

2. P. I. Dolin and B. V. Ershler, *Zhur. Fiz. Khim.*, **13**, 747 (1940).
3. B. V. Ershler, *Zhur. Fiz. Khim.*, **22**, 683 (1948).
4. A. A. Sutyagina and K. M. Gorbunova, *Zhur. Fiz. Khim.*, **33**, 1982 (1959) [*Russ. J. Phys. Chem.*, **248** (1959)].
5. A. F. Bogoyavlenskii, B. E. Ivanov, and V. A. Khudyakov, *Zhur. Prikl. Khim.*, **33**, 368 (1960).
6. N. A. Izgaryshev and S. V. Gorbachev, "Kurs Teoreticheskoi Elektrokhemii" (Course of Theoretical Electrochemistry), Goskhimizdat, 1951.
7. H. Gerischer, *Z. phys. Chem. (Frankfurt)*, **1**, 278 (1954).
8. I. M. Ryzhik, "Tablitsy Integralov, Summ, Ryadov i Proizvedenii" (Tables of Integrals, Sums, Series, and Products), OGIZ, 1948.
9. G. M. Fikhtengol'ts, "Kurs Differentsial'nogo i Integral'nogo Ischisleniya" (Course of Differential and Integral Calculus), Fizmatgiz, 1959.
10. S. Glasstone, K. G. Laidler, and H. Eyring, "Theory of Rate Processes" (Translated into Russian), Inostr. Lit., 1948.

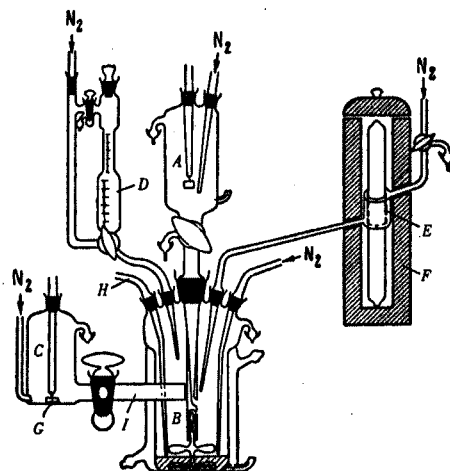


Fig. 1. Diagram of the apparatus.

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RADIOCHEMICAL AND ELECTROCHEMICAL STUDIES OF ELECTRODE PROCESSES ON AMALGAMS. II

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It has been shown¹ that electrode processes on amalgam electrodes with substantial exchange currents can be studied by a combination of radiochemical and electrochemical measurements. The previously developed method^{2,3} has been elaborated to measure exchange currents in the absence of surface-active additives and employed in the measurements of exchange currents, transfer coefficients, limiting anodic and cathodic currents, and the potential dependence of the true rates of anodic processes on zinc, thallium, and indium amalgams. The reason for this choice was that the electrode processes on zinc amalgam have been studied by a combination of radioactive tracer and electrochemical methods only in the presence of surface-active additives^{2,3} and, as stated earlier¹, the data obtained by the radiochemical method in pure solutions⁴ cannot be fully explained in terms of the theory of retarded discharge-ionisation. Moreover it will be possible to compare the results obtained by different methods since for zinc amalgam reliable data have been obtained on the exchange currents and transfer coefficients by various electrochemical methods⁵⁻⁹. In order to compare the electrode processes for amalgams of metals of different valencies we have also studied the systems In-In^{3+} and Tl-Tl^{+} .

EXPERIMENTAL

The apparatus is shown in Fig. 1. An amalgam of required concentration was prepared in cell A by electrolysis with a mercury cathode of a salt solution of the metal

investigated containing its radioactive isotope. The amalgam obtained was poured into the measuring cell B which was then filled with acidified solution of an inert electrolyte from the auxiliary vessel C. Then the hydrogen overvoltage curve for the amalgam was determined in order to check the purity of the solution and the electrochemical activity of the amalgam. At the same time the radioactivity of a sample of the solution was measured. When the radioactivity exceeded the usual background level under the given conditions (for example, due to dissolution from the amalgam surface of traces of metal oxide that could have formed in the preparation of the amalgam or during its transfer from cell A into the measuring cell B), cathodic polarisation of the amalgam was continued until the radioactivity of the subsequent samples of the solution fell to the usual value. Next the cell B was filled with a salt of the metal to be investigated from the burette D†. The true rates of the anodic dissolution of the metal with polarisation of the electrode or at equilibrium were determined from the rate of rise of the radioactivity of the solution measured by taking periodically small samples of the solution into cell E which had the form of a glass cylindrical jacket surrounding the counter tube and situated in the lead shielding chamber F. After each measurement the sample was returned to cell B. In the case of thallium, whose radioactivity was measured using the β -radiation of ^{204}Tl , the cylindrical glass jacket had a narrower annular space and was provided with a thin-walled membrane‡. The specific radioactivity of the solution used in the preparation of an amalgam was determined in the same cell under strictly reproducible geometric conditions. In parallel with the

† Incorporation of this burette made it possible to measure, in a single experiment, the exchange currents (or limiting currents) at several concentrations of the solution.

‡ The principal advantage of the all-glass closed system described is that it makes it possible to work with radioactive tracers without the necessity of dealing with exposed surfaces of radioactive solutions and amalgams and no special arrangements are required for sampling and preparing specimens for counts. Furthermore, the system ensures fixed geometric conditions for measurements of radioactivity of samples and also maintaining the volume of the solution constant.

radiochemical measurements, the anodic and cathodic polarisation curves were obtained in each experiment by means of the auxiliary platinum electrode G. The potential of the amalgam was measured relative to the reference electrode $\text{Hg}/\text{Hg}_2\text{SO}_4$ (1 N H_2SO_4) connected with cell B by means of the bridge H and recalculated relative to the standard hydrogen electrode. In order to avoid non-uniform polarisation of the amalgam surface, which may occur at high current densities, solutions of high electrical conductivity were employed and the outlet of tube I was as near as possible to the vertical axis of cell B and away from the amalgam surface. The solution and amalgam were stirred with a propellor-type glass stirrer rotated at 400 rev/min.[§] Preparation of the amalgams and all the measurements were made in an atmosphere of purified nitrogen. Experiments were made at a constant temperature ($\pm 0.1^\circ$) and constant high ionic strength which was achieved by using an excess of an inert electrolyte (see Ref. 1, p. 579). All the solutions were prepared with doubly distilled water. ZnSO_4 , MgSO_4 , TiClO_4 , and NaClO_4 were twice recrystallised from doubly distilled water and preheated to a high temperature (to avoid decomposition, NaClO_4 was dried at 110°). Indium perchlorate was prepared by dissolving metallic indium (99.99%) in concentrated doubly distilled HClO_4 with heating and then dissolving in HClO_4 the indium hydroxide precipitated from the solution.^{||}

The rates of exchange and the true rates of the anodic process (in A cm^{-2}) during polarisation were calculated, mainly from the slopes of the initial linear parts of the curves showing the rate of rise of radioactivity of the solution, using the following approximate formula^{2,3}:

$$i_a = \left(\frac{v_2}{v_1} \right) \frac{m_a n F I}{I_0 S t}, \quad (1)$$

where v_2 and v_1 are the volumes of solutions in cells A and B, m_a is the metal content in the amalgam in g-atoms, S the area of the amalgam, t the time in sec, and I_0 and I are the radioactivities of the samples of solution in cells A (initial) and B. In a few measurements of exchange currents with zinc and thallium the calculation of the final concentration was made by the complete logarithmic formula taking into account the reverse (cathodic) process of transfer of radioactivity from the solution into the amalgam³.

An important question is the nature of the potentials of amalgams of the metals investigated in solutions of their salts. Generally speaking, as the equilibrium potentials of zinc, indium, and thallium amalgams are negative with respect to the potential of the hydrogen electrode, the exchange process between the amalgam and ions of the metal investigated should be accompanied, in the absence of external polarisation, by self-dissolution of the amalgam due to evolution of hydrogen. This should shift the amalgam potential in the positive direction compared with the equilibrium potential in a given solution. However, examination of published data (see, for example, Kravtsov and Ermolova¹²), extrapolation of the hydrogen overvoltage

curves to these potentials, and direct measurements of the self-dissolution of the amalgams investigated[†] have shown that the rate of this process is negligible (approximately $4.6 \times 10^{-6} \text{ A cm}^{-2}$ for zinc and not exceeding $7 \times 10^{-7} \text{ A cm}^{-2}$ for thallium and indium[†]) by comparison with the exchange rates and that the dependence of the equilibrium potential of the amalgam on the corresponding metal ion concentration in solution satisfies Nernst's equation for all the amalgams investigated. Therefore the experimental amalgam potentials, for all the three metals over the whole range of the amalgam and solution concentrations investigated, are practically equilibrium potentials.

Measurements of the exchange current for zinc were made at 25° over the range of amalgam concentrations from 8×10^{-5} to 0.97 M and solution concentrations from 10^{-4} to 0.2 M ZnSO_4 with MgSO_4 added to attain constant ionic strength (2 M) and H_2SO_4 (0.005 M) to prevent hydrolysis. Preliminary measurements have shown that at an amalgam concentration 0.13 M and solution concentrations 0.01–0.2 M ZnSO_4 the exchange current changes little with rate of stirring in the range 200–500 rev/min. A slight rise in the exchange current with increase in rate of stirring is probably due to an increase in the amalgam surface. The results of one of the experiments on the rise of radioactivity of the solution with time at several concentrations of the solution and constant amalgam concentration under equilibrium conditions are plotted in Fig. 2. The zinc ion concentration in the solution was increased progressively by adding small quantities of concentrated ZnSO_4 solution. As the concentration increases, the equilibrium potential shifts in the positive direction and the slope of the I - t curve rapidly increases. After the exchange has proceeded for a fairly long time in the solution of the highest ZnSO_4 concentration, the slope of the I - t curve gradually begins to

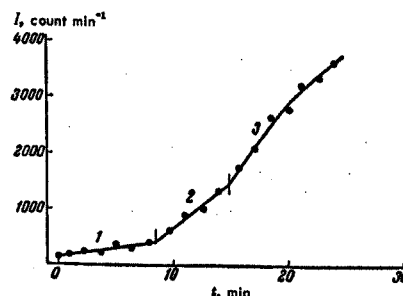


Fig. 2. Rate of increase of radioactivity of solutions at various ZnSO_4 concentrations (c_s) for one amalgam sample ($c_a = 0.13 \text{ M}$): 1) 0.005 M; 2) 0.05 M; 3) 0.18 M. Vertical lines show the times when the concentration was changed.

§ An estimate of the Reynolds number and also the observed proportionality between the limiting anodic current for Zn amalgams and the rotational speed of the stirrer in the range 100–430 rev/min have shown that the conditions of stirring were turbulent under the experimental conditions employed^{10,11}.

|| The concentration of this $\text{In}(\text{ClO}_4)_3$ solution was at our request kindly checked by S. I. Sinyakova by a polarographic method, for which we express our thanks.

† The rates of self-dissolution of the amalgams were determined in the same solutions, by the radiochemical method described above, in the absence of ions of the corresponding metals.

‡ These rates of self-dissolution of the amalgams could be produced by 0.01% of oxygen in the nitrogen. Thus the oxygen content in nitrogen did not exceed the above value under the conditions employed.

decrease (see part 3 of the curve in Fig. 2) because of appreciable participation of radioactive species in the reverse (cathodic) process.

Figs. 3 and 4 show the variation of the exchange currents and the limiting diffusional anodic and cathodic currents with concentrations of the amalgam (c_a) and the solution (c_s). The $\log i_0 - \log c_a$ and $\log i_0 - \log c_s$ curves have two regions with different slopes, the low concentration regions being parallel to the limiting current lines and having slopes close to unity. Evidently in this concentration range the exchange rate is controlled by diffusion in the amalgam (Fig. 3) and in the solution (Fig. 4). In the second region, which starts at concentrations close to 10^{-2} M, the slopes of the lines are smaller, i.e. the exchange current increases with concentration more slowly. It can be easily shown that the exchange rate in this region is still unaffected by diffusion of species in the second phase; for this purpose, the limiting cathodic and anodic currents (i_d^c and i_d^a) at the solution and amalgam concentrations stated above are plotted in the figures (broken lines). Their values are in both cases considerably higher than the measured exchange rates. The transfer coefficients, calculated from the slopes of the $\log i_0 - \log c_a$ and $\log i_0 - \log c_s$ lines in the second region using Eqn. (12) given in a previous paper¹, are $\alpha = 0.52 \pm 0.04$ and $\beta = 1.40 \pm 0.05$; thus the sum $\alpha + \beta$ is equal to 1.92, i.e. close to 2. The experimental data for the kinetic regions of Figs. 3 and 4 may therefore be expressed by

$$i_0 = i_0^0 [\text{Zn}]^{0.26} [\text{Zn}^{2+}]^{0.70}, \quad (2)$$

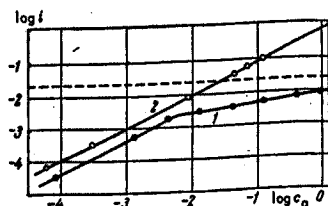


Fig. 3. Effect of amalgam concentration at $c_s = 0.025$ M ZnSO_4 on: 1) exchange rate; 2) limiting anodic current. The broken line shows the cathodic limiting current.

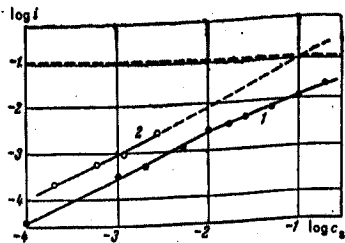


Fig. 4. Effect of the concentration of ZnSO_4 solution at $c_a = 0.13$ M on: 1) exchange rate; 2) limiting cathodic current. The broken line shows the limiting anodic current.

where $i_0^0 = 0.11$ A cm^{-2} . The exchange currents which we found agree with radiochemical data⁴ for the higher solution concentrations and are slightly lower than the values obtained by other methods⁵⁻⁸; the values of the transfer coefficients are in satisfactory agreement with published data^{4,6,7, 13-15}. The dependence of the exchange currents on temperature at the two amalgam concentrations corresponding to the two regions of the $\log i_0 - \log c_a$ curve is plotted in Fig. 5. The activation energies, calculated from the slopes of the lines, are 7.4 and 5.0 kcal mole^{-1} for the kinetic and the diffusion-controlled stages respectively; the activation energy for the kinetic stage is slightly lower than that obtained by Gerischer⁷ (9.1 kcal mole^{-1}).

In Fig. 6 the experimental anodic and cathodic polarisation curves for three amalgam concentrations are compared with theoretical curves calculated by approximate formulae obtained from Eqn. (16) published previously^{1,16}. The exchange currents corresponding to these concentrations are also plotted[†]. The experimental points are in good agreement with the theoretical curves[†].

An important conclusion follows from an examination of the polarisation curves and Eqn. (16) of Ref. 1. The limiting current varies linearly with the concentration of the depolariser, but under the same conditions the variation of the exchange current with the concentration is very much slower [see Eqn. (12) of the previous paper¹]. Because of this effect an increase in the concentration of the reacting species in only one of the phases, for example in the amalgam, may be sufficient to cause a transition from the diffusional to the kinetic region^{16,17}. In fact, Eqn. (16) of Ref. 1 shows that when $i_0 > i_d^a$ (assuming for simplicity that $[\text{M}^{n+}] = \text{const}$ and $i_d^a \gg i_d^c$), the first term in the denominator is small by comparison with the second and the rate of the anodic process is mainly diffusion controlled; as the amalgam concentration increases, the condition $i_0 < i_d^a$ may be attained and when $\Delta\phi$ is not very large, we may

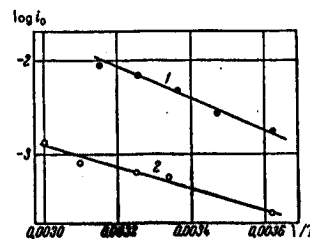


Fig. 5. Temperature dependence of the exchange current for zinc amalgam at $c_s = 0.025$ M ZnSO_4 and various values of c_a : 1) 0.13 M; 2) 0.0013 M.

§ The discrepancy is probably due to differences in anionic compositions and ionic strengths of the solutions employed.

† Values of the exchange currents corresponding to dilute amalgams have been determined by extrapolation of the kinetic region of the $\log i_0 - \log c_a$ curve (Fig. 3).

‡ The slight discrepancy on curve 3 is due to the fact that the accuracy of determination of i_0 and i_d^a becomes inadequate with such a dilute amalgam.

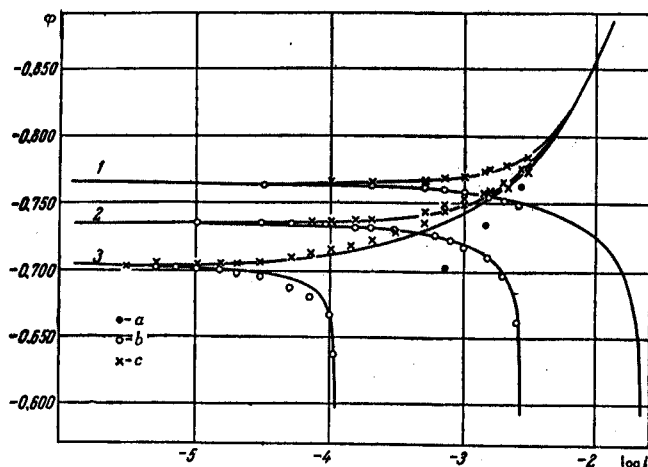


Fig. 6. Polarisation curves at $c_s = 0.025$ M ZnSO_4 and various amalgam concentrations c_a : 1) 0.026 M; 2) 0.0029 M; 3) 0.00011 M. Experimental points: a) exchange current; b) anodic part of polarisation curve; c) cathodic part of polarisation curve. The curves have been calculated from the experimental values of i_0 , α , β , i_d^a and i_d^c .

neglect the second term in the denominator, i.e. the discharge-ionisation stage is the controlling one. This conclusion agrees with our experimental data. For curve 3 (Fig. 6) we have $i_d^a/i_0 \sim 0.1$, i.e. the rate of the anodic process is diffusion controlled, but for curve 1 we have $i_d^a/i_0 \sim 10$, i.e. the controlling stage is the discharge-ionisation. Thus an increase in the amalgam concentration (~ 200 times), with other conditions remaining the same, caused a transition from the diffusional to the kinetic region. This effect is favoured by low values of the corresponding transfer coefficient, in particular of α , observed with bivalent metals. In general the effect may be employed for choosing reactant concentrations in order to reduce the influence of the diffusion stage on the results of measurements of the exchange current and transfer coefficient. Thus it follows that in the case of the amalgam electrodes and also in oxidation-reduction processes on inert electrodes the conditions for measuring the exchange current will be most favourable at equal concentrations of the oxidised and reduced species.

SUMMARY

1. A method of studying the kinetics of electrode reactions on amalgam electrodes, based on a combination of electrochemical and radiochemical measurements, has been described.
2. The electrode processes on zinc amalgam have been studied in zinc sulphate solutions. Exchange currents have been determined as a function of amalgam and solution concentrations and temperature. The transfer coefficients of the anodic and cathodic processes have been determined as $\beta = 1.40 \pm 0.05$ and $\alpha = 0.52 \pm 0.04$ and the apparent activation energies as $7.4 \text{ kcal mole}^{-1}$ for the discharge-ionisation stage and 5 kcal mole^{-1} for the diffusion-controlled stage.

1. V. V. Losev and G. M. Budov, *Zhur. Fiz. Khim.*, **37**, 578 (1963) [*Russ. J. Phys. Chem.*, **297** (1963)].
2. V. V. Losev, *Dokl. Akad. Nauk SSSR*, **100**, 111 (1955); V. V. Losev and A. M. Khopin, "Trudy IV Elektrokhimicheskogo Soveshchaniya" (Proceedings of the Fourth Electrochemical Conference), 1956, p. 116.
3. V. V. Losev, *Trudy Inst. Fiz. Khim.*, No. 4, 20 (1957).
4. N. B. Miller and V. A. Pleskov, *Dokl. Akad. Nauk SSSR*, **74**, 323 (1950); V. A. Pleskov and N. B. Miller, "Trudy Soveshchaniya po Elektrokhimii" (Proceedings of the Electrochemical Conference), 1953, p. 165; N. B. Miller, Thesis, 1953.
5. J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 951 (1952).
6. B. V. Ershler and K. I. Rozental', "Trudy Soveshchaniya po Elektrokhimii" (Proceedings of the Electrochemical Conference), 1953, p. 446.
7. H. Gerischer, *Z. phys. Chem. (Leipzig)*, **202**, 302 (1953).
8. H. Gerischer, *Z. Elektrochem.*, **59**, 604 (1955); *Z. phys. Chem. (Frankfurt)*, **10**, 264 (1957).
9. H. Gerischer and W. Vielstich, *Z. phys. Chem. (Frankfurt)*, **3**, 16; **4**, 10 (1955).
10. V. G. Levich, "Fiziko-Khimicheskaya Gidrodinamika" (Physicochemical Hydrodynamics), Moscow, 1959.
11. A. I. Fedorova and G. L. Vidovich, *Dokl. Akad. Nauk SSSR*, **109**, 135 (1956).
12. V. I. Kravtsov and A. F. Ermolova, *Dokl. Akad. Nauk SSSR*, **136**, 1146 (1961).
13. J. H. Sluyters and J. J. Coomen, *Rec. Trav. chim.*, **79**, 1101 (1960).
14. O. A. Esin, *Zhur. Fiz. Khim.*, **17**, 159 (1943).
15. J. Koryta, *Coll. Czech. Chem. Comm.*, **19**, 433 (1954).
16. G. M. Budov and V. V. Losev, *Dokl. Akad. Nauk SSSR*, **122**, 90 (1958).
17. V. V. Losev, *Zhur. Fiz. Khim.*, **30**, 1402 (1956).

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SURFACE TENSION AND VAPOUR PRESSURE OF LIQUID ORGANIC COMPOUNDS. I. HYDROCARBONS, ETHERS, AND ESTERS

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The present paper deals with the conditions of equilibrium between liquid and vapour at a constant temperature with the aim of establishing the relation between the vapour pressure and the surface tension in homologous series of organic compounds. It is assumed that the free energies of the vapour and of the liquid surface are equal and that the vapour obeys the ideal gas laws. Then for 1 mole we obtain

$$G_0 + RT \ln p = G_0^l + A\gamma, \quad (1)$$