

therefore mistaken, and the concept of the λ -transition is devoid of clear physical meaning.

- Many changes in alloys represented by λ -points are in fact first-order phase transitions, with a large proportion of order-disorder processes, close to second-order phase transitions.
- The definition of second-order phase transitions proposed by Ehrenfest is inadequate, since similar discontinuities in properties are observed also with changes that are not phase transitions (vitrification).

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A METHOD FOR SEPARATING TWO SIMULTANEOUS ELECTRODE PROCESSES

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In electrochemical investigations it is often necessary to separate two processes occurring simultaneously at an electrode within a given potential range. Thus, for example, the polarographic reduction or oxidation waves for various substances at a dropping mercury electrode are distorted at high negative potentials by the simultaneous evolution of hydrogen or discharge of ions from the supporting electrolyte, and at potentials which are more positive than 0.3 V by dissolution of the mercury. It has proved extremely difficult to separate by electrochemical methods the main process under investigation from the subsidiary process. Such a separation may be accomplished by means of a rotating disc electrode¹, provided that the rate of one of the processes is limited by diffusion and hence depends, for a given potential, on the rate of stirring, while the rate of the other process does not depend on stirring. Among electrode processes of the latter type are, for example, the anodic dissolution of many metals, and the evolution of

hydrogen from acid solutions and of oxygen from alkaline solutions at not too high current densities.

According to Levich's theory of convective diffusion², when the rate of a process is governed by diffusion of the reactant to the electrode, the current density at a rotating disc electrode is given by the equation

$$i_1 = 0.62 n F D^{1/2} \omega^{1/2} \nu^{-1/4} (c_0 - c_s) = k \omega^{1/2}, \quad (1)$$

where n is the number of electrons taking part in the process, F is Faraday's constant, D the coefficient of diffusion of the reactant ions or molecules, c_0 their concentration in the bulk of the solution, and c_s the concentration near the electrode, ν is the kinematic viscosity of the solution, and ω the angular velocity of rotation of the electrode. In a reversible process, c_s depends solely on the electrode potential, and hence k is constant for a given potential, so that i_1 is proportional to $\omega^{1/2}$. If the concentration at the electrode surface c_s falls to zero, a limiting diffusion current is observed:

$$i_1^{\text{lim}} = 0.62 n F D^{1/2} \omega^{1/2} \nu^{-1/4} c_0. \quad (2)$$

It can be seen from (1) and (2) that in the case of a diffusion mechanism the velocity of the process is directly proportional to $\omega^{1/2}$. If, however, the rate of the second process is not limited by diffusion and does not depend on stirring, i.e. $i_2 = \text{const.}$, the total current varies linearly with $\omega^{1/2}$:

$$i = i_1 + i_2 = k \omega^{1/2} + i_2. \quad (3)$$

In the absence of convection, $\omega = 0$ and $i = i_2$. Thus by extrapolating the straight-line plot of i against $\omega^{1/2}$ to the value $\omega = 0$, it is possible to isolate that part (i_2) of the total current which does not depend on mixing and corresponds to a non-diffusion process. Subtraction of i_2 from the total current i (for a given value of ω) yields the other component i_1 for given conditions of mixing.

It must be emphasised that such a separation can be made by extrapolation to $\omega = 0$, but not by direct measurement of i in the absence of artificial mixing, since Eqns. (1) and (2) no longer hold at low values of ω because of the presence under normal experimental conditions of natural convection. This is the reason why the rate of a process with diffusion kinetics is not zero when measured experimentally at $\omega = 0$.

With $c_s > 0$, i.e. for $i_1 < i_1^{\text{lim}}$ (on the ascending portion of the wave), i_1 is proportional to $\omega^{1/2}$ only in reversible processes. For irreversible reactions, as Frumkin and Tedomradze³ have shown, this relationship is not maintained; however, even in this case it is possible, by (non-linear) extrapolation of the i vs. $\omega^{1/2}$ curve to $\omega = 0$, to separate i_1 and i_2 , although with a lower degree of accuracy.

A few examples of the application of the method are given below. Potential values are given relative to the normal hydrogen electrode.

EXPERIMENTAL

Ionisation of Oxygen at a Gold Electrode

Polarisation curves were recorded for a $N H_2SO_4$ solution saturated with oxygen at its usual partial pressure in air. The electrode was a gold disc of diameter 6.65 mm fixed to a vertical spindle; the sides of the spindle and the disc were sealed with a Teflon sheath. The electrode was rotated by a synchronous electric motor through a system



Fig. 1. Cathodic polarisation curves obtained with a gold disc electrode rotated at 2550 rev/min in NH_4SO_4 saturated with air: 1) experimental curve; 2) calculated curve for H_2 evolution; 3) calculated curve for ionisation of O_2 .

of pulleys, allowing the rate of rotation to be varied within wide limits. The number of rotations of the electrode per minute was measured by means of a tachometer.

Owing to the low overvoltage for hydrogen evolution on gold, the experimental polarisation curve for the ionisation of molecular oxygen is distorted by the simultaneous process of hydrogen evolution (Fig. 1, curve 1). Both these reactions are irreversible; but since in our case $[O_2] \ll [H^+]$, the rate of ionisation of O_2 is governed by diffusion and depends on ω , but the rate of evolution of H_2 (for low values of i) does not depend on stirring.

The relationship between the current i at various potentials and $\omega^{1/2}$ is shown in Fig. 2. Extrapolation of the straight lines in Fig. 2 to $\omega = 0$ separates that part of the total current which does not depend on the rate of stirring, and the resulting values are plotted in Fig. 1 (curve 2). The calculated curve 2 corresponds to hydrogen evolution. Subtraction of the values of the current density corresponding to curve 2 from the total current (curve 1) yields the calculated curve 3 for the ionisation of molecular oxygen.

Oxidation of Monovalent Silver Ions at a Gold Electrode in Potassium Hydroxide Solution

Oxidation of $Ag(I)$ ions at the electrode is accompanied by oxygen evolution, and the experimental polarisation curve does not show a sufficiently well marked wave for the oxidation of silver ions (Fig. 1 in the previous communication¹). The above method was used to obtain calculated curves for the evolution of oxygen (the rate of which does not depend on the rate of stirring) and the oxidation of Ag_2O . The latter curve has two well marked waves, the height of which (the value of the limiting current) is proportional to $\omega^{1/2}$ and the concentration of Ag_2O . The height of the first wave is equal to the height of the cathodic wave for the reduction of $Ag(I)$ ions in the same solution to metallic silver. The first wave thus represents the single-electron process of the oxidation of univalent silver ions to Ag_2O . The second wave is twice as high as the first, and corresponds to the oxidation of $Ag(I)$ ions to an oxide of trivalent silver.

The accuracy of the determination of the limiting current from the calculated curve for the oxidation of Ag_2O is about

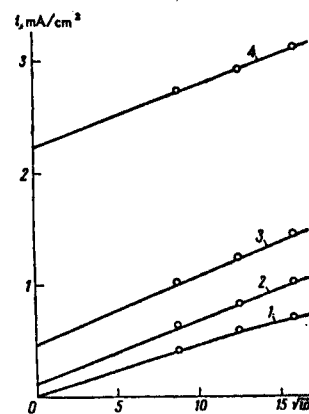


Fig. 2. Variation of current density (Fig. 1, curve 1) with angular velocity of rotation of electrode for various values of the potential: 1) -0.22 V; 2) -0.32 V; 3) -0.42 V; 4) -0.52 V.

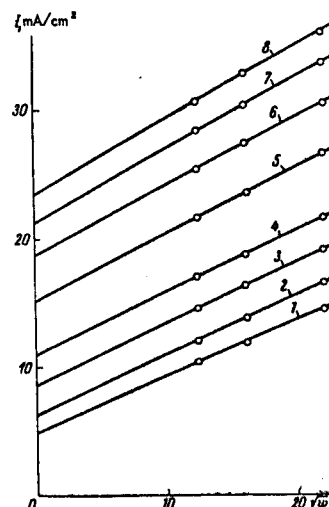


Fig. 3. Variation of current density for oxidation of V^{2+} ions at a germanium electrode in a solution of 0.067 M $VSO_4 + 2.2$ M $H_2SO_4 + 0.9$ M $ZnSO_4$ with angular velocity of rotation of electrode: 1) 0.58 V; 2) 0.78 V; 3) 1.28 V; 4) 1.78 V; 5) 2.78 V; 6) 3.28 V; 7) 3.78 V; 8) 4.28 V.

5%; the method can be applied even if the rate of oxygen evolution is 10–15 times the rate of oxidation of silver ions.

Oxidation of V^{2+} Ions at a Germanium Electrode

A solution of V^{2+} was prepared by reduction of V_2O_5 in H_2SO_4 solution with amalgamated zinc. Because of the ready oxidisability of V^{2+} , measurements were carried out in an atmosphere of nitrogen purified from traces of oxygen.

A germanium disc electrode of diameter 6.5 mm was prepared, in a manner similar to that described above for the gold electrode, from a single crystal of n -type germanium (resistivity 1.8Ω cm, diffusion length of holes 0.3 mm).

The oxidation of V^{2+} ions at a germanium anode is accompanied by dissolution of the germanium. The total current varies linearly with $\omega^{1/2}$ (Fig. 3). Application of the above method enabled the polarisation curve for the dissolution of Ge, the rate of which does not depend on mixing the solution, to be separated from the curve for the oxidation of V^{2+} ions, the rate of which is limited by the diffusion of the ions to the electrode and is proportional to $\omega^{1/2}$. The limiting current density in the calculated curve for the oxidation of V^{2+} is equal to the limiting current density in the experimental curve for the oxidation of V^{2+} ions at a rotating platinum electrode in the same solution. The results of the investigation of this system have already been reported in detail⁴.

SUMMARY

1. A method has been worked out for separating two processes occurring simultaneously at an electrode when the rate of one of the processes is limited by diffusion of the reactant to the electrode, and consequently depends on the efficiency of mixing of the solution, while the rate of the second process is independent of stirring.
2. The method has been applied to a study of the oxidation of Ag_2O in KOH solution, the ionisation of molecular oxygen at a gold electrode, and the oxidation of divalent vanadium at a germanium electrode.

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A SPECTROPHOTOMETRIC STUDY OF THE REACTION BETWEEN SODIUM 1,8-DIHYDROXY-2-(2-HYDROXYAZO-BENZENE)NAPHTHALENE-3,6-DI-SULPHONATE AND CADMIUM AND MERCURIC IONS

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We have recently undertaken a systematic study of the reaction in aqueous solution of cations of the Second Group of the Periodic System with sodium 1,8-dihydroxy-2-(2-hydroxyazobenzene)naphthalene-3,6-disulphonate, which is widely used in analytical chemistry as a "metal indicator" in complexometric titration¹. The reagent behaves as a tribasic weak acid H_3R^{2-} , whose successive dissociation constants are $K_1 = 2.8 \times 10^{-8}$, $K_2 = 5.3 \times 10^{-10}$, and $K_3 = 4.0 \times 10^{-13}$.² Our studies have shown that with ions of magnesium³, calcium, strontium, barium⁴, and zinc⁵, the dyestuff forms complexes of the same composition, $M(HR)_2^{2-}$,

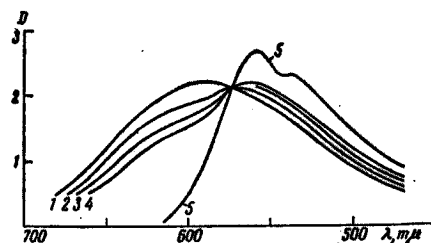


Fig. 1. Absorption curves of solutions containing the reagent ($C_R = 1 \times 10^{-4}$ M) and varying concentrations of cadmium ions at pH 9.3: 1) pure reagent; 2) $C_{Cd} = 1 \times 10^{-5}$ M; 3) $C_{Cd} = 3 \times 10^{-5}$ M; 4) $C_{Cd} = 5 \times 10^{-5}$ M; 5) excess of cadmium ions. Thickness of solution 3.0 cm.

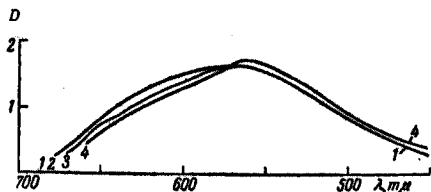


Fig. 2. Absorption curves of solutions containing the reagent ($C_R = 1.5 \times 10^{-4}$ M) and varying concentrations of mercuric ions at pH 9.3: 1) pure reagent; 2) $C_{Hg} = 3.4 \times 10^{-5}$ M; 3) $C_{Hg} = 6.8 \times 10^{-5}$ M; 4) $C_{Hg} = 6.8 \times 10^{-5}$ M. Thickness of solution 1 cm.

whose instability constants are 3.1×10^{-9} , 5.3×10^{-10} , 7.7×10^{-8} , 7×10^{-6} , and 3.0×10^{-11} respectively. The present paper concerns its reaction with cadmium and mercuric ions.

EXPERIMENTAL

The procedure for studying the equilibria, the apparatus, and the preparation of the dyestuff have already been described^{2,3}. Cadmium sulphate and mercuric nitrate were purified by appropriate methods. The cadmium-ion concentration was taken from the weight of sample, and the mercuric-ion concentration was found by titration.

Figs. 1 and 2 show the influence of cadmium and mercuric ions on the absorption curves of the reagent; the measurements were carried out at pH 9.3, analogous results being obtained at pH 11.5. The absorption curves change considerably on introducing increasing amounts of cadmium ions; with excess of the latter the absorption curve has $\lambda_{max} = 558$ mμ, the position of the maximum and the form of the curve remaining unchanged when the pH is increased to 11–12. Mercuric ions have a considerably smaller effect on the absorption curves of the reagent, but the general character of the changes is the same as for cadmium.

As in our earlier studies, the composition of the complex was determined by Ostromyslenskii's method at pH 8–12 (ammonia buffer). The optical densities of the solutions were measured at $\lambda = 620$ mμ on the monochromator UM-2 in 0.05 cm cells. The concentration of the original equimolar solutions varied from 1.0×10^{-3} to