

408. *Dissolution of Metals and Alloys. Part II.*¹ *The Dissolution of Iron, Cobalt, and Copper, and of Some Nickel-Copper Alloys in Solutions of Sodium Persulphate.*

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Iron, copper, and cobalt foils dissolve in solutions of sodium persulphate near room temperature, their reactivity decreasing in the order listed. Rates free from transport-limitation resulted on use of M-solutions and rotation of the foils at 500 r.p.m., and the following activation energies were found: Fe, 6.5; Co, 11.9; Cu, 11.2 kcal. mole⁻¹. Rates of dissolution of the three metals have been measured over at least the concentration range 0.1—1M, with rates of rotation of zero, 250, and 500 r.p.m. at three temperatures, and the results have been interpreted.

Nickel is unreactive.

The activation energies for the transport-free dissolution of nickel-copper alloys fall with increasing nickel content to a limiting value of 7.2 kcal. mole⁻¹ which holds for nickel contents between 40 and 90%. The rates vary irrationally from one alloy to another owing to development of different degrees of surface roughness. The rate-limiting step, for both alloys and metals, is probably the transfer of an electron therefrom to a persulphate ion.

IN Part I¹ we described preliminary experiments on the dissolution of copper in solutions containing persulphate ion: these were performed to assess whether this reaction could be used for studying the role of electronic factors in dissolutions. It was predicted that rates free from transport-limitation should be obtainable near room temperature, at high concentrations of persulphate ion (~ M), and with rapid stirring (500 r.p.m.).

¹ Part I, Bond, Hill, and Tennison, *J.*, 1959, 33.

This prediction has been confirmed, and this paper describes the kinetics of the chemically controlled reaction of iron, cobalt, and copper, and of some nickel-copper alloys, with solutions of sodium persulphate; the rates were all readily measurable between 0° and 25°. An attempt to study the kinetics of the dissolution of nickel was frustrated by the extreme slowness of the reaction.

EXPERIMENTAL

The apparatus and procedure were essentially as described in Part I.¹ Solutions of sodium persulphate (from British Drug Houses Ltd.) were used; the ratio of their estimated to their expected concentrations over the range 0.1—1M was constant at 1:0.955. No evidence was found for dependence of this ratio on the expected strength, as reported earlier.¹

Cobalt specimens were cut from foil (99.99%; 0.105 mm. thick) supplied by Johnson, Matthey and Co. Ltd., iron specimens from foil (99.9%; 0.11 mm. thick) supplied by the British Iron and Steel Research Association, and the alloy specimens from foils (~0.105 mm. thick)

TABLE I.
Treatment and analysis of nickel-copper alloys.

Nominal % Cu	Etching conditions		X-Ray fluorescence analysis				Volumetric analysis Cu (%) in alloy
	[HNO ₃] (M)	Time of etch (sec.)	Before reaction		After reaction		
			Mean % Cu	Δ †	Mean % Cu	Δ †	
100	8	10	—	—	—	—	100.1
90	9	10	90.1	0.2	89.9	0.1	—
80	9	10	80.6 ₅	0.7	79.4	0.0	80.2
70	9.5	8	71.2 ₅	2.5	70.0 ₅	0.3	71.7
60	9.5	10	62.4 ₅	0.3	60.3 ₅	1.3	62.9
50	9.5	10	51.6 ₅	1.3	49.2	0.4	52.3 *
40	9.5	15	42.2 ₅	0.5	39.8	0.0	42.6
30	10.5	40	31.6	1.2	36.2	2.0	32.7
20	10.5	50	19.9	0.2	20.8 ₅	2.1	19.9
10	13.0	70	10.0	0.0	7.5	1.6	10.0 ₅
0	16.0	40	—	—	—	—	—

* See text. † Difference between the two sides of the sheet.

supplied by the Mond Nickel Co. All the metal specimens were cut to a standard size (1.5 × 1.0 cm.), cleaned with a commercial metal polish, polished, washed with acetone, and etched with nitric acid: the etching conditions were adjusted as far as possible to remove about 5 mg. of the alloy or metal. These conditions are summarised in Table I.

RESULTS

For each metal, the rate of dissolution was assumed to be proportional to the area of the specimen, small deviations from the standard area being allowed for by expressing the rates as a percentage loss in weight ($100 \Delta w/w_0$), where w_0 is the initial weight (after etching) and Δw is the change in weight in the same units. Thus a rate of 1% min.⁻¹ corresponds to the dissolution of 7.56×10^{-7} g.-atom of copper cm.⁻² min.⁻¹, 8.07×10^{-7} g.-atom of cobalt cm.⁻² min.⁻¹, and 7.98 g.-atom of iron cm.⁻² min.⁻¹.

The values reported for the activation energies and for $\log_{10} A$ were calculated from the Arrhenius plots by the method of least squares, the limits quoted being the standard deviations.

Further Results for Copper.—For all solutions other than 1.0M, the graphs of percentage weight loss against time were linear until more than 80% of the copper had dissolved. With 1.0M-solutions the rate increased during the initial stages of reaction before reaching a constant value. The amount of copper dissolved before this constant rate was obtained was 53 ± 6 mg. irrespective of the rate of rotation and of temperature. From the observations made during the non-linear period, it was possible to estimate initial rates of reaction, which are further discussed below. The remainder of this section is concerned only with the constant rates.

The results reported earlier¹ indicated that the use of higher concentrations of sodium persulphate and rotation of the copper specimen would enable the chemically controlled rate

of dissolution to be determined. Figs. 1—3 show the dependence of the rate on the sodium persulphate concentration and on the rate of rotation at $25.0^\circ \pm 0.2^\circ$, $12.0^\circ \pm 0.2^\circ$, and $0.0^\circ \pm 0.2^\circ$, respectively. These Figures include the results from Part I (filled circles; the curves are those calculated on the basis of a theoretical treatment presented in the Discussion.

The critical test for the absence of transport control in reactions at solid-liquid interfaces is the lack of dependence of the rate of dissolution on the rate of rotation of the solid. At 0° the reaction is chemically controlled at concentrations of 0.1M and above, and at rates

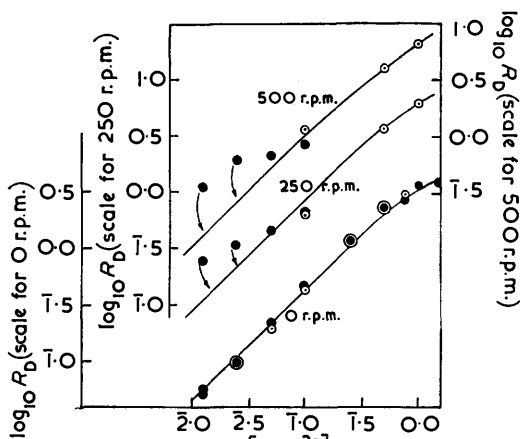


FIG. 1.

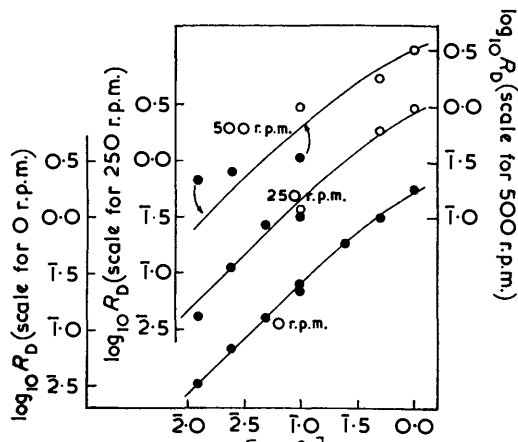


FIG. 2.

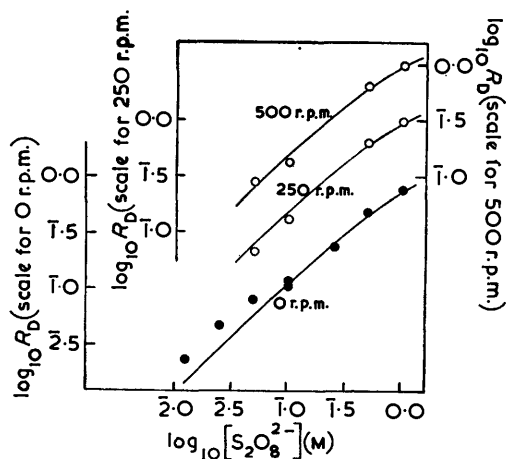


FIG. 3.

FIGS. 1—3. The dependence of \log (rate of dissolution, R_D) on \log (concentration of sodium persulphate) for copper at various rates of rotation at 25.0° (Fig. 1), 12.0° (Fig. 2), and 0.0° (Fig. 3). Open points, this work; filled points, from Part I. The curves are calculated (see Discussion).

of rotation at and above 250 r.p.m. However, as expected, the minimum concentration required to give chemical control increases with temperature, so that at 12.0° and 25.0° the rates at 250 and 500 r.p.m. are the same only at a concentration of 1.0M. Pairs of experiments in which the rates of rotation were 250 and 500 r.p.m. were also performed at this concentration at 5.5° , 19.0° , and 30.8° . All these results are given in Table 2. From the mean rates the

TABLE 2.

Rates of dissolution of copper in M-sodium persulphate at various temperatures.

Temperature	0.0°	5.5°	12.0°	19.0°	25.0°	30.8°
Rate at 250 r.p.m. (% min. ⁻¹)	1.00	2.05	2.98	4.54	6.25	9.00
Rate at 500 r.p.m. (% min. ⁻¹)	1.00	2.11	3.05	4.66	6.60	9.50
10 ⁶ × Mean rate (g.-atom of Cu cm. ⁻² min. ⁻¹)	0.76	1.57	2.28	3.48	4.86	6.99

value of the activation energy is 11.21 ± 0.07 kcal. mole⁻¹ and of $\log_{10} A$ is 2.93 (A being in g.-atom of Cu cm.⁻² min.⁻¹).

Results for Cobalt.—The rates of dissolution of cobalt were markedly slower than the corresponding rates for copper, under all conditions. The plots of percentage loss in weight against time were always linear. The results (Figs. 4—6) show that at each temperature, with a concentration of 1.0M, the rates at 250 and 500 r.p.m. are closely similar, and thus the reaction is chemically controlled under these conditions. This is also the case at concentrations of

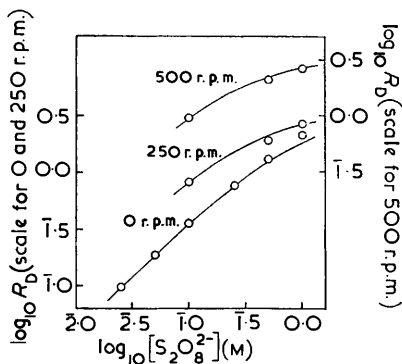


FIG. 4.

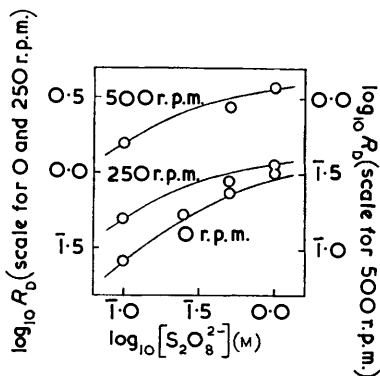


FIG. 5.

Figs. 4—6. The dependence of \log (rate of dissolution, R_p) on \log (concentration of sodium persulphate) for cobalt at various rates of rotation at 25.0° (Fig. 4), 13.5° (Fig. 5), and 0.0° (Fig. 6). The curves are calculated (see Discussion).

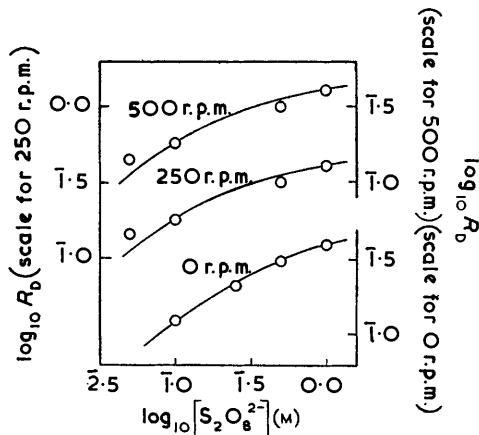


FIG. 6.

0.5M and 0.1M at 13.5° and below. The rates at 250 and 500 r.p.m. for 1.0M-sodium persulphate are as follows:

Temperature	0.5°	13.5°	25.0°
$10^7 \times$ Rate (g.-atom of Co cm. ⁻² min. ⁻¹): 250 r.p.m.	3.31	9.29	21.4
500 r.p.m.	3.32	9.45	21.8

From the mean rates we calculate an activation energy of 12.21 ± 0.001 kcal. mole⁻¹ and $\log_{10} A$ of 3.35 (A being in g.-atom of Co cm.⁻² min.⁻¹).

Results for Iron.—The rates of dissolution of iron were found to be faster than those for copper, especially when the iron specimens were rotated. No evidence for an initial increase in rate was found in any experiment. Greater difficulty in overcoming transport control was encountered with iron than with either copper or cobalt, as can be seen from the results shown

in Figs. 7—9: the rates obtained with 1.0M-solutions at 250 and 500 r.p.m. are shown in the following Table.

Temperature	0.5°	13.5°	25.0°
$10^6 \times \text{rate (g.-atom of Fe cm.}^{-2} \text{ min.}^{-1})$: 250 r.p.m.	4.30	6.55	10.8
500 r.p.m.	4.35	6.75	11.1

From the mean rates we calculate an activation energy of 6.49 ± 0.28 kcal. mole⁻¹ and a $\log_{10} A$ of -0.199 (A being in g.-atom of Fe cm.⁻² min.⁻¹).

Results for Nickel-Copper Alloys.—The composition of both sides of each alloy sheet had been determined before use by X-ray fluorescence spectrography: the results are given in

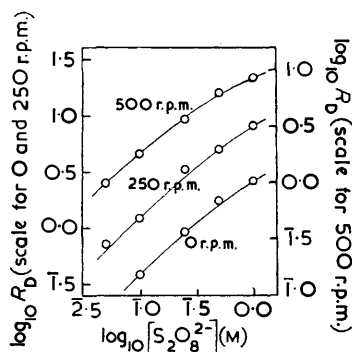


FIG. 7.

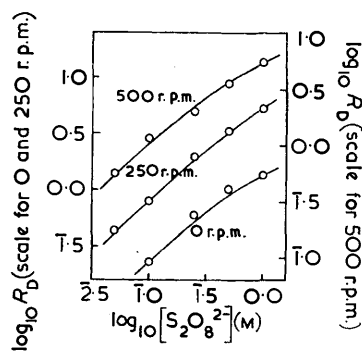


FIG. 8.

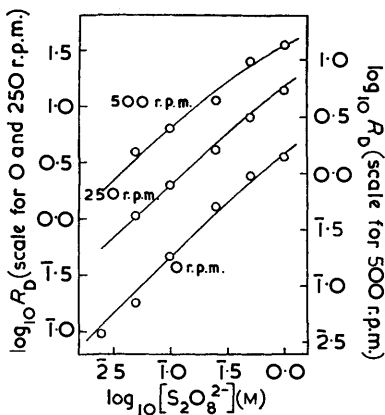


FIG. 9.

FIGS. 7—9. The dependence of \log (rate of dissolution, R_D) on \log (concentration of sodium persulphate) for iron at 0.5° (Fig. 7), 13.5° (Fig. 8), and 25.0° (Fig. 9). The curves are calculated (see Discussion).

Table 1, the fourth column showing the mean copper content of the two sides and the fifth the difference. The concentration gradients, which are particularly large for the alloys containing about 70, 50, and 30% of copper, arose because the sheets had been annealed in close contact. To investigate whether preferential dissolution of either component occurred in the reaction, both sides of specimens of each alloy were re-analysed by the same method after about 25% of their original weight had been removed by reaction: these results are given in columns 6 and 7 of Table 1. As an additional check the composition of the dissolved alloy was determined volumetrically, by placing a specimen of each alloy in a solution containing only sufficient sodium persulphate to dissolve some 20% of it. When reaction was complete, the copper in solution was determined iodometrically and thence, assuming the correctness of the figures in col. 4, we obtained the percentage of copper in the undissolved alloy (column 8 of Table 1). The volumetric analysis of the 50% copper alloy was performed on a specimen from which about 40% of its weight had already been removed by reaction. It was also established that

omission of the normal etching procedure was without significant effect in the volumetric analysis. Table 1 provides no evidence that either component is preferentially dissolved.

Since we were only interested in the reaction that was completely under chemical control, all rate measurements were carried out with 1.0M-sodium persulphate, the alloy specimen being rotated. The rates of dissolution of each alloy at 250 and 500 r.p.m. were the same within experimental error and thus all the reactions studied were chemically controlled.

Mention was made earlier of the initial increase in the rate of dissolution of copper in 1.0M-solutions. This also occurred with all the alloys, the time taken to reach a constant rate generally increasing with decrease in the copper content of the alloy. We consider first, however, measurements of rates which have attained a constant value.

Constant rates. Table 3 shows the activation energies and their standard deviations, and the values of $\log A$, as a function of alloy composition. To calculate the rates, and hence A , in g.-atom of alloy $\text{cm.}^{-2} \text{ min.}^{-1}$, the mean atomic weight of each alloy was computed from the initial composition as given in Table 1. While the activation energy declines steadily with decreasing copper content to a limiting value of about 7.4 kcal. mole^{-1} , the rates at any temperature vary irrationally with composition. It is interesting that, as with many heterogeneous reactions, the plot of E against $\log A$ is accurately linear if we exclude the alloys containing 40–70% of copper; for these alloys, $\log A$ is higher than their activation energies would lead us to expect from the results for the other alloys, and hence we conclude that these alloys are reacting abnormally rapidly. Since E varies understandably with composition, we are justified in assuming that the abnormality lies entirely in the $\log A$ terms, and if we substitute in the equation for the compensation effect, which is $\log A = 0.826E - 6.34$, the activation energies of the abnormal alloys to obtain "corrected" values of $\log A$, we find that the "corrected" rates at 25° are then constant at $2.2 (\pm 0.1) \times 10^{-8}$ g.-atom $\text{cm.}^{-2} \text{ min.}^{-1}$ for all alloys containing >60% of copper. If the abnormality is indeed only in the $\log A$ term, this would suggest that the abnormal alloys develop an unusually rough surface during their dissolution, and the above procedure therefore amounts to correcting the rates to unit true surface area.

Initial rates. A typical plot of weight loss against time, showing the increase in rate during the initial stages of the reaction, is shown in Fig. 10. The initial rates of dissolution of copper and of all the alloys have been calculated by graphical differentiation of the weight loss against time curves: the instantaneous rate obtaining at any time was plotted against the total weight of alloy dissolved in that time, and Fig. 11 is an example of the resulting curve (obtained by using the results shown in Fig. 10). Now because some 5 mg. were removed from all specimens by the etching treatment, the evaluation of the true initial rate involves a somewhat lengthy and uncertain extrapolation: therefore the initial rate is better defined as that rate obtaining when 5 mg. of metal have been removed, by either etching or reaction (see Fig. 11). Initial rates so computed are much less reliable than the subsequent constant rates discussed above; and because the reliability is variable (depending on the number of measurements made during the accelerating phase), no attempt is made to assess it.

The mean initial rates found by using rates of rotation of 250 and 500 r.p.m. and 1M-solutions were computed for the three temperatures, and the derived activation energies and values of $\log A$ are also shown in Table 3. The activation energies all lie between 8.5 and 11.5 kcal. mole^{-1}

TABLE 3.

Kinetics of the dissolution of nickel-copper alloys in 1M-sodium persulphate.

Nominal % Cu	From constant rates		From initial rates	
	E (kcal. mole^{-1})	$\log_{10} A$ *	E (kcal. mole^{-1})	$\log_{10} A$ *
100	11.21 \pm 0.13	2.93	10.5	2.10
90	9.68 \pm 0.21	1.67	9.6	1.24
80	8.14 \pm 0.19	0.39	11.0	2.22
70	8.14 \pm 0.02	0.68	10.4	2.02
60	7.39 \pm 0.05	0.02	8.9	0.74
50	7.38 \pm 0.30	1.90	11.4	2.63
40	7.12 \pm 0.09	1.89	9.8	1.41
30	7.25 \pm 0.02	1.64	8.5	0.65
20	7.55 \pm 0.10	1.88	9.6	0.73
10	7.41 \pm 0.39	1.81	11.2	1.13

* A in g.-atom $\text{cm.}^{-2} \text{ min.}^{-1}$.

and in contrast to those derived from the constant rates (see also Table 3) they show no regular trend with the composition of the alloy: we therefore assume that the activation energy for the initial stage of the dissolution is 10.0 ± 1.5 kcal. mole⁻¹ and that this is within experimental error independent of alloy composition. The manner in which the initial rates vary with alloy composition is rather more rational than that for the constant rates. At each temperature the rates shown by the alloys containing 90%, 80%, 60%, 50%, 40%, and 30% of copper are almost the same: pure copper and the 70% copper alloy react faster, while below 30% there is a progressive decrease in initial rate with copper content. These results are discussed below.

On the assumption that, to attain a constant rate, the surface of the metal must be roughened to a certain extent, the increase in rate could be due to the failure of the etching procedure adopted to give a sufficiently roughened surface. Thus the initial stages of the reaction would involve a further increase in the degree of roughness. An attempt was made to verify this hypothesis by performing experiments with the alloys containing 20% and 60% of copper at

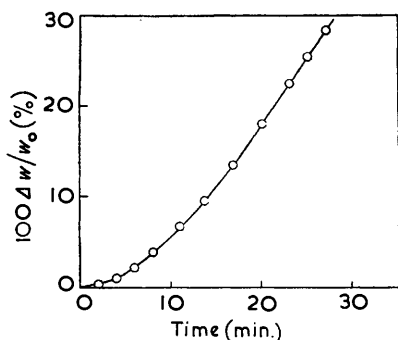


FIG. 10. Dependence of weight loss (mg.) on time for the dissolution of 20% copper alloy at 12.0° and 500 r.p.m. in 1M-sodium persulphate.

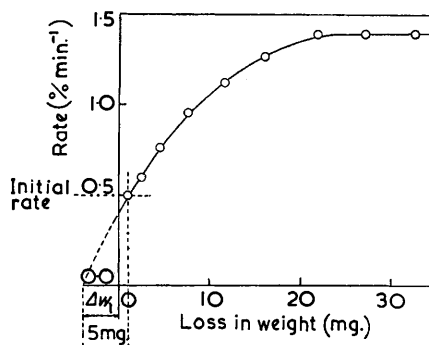


FIG. 11. Dependence of rate on time for the dissolution of 20% copper alloy, based on results shown in Fig. 10.

25° and 500 r.p.m. in which the extent of the etching was varied. The results are contained in Table 4 which shows the weight removed in the etch (Δw_e), the further weight removed in the reaction before the rate became constant (Δw_1), the sum of these two, the initial rate ($R_{D(0)}$) and the subsequent constant rates (R_D). The initial rate is here the rate at the beginning of the reaction irrespective of the amount removed in the etch.

Three significant points emerge from these results: (i) The total weight ($\Delta w_e + \Delta w_1$) which it is necessary to remove either by etching or by reaction before a constant rate obtains is a constant quantity for each alloy (~ 70 mg. for the 60% copper alloy and ~ 50 mg. for the 20% copper alloy). (ii) This quantity is larger for the alloy which was thought to be reacting "abnormally" rapidly than for the other. (iii) In both cases the initial rate increases with the weight removed by etching, Δw_e , and tends to the limiting constant value as Δw_e increases and as Δw_1 tends to zero. These three points confirm the validity of the hypothesis stated at the beginning of the last paragraph. The reason for the slight dependence of the constant rate R_D on etching conditions (see columns 5 and 10 of Table 4) is unknown.

Attempted Dissolution of Nickel, and the Effect of Sulphuric Acid on the Rate of Dissolution of

TABLE 4.

Results for the variation of etching conditions.

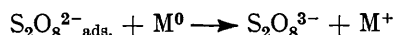
60% Copper alloy					20% Copper alloy				
Δw_e (mg.)	Δw_1 (mg.)	$\Delta w_e + \Delta w_1$ (mg.)	$R_{D(0)}$ (% min. ⁻¹)	R_D (% min. ⁻¹)	Δw_e (mg.)	Δw_1 (mg.)	$\Delta w_e + \Delta w_1$ (mg.)	$R_{D(0)}$ (% min. ⁻¹)	R_D (% min. ⁻¹)
35.1	35.5	70.6	3.80	5.30	20.9	27.5	48.4	1.15	3.25
16.6	53.0	69.6	2.50	5.20	5.1	45.0	50.1	0.45	2.90
6.0	65.0	71.6	1.92	4.35	3.7	47.5	51.2	0.35	2.70
4.0	64.0	68.0	1.27	4.35					
0.0	75.0	75.0	0.80	5.05					

Copper.—No loss of weight occurred after immersion of an etched nickel specimen in M-sodium persulphate at 25° for 48 hr. Neither omission of the etch nor making the solution 0.1N in sulphuric acid had any effect. We conclude that nickel is inherently inactive in this reaction (despite one report to the contrary²), and this is discussed below.

The rate of dissolution of copper at 500 r.p.m. in M-sodium persulphate made 0.1N in sulphuric acid was ~1.6 times faster than in neutral solution, but the activation energy (11.5 kcal. mole⁻¹) was not significantly changed.

DISCUSSION

The Kinetics and Mechanism of the Dissolution of Metals in Sodium Persulphate Solutions.—The reaction of a molecule with a solid surface is conventionally broken down into five steps: (i) transport of the molecule to the neighbourhood of the surface, (ii) adsorption of the molecule on the surface, (iii) reaction of the molecule with the surface, (iv) desorption of the products, and (v) transport of the products away from the surface. In the present case, where the reacting species is an ion in solution, step (ii) may also involve partial dehydration of the ion, and step (iv) its rehydration, and the hydration or complexing of the newly formed cation. Step (iii) must consist of a number of one-electron transfers, of which at least the last in the case of iron and cobalt is likely to occur homogeneously, *i.e.*, after stage (iv). We recognise that the rate of step (i) was important for most of the conditions under which the metals were studied. When complete chemical control was attained, one of the electron transfers constituting step (iii) must have been rate-limiting, and we shall assume that it was the first of these, *viz.*:



The rate of the chemical reaction is thus proportional to the fraction (θ_s) of surface covered by adsorbed persulphate ions. That rates were constant up to about 80% reaction (except at low persulphate ion concentrations) is good evidence that neither step (iv) nor (v) was ever rate-limiting.

A simple theoretical treatment has been developed to interpret the results. We consider two adjacent layers lying between the surface of the metal and the bulk of the solution: layer I contains the species actually adsorbed on the surface, while species residing in layer II may become adsorbed by a process not involving transport. We then assign rate constants as follows. (i) For the transport of persulphate ions from layer II to the bulk solution, and *vice versa*, k_T . (ii) For adsorption of persulphate ions (*i.e.*, removal from layer II to layer I), k_a , and for desorption of persulphate ions (*i.e.*, removal from layer I to layer II), k_d . (iii) For chemical reaction of adsorbed persulphate ions, k_c . The steady-state treatment of this system, after elimination of the concentration of persulphate ions in layer II, gives the following equation, which is quadratic in θ_s :

$$\theta_s \left(\frac{k_c + k_d}{k_a} \right) = (1 - \theta_s) \frac{k_T S + k_d \theta_s}{k_T + k_a}, \quad (1)$$

where S is the concentration of persulphate ion in the bulk of the solution. In order readily to proceed further, it is necessary to introduce two simplifying assumptions. (a) If the persulphate ions are very strongly adsorbed on the metal surfaces used, *i.e.*, if $k_a \gg k_d$, then we can afford to neglect terms in k_d . Equation 1 then becomes

$$\theta_s \left(\frac{k_c}{k_a} + \frac{k_T S}{k_T + k_a} \right) = \frac{k_T S}{k_T + k_a}. \quad (2)$$

(b) If further we assume $k_a \gg k_T$ (which is very probable), equation (2) reduces to

$$\theta_s = \frac{(k_T/k_c)S}{1 + (k_T/k_c)S}. \quad (3)$$

² Levi, Mighiovini, and Ercolini, *Gazzetta*, 1908, **38**, 583.

We have now a simple equation which enables us to estimate θ_s for any concentration (S) of persulphate ion; it involves the one parameter, k_T/k_c . Moreover, the rate of reaction R_D must be given by

$$R_D = k_c \theta_s, \quad (4)$$

and the procedure adopted was to fit the experimental results on the variation of rate with concentration and with rate of stirring to these equations, and hence to obtain optimum values of k_T and k_c . If this simple treatment is essentially correct, then the following consequences ensue. (i) At constant temperature and rate of stirring (R_R), k_T will be the same for each metal. (ii) Values of k_T will increase with R_R , and may attain a limiting value equal approximately to k_c . (iii) The activation energies E_T derived from values of k_T should be about 5 kcal. mole⁻¹. (iv) The activation energies E_c derived from values of k_c for each metal should correspond to those (quoted in the Results section) as obtained directly from chemically controlled rates.

The fitting procedure was as follows. Plots of $\log \theta_s$ against $\log S$ (equation 3) are curves, whose degree of curvature increases with increasing k_T/k_c . Based on a number of calculations, a plot of $\Delta(\log \theta_s)$ for the concentration interval 0.1M to 1M against k_T/k_c was constructed, and, by interpolation of an observed value of $\Delta(\log R_D)$ for this concentration range, the corresponding value of k_T/k_c was found. This was done for each series of measurements in which the concentration was varied. The normalisation factor which it was then necessary to use in order to superimpose the calculated curve on the experimental points (*i.e.*, $\log k_c$) was then found: hence k_c and, with k_T/k_c known, k_T were found.

Rigorous application of this procedure gave values of k_c which sometimes varied with R_D ; this, when it occurred, was traced to experimental error in the rate measurements (especially at 0.1M-concentration), which led to an inappropriate value of $\Delta(\log R_D)$ and hence to an erroneous value of k_T/k_c . Better consistency of k_c was obtained in such cases by selecting some other value of $\Delta(\log R_D)$, and hence of k_T/k_c , which gave optimum agreement with the experimental results over the whole concentration range. The curves shown in Figs. 1—9 were calculated on the basis of the values of k_c and k_T shown in Table 7.

TABLE 7.
Optimum values of k_c and k_T .

Iron				Cobalt				Copper			
R_R	k_T	k_c	\bar{k}_c	R_R	k_T	k_c	\bar{k}_c	R_R	k_T	k_c	\bar{k}_c
At 25.0°				At 25.0°				At 25.0°			
0	4.43	29.5	} 29.1	0	3.90	3.55	} 3.47	0	4.45	17.8	} 18.2
250	21.0	30.2		250	10.5	3.55		250	9.50	19.0	
500	27.5	27.5		500	13.2	3.31		500	10.7	10.7	
At 13.5°				At 13.5°				At 12.1°			
0	3.64	18.2	} 18.2	0	3.30	1.32	} 1.34	0	2.66	7.41	} 7.36
250	14.2	17.8		250	8.10	1.35		250	4.25	7.08	
500	18.6	18.6		500	8.10	1.35		500	5.30	7.59	
At 0.5°				At 0.5°				At 0.0°			
0	2.75	11.0	} 10.9	0	1.56	0.52	} 0.50	0	1.21	2.69	} 2.78
250	9.6	10.7		250	2.95	0.49		250	1.69	2.82	
500	11.0	11.0		500	2.95	0.49		500	1.69	2.82	

The following conclusions emerge. Values of k_c for each metal at each temperature are satisfactorily constant, and the activation energies (based on the mean values of k_c , *i.e.*, \bar{k}_c) are calculated to be: for iron, 6.5; for cobalt, 11.9; and for copper, 12.2 kcal. mole⁻¹. The values based on transport-free rates in 1M-solutions were respectively 6.5, 12.2, and 11.2 kcal. mole⁻¹. The agreement is satisfactory, and one of the expected consequences of the theory is thus fulfilled.

The situation with regard to the calculated values of k_T is somewhat less satisfactory. For each metal at each temperature they certainly increase with R_R as expected, but the limiting values they appear to attain are sometimes six times greater than k_c (as with cobalt at 0.5° and 13.5°) and sometimes less than k_c (as with copper at 0°). No substantial alteration in these values of k_c and k_T can be justified. However, the agreement between the value of k_T for the three metals at each temperature when R_R is zero is not unreasonable, and is indeed quite good at 25°. From the mean values of k_T at $R_R = 0$, we calculate an activation energy E_T of 5.5 kcal. mole⁻¹; this is about as expected. However, the divergence between the values of k_T for the three metals becomes more serious when R_R is 250 or 500 r.p.m.: the values for cobalt and copper are not greatly different, but those for iron are much higher. If we take values of k_T for iron at the three temperatures, we find good Arrhenius plots for $R_R = 250$ and for $R_R = 500$ r.p.m.; the values of E_T are, respectively, 5.1 and 6.0 kcal. mole⁻¹, which suggest that these values of k_T are reliable and that the values applying to cobalt and copper are low.

Three possible factors contribute to this situation. (i) By the form of the theory, $\Delta(\log \theta_s)$ for a given concentration range decreases with increasing k_T/k_c , and the scatter of the experimental results is such that each value of k_T/k_c selected for a given value of $\Delta(\log R_R)$ is uncertain by at least $\pm 10\%$. This uncertainty, however, cannot be wholly responsible. (ii) The second assumption made in the theory (namely, that $k_a \gg k_T$), while probable, is not necessarily true, and the calculated values of k_T will be low to an extent which depends on the extent to which the inequality is untrue. (iii) Finally, and most probably, low values of k_T result when low values of k_c are found, *i.e.*, when chemical control is readily attained. Thus, for example, with cobalt at 0.5° and 13.5°, where R_D is independent of R_R over the entire concentration range studied, the treatment *must* give values of k_c and k_T which are independent of R_R . Once k_T exceeds k_c by a certain factor (which appears here to be about six), further increase in k_T with increasing R_R is irrelevant to R_D and is not therefore sensed by the experimental measurements. For this reason also the low values of k_T must be minimum ones, although it is not apparent why k_T seems to achieve a limiting value less than k_c with copper at 0°.

We therefore conclude that the theoretical treatment described above, although not without defect, provides a reasonable interpretation of the experimental results.

The Dissolution of Nickel-Copper Alloys, and the Relative Reactivities of the Metals.—The sequence of reactivities of the metals studied is Fe > Cu > Co \gg Ni, and, although the substantial differences in reactivity confirm that we have indeed been measuring chemically controlled rates, the precise nature of the rate-limiting step is not at once evident. The results for the nickel-copper alloys, however, illuminate this problem.

The constant rates (after correction for variations in surface areas), the activation energies, and hence also the pre-exponential factors, decrease with decreasing copper content, but after this has reached 60% (at which composition the *d*-band begins to empty and ferromagnetism first appears), they remain essentially constant down to 10% of copper (see Table 4 and text). Before proceeding to an interpretation, we first note three additional points. (i) The initial rates present a broadly similar picture, although they again decline when the copper content is less than 30%, and the activation energies seem to be invariant. (ii) Table I shows qualitatively that copper-rich alloys are more reactive towards nitric acid than are nickel-rich alloys, and this is supported by an old study³ which shows reactivity increasing sharply as the *d*-band empties. A change in the rate of oxidation of these alloys also occurs at this point.^{4,5} (iii) In the catalytic decomposition of hydrogen peroxide, where electron transfer from the metal is thought to be rate-determining, the activity of nickel-copper alloys decreases with decreasing copper content,

³ See Partington, "Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans, London, 1936, Vol. XV, p. 200.

⁴ Dowden, *J.*, 1950, 242.

⁵ Pilling and Bedworth, *Ind. Eng. Chem.*, 1925, 17, 372.

and the activation energy simultaneously rises.⁶ The electronic structure of nickel-copper alloys affects not only their catalytic properties, but clearly also their reactivities in dissolutions.

Now theory^{4,6} suggests that a surface reaction in which the rate-controlling step is the extraction of an electron from the metal will be favoured by (a) a low ionisation potential or work function of the metal, and (b) a large, negative rate of change of the electron-level density at the Fermi surface, $g(-\phi)$. The difference between the work functions, and between the ionisation potentials, for nickel and copper is not large, but measurements of the electronic specific heats at low temperature show that $g(-\phi)$ is almost constant from nickel to the 60% copper alloy, at which point it starts to fall rapidly. Our observations on the rates of dissolution, therefore, accord satisfactorily with this theory, but the activation energy is expected to decrease as the d -band is emptied (as found in the decomposition of hydrogen peroxide⁶) rather than increase, as found. The existence of a compensation effect is, however, a complicating feature.

We return now to the problem of the relative reactivities of the metals. The inactivity of nickel is surprising and possibly spurious, and the great difference between the reactivity of nickel and the 10% copper alloy finds no interpretation in the band theory: it is, however, not without precedent. Unpublished work⁷ has shown that, while copper and cobalt dissolve in aqueous solutions of, respectively, cuprammonium and hexaminecobaltic nitrate in the presence of air, nickel does not react with solutions of hexamine-nickel nitrate. Both copper and cobalt dissolve rapidly in solutions of dinitrogen tetroxide⁸ and of nitrosyl perchlorate⁹ in methyl cyanide, but nickel (and iron) do not dissolve. However, from the known variation in $g(-\phi)$ ^{4,6} we should expect iron to be somewhat more reactive than cobalt and to show a somewhat lower activation energy, and both to be more reactive than nickel: but the reactivity of copper relative to these metals is not easy to predict.

We may summarise our conclusions as follows. The reaction shows some of the features expected on the basis of band theory for one in which the rate-controlling step involves the extraction of an electron from the metal or alloy. The kinetics of the dissolution of the metals, and the change in the kinetic parameters for the nickel-copper alloys at the point where the d -band becomes filled, both support this view. The lack of reactivity shown by nickel is not thereby interpreted, and we feel that a study of nickel-copper alloys containing less than 10% of copper, and of nickel-cobalt alloys, should prove rewarding.

We thank the Mond Nickel Company for providing the nickel-copper alloys and nickel foil, and for performing the X-ray fluorescence analyses; also the British Iron and Steel Research Association for providing the iron foil.

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[Received, September 28th, 1961.]

⁶ Dowden and Reynolds, *Discuss. Faraday Soc.*, 1950, **8**, 184.

⁷ Bond, Griffin, and Lacey, unpublished work.

⁸ Addison, Sheldon, and Hodge, *J.*, 1956, 3900; also Addison, unpublished work.

⁹ Hathaway and Underhill, *J.*, 1960, 3705.