

4. Absorption bands at 1740 and 1395 cm^{-1} , due to the doubly ionised form, appear in solutions containing more than 30% of potassium hydroxide.
5. The spectrum of caprolactam in alkaline solutions up to 20% KOH is the same as in water. It is concluded therefore that up to 20% KOH almost all the caprolactam is present as the unionised form.
6. Data from the infrared and ultraviolet spectroscopy were used to determine the equilibrium constants for the formation of the monoanion ($K_p = 7$) and the dianion ($K_p' = 190$).
7. A mechanism for the ionisation of lactams in alkaline solutions is suggested.

1. G.I. Batyukov and S.G. Entelis, Russ. P. 736105/26 (1962).
2. R. Mecke and R. Mecke, Chem. Ber., **89**, 343 (1956).
3. A.E. Parsons, J. Mol. Spectroscopy, **6**, 201 (1961).
4. Yu. V. Moiseev, G.I. Batyukov, and M.I. Vinnik, Izv. Akad. Nauk SSSR, Ser. Fiz., **26**, 1309 (1962).
5. R.C. Gore, R.B. Barnes, and E. Petersen, Analyt. Chem., **21**, 282 (1949).
6. M.L. Bender and R.D. Ginger, J. Amer. Chem. Soc., **77**, 348 (1955).
7. J.M. Hunt, M.P. Wisherd, and L.C. Banham, Analyt. Chem., **22**, 1478 (1950).
8. M.I. Vinnik, Yu. V. Moiseev, and L.V. Palagina, Dokl. Akad. Nauk SSSR, **143**, 1427 (1962).
9. M.I. Vinnik, Yu. V. Moiseev, and L.V. Palagina, Dokl. Akad. Nauk SSSR, **138**, 149 (1961).

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Received 27th December 1961

RADIOCHEMICAL AND ELECTROCHEMICAL STUDIES OF ELECTRODE PROCESSES ON AMALGAMS. I

V. V. Losev and G. M. Budov

In investigations of the mechanism of any electrode process, including the anodic dissolution and the electro-deposition of metals, the overall process must be divided into elementary stages, and which is the slowest among them must be established, i.e. which stage determines the polarisation in practice, and also the kinetics of direct charge transfer at the interface (discharge-ionisation stage) must be studied. This last is especially important, as regularities in the exchange of charge constitute the basis of the theoretical interpretation of electrode processes. Study of the rules governing the discharge-ionisation stage of metals on solid electrodes is associated with great difficulties. Many of these can be overcome by using amalgam instead of solid electrodes, which enables the stages of diffusion along the surface and crystallisation (the rates of which may be considerably lower than that of the discharge-ionisation stage¹) to be replaced by diffusion of the discharged species into the interior of the amalgam. Thus in

the case of the amalgam electrode the problem of elucidating the laws of the discharge-ionisation stage reduces to eliminating the effect of two analogous diffusion stages (in the solution and in the amalgam). In the case of the amalgam it is considerably easier to ensure a clean surface and to prevent its passivation, and moreover the surface of the amalgam electrode is smooth and uniform. The high hydrogen overpotential of mercury and amalgams may facilitate the study of electrode processes for those metals the hydrogen overpotential of which is low. Finally, a substantial advantage of amalgams over solid electrodes is that the rate of the anodic process and the exchange current can be studied as a function of the concentration of metal in the amalgam, hence determining the reaction order for the anodic process.

In the analysis of the discharge-ionisation stage for electrode processes in which more than one electron takes part the question arises whether their addition (and hence removal) takes place simultaneously or in stages. It is usually supposed that the transfer of more than one electron is accomplished in one elementary act²⁻⁴. Nevertheless, theoretical considerations of the small probability of the simultaneous transfer of several electrons to a reactant species⁵⁻⁹ suggest that the discharge-ionisation stage in many-electron electrode processes most likely represents the net effect of several consecutive one-electron steps†. Direct confirmation of this hypothesis is provided by the detection of species of intermediate valency in electrochemical reactions. During recent years the presence of such cations has been demonstrated with several metals¹²⁻²⁰.

The task of the present paper is to examine, on the postulate of a stepwise occurrence of the discharge-ionisation process, the kinetic laws of the anodic dissolution and cathodic deposition of metals on amalgam electrodes, by a method based on a combination of radiochemical and electrochemical measurements.

Kinetic Equations for Ionisation and Discharge Processes on Amalgam Electrodes

Let us consider the anodic dissolution of an amalgam of a given metal in a solution containing simple ions of the same metal‡:



Let us suppose that the solution contains an excess of a foreign electrolyte and that its ionic strength is constant; hence the activity coefficient of the M^{n+} ions remains constant when their concentration is varied, and activities are

† A similar problem arises also in the kinetics of oxidation-reduction reactions in a solution, where the hypothesis of one-electron transfers in these reactions, which was put forward long ago by Haber¹⁰, has recently obtained fresh experimental support. Thus it has been shown that reactions between two-equivalent and one-equivalent oxidants and reductants in solution occur in such a way that two-equivalent ions (for example Ti^{3+}) are reduced to their stable state of lower valency in two stages involving the formation of unstable intermediate species (for example Ti^{2+})¹¹.

‡ For simplicity, we shall examine the case in which the anodic and cathodic processes are of first order with respect to the corresponding reactant species, and only simple metal ions take part in the electrode process. It is also assumed that chemical reactions in the solution, preceding the discharge process, are absent.

proportional to concentrations (in all equations, therefore, activity coefficients will always be included in constants[§]). If under these conditions specifically adsorbed anions are also absent from the solution, the ψ_1 -potential is greatly lowered and is practically independent of the electrode potential. It is also postulated that reaction (1) represents a combination of successive one-electron stages. In general the rates of these stages may be comparable²¹, but it is convenient to assume that the rate of one of these stages is considerably lower than those of the remainder, which can be regarded as equilibrium stages. This hypothesis is justified experimentally, the slowest stage of process (1) usually proving to be elimination of the last electron²²⁻²⁴. We therefore assume further that the rate-determining stage in process (1) is the reaction



The true rate of the anodic process is represented²⁵ by the equation

$$i_a = k' [M^{(n-1)+}] e^{\beta_n F \varphi / RT}, \quad (3)$$

while the true rate of the cathodic process is

$$i_c = k'' [M^{n+}] e^{-\alpha_n F \varphi / RT}, \quad (4)$$

where α_n and β_n are the transfer coefficients of stage (2), k' and k'' are constants, and the concentration of the intermediate species $M^{(n-1)+}$ is governed by the equilibrium conditions of the stages involving removal from the metal atom of all the electrons other than the last:

$$[M^{(n-1)+}] = K [M] e^{(n-1) F \varphi / RT}, \quad (5)$$

where $[M]$ is the concentration of metal in the amalgam, and K a constant depending on the standard equilibrium potential of the system. After substituting $[M^{(n-1)+}]$ from Eqn. (5) in (3), we obtain

$$i_a = k' K [M] e^{(n-1+\beta_n) F \varphi / RT} = k' K [M] e^{\beta F \varphi / RT}, \quad (6)$$

where $\beta = n - 1 + \beta_n$ is the experimentally determined apparent transfer coefficient. Sometimes it is more convenient to use Eqns (6) and (4) in semilogarithmic form:

$$\varphi = \text{const} + \frac{RT}{\beta F} \ln i_a, \quad (7)$$

$$\varphi = \text{const} - \frac{RT}{\alpha F} \ln i_c. \quad (8)$$

It appears from Eqn. (6) that, on our hypothesis of the stepwise occurrence of the electrode process, only the coefficient β can be directly found by means of Eqn. (7), from the experimental data, whereas the true coefficient β_n , corresponding to the ionisation in stage (2), can be determined only by means of the relation $\beta_n = \beta - (n - 1)$.²³ The coefficient α_n coincides with the experimentally determined coefficient α , as can be seen from Eqn. (4), and can be found directly from experimental data by means of Eqn. (8). At equilibrium the rates of the anodic and

cathodic processes are the same and equal to the exchange current:

$$i_0 = k' K [M] e^{\beta F \varphi_{eq} / RT} = k'' [M^{n+}] e^{-\alpha F \varphi_{eq} / RT}. \quad (9)$$

If we solve Eqn. (9) for the equilibrium potential

$$\varphi_{eq} = \frac{RT}{(\alpha + \beta) F} \ln \left(\frac{k' [M^{n+}]}{k' K [M]} \right) \quad (10)$$

and compare Eqn. (10) with the Nernst equation for process (1), we obtain the relation

$$\alpha + \beta = n. \quad (11)$$

After substituting in Eqn. (9) the value of φ_{eq} from the Nernst equation and carrying out a simple rearrangement taking into account the relation (11), we obtain the equation

$$i_0 = i_0^* [M]^{\alpha/n} [M^{n+}]^{\beta/n}, \quad (12)$$

where i_0^* is the normal or standard exchange current^{3,4}. It is readily shown that, on our postulates, relations are obtained between the experimentally determined coefficients α and β from which the nature of the slow one-electron stage can be assessed. Actually, in our case it is not difficult to obtain from relation (11), in view of the conditions $\alpha_n \times \beta_n = 1$ and $\alpha_n = \alpha$, the inequality $\beta > n - 1$, and hence $\beta > \alpha$. Thus in the case of metals which dissolve to form multivalent ions, the coefficient β should appreciably exceed α : in other words, the slope of the anodic polarisation curve plotted as φ against $\log i_a$ should be considerably smaller than that of the corresponding cathodic curve. This difference should be more marked the higher the valency of the metal ions which are formed. Consequently the experimental determination of transfer coefficients for many-electron electrode processes may help to elucidate their detailed mechanism.

The initial equations (4) and (6) for electrode processes at an amalgam electrode represent the true rates of the cathodic and anodic processes respectively. Nevertheless, the experimentally measured external polarising current i is always equal to their difference, since both conjugate processes take place at the electrode whatever its potential:

$$i = i_a - i_c = k' K [M] e^{\beta F \varphi / RT} - k'' [M^{n+}] e^{-\alpha F \varphi / RT}. \quad (13)$$

Relation (13) represents the equation to the steady-state polarisation curve; at a sufficient distance from the equilibrium potential, in either a positive or a negative direction this relation passes into Eqn. (6) or (4) respectively. By utilising Eqn. (9), we can express (13) in the more convenient form

$$i = i_0 (e^{\beta F \Delta \varphi / RT} - e^{-\alpha F \Delta \varphi / RT}), \quad (14)$$

where $\Delta \varphi = \varphi - \varphi_{eq}$; we assume that $i > 0$ for the anodic process, and therefore $\Delta \varphi > 0$ for the anodic process and $\Delta \varphi < 0$ for the cathodic process. The above relations can be utilised for the experimental determination of the kinetic parameters i_0 , α , and β , and also the reaction order of the anodic and cathodic processes. Thus in order to determine the reaction order in the former case, by means of Eqn. (6), it is necessary to measure the rate of the anodic process

§ When considering dilute amalgams, we can also disregard the difference between activities and concentrations of the metal in the amalgam.

¶ This difference in physical meaning between the coefficients α and β for many-electron electrode processes is associated with the fact that, on our postulate, the slow stage is preceded by the equilibrium stages in the case of the anodic process, whereas in the cathodic process the first stage in the overall process is rate-determining. If a different stage is rate-determining, and also in the case of two or more stages having comparable rates²¹, the physical meaning of the coefficients α and β will be different.

† In view of the expression obtained previously $\beta = n - 1 + \beta_n$, we hence find the usual relation between the true transfer coefficients: $\alpha_n + \beta_n = 1$.²⁵

‡ Eqn. (12) differs from the expressions usually employed^{3,4} in that the latter assume that the rate-determining stage of the electrode process is the simultaneous removal or addition of electrons, corresponding to the condition $\alpha + \beta = 1$, whereas in the above derivation it is assumed that $\alpha + \beta = n$.

i_a with amalgams of different concentrations at constant potentials. When steady-state polarisation curves are employed for the solution of these problems, they must be recorded at potentials remote from equilibrium, *i.e.* right up to current densities i exceeding the exchange current by 2–3 orders of magnitude. Actually, Eqns. (13) and (14) pass into Eqns. (6) and (4) [or into Eqns. (7) and (8) respectively] only when $i \gg i_0$. Under these conditions the concentrations of the reactant species at the electrode surface may differ from the corresponding concentrations in the bulk of the solution and the amalgam. After correction of Eqn. (9) for concentration polarisation²⁸, the equation to the steady-state polarisation curve (14) becomes

$$i = i_0 \left[(1 - i/i_a^0) e^{\beta F \Delta \phi / RT} - (1 + i/i_c^0) e^{-\alpha F \Delta \phi / RT} \right], \quad (15)$$

where i_a^0 and i_c^0 are the anodic and cathodic limiting currents. This equation can be converted by simple rearrangement into a form which is more convenient for comparison with experimental data:

$$i = \frac{e^{\beta F \Delta \phi / RT} - e^{-\alpha F \Delta \phi / RT}}{1/i_0 + (1/i_a^0) e^{\beta F \Delta \phi / RT} + (1/i_c^0) e^{-\alpha F \Delta \phi / RT}}. \quad (16)$$

Study of Electrode Processes on Amalgams by a Radioactive Tracer Method

The radioactive tracer method occupies a special position among the various methods for studying electrode processes, since it enables the exchange current to be measured directly from the rate of transfer of radioactive species from one phase to another. With systems having very large exchange currents, of course, the uniform distribution of radioactive species, which is the fundamental condition for the correct measurement of the exchange current, may break down in one or both phases even with vigorous stirring of amalgam and solution during exchange; the experimental rate of isotopic exchange may then prove to be determined not by the ionisation-discharge stage but by the rate of diffusion of the radioactive species. However, the results of the measurements are much less distorted by difficulties due to diffusion in the radioactive tracer method than in ordinary polarisation measurements. Actually, since the steady-state polarisation curve for a given process (for example the anodic process) is distorted at high current densities by concentration polarisation, and at low current densities by the occurrence of the reverse cathodic process, the anodic and cathodic limiting currents should exceed the exchange current by 2–3 orders of magnitude²⁸ in order to obtain on the curves (ϕ plotted against $\log i$) a sufficiently long linear portion for determination of the exchange current (by extrapolation to the equilibrium potential) and of

the transfer coefficients. Nevertheless, a simple calculation[†] shows that, in the case of the radiochemical method, it is sufficient that the limiting currents should exceed the exchange current by a factor of 3–5 to obtain a reliable measurement of the exchange current.

In some work on the rate of isotopic exchange[†] a dropping amalgam has been utilised^{30–32}. In the case of lead and cadmium amalgams studied by this method, and also with pure mercury²⁷, the rate of isotopic exchange was governed mainly by the diffusion stage, and the true exchange currents could not be determined. A systematic investigation of rates of exchange on zinc, bismuth, lead, and thallium amalgams was made by Miller and Pleskov³³, who employed a considerably better technique. A detailed study was made of the dependence of the rate of isotopic exchange on the concentration in the amalgam and in the solution and of the effect of temperature, nature of solvent, and complex formation on the rate of exchange, the latter being observed to decrease in the presence of added organic surface-active agents. In the case of zinc amalgam the values of the exchange current and of the transfer coefficient α agree satisfactorily with the results obtained by non-steady-state methods,^{3, 35, 36} whereas with bismuth amalgam in $\text{BiCl}_3 + 1 \text{ N HCl}$ solution and lead amalgam in $\text{Pb}(\text{NO}_3)_2$ solution the values of the rate of exchange are smaller by about three orders of magnitude than the exchange currents obtained by an a.c. method³⁵. With solutions more dilute than 0.1 N, the rate of exchange was directly proportional, with all the amalgams, to the concentration of the salt of the metal in solution. This result is inconsistent with the theoretical concentration dependence of the exchange current [Eqn. (12)], according to which the exchange current should increase more slowly than linearly with the concentration of metal ions. It is probable that in dilute solutions the rate of exchange is limited mainly by the diffusion of radioactive species in the solution, not by the electrochemical stage. Nevertheless, the deviation from this linear dependence in more concentrated solutions, and also the dependence of the rate of exchange on the concentration of the zinc amalgam in such solutions, the latter agreeing well with theory, indicate, in our view, that with zinc amalgam in more concentrated solutions the rate of exchange is governed mainly by the ionisation-discharge stage, not by diffusion[‡].

† The rate of isotopic exchange i'_0 measured by the radiochemical method is linked with the true exchange current i_0 by the relation $1/i'_0 = 1/i_0 + 1/i_a^0 + 1/i_c^0$.^{32, 34}

‡ We shall not consider work on isotopic exchange between solid metals and solutions of the corresponding salts, since it has not yet proved possible to use such measurements for calculating the exchange current. In view of the low rate of diffusion in the solid phase, the rate of exchange in these systems is usually governed, not by the electrochemical stage, but by the diffusion of radioactive species into the interior of the electrode or along its surface. Thus in the case of a silver electrode in 0.1 N AgClO_4 solution the true exchange current measured by a non-steady-state potentiostatic method is 4.5 A cm^{-2} ,¹ whereas the rate of isotopic exchange under the same conditions was lower by 3–6 orders of magnitude^{1, 29}, and its value is certainly no indication of the rate of the ionisation-discharge stage.

‡ Actually, in the case of purely diffusion-dependent kinetics, for example with respect to the solution, the rate of exchange should vary linearly with the concentration of metal ions in the solution and be independent of the concentration of the amalgam, as has been observed, for example, with a concentrated cadmium amalgam in dilute $\text{Cd}(\text{ClO}_4)_2$ solutions³¹.

§ We have assumed that anodic and cathodic reactions are of first order (see next Section), but in general the reaction order can, of course, differ from unity. In order to determine the order of the reaction, it is necessary to measure the dependence of the rate of the given process (for example anodic) on the concentration of reactant species at constant potential (ϕ constant) and not at constant polarisation ($\Delta \phi$ constant), as is sometimes done²⁸. In the latter case we actually obtain from Eqns. (14) and (12) a fractional reaction order with respect to the amalgam concentration, which contradicts theory, and even a dependence of the rate of the anodic process on the concentration of the solution, which is clearly inconsistent with Eqn. (6).

A certain disadvantage in the above methods is that the radiochemical measurements were not accompanied by electrochemical measurements, and were made only under equilibrium conditions. However, a complete description of the electrode process requires knowledge of the transfer coefficients α and β , and also, when concentration polarisation is present, the anodic and cathodic limiting currents [see Eqn. (16)]. This problem can be solved by combining radiochemical with electrochemical measurements. Actually, it is possible, by measuring the rate of growth of radioactivity in the solution in contact with the labelled amalgam during passage of an external current, to isolate one of the conjugate processes occurring on the amalgam (in this case the anodic process), and determine its velocity not only at the equilibrium potential (the exchange current) but also at various potentials under non-equilibrium conditions; in particular, the rate of the anodic process can be measured during cathodic polarisation, *i.e.* under conditions such that the corresponding reverse process predominates. From the slope of the polarisation curve thus obtained for the anodic process (φ plotted against $\log i_a$), the transfer coefficient β can be found, and the reaction order for the anodic process determined from the change in its value with variation of the concentration of the amalgam (at constant φ). By measuring anodic and cathodic limiting currents under the same conditions, a reliable estimate can be obtained for the effect of the diffusion stage on the radiochemical measurements, and appropriate corrections can be made if necessary. Furthermore, the agreement of the experimental polarisation curve with the curve calculated from Eqn. (14) using values of i_0 , α , and β obtained by the radiochemical method serves as a proof of the electrochemical mechanism of exchange represented by Eqn. (1) and the absence of exchange by any non-electrochemical mechanism. Finally, such agreement may serve as evidence that the process has the same mechanism under equilibrium conditions and at an appreciable distance from equilibrium, which is not always the case^{1,37}.

A method of combining radiochemical with electrochemical measurements was worked out by one of us²² in the case of the ionisation and discharge of zinc ions at a stationary zinc amalgam electrode[†], the exchange current being artificially lowered, in order to eliminate the effect of the diffusion stage, by addition of a surface-active agent. Over a wide range of potentials in the region of the equilibrium value a linear relation was observed between the potential of the amalgam and the logarithms of the true rates of the anodic and cathodic processes²³. It was concluded from the results, in view of the fact that the slope of the anodic polarisation curve was considerably less than that of the

cathodic curve ($\beta > \alpha$), that the ionisation of zinc takes place in stages, the rate of the overall process being limited by the stage $\text{Zn}^+ \rightarrow \text{Zn}^{2+} + e$.²²

Since surface-active substances can greatly complicate the occurrence of electrode processes, it is of interest to apply this method to amalgam electrodes in pure solutions of the corresponding salts with the aim of determining the exchange current, transfer coefficients, and reaction order. A comparison of the results of such measurements for metals of different valencies should help to elucidate the mechanism of the ionisation and discharge processes, and in particular reveal the rate-determining stage of many-electron electrode processes.

SUMMARY

1. Kinetic equations have been derived for ionisation and discharge at an amalgam electrode based on the hypothesis of the multistage transfer of electrons in many-electron electrochemical reactions.
2. Foundations have been laid for a method of investigating the kinetics of electrode processes on amalgams by combining radiochemical with electrochemical measurements.

1. H. Gerischer *et al.*, *Z. Elektrochem.*, **58**, 819 (1954); **61**, 1159 (1957); *Analyt. Chem.*, **31**, 33 (1959).
2. P. Delahay, "New Instrumental Methods in Electrochemistry" (Translated into Russian), Inostr. Lit., Moscow, 1957.
3. H. Gerischer, *Z. phys. Chem. (Leipzig)*, **202**, 292, 302 (1953).
4. A. G. Stromberg, *Zhur. Fiz. Khim.*, **29**, 409 (1955).
5. A. N. Frumkin, "Voprosy Khimicheskoi Kinetiki" (Problems of Chemical Kinetics), Moscow, 1955, p. 402.
6. N. N. Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki" (Some Problems of Chemical Kinetics), Moscow, 1958, p. 258.
7. D. C. Grahame, *Ann. Rev. Phys. Chem.*, **6**, 337 (1955).
8. F. H. Westheimer, "Symposium on the Mechanism of Enzyme Action", 1954, p. 321.
9. F. Basolo and R. Pearson, "Mechanism of Inorganic Reactions", Vol. 4, 1958, p. 315.
10. F. Haber and J. Weiss, *Proc. Roy. Soc.*, **147A**, 332 (1934); L. Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937).
11. W. C. E. Higginson *et al.*, *J. Chem. Soc.*, 3044 (1953); 343 (1956); 477 (1957); *Discuss. Faraday Soc.*, No. 29, 49 (1960); R. H. Betts, *Canad. J. Chem.*, **33**, 1780 (1955); J. Halpern, *ibid.*, **37**, 148 (1959).
12. W. Kangro and F. Weingärtner, *Z. Elektrochem.*, **58**, 505 (1954).
13. A. W. Davidson, *J. Amer. Chem. Soc.*, **72**, 170 (1950); **76**, 363 (1954); **78**, 556, 559 (1956); *J. Inorg. Nuclear Chem.*, **13**, 64 (1960).
14. D. V. Kokouline and B. N. Kabanov, *Dokl. Akad. Nauk SSSR*, **112**, 692 (1957); *Zhur. Fiz. Khim.*, **34**, 2469 (1960) [*Russ. J. Phys. Chem.*, 1165 (1960)].
15. J. Epelboin *et al.*, *Z. Elektrochem.*, **59**, 689 (1955); *Compt. rend.*, **239**, 1695 (1954); *Métaux*, No. 387, 3 (1957).
16. H. Imai, *J. Electrochem. Soc. Japan*, **23**, 583 (1955).
17. R. H. Sanborn and E. F. Orlemann, *J. Amer. Chem. Soc.*, **78**, 4852 (1956).
18. A. Vlcek, *Coll. Czech. Chem. Comm.*, **22**, 948, 1747 (1957); *Nature*, **180**, 753 (1957); **189**, 393 (1961).
19. L. D. Hepler, Z. Z. Hugus, and W. M. Latimer, *J. Amer. Chem. Soc.*, **75**, 5672 (1953).

§ The possibility of obtaining the curves for the true rate of the anodic process in the vicinity of the equilibrium potential is especially important in studying the mechanism of many-electron processes. In fact, with a two-electron process, for example, when the rates of the two stages are comparable while the slopes of the true curves corresponding to these stages are different, the exchange currents obtained by extrapolating anodic and cathodic polarisation curves to φ_{eq} should be different²¹. In this case the slope of the true anodic curve should be different in the cathodic and anodic regions, and consequently the complete curve for the true rate of the anodic process obtained over a wide potential range should undergo a break in the region of the equilibrium potential.

† An analogous method was used by Audubert³⁸ to determine the slope of the curve relating the true rate of the anodic process with potential during cathodic polarisation of a solid copper electrode in CuSO_4 solution.

20. G. Biedermann and T. Wallin, *Acta Chem. Scand.*, **14**, 594 (1960).
21. K. J. Vetter, *Z. Naturforsch.*, **7a**, 328 (1952); **8a**, 823 (1953); *Z. Elektrochem.*, **56**, 797 (1952); **64**, 805 (1960); "Elektrochemische Kinetik", 1961, p. 129.
22. V. V. Losev, *Dokl. Akad. Nauk SSSR*, **100**, 111 (1955).
23. V. V. Losev and A. M. Khopin, "Trudy IV Elektrokhimicheskogo Soveshchaniya" (Transactions of the Fourth Electrochemical Conference), 1959, p. 116.
24. G. M. Budov and V. V. Losev, *Dokl. Akad. Nauk SSSR*, **122**, 90 (1958); **129**, 1321 (1959).
25. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, "Kinetika Elektroodnykh Protsessov" (Kinetics of Electrode Processes), Moscow, 1952.
26. S. V. Gorbachev and A. G. Atanasyants, *Nauch. Dokl. Vys. Shkoly, Khim. i Khim. Tekhnol.*, **3**, 430 (1958).
27. M. Haissinsky *et al.*, *J. Chim. phys.*, **45**, 224 (1948); **46**, 476 (1949).
28. B. E. Conway, *Chem. Can.*, **9**, 45 (1957); M. Stern and A. L. Geary, *J. Electrochem. Soc.*, **104**, 56 (1957).
29. S. E. Vaisburd, N. M. Kozhevnikova, and V. L. Kheifets, *Zhur. Prikl. Khim.*, **32**, 2507 (1959).
30. J. Groh, *Z. phys. Chem.*, **128**, 449 (1927).
31. S. Fronaeus *et al.*, *Acta Chem. Scand.*, **7**, 746 (1953); **8**, 412, 961 (1954); **10**, 490 (1956).
32. A. M. Baticle and M. J. Thouvenin, *Compt. rend.*, **248**, 794 1330 (1959).
33. N. B. Miller and V. A. Pleskov, *Dokl. Akad. Nauk SSSR*, **74**, 323 (1950); "Trudy Soveshchaniya po Elektrokhimii" (Transactions of the Electrochemical Conference), 1953, p. 165; N. B. Miller, Thesis, 1953.
34. G. M. Budov, Thesis, Moscow, 1962.
35. J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 951 (1952).
36. H. Gerischer and W. Vielstich, *Z. phys. Chem. (Frankfurt)*, **3**, 16; **4**, 10 (1955).
37. E. Mattson and J. O'M. Bockris, *Trans. Faraday Soc.*, **55**, 1586 (1959).
38. R. Audubert, *Compt. rend.*, **238**, 1997 (1954).

Institute of Electrochemistry,
USSR Academy of Sciences,
Moscow

Received 29th December 1961

Karpov Physicochemical Institute,
Moscow

MECHANISM AND EQUILIBRIUM IN THE REDUCTION OF NICKEL FERRITE WITH HYDROGEN

G. P. Popov and G. I. Chufarov

A number of studies have been made of the properties of nickel ferrite. It has been shown that NiFe_2O_4 has a spinel structure with a lattice constant of 8.333 Å. The constant for the distribution of iron(III) ions in NiFe_2O_4 between the tetrahedral and octahedral sublattices has been found to be 0.5.² The resistivity of nickel ferrite³ and the temperature variation of its heat capacity⁴ have been measured.

Nickel ferrite exhibits a region of homogeneity at 1300°.⁵ Studies have been made on the reduction of NiFe_2O_4 with carbon monoxide⁶, and on the ferritisation of $\text{NiO} + \text{Fe}_2\text{O}_3$ oxide mixtures^{7,8}. It has been shown^{9,10} that the mechanism of the reduction of NiFe_2O_4 with hydrogen and graphite under conditions far removed from equilibrium is variable and greatly depends on the relation between the rates of the chemical reaction and diffusion in the solid phase. No information is available about the mechanism of the reduction of NiFe_2O_4 under equilibrium conditions. The thermodynamic properties of this system have not been determined, apart from the standard enthalpy of formation of NiFe_2O_4 from the elements which has been calculated. The present paper describes a determination of the equilibrium conditions in the reduction of nickel ferrite with hydrogen.

EXPERIMENTAL

The reduction with hydrogen was carried out in a closed vacuum apparatus in which an $\text{H}_2 + \text{H}_2\text{O}$ mixture circulated. The pressure of water vapour was maintained equal to the saturated vapour pressure at 0°. After attainment of equilibrium, the weighed sample of ferrite was removed from the furnace by an electromagnetic device, the water vapour was frozen out in a trap immersed in liquid nitrogen, and the hydrogen pressure was measured. Equilibrium was approached both from the oxidation and the reduction side, the mean hydrogen pressure being taken as the equilibrium value. The degree of reduction was determined from the amount of hydrogen used up. The nature of the solids coexisting with the gas phase was determined by X-ray diffraction (Debye powder method) using $\text{Fe K}\alpha$ radiation and an MnO filter. The lattice constants were determined using the graphical extrapolation of Bradley and Jay.

Nickel ferrite was obtained by sintering an equimolar $\text{NiO} + \text{Fe}_2\text{O}_3$ mixture at 1200° in air for 30 h. The X-ray diffraction analysis showed that nickel ferrite is single-phase and has a lattice constant of 8.332 ± 0.005 Å, in agreement with the literature^{1,10}.

Mechanism of the Reduction of Nickel Ferrite

Fig. 1 shows the variation of the lattice constants of the phases which are present during the reduction of NiFe_2O_4 . Since the lattice constant of nickel ferrite is 8.333 Å and that of Fe_3O_4 is 8.38 Å,¹² we may conclude from the shape of curve 1 in Fig. 1 that NiFe_2O_4 is reduced to Fe_3O_4 , forming a continuous series of solid solutions which are gradually enriched in magnetite as reduction proceeds. The X-ray diffraction pattern at the same time reveals also the lines of metallic nickel, whose lattice constant remains almost unchanged up to 20% reduction. During this time removal of oxygen from the ferrite results in the formation of almost pure nickel. Later the lattice constant of the metallic phase increases, reaching 3.56 Å at 60% reduction. According to Bradley *et al.*¹³, this indicates the enrichment of the metallic phase in iron. When the extent of reduction reaches 60%, the reduction of the spinel phase terminates, and the second stage of the process begins in which FeO (with an admixture of nickel) is reduced to iron. The iron formed in this process continues to increase the lattice constant of the metallic phase, up to 3.584 Å at 75% reduction. Subsequently the lattice constant apparently varies, in accordance with the results of Bradley *et al.*¹³, along the