

SUMMARY

The composition of CO-CO₂ equilibrium mixtures for reaction (1) has been determined over the range 850°-1150° and found to vary little with temperature. An equation relating $\log K_p$ to $1/T$ has been derived [Eqn. (1a)]. The standard thermodynamic functions for reactions (3)-(5) are as follows:

$$\begin{aligned}\Delta H_{298}^0(3) &= -10.3 \text{ kcal mole}^{-1}, \quad \Delta G_{298}^0(3) = -9.1 \text{ kcal mole}^{-1}; \\ \Delta H_{298}^0(4) &= -138.3 \text{ kcal mole}^{-1}, \quad \Delta G_{298}^0(4) = -127.4 \text{ kcal mole}^{-1}; \\ \Delta H_{298}^0(5) &= -343.7 \text{ kcal mole}^{-1}, \quad \Delta G_{298}^0(5) = -319.8 \text{ kcal mole}^{-1}.\end{aligned}$$

1. K. Kelley, J. Amer. Chem. Soc., **63**, 2750 (1941).
2. R. L. Orr, J. Amer. Chem. Soc., **75**, 528 (1953).
3. W. Roth and H. Troitsch, Z. anorg. Chem., **260**, 337 (1949).
4. R. Schenck and K. Leiman, DOMEZ, **10** (1932).
5. A. N. Vol'skii, "Osnovy Teorii Metallurgicheskikh Plavok" (Fundamentals of the Theory of Metallurgical Smelting), Metallurgizdat, 1943, pp. 145-160.
6. B. G. Lebedev and V. A. Levitskii, Zhur. Fiz. Khim., **35**, 2788 (1961) [Russ. J. Phys. Chem., **1380** (1961)].
7. O. A. Esin and P. V. Gel'd, "Fizicheskaya Khimiya Pirometallurgicheskikh Protseessov" (Physical Chemistry of Pyrometallurgical Processes), Part I, Metallurgizdat, 1950, pp. 438-440.
8. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry" (Translated into Russian), Inostr. Lit., 1954.
9. F. D. Richardson and J. H. E. Jeffes, J. Iron Steel Inst., **163**, 4, 717 (1949).
10. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", 3rd Series, U. S. Nat. Bur. Stand., Circ. No. 500, Washington, 1952.

Moscow Steel Institute and
Lomonosov Moscow State University

Received 5th July 1961

POLARISATION OF THIN POROUS ELECTRODES

O. S. Ksenzhek

The problem of the distribution of polarisation within a porous electrode has been examined in a number of studies¹⁻⁴. It was usually assumed that the electrode is sufficiently thick to justify the following boundary condition at infinity in the solution of the differential equations:

$$\eta = 0 \text{ at } x = \infty,$$

where η is the polarisation. This condition holds sufficiently well when the electrode thickness is at least 2-3 times as great as the effective depth of penetration of the process into the porous electrode. The depth of penetration

depends on the structural characteristics of the electrode process, and is determined by the expression⁴

$$x_e = \sqrt{\frac{b}{2Si_0\rho}}, \quad (1)$$

where S is the specific surface area of the electrode, ρ the effective resistance of the electrolyte in the electrode pores, i_0 the exchange current, and b a constant (of the order of $2RT/F$).

The distribution of the process intensity within a porous electrode is non-uniform. The process occurs with maximum intensity in the surface layer of the electrode and at a depth of the order of x_e its intensity falls off sharply. It is therefore undesirable in practice to use porous electrodes which are thick compared with x_e , and we shall consider only the polarisation of electrodes which are thin in this respect.

The differential equation describing the steady-state operation of the porous electrode (under the condition of sufficiently intense internal convection ensuring constant concentration) may be written as follows⁴:

$$\text{div grad } \eta = 2Si_0\rho \sinh \frac{\eta}{b}. \quad (2)$$

In the subsequent treatment the one-dimensional case (planar electrode) will be examined and the following dimensionless quantities defining the polarisation, current density, and the linear dimension will be employed:

$$\psi = \frac{\eta}{b}, \quad J = \frac{i}{i_0}, \quad X = \frac{x}{x_e},$$

where

$$i_0 = \frac{b}{x_e\rho} = \sqrt{\frac{2Si_0b}{\rho}}.$$

On substituting these quantities in Eqn. (2), the latter can be transformed in the following way:

$$\frac{d^2\psi}{dX^2} = \sinh \psi. \quad (3)$$

The fact that the current across the back surface of the electrode (or across the plane passing through the middle of the electrode thickness in the case of two-sided operation) is zero may be used as the boundary condition in the case of a thin electrode. In order to integrate Eqn. (3), an expression for Ohm's law, which in terms of the above dimensionless quantities takes the form

$$\frac{d\psi}{dX} = -J, \quad (4)$$

is substituted. Single integration of (3) yields

$$J = \sqrt{2(\cosh \psi - \cosh \psi')}, \quad (5)$$

where ψ' is the polarisation of the back electrode surface. Second integration gives an expression for X :

$$X = kF(\varphi, k), \quad (6)$$

where $F(\varphi, k)$ is an elliptic integral of the first kind, k its modulus, and φ its amplitude. These quantities are given by the following expressions:

$$k = \frac{1}{\cosh \frac{\psi'}{2}}; \quad (7)$$

$$\varphi = \cos^{-1} \frac{\sinh \frac{\psi'}{2}}{\sinh \frac{\psi}{2}} = \sin^{-1} \frac{J}{2 \sinh \frac{\psi}{2}}. \quad (8)$$

For practical calculations it is more convenient to use X as an independent variable or parameter. The data calculated by formulae (5) and (6) are shown in Figs. 1–3 in this form. The relative quantity h characterising the efficiency of the electrode, is plotted as ordinate in Fig. 1. This quantity represents the ratio of the thickness of a fictitious porous electrode, such that the intensity of the process is distributed uniformly through its thickness, to the actual thickness of a real electrode at the same polarisation and current in both cases. The efficiency of the electrode h may also be defined as the ratio of the current at a porous electrode of the given thickness to the current which would pass, at the same polarisation, through a smooth (non-porous) electrode with surface area equal to the total surface area of the porous electrode:

$$h = \frac{J}{X \sinh \psi} \quad (9)$$

It is evident from Fig. 1 that at low currents the efficiency of a porous electrode is high (about 70%) at a thickness of the order of x_e , and gradually decreases — roughly in inverse proportion to the thickness. At very small currents expression (9) for h reduces to:

$$h = \frac{\tanh X}{X} \quad (10)$$

In this form the expression is convenient for the calculation of the efficiency of a thin porous electrode when the operation of the latter is determined by diffusion⁵. At large currents the efficiency of relatively thick electrodes falls off sharply.

Fig. 2 shows how the ratio of the current at a thin electrode to that at a similar electrode of unlimited thickness varies with the electrode thickness when the polarisation is the same for both. At small polarisations this ratio is proportional to $\tanh X$, but at higher polarisations the rate of increase is more rapid. For example at $\psi = 10$ an electrode with the thickness $X = 0.2$ is virtually indistinguishable in its characteristics from an electrode of unlimited thickness. Obviously, the use of a thicker electrode in this case is unjustified.

In industrial calculations of the minimum electrode thickness necessary to ensure an efficiency close to that of an electrode of unlimited thickness, the following approximate formula may be employed:

$$X_{\min} = \frac{5.5}{e^{\psi/2} + 2} = \frac{5.5}{J + 3} \quad (11)$$

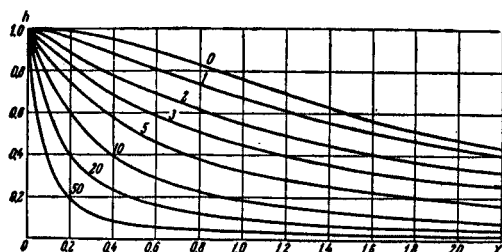


Fig. 1. Efficiency of a porous electrode as a function of its thickness at various currents. The numbers on the curves denote J .

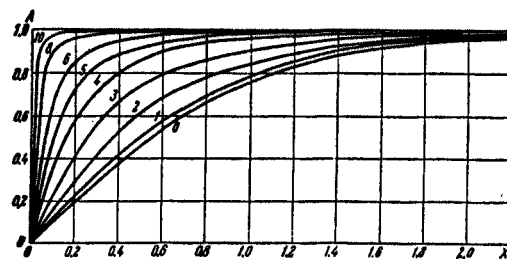


Fig. 2. Dependence of the ratio I_X/I_∞ on the thickness of the electrode at various polarisations. The numbers on the curves denote ψ . $A = I_X/I_\infty$. For example: $I_0/i_0 = 10^4$, $X = 0.01$, $J = 2 \times 10^2$ or 0.5×10^{-2} ; we find that $\Delta\psi = 3.75$.

At the electrode thickness $X_{\min}$ the efficiency is about 90% of that obtainable with a thick electrode.

Fig. 3 shows to what extent the polarisation of a porous electrode is smaller than that of a smooth electrode. In the case of an infinitely thick electrode the maximum decrease in polarisation compared with a smooth electrode occurs when $J = 1$. The polarisation of a smooth electrode is then given by

$$\psi_{\text{sm}} = \sinh^{-1} \frac{I_0 J}{2i_0} = \sinh^{-1} \frac{I_0}{2i_0} \approx 2.3 \log \frac{I_0}{i_0} \quad (12)$$

and that of a porous electrode by

$$\psi_{\text{por}} = 2 \sinh^{-1} \frac{J}{2} = 2 \sinh^{-1} \frac{1}{2} \approx 1. \quad (13)$$

The difference between the polarisations is

$$\Delta\psi_{\max} = 2.3 \log \left(\frac{I_0}{i_0} \right) - 1. \quad (14)$$

At current density J greater or smaller than unity the reduction of polarisation symmetrically decreases by 2.3 (ln 10) units of ψ when J changes by a power of ten.

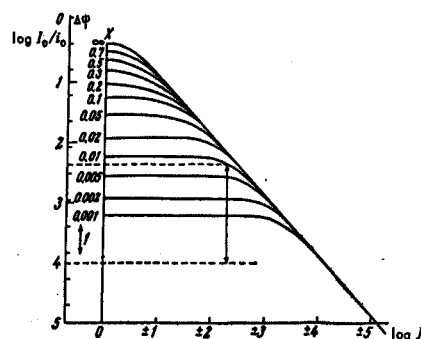


Fig. 3. Drop in polarisation at a porous electrode, compared with a smooth electrode, in relation to the current density, thickness of the porous electrode, and the ratio I_0/i_0 . For example: $I_0/i_0 = 10^4$, $X = 0.01$, $J = 2 \times 10^2$ or 0.5×10^{-2} ; we find that $\Delta\psi = 3.75$.

The current-density range in which the polarisation of a porous electrode is smaller than of a smooth one is, in logarithmic units, $2 \times 2.3 \log(I_0/i_0)$, i.e. it extends from $J = i_0/I_0$ to $J = I_0/i_0$ or from $I = i_0$ to $I = 2Sb/\rho$. Beyond the limits of this current-density range there is no point in using a porous electrode since no decrease in polarisation is obtained. The ratio I_0/i_0 , determining the useful current-density range, can be expressed in terms of quantities related to the structure of the porous electrode and to the electrode-process kinetics:

$$\frac{I_0}{i_0} = \frac{b}{x_e \rho i_0} = \sqrt{\frac{2Sb}{\rho i_0}} \quad (15)$$

The polarisation characteristics of electrodes whose thickness exceeds $(2-3)x_e$ are virtually indistinguishable from those of infinitely thick electrodes, regardless of the current density. With thinner electrodes the maximum decrease in polarisation in the neighbourhood of $J = 1$ becomes smoothed out and at $X \leq 0.1$ there is a current density range in which the decrease of polarisation remains constant (horizontal parts of the curves in Fig. 3). This means that at such current densities the polarisation curve for a porous electrode is parallel to that of a smooth electrode, being displaced towards higher current densities by $\log(Xx_eS)$. In other words the entire surface of the thin electrode is equally accessible under these conditions and the electrode may be regarded as a smooth one but having an effective surface Xx_eS ($Xx_eS = xS = XI_0/2i_0$) times greater than its apparent surface. The decrease in polarisation is then given by

$$\Delta\eta = 2.3 \log xS = 2.3 \log \left(\frac{1}{2} X \frac{I_0}{i_0} \right) \quad (16)$$

Obviously a decrease in polarisation in relation to a smooth electrode can only occur when the following condition holds:

$$X > \frac{2i_0}{I_0} \quad \text{or} \quad x > S^{-1} \quad (17)$$

This condition determines the minimum thickness of the electrode which can still be regarded as porous. Since the dimensions of the structural elements of a porous electrode (pores, grains) are of the order of S^{-1} , condition (17) corresponds to an electrode thickness commensurate with the dimensions of its constituent grains.

The current-density range in which the internal surface of a thin porous electrode may be regarded as practically equally accessible extends on the high current side to $J \approx X^{-1}$ ($I \approx b/x\rho$). At $J > 4X^{-1}$ a "thin" porous electrode may be regarded as infinitely thick, but at $X^{-1} < J < 4X^{-1}$ account must be taken of its finite thickness by using the exact formulae (5) and (6).

As an illustration of the above calculations consider the following concrete example: a porous electrode 3 mm thick with specific surface area $S = 2500 \text{ cm}^2 \text{ cm}^{-3}$ and the resistance of the electrolyte in the pores $\rho = 100 \Omega \text{ cm}$. The electrode process is characterised by the exchange current $i_0 = 10^{-8} \text{ A cm}^{-2}$ and $b = 0.05 \text{ V}$. We find that $x_e = (b/2Si_0\rho)^{1/2} = (0.05/2 \times 2500 \times 10^{-8} \times 100)^{1/2} = 3.16 \text{ cm}$, $I_0 = b/x_e\rho = 0.05/3.16 \times 100 = 1.58 \times 10^{-4} \text{ A cm}^{-2}$, $X = x/x_e = 0.3/3.16 \approx 0.1$, and $I_0/i_0 = 1.58 \times 10^{-4}/10^{-8} = 1.58 \times 10^4$. A decrease in polarisation (compared with a smooth electrode) may be observed between $J = 1/1.58 \times 10^4 = 0.63 \times 10^{-4}$ and $J = 1.58 \times 10^4$, i.e. between $I = 10^{-8} \text{ A cm}^{-2}$ and $I = 2.5 \text{ A cm}^{-2}$, which corresponds to the entire range of current densities obtainable in practice. The electrode polarisation at current densities up to $J \approx 0.1$ ($I \approx 1.5 \times 10^{-3} \text{ A cm}^{-2}$) is small;

between $J \approx 0.1$ and $J \approx 10$ ($I \approx 1.5 \times 10^{-3} \text{ A cm}^{-2}$) the polarisation increases by $2.3 \times 0.05 = 0.115 \text{ V}$ when the current increases tenfold, there being no significant difference in polarisation along the thickness of the electrode. The decrease in polarisation in this current-density range is $\Delta\eta = 2.3 \times 0.05 \log 0.3 \times 2500 = 0.33 \text{ V}$. Above $J \approx 40$ ($I \approx 6.3 \times 10^{-3} \text{ A cm}^{-2}$) the electrode behaves as a "thick" porous electrode; the slope of the polarisation curve in semilogarithmic coordinates increases twofold (0.23 V); the potential is distributed non-uniformly along the thickness of the electrode; the decrease in polarisation is less than 330 mV.

SUMMARY

The characteristic features of the polarisation of porous electrodes whose thickness is commensurate with the effective depth of penetration of the process into the electrode have been examined. Calculations have been made of the effectiveness of porous electrodes in relation to their thickness. The range in which porous electrodes are useful has been determined.

1. V.S. Daniel'-Bek, Zhur. Fiz. Khim., **22**, 697 (1948).
2. A.N. Frumkin, Zhur. Fiz. Khim., **23**, 1477 (1949).
3. O.S. Ksenzhek and V.V. Stender, Dokl. Akad. Nauk SSSR, **107**, 280 (1956).
4. D.A. Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), Izd. Akad. Nauk SSSR, Moscow-Leningrad, 1947.
5. O.S. Ksenzhek, Zhur. Fiz. Khim., **36**, 243 (1962) [Russ. J. Phys. Chem., **121** (1962)].

Dnepropetrovsk Institute of
Chemical Technology

Received 5th July 1960

THERMODYNAMIC INVESTIGATION OF ALLOYS BY AN E.M.F. METHOD USING A SOLID ELECTROLYTE WITH ANIONIC (OXYGEN) CONDUCTIVITY. I. Co_3W

T.N. Rezhukhina and Z.V. Proshina

At present the thermodynamic properties of intermetallic compounds for alloys not containing a volatile component are usually determined by an e.m.f. method using a liquid or solid electrolyte containing cations of the more active metal of the alloy. However, there is always the possibility that current can be conducted by ions of various charge types if the more active metal is capable of exhibiting valency greater than unity. Then in order to determine n in the formula $\Delta G^0 = -nFE$, it is necessary to perform additional electrochemical experiments, or the heat of formation of the alloy must be determined calorimetrically to correct the thermodynamic data obtained by the e.m.f. method. The indeterminacy is eliminated if