

123. *The Kinetics of the Reaction between Copper and Iodine in Aqueous (Potassium Iodide) Solution. Part I.*

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The reaction between copper and iodine solutions containing initially iodine and potassium iodide in the ratio 1 atom. : 4 mols. has been studied and the following points have been established: (1) For a large range of concentrations of iodine the rate of reaction is unaffected by the presence or thickness of the cuprous iodide film formed on the copper as a result of the reaction; (2) the reaction is unimolecular with respect to the iodine; (3) when the reaction proceeds at constant concentration of iodine the graph of time against weight of cuprous iodide is a straight line; (4) the reaction rate is unaffected by the method of preparation or degree of smoothness of the metal surface or by the presence of a cuprous oxide film formed on the copper at 100°; (5) from the temperature coefficient the "critical increment" has been calculated to be 6500 cal. per g.-atom; (6) in the case of N/50-solutions of iodine, if over 300 g./l. of potassium iodide are present the cuprous iodide is not deposited as a film on the metal but is retained in solution, the copper being left in a finely etched condition and oxidising rapidly on drying in the air; (7) the increase in reaction rate on increasing the potassium iodide concentration over a large range of concentrations has been identified with the increase in the rate of diffusion of iodine in higher concentrations of potassium iodide; (8) it is believed that the reaction proceeds by the passage of both iodine and solvent through the cuprous iodide film, and not by the diffusion of copper.

EARLY work on the reaction between aqueous potassium iodide and certain metals including copper was carried out by Van Name and his collaborators (Van Name and Edgar, *Amer. J. Sci.*, 1910, **19**, 45, 237; 1911, **32**, 207; 1917, **43**, 449), who considered that the rates of solution of mercury, cadmium, zinc, copper, and silver in aqueous solutions of iodine containing a large excess of potassium iodide are practically equal, as would be anticipated according to Nernst's diffusion theory. The temperature coefficient between 10° and 35° was found to be 1.3. Increase of potassium iodide concentration accelerated the reactions. In the case of copper and silver large quantities of potassium iodide were used to dissolve the cuprous and silver iodides, as Van Name wished to study the reaction without the presence of the iodide film which he considered would lower the rate of solution of the metal.

For all the metals investigated his method was the same. Strips of the metal foil were placed in the liquid which was stirred at a fixed rate, and the course of the reaction was followed by titration of portions of the solution withdrawn at definite time intervals. The method involved a change of volume of the solution from step to step. If v = volume of solution at a time t , m = total weight of available iodine, c = concentration of iodine, and the reaction is unimolecular with respect to the iodine, the rate of reaction will be defined by $k = [v/(t_2 - t_1)] \log_e c_1/c_2$. This equation was found to hold, and values of k were found to be approximately equal at 25° for all the metals investigated; Van Name therefore considered that the rates of reaction were governed by the rate of diffusion of iodine in the solution.

More recently, interest has centred in the function of the films formed on metal surfaces as the result of chemical action. Pilling and Bedworth (*J. Inst. Met.*, 1923, **29**, 529) have postulated that in many cases in the oxidation of metals the rate of reaction is controlled by the diffusion of oxygen through the protective layer of oxide film formed on the metal surfaces. Hence at constant concentration of oxygen, if x is the mass of the gas combined with the metal at the time t , the rate of reaction $dx/dt = k/x$ which integrates to $\frac{1}{2}x^2 = kt$. This well-known parabolic law, sometimes called the Tammann-Pilling-Bedworth equation, has been found to hold for many cases of corrosion, oxidation, and reactions giving a film of reaction product on the surface of the solid reactant.

Evans and Bannister (*Proc. Roy. Soc.*, 1929, *A*, **125**, 370) have recorded results of experiments on the reaction between silver and iodine in various organic solvents. With constant concentration of iodine, the parabolic law is obeyed save for very small thicknesses of silver iodide. From the effect of concentration it was concluded that the state of the iodine adsorbed on a layer of the silver is not less than I_2 but the small temperature coefficient excludes the idea of "gaseous" diffusion through large apertures. The effect of varying the

solvent indicated that the process is not controlled by the solvent entering pores, and they considered that the iodine passes through pores of a few molecular diameters in loose union with the silver iodide, a process intermediate in character between diffusion in solid solution and gaseous leakage through definite cracks.

The reaction between copper and sulphur in carbon tetrachloride solution has been studied by Bradley (*Trans. Faraday Soc.*, 1938, **34**, 278), who found that, although a film of cuprous sulphide was deposited on the copper surface, the reaction was unimolecular with respect to the sulphur concentration and the film did not affect the rate.

In general, it appears that heterogeneous reactions which result in formation of a film on the surface of one reactant fall into two classes: (i) in which the velocities are controlled by the diffusion of one or more reactants through the film; (ii) in which the rate is independent of the thickness of the reactant film. Interest in this question has recently been revived by the work of Wagner (*Z. physikal. Chem.*, 1933, **B**, **21**, 37) on the reaction between silver and sulphur at 400°; he concluded that, contrary to expectation, it is mainly the silver, and not the sulphur, which diffuses through the film of silver sulphide. A similar phenomenon was noted previously by Pfeil (*J. Iron Steel Inst.*, 1929, **119**, 501), who showed that in the oxidation of iron there is considerable diffusion outwards through the already existing film of oxide.

The present work records values of the rates of reaction between copper and iodine dissolved in aqueous potassium iodide, and the following variables were investigated: (1) The initial concentration of the iodine, from 0.04*N* to 0.0025*N*; in all cases unless otherwise stated the solutions contained 4 mols. of potassium iodide per atom of iodine. (2) The nature and treatment of the surface of the copper foil. (3) The concentration of the potassium iodide. (4) The temperature, 20°, 25°, 30°, and 35°. (5) The rate of stirring. One of the chief objects was to obtain information on the influence of the cuprous oxide film on the course of the reaction, especially with regard to Wagner's work.

EXPERIMENTAL.

Materials.—"AnalaR" Iodine (Hopkin and Williams) was used throughout. The impurities consisted only of 0.01% non-volatile matter, 0.005% chloride and bromide, 0.005% cyanide, 0.01% sulphate, so further sublimation over potassium iodide was considered unnecessary. "AnalaR" Potassium iodide was also used, and the "AnalaR" sodium thiosulphate contained sulphate and sulphite 0.01%, sulphide 0.0005%, heavy metals 0.0015%. The copper foil was of extremely high purity and was kindly supplied by I.C.I. Metals, Ltd., through the courtesy of Dr. Maurice Cook. All burettes and pipettes were checked by gravimetric means, and one pipette was used throughout the entire work for the withdrawal of the 5-c.c. samples.

Preparation of the Copper Surface.—Pieces of copper 4.0 × 4.5 cm. and 0.25 mm. thick, were used. This thickness ensured a strong foil which would not bend on rapid rotation in the liquid, yet the total weight of metal was small enough to ride easily in the fragile glass saddle. The standard polished surface was always prepared as follows except where otherwise stated. The copper was cut into the requisite area by means of a razor blade and a copper guide block of accurate dimensions. The foil was then washed free from grease with carbon tetrachloride. A pad of washed linen containing carborundum powder grade 3F was soaked in carbon tetrachloride and used to polish the metal in one direction only for 3 mins. on each side of the foil. This method ensured the removal of all surface impurities and oxide. The foil was then well washed with carbon tetrachloride and kept under the liquid until used. In every case the foil was prepared immediately before the start of each experiment. This method of polishing will be referred to as "carborundum straight polishing" (C.S.P.).

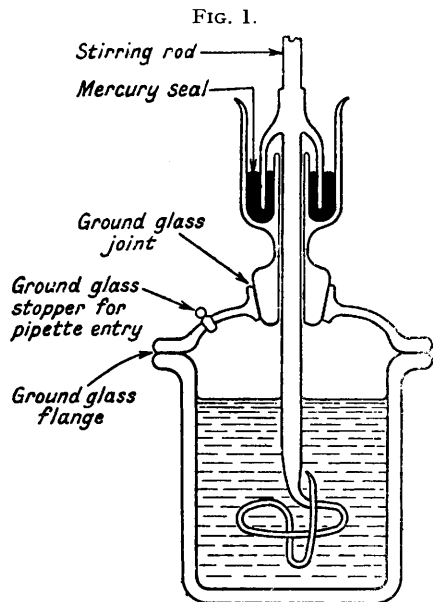
Apparatus.—The reaction vessel is shown in Fig. 1 and is self-explanatory. The metal specimen is held in the saddle, constructed from drawn-out glass rod (0.1 cm. thick), so that the edges of the specimen only touch the glass at three points. The vessel is made completely of glass, with ground glass flanges and joints, and the interior is closed by a mercury seal. The area of mercury exposed to iodine vapour within the vessel is so small as to be negligible. The vessel is readily opened by sliding the part above the ground glass flange, and the glass stopper in the top portion exists for the entry of the pipette. This stopper is removed momentarily at given intervals, but the duration of each removal is so small that no appreciable evaporation takes place.

The rotation of the stirrer was effected by an electric motor connected to the glass rod through a reduction gear. This ensured more regular rotation than if no reduction gear were used, and by introducing a rheostat into the motor circuit the rate of rotation could be varied to obtain close reproduction of results.

In all experiments, except those carried out in constant concentration of iodine, the procedure was the same. 300 C.c. of the solution were measured into the reaction vessel, which was immediately closed and placed in the thermostat at the particular temperature. At the start of the reaction the copper foil was placed in the saddle, and rotation carried out at a fixed rate. At given intervals 5 c.c. samples were pipetted out and titrated directly with sodium thiosulphate solution, the concentration of which was $\frac{1}{2}$ that of the initial concentration of the iodine solution. The initial titration figure (20 c.c.; $t = 0$) was large enough to ensure a reasonable accuracy. The titrations of iodine by thiosulphate entailed using solutions of the latter between ranges of concentration of $N/100$ and $N/1600$. It was found that the use of such dilute solutions in no way vitiated the accuracy of the titrations. Very dilute starch solutions were used and the pale sky-blue colour disappeared with extreme sharpness at the end-point.

Analysis of the Film.—A piece of copper foil was cleaned and polished (C.S.P.) and rotated in an $N/100$ -solution of iodine in $N/25$ -potassium iodide for 1 hour. It was then removed, washed, and dried, and the film removed and its copper content determined by the thiocyanate method (Found: Cu, 33.28. Calc. for Cu_2I_2 : Cu, 33.34%).

The Direction of Diffusion through the Film of Cuprous Iodide.—Wagner's method (*loc. cit.*) failed, for whereas silver



sulphide forms stable, hard pellets, those formed when cuprous iodide is compressed are soft and crumble readily. An alternative method was therefore tried. When copper reacts with iodine, the resulting film has a faint yellow tinge if aqueous potassium iodide is the solvent, but is almost colourless if thiophen-free benzene is the solvent. If, however, iodine solution in benzene containing slight traces of thiophen is used, the resultant film is black. This may be due to the presence of minute traces of cuprous sulphide in the film, but the amount is too small to be detected.

Two sheets of copper foil were polished (C.S.P.). A double saddle was constructed on the end of the stirring rod, and one piece of copper placed in each compartment. These were rotated in an $N/100$ -solution of iodine in benzene (not thiophen-free) for 24 hours, and a stable black film was formed over the surface of both pieces of copper. These were removed and dried. One specimen was then rotated in $N/200$ -iodine in $N/50$ -potassium iodide for 20 minutes, removed, and dried. Inspection of the primary film showed it to be black throughout. The film on the further-treated specimen, however, showed a black outer film characteristic of the action of iodine in benzene, and underneath, an inner white film characteristic of the action of aqueous iodine. A portion of the outer black film was chipped off with a razor and a photomicrograph is shown in Fig. 2. The black film is superimposed on the white film. In the bottom left-hand corner a little of the white film has also been broken away and shows the copper surface underneath. Apparently the iodine diffuses through the film to the copper.

The experiment was then reversed. Two copper sheets were prepared as before and rotated in a similar iodine solution, two stable white films being produced. The foils were removed and dried, and one was rotated in a solution of iodine in benzene for 36 hours, removed, and dried. The first specimen showed a homogeneous white film, but the second showed, beneath this white film, a black film characteristic of the action of iodine in benzene. A photomicrograph of the foil, with a portion of the white film chipped away, is shown in Fig. 3. Here again the iodine appears to diffuse through the cuprous oxide film. It must be remembered that the reaction for which Wagner showed a reverse mechanism, *i.e.*, the diffusion of the cation rather than the anion, takes place at a high temperature (400°).

Table I shows the complete readings for the reaction with solutions of iodine of initial concentration $N/400$ at 25° . For other concentrations at 25° and a number of experiments at 20° , 30° , and 35° , only the times and the values of k are given. In all cases, $[KI]/[I] = 4$. Col. 2 gives the thiosulphate titration ($a - x$). Col. 3 gives c , iodine concentration (g.-atoms/l.) at time t , calculated from the titration value. Col. 4 shows x , which is proportional to the amount of iodine which has reacted with the copper at time t save for a small correction to be made in each reading for the effect of the change of volume after each titration. In col. 5, χ represents the total amount of iodine (in g.-atoms $\times 10^{-6}$) present as cuprous iodide per sq. cm. of copper surface at time t , corrections having been made for the change in volume of solution mentioned above and for the area of copper (36 sq. cm.), as given by

$$x = \frac{1}{1000 \times 36} \left\{ \left(300c_0 \times \frac{x_1}{20} \right) + \left(295c_0 \times \frac{x_2 - x_1}{20} \right) + \left(290c_0 \times \frac{x_3 - x_2}{20} \right) \dots \dots \dots \right\}$$

In Col. 6, k is calculated from $k = [2.303v/(t_2 - t_1)] \log_{10} c_1/c_2$.

The Influence of the Copper Surface on the Rate of the Reaction.—The method of polishing the copper surface has been described. Microscopic examination (mag. 50) showed unbroken parallel scratches on the metal. Three other methods

for the preparation of the surface were used, and their effect on the reaction rate investigated. (1) The surface was washed as before and a similar pad made. The polishing was carried out, however, with a circular motion. The strip was then washed again as in the first method. Surfaces so treated showed under the microscope deep scratches. (2) The copper surface was washed with carbon tetrachloride and first polished with a revolving pad of washed lamb's wool and soft brick dust. Final polishing was carried out with jeweller's rouge. The final surface showed excellent optical reflection and no scratches (mag. 50). (3) The surface was washed with cotton wool soaked in very dilute nitric acid until it was of uniform colour, then washed well with water and finally with carbon tetrachloride. Surfaces so prepared showed no scratches.

Vernon (J., 1926, 2273) has shown that when copper is heated in air for a short time at 100° a film of oxide is formed, which has extraordinary protective properties. It was considered of interest to determine if this film had any influence on the present reaction. A deep red film was produced on the metal by heating it for 30 mins. in a closed glass vessel in an air-bath at 100° . Care was taken not to damage the film in removal.

All these differently prepared specimens were tested in $N/50$ -iodine at 25° . The results are shown graphically in Fig. 4, x being plotted against t ; x is comparable in all cases, and it will be seen that the preparation of the copper surface has no effect on the rate of reaction. If, after a few minutes' reaction between the oxidised copper and the iodine, the cuprous iodide layer be removed with a razor, no sign of the oxide film can be seen. Probably this very thin oxide film is immediately removed by iodine.

The Reaction in Solutions containing Large Quantities of Potassium Iodide.—It has been shown by Van Name and Edgar (*loc. cit.*) that if copper reacts with iodine containing about 400 g. of potassium iodide per l., cuprous iodide is not deposited but remains in solution.

Such a solution of potassium iodide was therefore used in studying the reaction at four temperatures, 20° , 25° , 30° , and 35° , the object being to compare the rate of reaction with the rates in solution of low iodide concentration where the iodide film is present. The surface of the metal after reaction presented some features of interest: it was completely free from cuprous iodide but pale pink and very rough. On washing and drying the metal and examining it in air, the surface was found to be reddish-brown, probably owing to oxidation, the surface of the copper being so pitted that when the layer of protective moisture evaporated, the copper surface spontaneously oxidised. The results are shown in Table II. The column headed χ has a slightly different significance and may be considered to represent the weight of iodine lost from solution as I_2 or KI_3 , per sq. cm. of copper surface.

The Reaction at Constant Concentration of Iodine.—The experimental difficulties of keeping the concentration of iodine in solution constant throughout are considerable. Since these experiments preclude following the reaction by titration, it must be followed by weight increments. The use of a large concentration of iodine and small strips of copper would

FIG. 4.

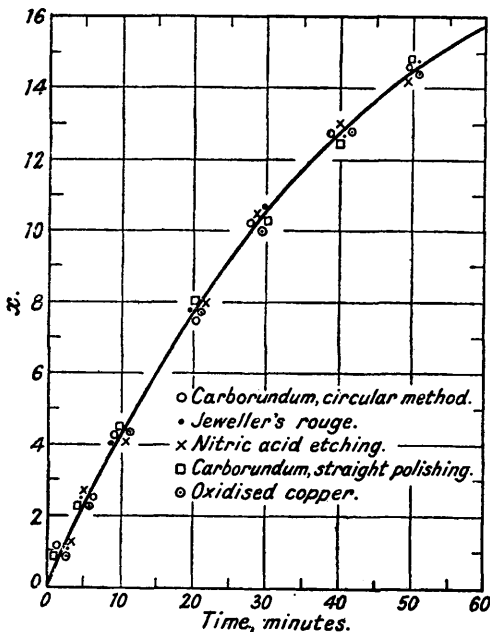
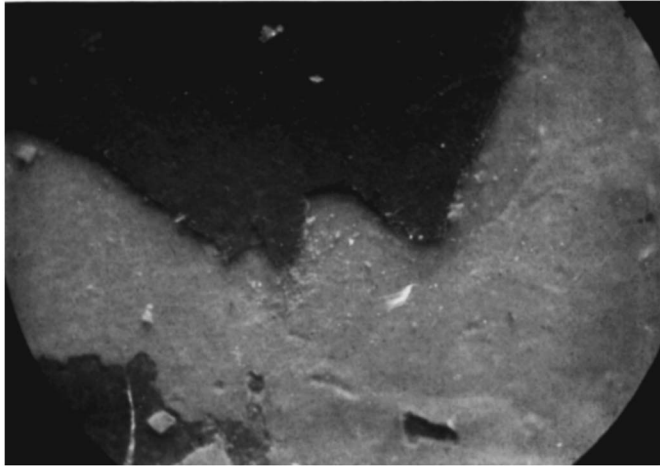
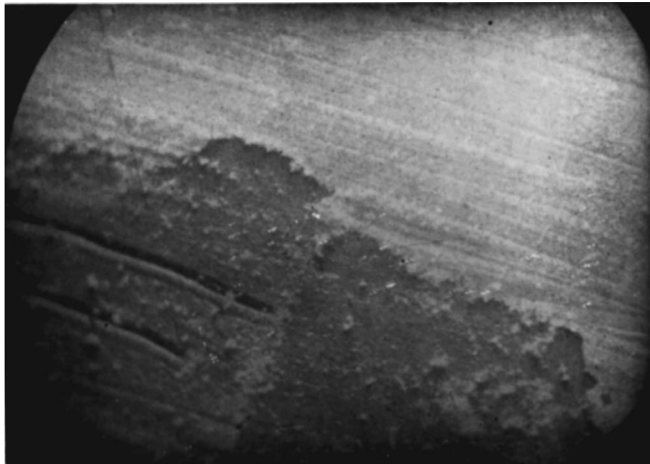


FIG. 2.



Magnification 50 diameters.

FIG. 3.



Magnification 50 diameters.

[To face p. 600.]

TABLE I.

N/400-Iodine at 25°.

Time, mins.	(a - x). c × 10 ⁵ .	x.	χ × 10 ⁶ .	k.	Time, mins.	(a - x). c × 10 ⁵ .	x.	χ × 10 ⁶ .	k.
0	20.0	250	—	—	20	12.4	155	7.6	7.619
2	19.1	239	0.9	0.937	6.91	30	9.6	120	10.4
5	17.9	224	2.1	2.166	6.38	40	7.3	91	12.7
10	15.8	197	4.2	4.282	7.23	50	5.7	71	14.3
15	14.0	175	6.0	6.063	6.80	60	4.4	55	15.6
					Mean 6.99				

N/200-Iodine at 25°.

N/100-Iodine at 25°.

N/50-Iodine at 25°.

N/25-Iodine at 25°.

Time, mins.	k.	Time, mins.	k.	Time, mins.	k.	Time, mins.	k.
2	6.99	2	6.91	2	6.91	2	6.15
5	6.93	5	6.66	5	6.59	5	6.38
10	6.91	10	6.91	10	6.93	10	6.84
15	6.89	15	7.07	15	7.32	15	7.21
20	7.23	20	6.79	20	6.59	20	6.75
30	7.09	30	7.03	30	7.30	25	7.02
40	7.12	40	7.03	40	7.00	30	6.84
50	6.95	50	7.37	50	7.25	40	7.16
60	6.86	60	6.86	60	6.54	50	7.24
Mean 6.99		Mean 6.96		Mean 6.97		Mean 6.83	

N/400-Iodine at 20°.

N/200-Iodine at 20°.

N/100-Iodine at 20°.

N/50-Iodine at 20°.

N/25-Iodine at 20°.

Time, mins.	k.	Time, mins.	k.	Time, mins.	k.	Time, mins.	k.	Time, mins.	k.
2	6.22	2	5.78	2	5.71	2	5.35	2	5.71
5	5.11	5	4.84	5	5.39	5	5.51	5	5.51
10	5.41	10	5.18	10	5.94	10	5.49	10	5.67
15	6.07	15	6.22	15	5.39	15	6.09	15	5.61
20	5.76	20	5.53	20	5.85	20	5.50	20	5.69
30	5.62	30	5.80	30	6.08	30	5.85	30	5.61
40	5.92	40	5.57	40	6.15	40	6.21	40	5.84
Mean 5.73		Mean 5.56		Mean 5.78		Mean 5.71		Mean 5.66	

N/400-Iodine at 30°.

N/200-Iodine at 30°.

N/100-Iodine at 30°.

N/50-Iodine at 30°.

Time, mins.	k.	Time, mins.	k.	Time, mins.	k.	Time, mins.	k.
2	7.12	2	7.70	2	8.08	2	8.49
5	8.89	5	8.24	5	8.41	5	8.13
10	7.69	10	8.77	10	8.22	10	8.61
15	7.83	15	8.35	15	8.32	15	8.16
20	9.45	20	8.55	20	8.31	20	8.10
30	8.87	30	8.79	30	8.36	30	8.20
40	—	40	8.35	40	8.09	40	8.48
Mean 8.31		Mean 8.38		Mean 8.21		Mean 8.31	

N/400-Iodine at 35°.

N/200-Iodine at 35°.

N/100-Iodine at 35°.

N/50-Iodine at 35°.

Time, mins.	k.	Time, mins.	k.	Time, mins.	k.	Time, mins.	k.
2	9.30	2	9.68	2	8.75	2	8.75
5	9.80	5	10.22	5	9.99	5	9.59
10	9.63	10	9.69	10	10.57	10	9.16
15	9.92	15	9.99	15	9.17	15	10.71
20	10.12	20	9.65	20	10.59	20	10.96
30	10.08	30	9.69	30	9.89	30	9.98
Mean 9.81		Mean 9.82		Mean 9.827		Mean 9.86	

not give results of sufficient accuracy, since the weight increments would be so small. It is impossible to use a saturated solution of iodine in, say, N/200-potassium iodide solution, with solid iodine present in a linen bag, since its rate of dissolution in this solution is smaller than its rate of consumption by the reaction.

The following method was found satisfactory. About 25 c.c. of chloroform were placed in the bottom of a standard reaction vessel, and excess iodine added, giving a saturated solution. 300 C.c. of N/200-potassium iodide were added, and equilibrium was established by stirring with a glass sheet in the rotation saddle used previously for the copper strip. A certain concentration of iodine was set up, according to the partition coefficient, in the aqueous layer. The requisite number of copper strips were prepared (36 sq. cm. area), polished (C.S.P.), washed, dried, and weighed. When the solution had reached equilibrium the glass sheet was replaced by a copper strip, and the reaction carried on for a time t_1 , the copper then being removed, washed, dried, and weighed. A second copper strip was then rotated for a time t_2 , and so on. That the concentration of the iodine in the aqueous layer remained constant throughout was checked by titrations with thiosulphate. The equilibrium between saturated chloroform and N/200-potassium iodide was restored more rapidly than the iodine was removed by the reaction. These experiments were repeated with N/400-potassium iodide, and the temperature in each case was 35°. The results are shown graphically in Fig. 5, and it will be seen that the relation between weight increment and time is linear.

TABLE II.
($c_0 = 0.0200$ throughout.)

Time, mins.	(a - x).	$c \times 10^4$.	x.	$x \times 10^6$.	k.	Time, mins.	(a - x).	$c \times 10^4$.	x.	$x \times 10^6$.	k.
N/50-Iodine at 20°.						N/50-Iodine at 25°.					
2	19.2	192	0.8	6.67	6.12	2	19.05	190	0.95	7.92	7.31
5	17.9	179	2.1	17.32	6.89	5	17.6	176	2.4	19.80	7.78
10	15.9	159	4.1	33.43	6.87	10	15.35	153	4.65	37.92	8.11
15	13.95	139	6.05	48.87	7.45	15	13.35	133	6.55	53.76	7.79
20	12.25	122	7.75	62.09	7.29	20	11.5	115	8.5	68.15	8.35
30	9.55	95	10.45	82.72	6.84	30	8.4	84	11.6	91.83	8.65
Mean 6.91						Mean 8.01					
N/50-Iodine at 30°.						N/50-Iodine at 35°.					
2	18.8	188	1.2	10.00	9.19	2	18.6	186	1.4	11.67	10.89
5	17.15	1715	2.85	23.52	9.23	5	16.75	167	3.25	26.85	10.30
10	14.55	1455	5.45	44.46	9.44	10	13.65	136	6.35	51.80	11.87
15	12.3	123	7.7	62.27	9.79	15	11.3	113	8.7	70.40	10.77
20	10.3	103	9.7	77.82	9.86	20	9.25	92	10.75	86.34	11.21
30	7.3	73	12.7	100.75	9.51	30	6.1	61	13.9	110.40	10.44
Mean 9.50						Mean 11.08					

Retarding Films.—Evidence has been given that the film of cuprous iodide formed by the action of aqueous iodine on copper does not retard the reaction. In certain cases, however, retarding films have been observed and they may be divided into two sections.

FIG. 5.
Reaction between copper and iodine of constant concentration at 35°.

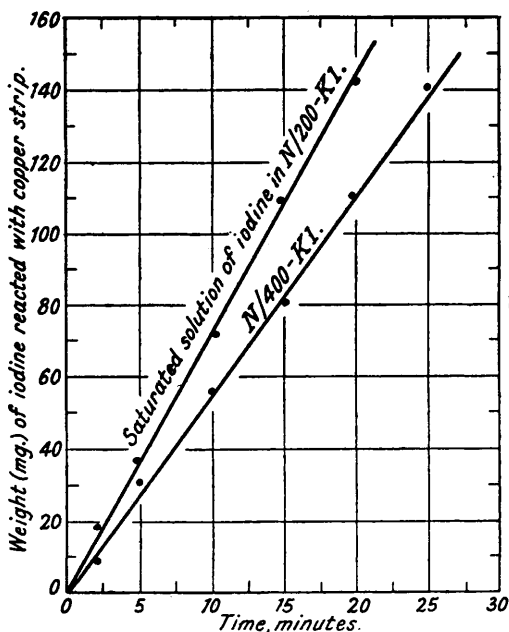
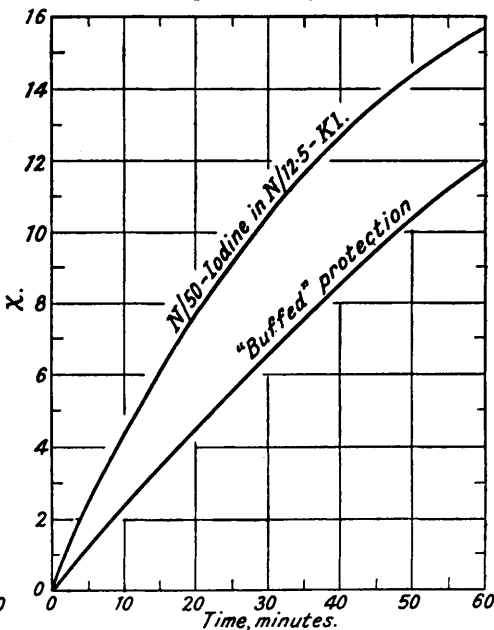


FIG. 6.
Graph showing retardation of reaction by buffing cuprous oxide film.



(1) *"Buffed" surfaces.* A piece of copper was prepared in the usual manner, placed in N/25-iodine in N/6.25-potassium iodide solution for 1 hour, removed, and dried. The surface was then "buffed" with the usual carborundum pad. Much of the outer film was removed, but the copper strip showed a brown lacquer-like finish. The strip was then tested with N/50-iodine solution as usual. The results are shown graphically in Fig. 6. It will be seen that with the "buffed" metal the reaction is slower. In some way a part of the iodide is ground into the copper surface and forms a partly protective layer. The protective nature of such a treatment was found in all cases investigated, and in one experiment the buffing produced a protective layer which almost prevented further action on the metal by aqueous iodine solution.

(2) *Rapidly deposited films.* In the foregoing tables, the readings for the reaction between copper and N/25-iodine in N/6.25-potassium iodide at 30° and 35° are omitted. They are given in Tables III and IV. In Table III k is fairly

TABLE III (30°).

Time, mins.	a - x.	k.	Time, mins.	a - x.	k.
0	20.0	—	15	14.2	6.54
2	19.2	5.80	20	12.75	5.89
5	17.9	6.98	30	10.55	5.29
10	15.9	6.96	40	8.9	4.59

TABLE IV (35°).

Time, mins.	a - x.	k.	Time, mins.	a - x.	k.
0	20.0	—	15	13.3	6.17
2	18.75	9.68	20	12.1	5.39
5	17.0	9.63	30	10.25	4.51
10	14.8	8.04	40	8.75	4.35

constant but lies well below the figure for 30° (8.31) obtained with the lower concentrations. In Table IV, k starts slightly below the value for 35° (lower concentrations), *viz.*, 9.83, and falls rapidly with time. This phenomenon was duplicated on repeating these experiments. That is, the reaction with $N/25$ -iodine does not obey the simple unimolecular law followed over the more dilute range of concentrations at these and lower temperatures. These solutions are the most concentrated used previously, so that the experiments at 30° and 35° are those in which the cuprous iodide film is most rapidly formed in its initial stages. In view of this, the reaction was studied with $N/10$ -iodine in $N/2.5$ -potassium iodide solution at 35°, 30°, 25°, and 20°. In all cases the velocity constant falls off rapidly with time, and the rate of fall increases with rise of temperature; moreover, all the cuprous iodide films are harder and less easily chipped away than the usual films. Table V shows M , the amount of iodine (g.) absorbed in 30 mins. from different concentrations at 25° and 30°.

TABLE V.

At 25°.						
Initial concn. of iodine, N	0.0025	0.005	0.01	0.02	0.04	0.1
M , g.	0.0475	0.0950	0.1882	0.3800	0.7434	0.8055
At 35°.						
Initial concn. of iodine, N	0.0025	0.005	0.01	0.02	0.04	0.1
M , g.	0.0589	0.1170	0.2367	0.4750	0.7115	0.8360

The Concentration of the Potassium Iodide.—The reaction between $N/50$ -iodine in potassium iodide solution of concentrations (g./l.) 13.28 ($N/12.5$), 50, 100, 150, 200, 300, 400, and 800 was carried out in the usual manner at 25°. The

FIG. 7.

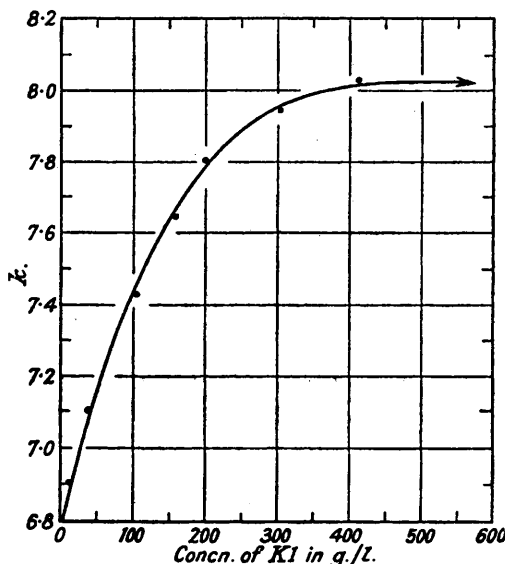
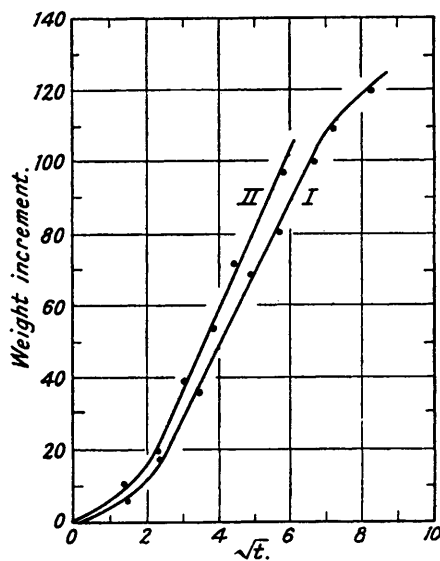


FIG. 8.



results are shown graphically in Fig. 7. With 200 g. of potassium iodide the film becomes patchy and shows evidence of having been partly attacked by the iodide. With 300 g. of potassium iodide no film of cuprous iodide is visible. Examination of the graph shows that the velocity constant increases gradually with increase of potassium iodide concentration up to 400 g./l., no further difference being shown at 800 g./l.

Rate of Stirring.—The effect of the rate of stirring on the rate of reaction was investigated but no change was detected as long as the rotation was maintained at a fairly high rate. A standard rate of 100 r.p.m. was adopted as giving reproducible results.

DISCUSSION.

The reaction which has been studied might be governed by any of the following mechanisms. (1) The rate might be independent of the concentration of iodine throughout, and controlled by diffusion of iodine through the film of cuprous iodide, in which case the reaction will follow the Tammann-Pilling-Bedworth equation $dx/dt = k/x$, whence $x^2 = kt$. (2) The rate might be independent of the thickness of the cuprous iodide layer but directly proportional to the concentration of the iodine. Hence, dealing, as we are here, with a constant surface area of copper, a unimolecular law, modified for the step-wise volume changes introduced in the course of the reaction, might apply; *i.e.*, $k = [v/(t_2 - t_1)] \log_e c_1/c_2$. (3) The rate might be proportional to the concentration of the iodine at any moment and might also be controlled by diffusion through the cuprous iodide layer so that $-dc/dt = kc/\chi$, where χ is proportional to the thickness of the iodide layer.

In Fig. 8 graphs for 25° of the weight increment against \sqrt{t} are shown. Curve I represents $N/50$ -iodine in $N/12.5$ -potassium iodide; Curve II shows the reaction with $N/50$ -iodine in aqueous potassium iodide containing 400 g./l. Curve I after a short initial period approximates to a straight line, and it might be assumed from this that the Tammann-Pilling-Bedworth law is approximately obeyed. When Curve II, representing the reaction

in the absence of an iodide film, is considered, however, the graph is seen to be of the same shape. Again, if the course of the reaction in dilute potassium iodide be governed by mechanism (1), the rate of reaction being independent of the concentration of iodine in solution, then the values of χ at any time t , in cases involving different initial concentrations of iodine solution, should be identical. This is not so: the values of χ are directly proportional to the initial concentration of iodine. The simple Tammann-Pilling-Bedworth equation is not therefore applicable to this reaction under our conditions.

The results given in Table II show that the equation $k_2[v/(t_2 - t_1)] \log_e c_1/c_2$, first derived by Van Name and Edgar, is obeyed quite well. The values of k increase slowly with rise of temperature, as observed by Van Name and Edgar. Consideration of the results of experiments in Table I shows, however, that the equation is equally well obeyed in those cases in which the copper is covered with a cuprous iodide film throughout the reaction. The value of k will be seen to be approximately independent of the initial concentration of the iodine, and it is concluded that, between the limits of temperature and under the conditions stated, the reaction between copper and iodine dissolved in aqueous potassium iodide is unimolecular with respect to the iodine and is independent of the presence or thickness of the cuprous iodide film formed on the copper in the course of the reaction.

It may be suggested therefore that the reaction proceeds by collisions between the iodine and the copper surface. The film of iodide has no impeding effect; hence the reactant appears to pass through the film readily. This is not unexpected, since cuprous iodide films so formed are easily wetted by water.

The physical condition of the surface of the copper does not affect the reaction rate. If the reaction were controlled by the diffusion of one reactant through the film, then it might be expected that the type of surface would affect the reaction rate; for various types of surface might initiate a particular orientation of the film of iodide. Since, however, the reaction is not controlled by diffusion through the film the results obtained are not unexpected.

The gradual increase in k with increase in iodide concentration in the reaction between various metals and iodine in aqueous potassium iodide was noted by Van Name and Edgar (*loc. cit.*). The problem was investigated further by Edgar and Diggs (*J. Amer. Chem. Soc.*, 1916, **38**, 253), who measured the rate of diffusion of iodine in potassium iodide solutions of various concentrations at 25°. They give a graph showing the relation between the diffusion constant and the concentration of the iodide which is similar in shape throughout its whole course to that of Fig. 7. The conclusion they reached, confirmed by the present work, is that the increased rate of reaction is connected in some way with the increased rate of diffusion of the iodine.

We now consider the more rapidly deposited films. The readings at 25° (Table V) show that the value of M for a 0.005*N*-solution is twice the value for the 0.0025*N*-solution. This direct proportionality holds up to and including 0.04*N*-solution. The value of M for 0.1*N*-solution is, however, barely greater than that for 0.04*N*-solutions, and moreover the reaction in 0.1*N*-solution does not obey the simple unimolecular law. The readings at 35° show strict proportionality up to and including 0.02*N*. The value of M for 0.04*N*-solutions is, however, much less than twice the value for 0.02*N*-solutions, and the value for 0.1*N*-solution is still further removed from the value expected if strict proportionality held. The reaction at 25° in solutions up to and including 0.04*N* is unimolecular with respect to iodine, but this does not hold at higher concentrations. At 35° this mechanism breaks down when solutions of 0.04*N* are reached.

For many reactions between solids and liquids it is considered that an adsorbed film of reactant is set up on the surface of the solid—Nernst's well-known theory. We might make the probable assumption that the concentration of iodine in the adsorbed layer is a function of that in the solution up to a certain value of the latter, after which it is independent of the bulk concentration of iodine. We should expect the reaction to be unimolecular up to this point, after which the velocity of the reaction would become constant (zero order). These assumptions would not explain such a result as that obtained at 35° with *N*/25-iodine (Table IV), where the unimolecular constant starts off at approximately the "correct" figure and falls rapidly with time. Although under the conditions of temperature and concentration detailed in Table I, the rate of reaction is not affected by the presence of the iodide film, yet it is possible that under conditions in which the film forms on the copper at a much greater rate, the structure of the film may be altered. It may be that, during relatively slow growth of the cuprous iodide, intercrystalline cracks and holes may exist in the film and these permit the passage of the reactant readily. During rapid film growth, however, these holes may be covered by further crystals laid haphazardly upon them. We have also the possibility of orientation of the crystals composing the film occurring at some rate of formation of the latter. *X*-Ray examination should throw some light on this question. We have, however, the experimental observations that the films produced at the higher concentration (Table IV) appeared harder and less easily removed from the metal than the usual films.

It is well known that apparently simple heterogeneous reactions of this type are extremely complex, usually involving the actual chemical reaction complicated by diffusion and adsorptive effects. In Part II, dealing with the kinetics of the reaction in organic media, the mechanism is further discussed.

The logarithms of the velocity constants of the reaction both for low concentrations of potassium iodide, where the cuprous iodide film is formed, and for higher concentrations of iodide (no film) have been plotted against the reciprocal of the absolute temperature and excellent straight lines are obtained in both cases. From the slopes of these, the critical increment has been calculated; for low concentrations of potassium iodide (4 times that of the initial concentration of iodine in each case) it is 6500 cal./g.-atom of iodine. At higher concentrations of potassium iodide (400 g./l.) the value is 5760 cal. This is in fair agreement with the

value calculated by Moelwyn-Hughes ("Kinetics of Reactions in Solution," p. 279) from Van Name's data, *viz.* 4040 cal.

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