211. The Kinetics of the Reaction between Copper and Iodine in Various Solutions. Part II. Solutions of Iodine in Organic Solvents.

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The kinetics of the reaction between copper and iodine when dissolved in carbon tetrachloride, chloroform, benzene, or diamyl ether has been investigated. In carbon tetrachloride and chloroform the rate appears to follow the equation $dx/dt = k(a - x)/x$, where the symbols have their usual significance. The influence of the state of the surface of the copper and the temperature coefficient has also been studied. Whereas in the work (Part I) on aqueous (potassium iodide) solutions of iodine it was shown for a large range of iodine concentrations that the rate of reaction is unaffected by the presence or thickness of the film of cuprous iodide, yet with the above solutions the rate appears to be partly controlled by the thickness of the iodide film.

In Part I (*J.*, 1942, 598) the results of a study of the rate of reaction of copper on iodine in aqueous (potassium iodide) solution were communicated. It was shown that for a large range of iodine concentration the reaction was unimolecular with respect to the iodine concentration, and the rate was unaffected by the presence or absence of a cuprous iodide film or by the method of preparation or degree of smoothness of the copper surface. The increase in reaction rate found on increasing the potassium iodide concentrations to very high values was identified with the increase in the rate of diffusion of iodine in these circumstances. It was also demonstrated that the reaction proceeds by the diffusion of both iodine and solvent through the cuprous iodide film and not by the diffusion of copper ions.

It is well known that iodine dissolved in aqueous potassium iodide is present largely in the form of the complex ion I_3^-, the proportion of free iodine molecules being very small. In the case of organic solvents giving violet solutions the iodine is considered to exist as simple molecules, whereas in the brown solutions obtained with ethers, ketones, or esters it exists mainly as a co-ordination complex with the solvent. The great difference in the state of the iodine in aqueous solutions on the one hand, and in organic solvents on the other, might be expected to have a considerable effect on the kinetics of the reaction between copper and iodine, and it was decided to extend the work to solutions of the latter type.

This work may be divided into the following sections : (1) Experiments carried out between copper and iodine in carbon tetrachloride solution at 25°. The initial concentration of the solutions varied from 0·0025 to 0·04 g.-atom/l. (2) Experiments at 25° in chloroform, benzene, and diamyl ether, showing the effect of change of solvent. (3) Experiments at 0°, 25°, and 30°, showing the effect of change of temperature. (4) Experiments at 25°, showing the influence of the state of the copper surface on the rate of reaction.

Experimental.

The experimental method has been described (Part I, *loc. cit.*). Briefly it consisted in rotating strips of thick copper foil of 36 sq. cm. area in the iodine solution at about 100 revs./min. The course of the reaction was followed by titration : 5 c.c. of the solution were pipetted into an excess of N/1600-sodium thiosulphate solution, shaken until all the iodine had reacted, and then back-titrated with N/1600-iodine solution. The copper strips showed a firm film of whitish-brown cuprous iodide which exhibited no crumbling.

Carbon tetrachloride. " AnalaR " Carbon tetrachloride was distilled over calcium chloride and then repeatedly over clean, polished strips of copper to remove any traces of sulphur present. Fractions boiling at 76·7° were used for the work. The results are given in Table I, where $k = \frac{2{\cdot}303v}{t_2 - t_1}\log_{10}\frac{C_1}{C_2}$ and χ is given in g.-atoms × 10^6, all the data relating to 25°.

Col. 7 in the readings for initial concentration N/400, contains the values of the simple unimolecular constant k (corrected for the volume change). In the reaction for copper with iodine in aqueous (KI) solution a constant is given by this equation, but in the present experiments it is seen that k falls rapidly with time. This suggests that the reaction is retarded by the cuprous iodide film. However, that the Tammann–Pilling–Bedworth equation $\chi^2 = kt$ is not obeyed is seen by an examination of Fig. 1, where χ is plotted against time. If this relation were obeyed, values of χ for a particular time t should all be equal and independent of the initial concentration of the iodine. It can also be seen that the ordinates are not proportional to the iodine concentration, which should be the case if the unimolecular relation is obeyed. It appeared probable that this reaction in organic media (*a*) was proportional to the iodine concentration, and (*b*) was inversely proportional to the thickness of the cuprous iodide film formed on the copper. Hence, if a = initial concentration of iodine and $a - x$ = concentration of iodine at time t,

$$dx/dt = k(a - x)/x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

since x is proportional to the thickness of the cuprous iodide film. The integrated form of this equation, giving k, the velocity constant, will only hold for the reaction at constant volume. In the present work

TABLE I.

Time, mins.	$(a - x)$.	[I], C.	x.	χ.	k_n.	k.
		300 C.c. of N/400-iodine in CCl_4.				
0	20·0	0·0025	—	—	—	—
10	17·5	0·00219	2·5	2·60	0·192	4·01
20	16·2	0·00202	3·8	3·94	0·265	2·28
30	15·5	0·00194	4·5	4·64	0·193	1·28
60	13·9	0·00174	6·1	5·52	0·196	1·03
90	12·65	0·00158	7·35	6·73	0·206	0·88
150	11·15	0·00139	8·85	8·17	0·161	0·58
				Mean	0·202	

Time, mins.	$(a-x)$.	[I], C.	x.	χ.	k_n.
	300 C.c. of N/200-iodine in CCl_4.				
0	20·0	0·005	—	—	—
10	18·2	0·0045	1·8	3·75	0·194
20	17·65	0·00441	2·35	4·877	0·140
30	17·15	0·00429	2·85	5·884	0·134
60	16·1	0·00402	3·9	7·962	0·149
120	14·3	0·00357	5·7	11·462	0·193
180	12·9	0·00322	7·1	14·135	0·217
				Mean	0·171
	300 C.c. of N/100-iodine in CCl_4.				
0	20·0	0·01	—	—	—
10	18·75	0·00937	1·25	5·25	0·185
20	18·25	0·00912	1·75	7·26	0·181
30	17·85	0·00892	2·15	8·69	0·174
60	16·95	0·00847	3·05	12·51	0·196
120	15·6	0·00780	4·4	17·60	0·205
180	14·5	0·00725	5·5	21·80	0·197
270	13·4	0·00670	6·6	25·93	0·193
390	12·3	0·00615	7·7	29·97	0·179
600	10·8	0·00540	9·2	35·39	0·177
				Mean	0·187

Time, mins.	$(a-x)$.	[I], C.	x.	χ.	k_n.
	300 C.c. of N/50-iodine in CCl_4.				
0	20·0	0·020	—	—	—
10	19·2	0·0192	0·8	6·67	0·150
25	18·7	0·0187	1·3	10·77	0·162
50	18·15	0·0181	1·85	15·2	0·165
100	17·35	0·0173	2·65	21·5	0·170
160	16·7	0·0167	3·3	16·6	0·187
250	16·0	0·0160	4·0	31·9	0·162
390	15·0	0·0150	5·0	39·4	0·183
				Mean	0·169
	300 C.c. of N/25-iodine in CCl_4.				
0	20·0	0·040	—	—	—
8	19·5	0·0390	0·5	8·33	0·144
40	18·8	0·0376	1·2	19·8	0·172
80	18·3	0·0366	1·7	17·9	0·167
140	17·7	0·0354	2·3	36·0	0·186
220	17·1	0·0342	2·9	45·3	0·183
				Mean	0·170

the volume of the reacting liquid varies with each reading owing to the extraction of 5·0 c.c. for the titration. The immediate problem is to insert this volume correction into equation (1).

If m is the mass of iodine in solution, and c and v are the concentration and volume respectively, then $m = cv$ and

$$- \mathrm{d}m/\mathrm{d}t = - \mathrm{d}(cv)/\mathrm{d}t$$

If c_0 = initial concentration and v_0 = initial volume then

$$- \mathrm{d}(cv_0)/\mathrm{d}t = kc/v_0(c_0 - c)$$

because $v_0(c_0 - c)$ is proportional to the thickness of the cuprous iodide film at any moment during the first interval; hence

$$k_1 = \frac{v_0^2}{t_1 - t_0}\left(c_0 \ln \frac{c_0}{c_1} - c_0 + c_1\right) \qquad (2)$$

At t_1, we remove 5 c.c., and with the new volume v_1 we have

$$- v_1 \frac{\mathrm{d}c}{\mathrm{d}t} = \frac{kc}{v_0(c_0 - c_1) + v_1(c_1 - c)}$$

because $v_0(c_0 - c_1)$, now constant, represents the thickness of the film at the beginning of the second interval. Additional amounts of iodine added during the second stage are represented by $v_1(c_1 - c)$. Integrating between the limits c_1 and c_2 and t_1 and t_2, we have

$$k_2 = \frac{v_1 v_0(c_0 - c_1) \ln (c_1/c_2) + v_1^2 c_1 \ln (c_1/c_2) - v_1^2(c_1 - c_2)}{t_2 - t_1} \qquad (3)$$

This equation gives k_2, the velocity constant for the second interval. Similarly for the third interval we have

$$- v_2 \frac{\mathrm{d}c}{\mathrm{d}t} = \frac{kc}{v_0(c_0 - c_1) + v_1(c_1 - c_2) + v_2(c_2 - c)}$$

which, integrated between the limits t_2 and t_3 and c_2 and c_3, gives

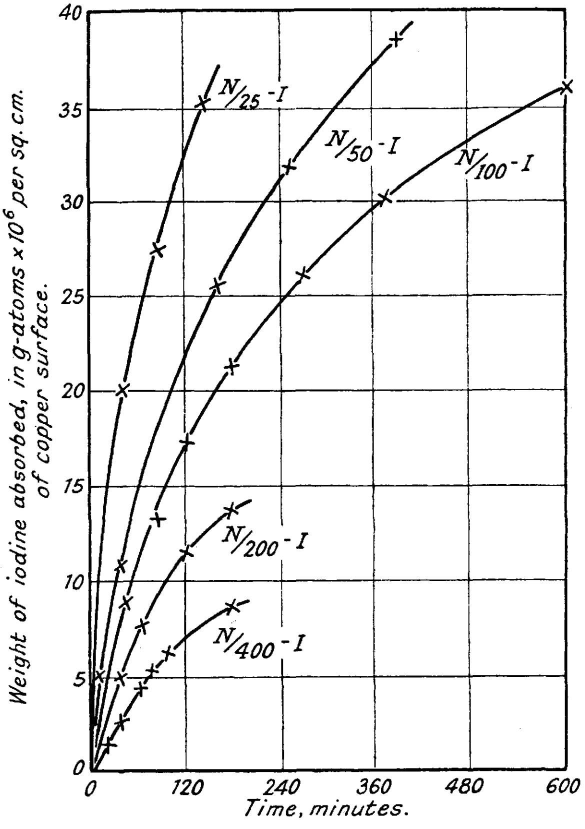
$$k_3 = \frac{v_2\{v_0(c_0 - c_1) + v_1(c_1 - c_2)\} \ln (c_2/c_3) + v_2^2 c_2 \ln (c_2/c_3) - v_2^2(c_2 - c_3)}{t_3 - t_2} \qquad (4)$$

the velocity constant for the third interval. For the *n*th interval we have,

$$k_n = \frac{v_{n-1}\{v_0(c_0 - c_1) + v_1(c_1 - c_2) + \ldots v_{n-2}(c_{n-2} - c_{n-1})\} \ln (c_{n-1}/c_n)}{t_n - t_{n-1}} + \frac{v^2_{n-1}\, c_{n-1} \ln (c_{n-1}/c_n) - v^2_{n-1}\, (c_{n-1} - c_n)}{t_n - t_{n-1}} \quad . \quad (5)$$

From equation (5) we can calculate k for any interval (corrected for the change of volume). It is noteworthy that if equation (2) is used for all intervals in the reaction the differences shown in the values of the constant so obtained are small, *i.e.*, the correction term for the change of volume is small. That equation (5) is similar to equation (2), save for the inclusion of the volume changes in (5), may be shown by putting $v_1 = v_2 = v_3 \ldots . = v_n$ in equation (5), whereupon it reduces to equation (2). The values of k_n are given in Table I. They are fairly constant, but the agreement is not excellent. When the average values are compared for different initial concentrations of iodine they show no regular drift.

FIG. 1.



Iodine in carbon tetrachloride at 25°.

A direct contrast between the reaction in aqueous potassium iodide and that in carbon tetrachloride can therefore be made. In the former case the reaction appears to be independent of the presence or thickness of the cuprous iodide film, whereas in the latter case the reaction is directly controlled by the film thickness.

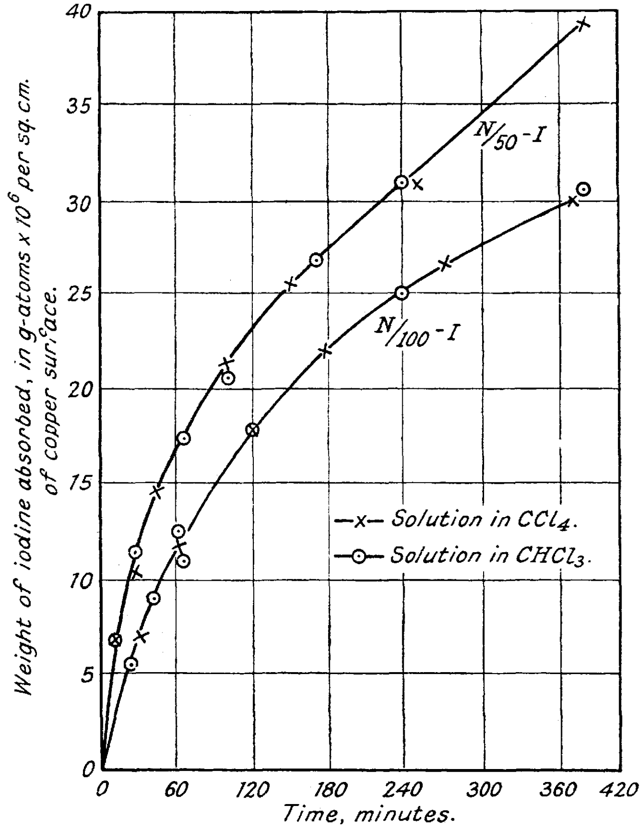
The Effect of the Solvent on the Reaction Rate.—In the determination of the effect of the solvent on the rate four organic liquids have been used.

" AnalaR " Chloroform containing no foreign matter detectable by analysis (free acid, Cl^-, Cl_2, CHO, $COCl_2$) was kept over calcium chloride for 36 hours, decanted, and distilled. The first fractions were discarded, and the bulk of the liquid, b. p. 60·2°, reserved for the experiments. Data were obtained for two concentrations of iodine, N/100 and N/50. The results are shown in Fig. 2, and it is seen that the rates in carbon tetrachloride and in chloroform are practically identical.

" AnalaR " Benzene containing 0·001% of thiophen and 0·002% of non-volatile matter was kept over copper foil for several days and then over fused calcium chloride. After decantation the liquid was distilled, and further purified by freezing. The m. p. of the final fraction was 5·5°, and this was used for the work. The copper surface was prepared by carborundum straight polishing (Part I, *loc. cit.*). Preliminary experiments showed that the rate in benzene is less than in carbon tetrachloride, so experiments were carried out over a range of concentration N/400—N/25. The results are shown graphically in Fig. 3, and it is seen that for concentrations greater than and including N/100 the rate of reaction in benzene is less than that in carbon tetrachloride; moreover, the difference in rate for the same concentration in the different solvents increases with increasing concentration. For solutions of N/200-iodine the rate in benzene is slightly greater than in carbon tetrachloride, and this difference is more pronounced in the case of N/400-solutions.

The solutions of iodine in certain oxygen-containing organic liquids, *e.g.*, ethers, esters, and ketones, show a deep brown colour when concentrated, changing to red at high dilutions. It is usually supposed that in such solutions co-ordination compounds exist between iodine and the solvent, the oxygen in the solvent acting as a donor element. It was desired to use such a solvent for this reaction. Of the common esters, ethers, and ketones, none is suitable. Acetone, which reacts with iodine in the presence of traces of alkali, was considered unsafe; diethyl ether and ethyl acetate have relatively high vapour pressures at 25°, and with the apparatus used, evaporation troubles would be encountered. The liquid eventually selected was diamyl ether. This, except for the reversible complex formation, is without action on iodine. Diamyl ether, obtained in large quantities, was purified by standing over calcium chloride, then copper foil, and by repeated distillation. The fraction of b. p. 168° was reserved for the experiments. It was intended to follow the course of the reaction in the usual way, *i.e.*, by titration, but this was found to be impossible, for the iodine in diamyl ether appears to react very slowly with sodium thiosulphate solution (possibly the dissociation of the iodine complex is very slow). On this account the rate was investigated gravimetrically. Copper strips were cut, polished, dried, and weighed. After reaction, the strip with the cuprous iodide film was washed well with diamyl ether, dried, and weighed again. The difference in weight gives the amount absorbed by the copper as cuprous iodide in time *t*. A new sheet of copper and a new solution of iodine were used for each experiment. The results are given in Table II, and the increases in weight are the means of two identical experiments; the iodine absorbed (col. 5) is given in terms of g.-atoms × 10^6 per sq. cm. of surface. The strips could be very accurately cut, and the slight variations in weight are due to slight variations in thickness. It can be seen that at all concentrations the rate in diamyl ether is much less than the rate in carbon tetrachloride.

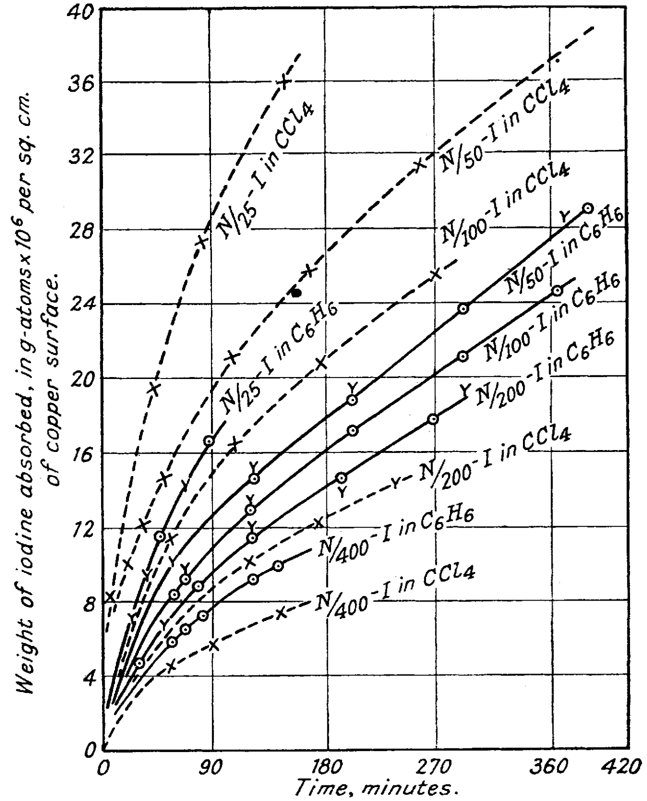
FIG. 2.



Comparison of reaction rates in chloroform and carbon tetrachloride at 25°.

Effect of Temperature.—The temperature coefficient of the reaction between copper and iodine in aqueous (potassium iodide) solution is small, but large enough to permit accurate measurement of the change of rate due to 5° increase to be taken. It was intended to study the reaction in organic solvents at 20°, 25°, 30° and 35°. Preliminary experiments showed, however, that the rate of reaction at 30° was very little greater than at 25°. The increase was too small to be shown accurately, and as it was undesirable to work at temperatures much above 25° it was decided to work at 0°. In this case, extreme care was taken to ensure the sealing of the reaction vessel, since at 0° the introduction of air would lead to water-vapour condensation. The temperature coefficient was investigated in this way with carbon tetrachloride and chloroform. The results are shown in Fig. 4, and it will be seen that the coefficient is very small.

FIG. 3.



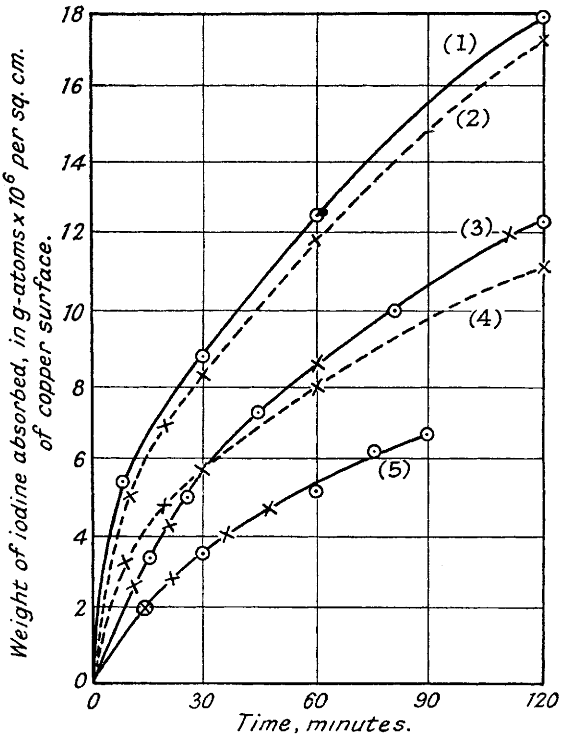
Comparison between rates of reaction in benzene and carbon tetrachloride at 25°.

TABLE II.

Time, mins.	Initl. wt. of Cu, g.	Wt. of Cu $+Cu_2I_2$, g.	Increase, g.	I absorbed.	Time, mins.	Initl. wt. of Cu, g.	Wt. of Cu $+Cu_2I_2$, g.	Increase, g.	I absorbed.
				N/50-Iodine.					
15	4·1900	4·2069	0·0169	3·696	60	4·1802	4·2110	0·0308	6·736
30	4·1580	4·1810	0·0230	5·031	75	4·1905	4·2240	0·0335	7·326
45	4·1827	4·2101	0·0274	5·992	90	4·1852	4·2210	0·0358	7·830
				N/200-Iodine.					
15	4·1906	4·2022	0·0116	2·537	75	4·2134	4·2386	0·0252	5·511
30	4·3256	4·3425	0·0169	3·696	90	4·2616	4·2890	0·0274	5·992
45	4·2016	4·2217	0·0201	4·396	105	4·1558	4·1850	0·0292	6·386
60	4·1724	4·1950	0·0226	4·942	120	4·0154	4·1372	0·0318	6·955
				N/100-Iodine.					
15	4·2044	4·2200	0·0156	3·441	75	4·1606	4·1897	0·0291	6·364
30	4·0996	4·1185	0·0195	4·264	90	4·1324	4·1636	0·0312	6·823
45	4·1678	4·1915	0·0237	5·183	105	4·1564	4·1906	0·0342	7·480
60	4·2110	4·2376	0·0266	5·817	120	4·1888	4·2258	0·0370	8·092

Effect of Surface Condition of the Copper on the Rate.—The presence of an oxide film or different methods of preparing the surface of the metal have no effect on the rate of reaction in aqueous (KI) solution. It has been shown also that the rate of reaction in such solutions under the conditions studied is independent of the presence or thickness of the cuprous iodide layer on the copper. For reactions in carbon tetrachloride and chloroform it has been shown that the reaction is controlled by diffusion through the cuprous iodide layer. The structure of the film might well be influenced by the condition of the surface of the copper. It was therefore decided to investigate the effect of the condition of the surface on the rate.

FIG. 4.



Effect of temperature on rate of reaction.

(1) N/100-I *in* CCl_4 *at* 30°.
(2) N/100-I *in* CCl_4 *at* 25°.
(3) N/100-I *at* 0° : {× *in* CCl_4. ○ *in* $CHCl_3$.
(4) N/200-I *in* CCl_4 *at* 25°.
(5) N/200-I *at* 0° : {× CCl_4. ○ $CHCl_3$.

The four different methods of preparing the surface have been described in Part I (*loc. cit.*), *i.e.*, (i) carborundum straight polishing, (ii) carborundum circular polishing, (iii) mirror finish with jeweller's rouge, (iv) etching with dilute nitric acid.

These experiments were all carried out in benzene solution, as it was considered that the films in benzene appeared rather more even and less liable to flaking than in other solvents. The results are shown in Fig. 5. Only slight differences could be detected, but it can be seen that: (1) The rates in the case of carborundum straight and carborundum circular polishing are identical; (2) the rate on the mirror surface is slightly less, (3) the acid-etched surface gives an even lower reaction rate. That is, the rate is less with the smooth surfaces, coarseness of abrasion tending to increase the velocity of the reaction.

The presence of an oxide film on the copper. Copper strips of the correct area were polished by carborundum straight polishing and heated to 100° for 30, 20, and 10 mins. as described in Part I. The oxidised copper was placed in the reaction vessel, and the reaction followed in the usual way by titration. The results are shown in Fig. 6, and it will be seen that the rate in both carbon tetrachloride and benzene is considerably decreased by the presence of an oxide film.

Films formed in Aqueous and Organic Solvents.—It has been shown that for a large range of iodine concentrations the rate of reaction in aqueous solution is unaffected by the presence or thickness of the cuprous iodide film on the copper, whereas in the case of reactions carried out in organic solvents this film controls the reaction. The question arises as to whether this difference is due to a difference in the actual films formed in the two cases or to the nature of the solutions in the two different classes of solvent.

Strips of copper foil of the usual size were polished and then rotated in a solution of N/200-iodine in N/50-potassium iodide for 30 minutes. The strips of copper covered with cuprous iodide film were then removed from the solution and washed and dried carefully. Some of the strips showed small cracks in

FIG. 5.

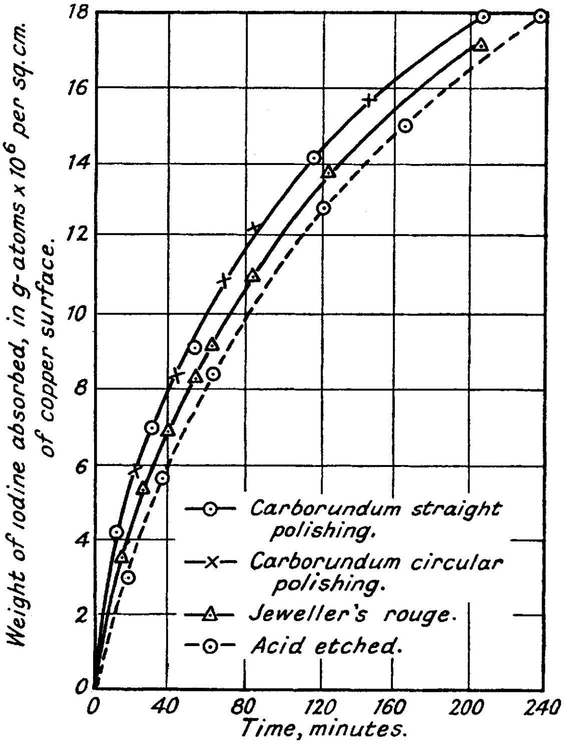
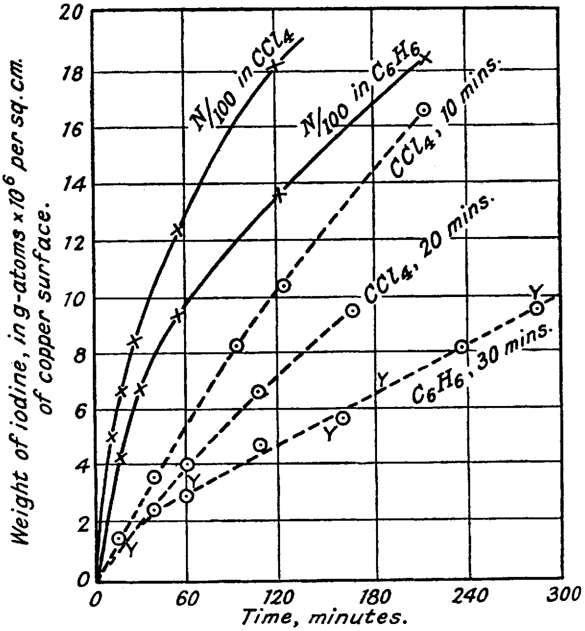


FIG. 6.



Rate of reaction on oxidised surface.

the films on drying and these were discarded. The "perfect" strips were then rotated in carbon tetrachloride, and the reaction followed by titration in the usual way. The results are given in Table III, (1) and (2), where χ is expressed as g.-atoms of I × 10^6.

TABLE III.

(1) *Copper covered by cuprous iodide film formed in aqueous solution rotated in* N/200-*iodine in carbon tetrachloride at* 25°.

Time, mins.	10	20	30	60	120	180
χ_0	0·83	1·45	1·85	3·04	5·57	7·48
χ (no previous film)	3·75	4·88	5·88	7·96	11·46	14·135

(2) *Copper covered by cuprous iodide film formed in carbon tetrachloride solution rotated in* N/200-*iodine solution at* 25°.

Time, mins.	2	5	10	15	20	30	40	50	60
χ_0	1·67	4·33	8·56	12·12	15·43	20·58	24·71	27·65	30·00
χ (no previous film)	1·87	4·54	8·57	12·13	15·43	20·78	24·91	28·04	30·38

The results described under (1) were not very reproducible owing to a certain amount of film-cracking, but they clearly showed that the rate in carbon tetrachloride solution is much decreased by the presence on the metal of a film deposited from an aqueous solution. The results described under (2) were easily reproducible and it is seen that the rate is unaffected by the presence of a cuprous iodide film formed in carbon tetrachloride.

DISCUSSION.

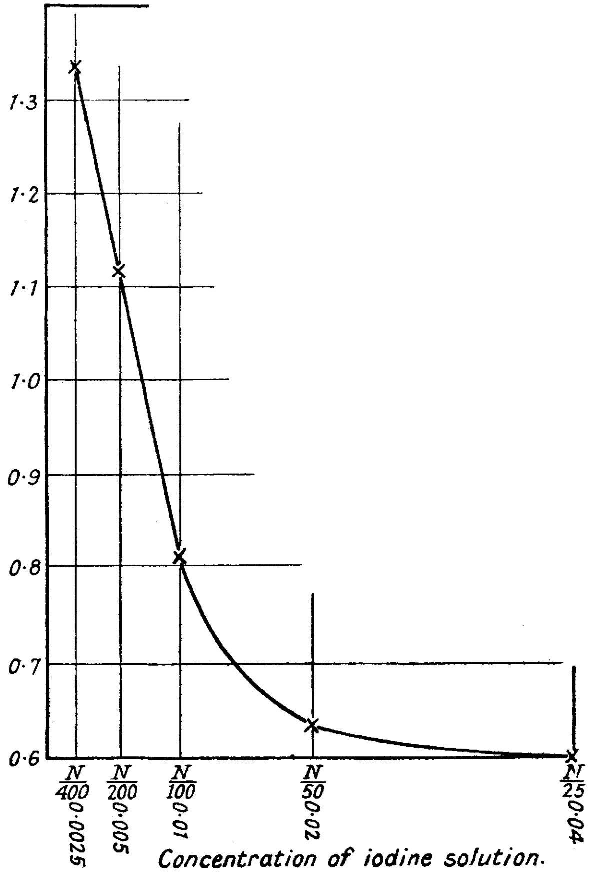
The actual rate of reaction observed in these experiments probably depends ultimately on the collisions of the iodine molecules on the copper surface, whatever the means by which the iodine travels through the cuprous iodide film. The rate of diffusion of the iodine molecules through the film will be a function of the concentration gradient of the molecules across the film, *i.e.*, the concentration of an adsorbed film of iodine on the liquid side of the cuprous iodide and the concentration, much lower, of iodine at the film (Cu_2I_2)–metal interface. The concentration of the adsorbed film of iodine will obviously depend on the state of the iodine in solution. Lachmann (*J. Amer. Chem. Soc.*, 1903, **25**, 50), after an examination of iodine solutions in 60 organic solvents, distinguished two types of solution: (1) violet solutions from substances like carbon tetrachloride, chloroform, etc. (substances called saturated by Lachmann); (2) brown solutions from ethers, esters, alcohols, and ketones (substances called unsaturated by him). This subject has been investigated by a number of workers but on the whole there seems to be little doubt that Lachmann's original classification was correct.

The problem of the benzene solution of iodine is not so simple, and on the collected evidence as a whole these solutions seem to fall directly into neither class. The problem has been investigated in recent years by Walker (*Trans. Faraday Soc.*, 1935, **31**, 1432). This solution was placed by both Lachmann and by Getman (*J. Amer. Chem. Soc.*, 1928, **50**, 2883) in the violet group, yet the colour is definitely reddish and very different from that in carbon tetrachloride, especially in concentrated solution: in more dilute solution the colours are more alike. From a study of the absorption spectrum, Walker concluded that there was some interaction between iodine and benzene. Hildebrand and Jenks (*ibid.*, 1920, **42**, 2180) also showed that benzene solutions of iodine are abnormal with respect to their solubility–temperature relationships compared with other violet solutions. The problem of the possible solvation of iodine in benzene solution is made more complex by the fact that the resulting dipole moment is zero; yet when the evidence as a whole is considered some type of interaction seems to be indicated.

Some simple experiments made by the authors are not without significance. The solutions in carbon tetrachloride or chloroform can be titrated readily with sodium thiosulphate, the end-point being reached with no period of delay; but if 20 c.c. of an N/100-iodine solution in diamyl ether are titrated with N/100-thiosulphate in the presence of starch, the blue colour fades after the addition of a few c.c. of titrant. After about one hour's standing the colour returns, but is again dispersed by the addition of a small amount of thiosulphate, returning again after standing. The theoretical volume of thiosulphate solution required for titration is reached only after several days. This suggests that the thiosulphate only reacts with the free iodine, and that the restoration of the equilibrium between the latter and the complex is slow. If with benzene a solvent–iodine complex is formed in the same way and the complex is of the same nature, the same difficulty might be expected in direct titrations. No such difficulty is experienced, however, so that, although iodine and benzene may form some sort of complex, it is not of necessity of the same type or of the same degree of stability as those formed in the brown solutions.

It is seen in Fig. 2 that the rates of reaction in carbon tetrachloride and chloroform are identical. This is in agreement with Evans and Bannister's results (*Proc. Roy. Soc.*, 1929, *A*, **125**, 370) for the reaction between silver and iodine: it might be expected, since the state of iodine in the two solvents is believed to be the same, *i.e.*, simple molecules. Table II shows that the rate in diamyl ether is much less than the rates in carbon tetrachloride at the same concentration. This might be due to any of the following causes : (1) Only the free iodine molecules diffuse through the cuprous iodide film and react with the metal. (2) Both the free iodine molecules and the complex molecules diffuse through the film but only the free iodine molecules react. (3) Both the free iodine molecules and the complex may react with the copper, but the passage of the complex through the cuprous oxide layer will almost certainly be much slower, owing to its large molecular size.

FIG. 7.



Ratio between ordinates for benzene to ordinates for carbon tetrachloride.

Fig. 3 shows the rate of reaction in benzene compared with the rate in carbon tetrachloride at the same concentrations. Consider first the experiments at concentrations 0·01, 0·02, and 0·04N. The rate of reaction is less than in carbon tetrachloride and the difference increases with increase of iodine concentration. However, the rate of 0·0025N-iodine in benzene is slightly greater than the rate at the same concentration in carbon tetrachloride. If, in Fig. 3, the ordinates of the graph of the reaction in 0·04N-iodine in benzene are compared with those of the graph of 0·04N-iodine in carbon tetrachloride, a fairly constant value of the ratio is obtained; *e.g.*, at time 390, 300, 210, 150, and 60 minutes this ratio is 0·60, 0·61, 0·60, 0·61, and 0·60, respectively. This is, of course, a perfectly arbitrary method of comparing the reaction rates. The average values of this ratio for all the concentrations are plotted against concentration and given in Fig. 7, and show the effect of concentration on the difference in reaction rate in the two solvents. Above concentrations of approximately N/200 the rate in benzene is less than that in carbon tetrachloride; below N/200 it is greater. It is difficult to see any obvious explanation of this inversion.

Graphs for results at 0°, 25°, and 30° are shown in Fig. 4 and it is seen that the temperature coefficient is very small, much less than in the aqueous solutions.

Unlike the reaction in aqueous solution, in organic liquids the rate is affected by the nature of the metal surface; in general, coarseness of surface tends to increase the rate of reaction. The rate of reaction in both benzene and carbon tetrachloride is decreased by the presence of an oxide film, the degree of reduction increasing with the period of oxidation.

Measurements of the rate in carbon tetrachloride of specimens covered with a cuprous iodide film deposited from aqueous solution showed that the rate was much lower than that obtained with a clean metal surface. Conversely, the rate in aqueous solution of a copper specimen covered with a film deposited from a carbon tetrachloride solution was the same as with the new metal specimen. Clearly, the difference is not due to a difference in the structure of the film deposited from the two types of liquid, aqueous and organic.

When the kinetics of this reaction in aqueous and organic solutions are compared, interest centres round the fact that in aqueous solutions the rate is unaffected by the film, whereas in organic solutions the film appears to control the reaction. It is necessary to explain this difference, which cannot be traced, as we have seen, to differences in the structure of the films of cuprous iodide formed in the two cases. It has been stated (Part I) that in reactions in aqueous solution both solvent and solute are believed to pass through the iodide film. It is possible, however, that in organic solvents these do not enter the film but only the solute diffuses through the iodide. These films are readily wetted by water, but on the other hand, it was found that when a sheet of copper was removed from an organic solution of iodine and the surface liquid drained off the film appeared dry and the weight did not decrease with time as might be expected if the liquid were in the pores of the film and hence evaporated slowly. Attempts were made to remove a portion of a film, to support it on a small stand made from thin glass rod, and touch its upper surface with a drop of carbon tetrachloride. The spreading of the liquid on the solid did not take place rapidly, and for some time the under side of the film showed no signs of the liquid soaking through. Owing to cracks formed in the films, they always collapsed after about a minute, so little reliable evidence was obtained. Some evidence for the fact that organic solvents do not enter the iodide film is obtained from a consideration of the reaction in different organic solvents. If the reaction proceeds by the passage of iodine and solvent through the film, then it might be supposed that in using organic solvents of different viscosities different rates might be obtained. The rates of reaction in carbon tetrachloride and in chloroform, in both of which solvents all the evidence points to the iodine existing as simple molecules, are identical, whereas the viscosities of the two solvents are widely different. As shown above, the state of iodine in benzene and diamyl ether is complex and so prevents a consideration of the rates carried out in them with respect to the above; but the evidence from solutions in chloroform and in carbon tetrachloride alone suggests that the organic solvents do not themselves diffuse through the cuprous iodide film.

Adopting this theory, we have still to consider the mechanism by which the iodine molecules diffuse through the film. Three mechanisms appear to be possible: (1) The iodine might diffuse through large cracks in the film (a type of gaseous diffusion); (2) it might diffuse through small pores in the film, possibly in loose union with the cuprous iodide; (3) the diffusions might take place through atomic holes in the cuprous iodide crystal lattice.

The diffusion mechanism of (1) would depend on the vapour pressure of the iodine, which would increase rapidly with rise of temperature, and this would result in a relatively large temperature coefficient. The very small temperature coefficient observed is evidence against this. Mechanism (2), passage of iodine through pores little larger than the molecules themselves, is not impossible. If some type of attraction exists between the iodine and the cuprous iodide little energy would be required for the diffusion. The small temperature coefficient found is some evidence for this. (3) According to the theories developed by Jost and Schottburg " atomic holes " exist as lattice defects in any crystalline material, and it is possible that diffusion of iodine may take place in this manner. This theory of diffusion has, of course, attracted much attention during recent years. Like mechanism (2), this process would require little energy, and it is not possible to distinguish between (2) and (3) by a consideration of the temperature coefficient.

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