment in the solution may be examined separately. The electronic wave function Φ_λ for any state λ lying between the initial and the final states, may be written in the form of a linear combination of atomic orbitals in the following way:

$$\Phi_\lambda = \frac{1}{\sqrt{N}}(c_1\lambda x_1 + c_2\lambda x_2). \tag{2}$$

From this equation it follows that the relation of the electrochemical free activation energy $\Delta\vec{G}^{\ddagger}$ of the reduction to overvoltage is expressed by the expression:

$$\frac{1}{F}\frac{\partial\Delta\vec{G}^{\ddagger}}{\partial\eta} = C_{2,t}\cdot C^{*}_{2,t}, \tag{3}$$

where $C_{2,t}$ is the coefficient x_2 in the transition state. From the form of the wave function (2) and the almost orthogonal state of functions x_1 and x_2 it is evident that $C_{2,t}\cdot C^{*}_{2,t}$ is the density of the probability of an additional electronic charge which is attached to nucleus M^{Z+} in the transition state, so that the total charge q# of the ion in the transition state, expressed in proton charge units, gives the equality:

$$q^{\neq} = Z - C_{2,t} \cdot C^{*}_{2,t}\,. \tag{4}$$

According to the Tafel equation, the left-hand part of equation (3) coincides with the transfer coefficient α for the process examined so that it is possible to write:

$$\alpha = Z - q^{\neq}. \tag{5}$$

Thus, the transfer coefficient is identified with the density of the probability of an electronic charge attached to the nucleus of the ion in the transition state of the given electron exchange process.

Analysis of the expression for the activation energy obtained by means of equation (5) shows that for ions whose interaction with water is purely electrostatic, the energy is maximal when

$$q^{\neq} = \frac{2Z - 1}{2}, \tag{6}$$

i.e., when $\alpha = 0.5$.

Calculation gives activation energies of 8–12 kcal/mole for radii of the ion M^{Z+} within the range 0.5–1.5 A, which are in reasonable agreement with experiment. The effect of the adsorption of ions, the potential of the diffuse double layer, and nonelectrostatic terms in the potential energy of the reaction of ion with water change these values in directions which may be predicted, but these effects are mainly second order.

From the result presented it is clear that the usual representation of activation barriers as potential energy curves for the initial and final states of the system formed by intersection is essentially misleading. For processes of the type discussed it obviously completely lacks substance as the transfer coefficient has no relation to the slopes of curves of the initial and final states of discharging particles. In actual fact, for electrostatically bound complexes of ions with water, it is found that energy forms corresponding to the internal hydration envelope make only a very small contribution to the activation energy of electron transfer, while the main term is produced by the interaction of the changing charge of the ion with the field of the unsaturated dielectric created by it. In this approach, essentially we regard the electron density associated with the nucleus of the ion as a reaction parameter. Neglect of this parameter in a representation of activation routes corresponding to the exchange of electrons leads to errors of the same type as the error pointed out by F. F. Vol'kenshtein in a case when the Lennard-Jones diagram is applied to molecular chemisorption processes, namely, the activation barrier drawn is, strictly speaking, an optical illusion as the energy profile contains two different limiting values of a continuously changing parameter.

L. I. Krishtalik. I wish to consider some problems connected with the theory of slow discharge. The first problem concerns the effect of the absolute values of the potential jump and the chemical potentials of charged particles, namely, electrons and hydrogen ions. It seems to me that R. M. Vasenin has made the error which was found previously in the work of A. K. Lorenz and some others. It consists of the fact that in writing the expression for the activation energy in the following form:

$$W = W_0 + \alpha\varphi F$$

and carrying out all subsequent operations, they forget that W_0 is the difference between the energies of the active complex and the initial state. Consequently, it includes both the chemical potential of an electron in the metal and the standard chemical potential of hydrogen ion. Therefore, when W_0 is moved into the constant, which is supposedly independent of the potential jump, an error is made as the potential jump is directly determined by the chemical potentials of the electron and the hydrogen ion, in particular, the solvation energy of the proton. A change in the solvation energy of the proton must produce a considerable change in activation energy. The increase in activation energy equals half of the increase in the solvation energy in the proton and this normally explains the relation of the overvoltage to the nature of the solvent. However, this does not make allowance for the fact that a change in the solvation energy is accompanied by a change in the potential jump and these two effects are strictly equal and opposite. In other words, to use the terminology proposed by M. I. Temkin, it can be stated that the ideal activation energy depends on the solvation energy, while the actual activation energy, which determines the magnitude of the overvoltage, does not depend on the solvation energy.

The second problem concerns the effect on the overvoltage of the adsorption energy not only of hydrogen atoms, but also hydrogen ions and water molecules. Naturally, these values should be included in the overvoltage equation, but normally they are small and are neglected. They cannot determine the order of magnitude of the overvoltage as they are actually small. However, it seems to me that they should not be neglected, firstly, because according to the estimate which may be made, they make an appreciable contribution to the overvoltage (of the order of 0.1 v) and secondly, because precisely these values chiefly characterize the change in overvoltage with a change in solvent. Besides, in connection with the fact that the absorption of ions is connected to a certain extent with their desolvation, there should be a qualitative parallelism between the adsorption energy and the solvation energy, i.e., a qualitative relation between the overvoltage and the solvation energy of a proton.

The final question concerns the calculation of activation energy by the normal method of potential curves. It seems to me that in such calculations there is always one inaccuracy. To be precise, for the construction of the Morse function for adsorbed hydrogen, the dissociation energy is taken as the energy of the hydrogen-metal bond and the parameter $\underline{a}$ is either taken as the coefficient obtained directly for the gaseous hydride or the coefficient calculated from the vibration frequencies of the gaseous hydride. However, these two values, the vibration frequency and the bond energy, are not independent. For the given class of compounds, metal·hydrides, they are directly proportional to each other. Therefore, when we take those two values from different sources and different conditions, we obtain considerably distorted potential curves. If this interrelation is considered, then the Morse function for hydrides may be represented in the form of an equation with one parameter, i.e., the bond energy. This eliminates the certain arbitrariness in the choice of the parameters of the Morse function. I would like to note that such a calculation shows the agreement of calculated and experimental values for the overvoltage and activation energy if a bond energy of the order of 30 kcal is adopted for cations with a high overvoltage.

S. V. Gorbachev. In recent years a new trend has arisen in our laboratory. The main idea of this trend is to use the experience of chemical kinetics in solving electrochemical problems. A. N. Frumkin stated that the investigation of temperature on the rate of electrochemical reactions has been found to be a fruitful method but, in his opinion, there are shortcomings in our work connected with the fact that the measurements were related to a definite potential, when it is desirable to relate them to a definite overvoltage or, more accurately, to a definite polarization potential. In our work we always emphasized that it is advantageous to make measurements by using as comparison electrodes, electrodes in the same solution, at the same temperature, and even in the same vessel, and not calomel half-cells. Therefore, in our work we used a vessel with three sections: an anode, a cathode and a comparison electrode. It is only when we are considering irreversible systems, for which it is impossible to obtain a comparison electrode with a stable potential, that it is necessary to use calomel electrodes. Naturally, use of such an electrode hampers the interpretation of the results.

J. O'M. Bockris. In connection with A. N. Frumkin's remarks on the mechanism of hydrogen liberation on metals with average overvoltage, it is interesting to note the following: Conway and Bockris recently showed that on some such transition metals the hydrogen exchange current falls with an increase in the heat of adsorption of atomic hydrogen. This result contradicts the hypothesis that the limiting stage is the discharge stage. For all metals investigated (for example, W, Ag, Fe, Ni, etc.), the slope in the Tafel equation was close to 0.12 v at 25°. This slope is characteristic of both the slow discharge mechanism and the slow desorption mechanism. Therefore, this relation between the exchange current and the heat of adsorption makes it possible to put forward the hypothesis that the slow stage in the liberation of hydrogen with a low current density on most metals with an average overvoltage is the electrochemical desorption stage. It is improbable that the limiting stage changes at high current densities as was proposed by A. N. Frumkin for nickel in acid solutions. With a displacement of the potential in a negative direction, the maximum of the potential curve during electrochemical desorption is also displaced. From this it follows that the electrochemical desorption mechanism does not change to a slow discharge mechanism and that the slow desorption mechanism is retained for all metals of the transition groups investigated.

The relation between the adsorption energy and the hydrogen overvoltage, which is derived from the work of Polanyi and Horiuti, is correct only for a definite class of metals. It may be confirmed experimentally for four metals: mercury, lead, tin, and thallium, where there is actually a regular fall in overvoltage with an increase in adsorption energy, which the theory of slow discharge requires.

In connection with the report of A. N. Frumkin, I would like to point out that although the electronic work function is not included directly in the equation of the theory of slow discharge, the relation between the overvoltage and the electronic work function may be established due to the fact that the adsorption energy of hydrogen is connected with the electronic work function.

A. N. Frumkin. I will not dwell in detail on the problem of introducing the electronic work function of the metal into the relation expressing the dependence of the constant a on the nature of the metal, considered in the articles with M. I. Temkin; I will limit myself to pointing out that in contrast to the work functions in vacuum, the work functions for the transfer of an electron from metals into the volume of the solution with these metals at the same measured potentials must be equal.

I agree with S. V. Gorbachev that it is necessary to use the general ideas of chemical kinetics to a maximum in examining the theory of electrode processes. I did not dwell on this in my report as I recently considered this problem in a separate communication [Coll: Problems of Chemical Kinetics, Catalysis, and Reactivity [in Russian] (Izd. AN SSSR, Moscow, 1955) p. 403]. However, contrary to the statement of S. V. Gorbachev, from material accumulated in the study of volume chemical processes it by no means follows that there is no relation between reaction energies and activation energies. On the contrary, the relation according to which in comparing reactions proceeding by an identical mechanism, an increase in reaction energy is accompanied by an approximately proportional fall in its activation energy, which is frequently associated with the name of Bronsted, is finding increasing new confirmation, in particular in the work of N. N. Semenov and his school [N. N. Semenov, Some Problems in Chemical Kinetics and Reactivity [in Russian] (Izd. AN SSSR, Moscow, 1954) p. 29].

Effect of Temperature on Electrolysis as a Kinetic Method of Investigating the Nature of Electrochemical Processes by S. V. Gorbachev

A. L. Rotinyan. In his report, S. V. Gorbachev presented a method of investigating the effect of temperature of the kinetics of electrode processes and also some results obtained by means of this method. In the form used up to the present time, this method has its faults. Since this method is finding increasing application, while errors, which in our opinion, were encountered previously, have not been eliminated, I consider it advantageous to make a few comments on behalf of myself and V. L. Kheifets.

In principle, the method examined may give definite information for individual reactions. However, with the simultaneous occurrence of two or several processes it is always necessary to determine the current yield of each of the processes and to construct polarization curves for each process on this basis. Only in this case is it possible to calculate the activation energy for any process. In making measurements in aqueous solutions at different temperatures, it is always necessary to remember that the liberation of hydrogen occurring on the cathode together with the main reaction and the liberation of oxygen on the anode together with the oxidation process studied vary strongly with temperature. In addition, other secondary processes may begin on the cathode with a change in temperature. Unfortunately, insufficient attention was paid to this in the work of S. V. Gorbachev. The following examples of the neglect of this phenomenon may be cited.

1. S. V. Gorbachev and N. P. Zhuk [Zhur. Fiz. Khim. 25, 841 (1951)] measured anode polarization curves in 0.1–5 M NaCl and proposed a new mechanism for the liberation of chlorine on the basis of these experiments. They considered that only chlorine was liberated on the anode under all conditions. This conclusion is contradictory to electrolysis practice. According to data which we obtained together with B. Ya. Sergeeva, the current yield of Cl_2 falls with a decrease in the NaCl concentration and is less than 10% in 0.1 N NaCl. The rest of the electricity is consumed largely in the liberation of oxygen. Consequently, the data and the conclusions of S. V. Gorbachev and N. P. Zhuk cannot be considered accurate.

2. In the work of S. V. Gorbachev and Yu. N. Yurkevich, no allowance was made for the fact that at low temperatures hydrogen is liberated on the cathode and at high temperatures, nickel.

3. In connection with the recently published work of G. A. Emel'yanenko [Doklady Akad. Nauk SSSR, 105, 1003 (1955)], in which it was shown that curves of the temperature dependence of overvoltage with a maximum are produced by the appearance of films on the cathode surface, "the phase polarization" discovered by S. V. Gorbachev, we are again moving into the region of postulates.

Moreover, it should be pointed out that in the work of S. V. Gorbachev and his co-workers, errors are also encountered which are not connected in principle with the method examined, but make the experimental data and conclusions in this work doubtful. These errors include, firstly, the measurement of potentials relative to an auxiliary electrode whose reversibility has not been confirmed by special experiments (for example, an auxiliary nickel electrode) and, secondly, measurement without the tip of the electrolytic connector clamped to the surface of the operating electrode.

Thus, the method of investigating the effect of temperature on the rate of electrode processes may be used if desired, but with the precautions pointed out.

N. P. Zhuk. A convenient experimental method of measuring polarization at different temperatures is the use as a comparison electrode of electrodes which are reversible with respect to the process studied in the same electrolyte and at the same temperature, as proposed by S. V. Gorbachev. It is true that in the study of some processes one encounters difficulties connected with the inadequate reversibility of the process on the comparison electrode, for example, in the study of the anode liberation of oxygen from aqueous solutions on platinum and nickel. We were able to reduce the irreversibility of an oxygen electrode on platinum to 0.2–0.3 v, but this was found to be inadequate. Therefore, it is difficult to overestimate the importance of the production of a reversible oxygen electrode on platinum by Bockris especially for the investigation of corrosion processes with oxygen depolarization.

Investigation of the temperature effect is being applied with increasing success in the study of corrosion processes and has already made it possible to proceed to their quantitative treatment in a number of actual cases. However, there have also been unsuccessful attempts. In particular, some investigators have attempted to evaluate absolute reaction rates (corrosion activity of media) solely from activation energy without allowance for the pre-exponential term, which is known to be incorrect.

In the corrosion of metals with hydrogen depolarization, all qualitative changes in the metal (its nature and structure, nature of impurities, etc.) affect the rate of the process by changing both the pre-exponential term and the activation energy, while quantitative changes affect the corrosion rate mainly through the change in the pre-exponential term. This may be illustrated by the data of N. S. Akulov and N. V. Khimchenko, who obtained very similar (± 1 kcal) activation energies for corrosion in 5% HCl at corrosion rates differing by a factor of 100 for a series of iron–carbon alloys, differing mainly in the carbon content. If we allow for the error they made in the calculation (the activation energies were too high by a factor of 2), the variations in activation energies are extremely slight. This shows that the carbon content affects the corrosion rate by the change in the pre-exponential factor.

I cannot agree with A. L. Rotinyan that we did not consider the possibility of oxygen liberation in the work he mentioned. We had experimental data for evaluating the role of oxygen liberation in the anode liberation of chlorine.

In conclusion, as one interested in corrosion, I wish that in the investigation of processes occurring on metal electrode, more attention were paid to the nature, structure, and state of the metal surface.

I. P. Anoshchenko. I would like to consider briefly the importance of the temperature factor in the investigation of metal corrosion.

For determining the activation energy of corrosion processes we attempted to use the method of S. V. Gorbachev, based on the Arrhenius equation. It was found that for cathode processes with the liberation of hydrogen, the relation of the logarithm of the current density log i to the reciprocal temperature $1/T$ was linear. Here, as in the liberation of metals (which was discussed by S. V. Gorbachev and A. V. Izmailov), the lines were parallel in some cases (for example, in pure H_2SO_4) and here we were dealing mainly with concentration polarization while in other cases they radiated from a point (for example in acid-containing additives). In the latter case we had chemical as well as concentration polarization. As regards anode processes lines were not always obtained in the same system of coordinates for corrosion in acids containing additives. We very often obtained broken lines, with one and even two breaks, and curves. This indicates a change in the anode process with a change in temperature. These data have not been interpreted fully as yet. Nonetheless, it is already clear that in the presence of surface-active substances, corrosion processes are more complex than can be explained solely by ideas on the presence of physical absorption alone. In particular, this is confirmed by the high activation energies of electrode processes. In using the method of S. V. Gorbachev, it is often necessary to work not with the polarization (overvoltage) potential but with the electrode potential. This is so when the process does not have a reversible potential.

L. I. Antropov. In electrochemical investigations in our country, some methods have fallen into undeserved oblivion. I am thinking primarily of optical methods. A brilliant example of what may be achieved by this method is provided by the work of A. G. Samartsev about twenty years ago. However, the optical method is hardly used by us nowadays in the study of the nature of chemical processes. The use of this method in particular schlieren microscopy, may be very profitable in the investigation of the anode solution of metals and anode polishing. Another such method is the use of the effect of ultrasonics on electrochemical processes. Intensive work is being carried out abroad, in particular in the USA, on the effect of ultrasonic and sonic vibrations on the course of electrochemical processes. Very few people here are studying this, possibly only in the laboratory of B. B. Kudryavtsev. We are paying quite inadequate attention to problems of the electrochemical synthesis of inorganic and organic substances and to the study of the kinetics of electrochemical reduction of organic compounds by means of polarography including oscillographic polarography.

The next method, on which much has been said during the discussion, is connected with the study of the temperature dependence of the rate of electrochemical reactions. As has already been noted, little attention has been paid to the temperature factor and comparatively few investigations have been carried out at high temperatures. S. V. Gorbachev's contribution lies in the fact that he is one of the first to consider the advantage of using this method. The basis here is the Arrhenius equation as transposed to apply to electrochemical reactions. Since charged particles participate in such reactions, the rate of these reactions depends not only on the concentration of the reacting particles, but also on the magnitude of the potential. As has been pointed out by M. I. Temkin, in this connection data which can be interpreted can be obtained only if the relation between current strength (rate of the electrochemical reaction) and temperature is studied at a given polarization. The latter is possible only when precisely the electrochemical reaction which proceeds under the given conditions has been established and an appropriate reference electrode chosen.

Moreover, since the Arrhenius equation contains the rate of the actual chemical reaction corresponding to that for which the relation of current strength to polarization is plotted at different temperatures, it is necessary to know the distribution of current between the reaction particles and to determine the fraction of the current pertaining to the process whose activation energy is to be calculated. Unfortunately, these requirements are not always observed and the activation energy values obtained have no real meaning. What I have said naturally does not lessen the importance that activation energy has not only in chemical processes but also in electrochemical processes. Therefore, it is natural that the criticism of S. V. Gorbachev's address provides no grounds for stopping the study of the temperature dependence of the rates of electrochemical reactions.

Application of Radioactive Tracers to the Study of Ionization and Discharge of Metal Ions on Amalgam Electrodes by V. V. Losev and A. M. Khopin

N. S. Hush. Together with Blackledge, I determined the relation of the rate of exchange of $Zn^{2+} \cdot | Zn (Hg)$ in $NaClO_4$ solution to the ionic strength μ and the temperature by measurement of the alternating-current impedance and also by direct-current measurements of the rate of solution of the amalgam. It was found that the activation energy of this process is independent of the ionic strength (10.0 kcal/mole at $\mu = 0.2-3.0$), while the rate constant increases sharply when the ionic strength falls below 2.0. Blackledge also measured the transfer coefficient α, determined by the equation

$$\alpha = -\frac{RT}{2F}\frac{\partial \ln \vec{k}}{\partial \eta},$$

where $\vec{k}$ is the rate constant of the reduction process. At cathode overvoltages and potentials close to the equilibrium value, $\alpha = 0.32$ (independent of temperature), while at high anode overvoltages and with a moderate ionic strength, it equals 0.66, in agreement with the results of V. V. Losev [Doklady Akad. Nauk SSSR, 100, 11 (1955)] obtained by another method. At low ionic strengths ($\mu < 1$) the cathode transfer coefficient increases with a fall in ionic strength. These results are most simply explained by a reaction mechanism with successive stages:

$$Zn^{2+} + e \rightleftarrows Zn^{+};$$
$$Zn^{+} + e \rightleftarrows Zn (Hg).$$

The rate of exchange was also studied in solutions of anions which are weak complex formers (Cl^-, Br^-, I^-, SCN^-). The data obtained indicated dual control of the rate. The rate of reduction of the simple hydrated ion Zn^{2+} differs little from the rates of reactions proceeding through the complexes $(ZnX)^+$ and ZnX_2. In this respect, the catalytic action of such anions is similar to their action in the catalysis of homogeneous transfers of an electron of ions of the transition group.

DISCUSSION

Electrode Processes in Molten Oxides by O. A. Esin

J. O'M. Bockris. To explain the values of the potentials, O. A. Esin assumes that Si^{2+} ions participate in the electrode reaction. However, this explanation involves certain difficulties. From x-ray diffraction determinations it is well known that silicon in silicates has four covalent bonds. SiO is known in a solid state. It is theoretically possible that in the system $FeO-SiO_2$ small amounts of Si^{2+} may exist close to the cathode under reducing conditions. However, the difficulty consists in the fact that if Si^{2+} were formed during the reduction, this ion would tend to enter the silicate lattice, which would lead to signs of the potential that do not agree with the experimental. It seems to me that the hypothesis on the participation of Si^{2+} in electrode reactions is analogous to the hypothesis on the participation of protons and not hydroxonium ions in processes in aqueous solutions.

O. A. Esin. Demonstrations of the existence of Si^{2+} in slags were given, for example, in the work of P. V. Gel'd (1950); this summarized the experimental arguments confirming that there is SiO in liquid slags of ferroalloy furnaces, sometimes in high concentrations. For its formation it is necessary that the slags contain a sufficiently high percent of SiO_2 and that they are in a strongly reducing atmosphere. [Doklady Akad. Nauk SSSR, 70, 473 (1950)].

The forms in which SiO exists in slags are not yet clear. Apparently, together with oxygen bridges of the type Si—O—Si, which are normal for SiO_2, they also contain others, namely, Si—Si. It is evident that in the equilibrium state, the potentials of di- and tetravalent silicon are the same.

In our case (an examination of the current yield and polarization), it was sufficient that the silicon could diffuse into the slag; its electrolytic transfer was not obligatory. The curves presented in the report show that at low SiO_2 contents (1.2%), the limiting currents were directly proportional to the SiO_2 concentration; at high concentrations (30 and 50% SiO_2), instead of falling, the polarization unexpectedly increased strongly. This curious circumstance is readily explained by the hypothesis that divalent silicon is formed at the cathode ($Si^{4+} + 2e \rightarrow Si^{2+}$) and at the anode ($Si - 2e \rightarrow Si^{2+}$) [Zhur, Fiz. Khim. 30, 374 (1956)].

Investigation of the Phenomenon of Overvoltage in Molten Salts by R. Piontelli et al.

J. O'M. Bockris. It is doubtful if the development of the method of directly measuring the potentials of polarized electrodes in molten media described in the work of R. Piontelli can find wide application as the exchange currents in aqueous solutions. Bockris, Hills, Young, and Hill recently showed that with a number of precautions in measurements in molten media,the alternating current method may be applied successfully. The applicability of this method to the study of fast electrode reactions makes it particularly suitable for molten media.

Investigation of Ion Exchange Between a Molten Metal and Its Salt with the Aid of Radioactive Isotopes by Yu. V. Baimakov and N. S. Nikitenko

S. I. Rempel'. My brief comment concerns the report of Yu. V. Baimakov on ion exchange in the system molten zinc—zinc chloride. Analogous work for aqueous solutions of electrolytes at boundaries with amalgams was carried out by V. A. Pleskov by using an apparatus in which the electrolyte was stirred strongly without a change in the area of the metal. This was done quite accurately. The rate of transfer of labeled atoms from one phase to the other should be determined solely by the exchange current and not by diffusion. In the procedure described here by Yu. V. Baimakov there was no stirring. The procedure may be criticized on this score. Had stirring been used, it would have been found that the measured exchange current would have been greater than in this work, the more so as the viscosity of the two phases is no less than in the work of V. A. Pleskov and zinc is liberated during electrolysis on liquid zinc without polarization (which indicates a very high exchange current).