8. *Dissolution of Metals and Alloys. Part I. The Dissolution of Copper in Solutions containing Persulphate Ion.*

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The reaction whereby metals dissolve in solutions containing persulphate ion has been examined for its suitability in assessing electronic factors in dissolution processes. Copper readily dissolves in such solutions near room temperature, but the reaction is transport-controlled at $[S_2O_8^{2-}] \leqslant 0\cdot025$M and at all concentrations up to 0·1M above 35°. The activation energy for transport control is 5·5 kcal./mole and the order of reaction increases with temperature to a limiting value of 1·2. At $[S_2O_8^{2-}] \geqslant 0\cdot25$M the activation energy is constant at 10·3 kcal./mole. Rotation of the copper increases the rate, the more markedly the higher the temperature and the concentration. The rate at 12° and 500 r.p.m. in 0·1M-solutions is substantially free from transport control, and under these conditions the order in persulphate ion is almost zero. The activation energy for the surface process is about 16·5 kcal./mole.

MUCH information has recently been obtained on the effect of the electronic constitution of metals and alloys on their ability to act as heterogeneous catalysts. The necessarily weak chemisorption through which efficient catalysis proceeds is shown by those metals (especially nickel, palladium, and platinum) which have both (i) nearly filled *d*-bands and (ii) a high density of energy levels at the Fermi surface.[1] It is generally assumed that in alloys of one of these metals with a Group IB metal the *d*-band is filled at a concentration of the latter of about 60%, but there is much evidence to show that the nickel–copper system is anomalous.[2]

Relatively little fundamental work has been performed on the effect of electronic constitution on the rate of dissolution of metals and alloys in liquids, although the matter is of great relevance to corrosion. The rate of dissolution of nickel–copper alloys in sea water [3,4] and in sodium chloride solution [5] increases very rapidly with increasing copper content above about 60%. No values for the Arrhenius parameters *A* and *E* were reported.

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[1] Dowden, *J.*, 1950, 242.
[2] See, *e.g.*, Coles, *Proc. Phys. Soc.*, 1952, **65**, *B*, 221.
[3] Friend, *J. Inst. Metals*, 1932, **48**, 109.
[4] LaQue, *Amer. Soc. Naval Engrs.*, 1941, **53**, 29.
[5] Uhlig, *Ann. New York Acad. Sci.*, 1954, **58**, 843.

Such systems do not however readily lend themselves to quantitative investigation, and alternative systems have been sought.

It has long been known that many metals dissolve in solutions containing persulphate ions, which act as electron acceptors: the more electropositive metals yield simple cations, *e.g.*, $Cu + S_2O_8^{2-} \longrightarrow Cu^{2+} + 2SO_4^{2-}$. Of the familiar metals, only platinum and gold do not so react.[6] It appeared that this process might be suitable as a means of assessing the electronic influence in dissolutions.

Reactions at solid–liquid interfaces are complicated by transport phenomena.[7] The chief object of this work was to determine under what conditions transport control could be overcome, thus enabling the surface reaction to be studied.

EXPERIMENTAL

Preparation and Estimation of Persulphate Solutions.—Initial experiments were performed with solutions of potassium persulphate, 0·1M-solutions of which were prepared only with difficulty at 18°; they became supersaturated at 0°. Concentrations were estimated by reducing the persulphate with excess of ferrous sulphate and back-titrating the unchanged ferrous ion with 0·1N-potassium permanganate.[8] Potassium persulphate solutions, initially of greater than 99% of the expected concentration, decomposed slowly at room temperature;[9] fresh solutions therefore were prepared daily.

Since it was later desired to carry out experiments with solutions more concentrated than 0·1M, attention was turned to other salts. Evolution of nitrogen was apparent during the attempted preparation of 0·1M-solutions of ammonium persulphate, presumably owing to oxidation of ammonium ion by persulphate ion. Such solutions had initially about 68% of the expected concentration, but thereafter decomposed only slowly: massive decomposition therefore occurs only during the dissolution, perhaps owing to the need to have solid present to nucleate the nitrogen bubbles. Ammonium persulphate solutions were clearly not acceptable for quantitative work.

The ratio of the estimated to the expected concentrations of sodium persulphate solutions is a minimum for solutions expected to be 0·25M (Table 1): no reason for the apparent dependence of this ratio on expected strength can be given. A graph was drawn, and the actual concentration of any solution was calculated by multiplying that expected by a factor obtained by interpolation within the graph. Sodium persulphate solutions decomposed only slowly on standing, but fresh solutions were prepared daily. All solutions were made up at the temperature at which they were to be used.

TABLE 1. *Expected and estimated concentrations of sodium persulphate solutions.*

Expected (M)	0·1	0·25	0·5	1·0
Estimated (M)	0·0932, 0·0930	0·2290, 0·2285	0·4645	0·940
Estimated/expected	0·932, 0·930	0·916, 0·914	0·929	0·940

Preparation of Copper Specimens.—Copper specimens (*ca.* 1·0 × 1·5 cm.) were cut from a sheet of "AnalaR" copper foil, 0·11 mm. thick. The removal of superficial tarnish and grease with a commercial metal polish, followed by polishing and washing with acetone, did not lead to reproducible rates. A variety of subsequent treatments was tried: treatment with concentrated hydrochloric acid led to faster but still irreproducible rates, and the finally adopted procedure was to etch the specimen for 20 sec. in 8M-nitric acid at 18° ± 2°. A standard specimen weighed 0·147 g. before and close to 0·140 g. after etching: the geometic area of the specimen after etching was estimated to be 3·05 cm.^{2}.

Procedure.—The reaction was followed by periodically determining the loss in weight of the copper. For experiments performed without rotation of the copper, 50 ml. of the solution were placed in a 100 ml. conical flask and brought to the required temperature: the copper was

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[6] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, London, 1930, Vol. X, p. 468.

[7] See, *e.g.*, Bircumshaw and Riddiford, *Quart. Reviews*, 1952, **6**, 157.

[8] Scott and Furman, "Standard Methods of Chemical Analysis," Technical Press Ltd. London, 1952, 5th edn., Vol. I, p. 922.

[9] Bawn and Margerison, *Trans. Faraday Soc.*, 1955, **51**, 925.

placed in a holder constructed from thin glass rod (Fig. 1*a*) and then inserted into the solution. The copper was removed, washed, dried and weighed at intervals of 5, 10, or 15 min.

In some experiments the copper was rotated in 75 ml. of the solution in a 100 ml. conical flask, a holder of the type shown in Fig. 1*b* being used. The holder was rotated by an electric motor whose speed was manually adjusted with a rheostat; rates of revolution were measured by a tachometer. Other procedures were as before.

Standard methods of temperature control and measurement were employed.

FIG. 1. (*a*) *Holder used when there was no rotation of the copper.* (*b*) *Holder used when the copper was rotated.*

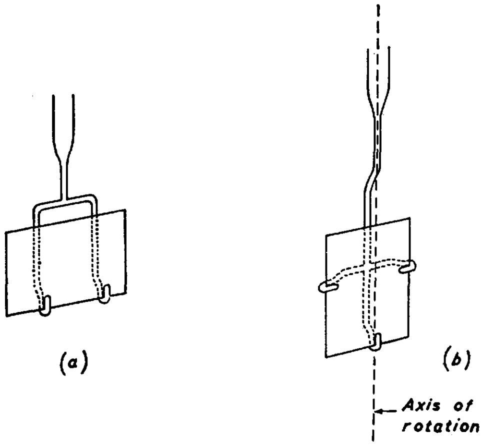
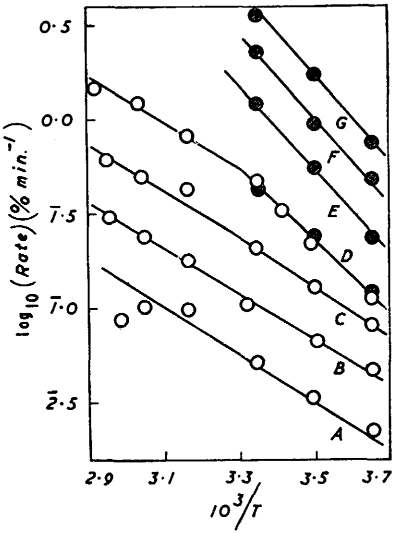


FIG. 2. *Dependence of* $\log_{10}$ *rate on reciprocal absolute temperature at various concentrations of persulphate ion.*



○ Potassium persulphate.
● Sodium persulphate.

A, 0·0125M; *B*, 0·025M; *C*, 0·050M; *D*, 0·10M; *E*, 0·25M; *F*, 0·50M; *G*, 1·00M.

RESULTS AND DISCUSSION

Expression of Rates and Shapes of Weight Loss–Time Curves.—The geometric area of a specimen is to a close approximation proportional to its weight for small deviations from standard size. The rate being assumed to be proportional to the area, such deviations were allowed for by expressing rates in terms of a percentage loss in weight, $(\Delta w/w_0) \times 100$, where w_0 is the initial weight (after etching) and Δw the change in weight in the same units. Thus a rate of 1·0% min.$^{-1}$ corresponds to the dissolution of 1·47 mg. of copper min.$^{-1}$ from a standard specimen, and therefore to 0·48 mg. of copper cm.$^{-2}$ min.$^{-1}$. This is equivalent to a rate of change in persulphate-ion concentration of $2{\cdot}62 \times 10^{-7}$ g.-ion l.$^{-1}$ min.$^{-1}$ cm.$^{-2}$. After 50% dissolution, the geometric area was decreased only by about 1% and no change in rate was noticed until more than 80% of the copper had dissolved, provided that the initial concentration of persulphate ion was sufficiently high. When this condition was not fulfilled ($[S_2O_8^{2-}] < 0{\cdot}025$M), rates decreased from the start and were proportional to the instantaneous concentration of persulphate ion. First-order rate constants were then determined and the initial rates calculated therefrom.

Dependence of Rates on Temperature and on Persulphate-ion Concentration with Potassium Persulphate and No Rotation of the Copper.—The results are shown in Fig. 2. The activation energies shown at the two lowest concentrations are constant over the whole range of temperature at 5·5 kcal./mole. At the two higher concentrations, the activation energies also have this value above about 35°, but between 0° and 35° the value for 0·05M-solutions is 6·5 and for 0·10M-solutions 9·1 kcal./mole. These and subsequently quoted activation energies are not uncertain by more than ±0·2 kcal./mole.

Now the activation energy of a process whose rate is determined by transport of ions through a solution will be approximately that for the diffusion of ions through the solution, typically about 1 kcal./mole greater than E_v, the activation energy for kinematic viscous flow.[10] E_v for water has been estimated as $4{\cdot}40 \pm 0{\cdot}05$ kcal./mole between 0° and 25° (Orr and Butler [11] give 4·2 kcal./mole between 0° and 45°), and for 0·1M-potassium persulphate solution as 4·1 kcal./mole in the same temperature range. The lower value in the latter case arises because the solution becomes progressively *less* viscous than water with decreasing temperature, presumably owing to the progressively increasing degree of hydration of the ions, which " de-polymerises " the water structure. The kinematic viscosity for the potassium persulphate solution is 1·480 centistokes at 5° as against 1·519 centistokes for water at this temperature.

It is concluded that under conditions where the activation energy of the dissolution is 5·5 kcal./mole the reaction is completely transport-controlled, and that for solutions greater than 0·025M below about 35° transport control in not complete.

These results also give the following values of the order of the reaction in persulphate-ion concentration at various temperatures in 0·0125—0·1M-potassium persulphate: 0·75 (0°), 0·92 (12·0°), 1·02 (25·0°), 1·10 (42·7°), 1·20 (55·0°), 1·19 (65·0°). A temperature-dependent order necessarily follows from a concentration-dependent activation energy: the order is independent of temperature when the reaction is transport-controlled at all concentrations, but no explanation can be offered for a limiting value greater than unity. The significance of reaction order will be reverted to later.

Dependence of Rates on Temperature and on Persulphate-ion Concentration with Sodium Persulphate and No Rotation of the Copper.—The above results show a concentration-dependent activation energy, and to determine whether a limiting value was attained with increasing concentration it was necessary to use a more soluble persulphate, namely, sodium persulphate. Results are shown in Fig. 2. Rates obtained by use of either the sodium or the potassium salt (0·1M) are closely similar at all temperatures: the activation energies are therefore also similar (8·8 as against 9·1 kcal./mole). At all concentrations higher than 0·1M the activation energy is constant at 10·3 kcal./mole, and this limiting value implies no change in the degree of transport control with increasing concentration greater than 0·1M. Whether transport control is completely absent under these conditions has yet to be established.

The dependence of order of reaction on temperature for 0·1—1·0M-sodium persulphate solutions is 0·78 (0°), 0·87 (12·0°), 1·06 (25·0°; 0·1—0·5M only). The values at each temperature correspond closely with those for potassium persulphate solutions. The full results for the dependence of the rate on concentration at 25° are shown in Fig. 3: the order is 1·06 for concentrations less than about 0·5M, whereafter there is a progressive decrease in order with increasing concentration. Now the degree of transport control varies with concentration below about 35°: apparent reaction orders less than unity are obtained where partial transport control operates, and they decrease with decreasing temperature, *viz.*, as the degree of transport control at constant concentration decreases. Orders at all temperatures should be unity at sufficiently low concentrations, and the implication is that zero orders would obtain at sufficiently high concentrations. The results in Fig. 3 show this trend clearly. The reaction might well be of zero order when there is no transport control if persulphate ions are adsorbed at the copper surface before reacting; a limiting rate would obtain when the persulphate-ion concentration in solution is high enough to form a monolayer of ions at the copper surface.

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[10] Riddiford, *J. Phys. Chem.*, 1952, **56**, 745.
[11] Orr and Butler, *J.*, 1935 1273.

Dependence of Rate on Temperature and on Persulphate-ion Concentration at Various Rates of Rotation of the Copper in Potassium Persulphate Solutions.—The critical test for the absence of transport control in reactions at solid–liquid interfaces is the independence of the reaction rate, R_D, of the rate of rotation of the solid, R_R (see Fig. 4). At 12° R_D becomes independent of R_R at rates greater than about 350 r.p.m.: R_D at 500 r.p.m. is 0·335% min.$^{-1}$, or 1·94 × 10^{-7} g.-ion of $S_2O_8^{2-}$ min.$^{-1}$ l.$^{-1}$ cm.$^{-2}$, and this is the rate of

FIG. 3. *Dependence of* log *rate on* log [$S_2O_8^{2-}$] *at* 25° *with sodium persulphate concentration.*

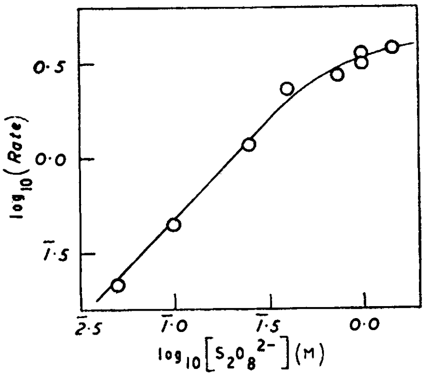
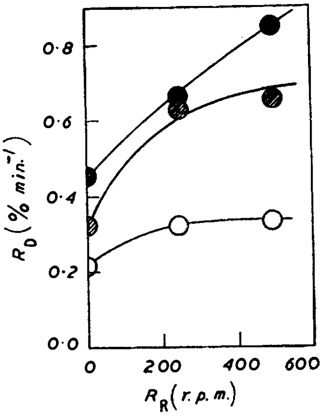


FIG. 4. *Dependence of rate R_D on rate of rotation R_R for* 0·1M-*potassium persulphate at various temperatures.*



○ 12·0°; ◍ 19·0°; ● 25·0°

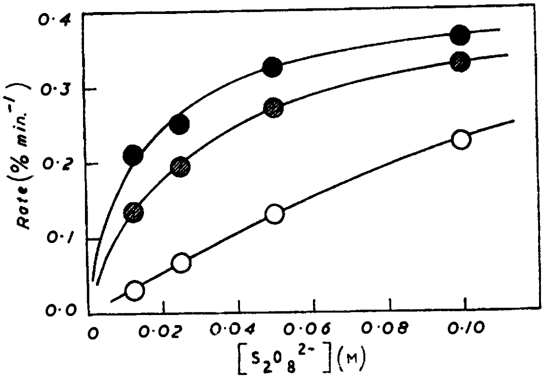


FIG. 5. *Dependence of rate on concentration at* 12·0° *with various rates of rotation.*

○ No rotation; ◍ 250 r.p.m.; ● 500 r.p.m.

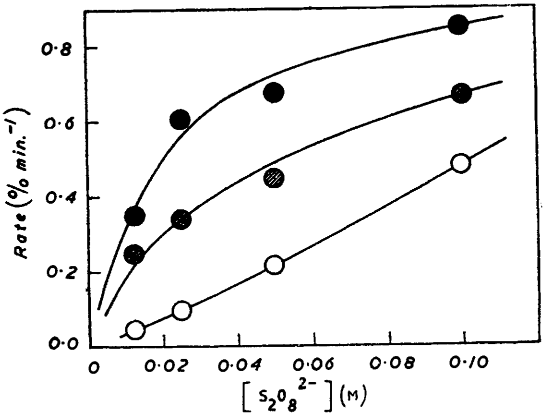


FIG. 6. *Dependence of rate on concentration at* 25·0° *with various rates of rotation.*

○ No rotation; ◍ 250 r.p.m.; ● 500 r.p.m.

dissolution at this temperature uninhibited by transport phenomena. Fig. 4 shows as expected that progressively higher values of R_R are required to overcome transport control as the temperature is raised, and while R_D at 19° and 500 r.p.m. (0·660% min.$^{-1}$) may be substantially free from such control, R_D is almost proportional to R_R at 25°. As it proved impossible to rotate the copper at speeds much in excess of 500 r.p.m., since turbulent flow sets in between 700 and 800 r.p.m. and eddies then form around it, there is only a small temperature range (15—20°) in which the activation energy of the true dissolution process can be determined, and little accuracy can therefore be expected. The rates at 12° and 19° at 500 r.p.m. correspond to an activation energy of about 16·5 kcal./mole, which is considerably greater than the limiting value found with concentrated solutions of sodium persulphate when the copper was not rotated (10·3 kcal./mole).

Experiments were also performed to determine the effect of persulphate-ion concentration (0·0125—0·1M) on reaction rates at various values of R_R at both 12° and 25°; the results are shown in Figs. 5 and 6 together with those found when the copper was not rotated. Fig. 5 confirms that the order in persulphate ion is low when transport control has been overcome (*i.e.*, in the region of 0·1M at 500 r.p.m.). Fig. 6 shows as expected that at 25° higher concentrations for a given value of R_R are required to attain the limiting rate. Experiments involving rotation of the copper have not been carried out in sodium persulphate solutions, but the results indicate that the use of, say, 1·0M-persulphate-ion concentration and an R_R of 500 r.p.m. would enable the true rate of the dissolution to be determined over a substantial temperature range.

We are grateful to Dr. John Shorter who first drew our attention to this reaction.

THE UNIVERSITY, HULL. [*Received, August 8th,* 1958.]