

ART. XXIV.—*On the Rates of Solution of Certain Metals in Dissolved Iodine, and their Relation to the Diffusion Theory*; by R. G. VAN NAME and ROWLAND S. BOSWORTH.

[Contribution from the Kent Chemical Laboratory of Yale Univ.—ccxxiii.]

IN a recent paper* it was shown that the metals mercury, cadmium, zinc, copper, and silver, all dissolve at the same rate in a solution of iodine in potassium iodide, a result which seems to prove that the velocity of the reaction is determined by the rate of diffusion of the iodine rather than the actual rate of combination of the iodine with the metal. Moreover, it was found that when the concentration of the potassium iodide is changed, or when bromine or cupric bromide is substituted for the iodine, the reaction velocity is altered in the direction which would be expected from the rates of diffusion of the active substances.

The present investigation is an extension of the work of Van Name and Edgar, intended to further test the applicability of the Diffusion Theory to this type of reaction. It covers, (1), a comparison of the rates of solution of several more metals in iodine; (2), a study of the effect of substituting other metallic iodides for potassium iodide; and (3), of the effect of varying acidity.

The method and apparatus employed were substantially the same as those used and described by Van Name and Edgar, but with several minor modifications which increased the regularity and reproducibility of the results. Disks of the different metals, of like size, were held in a fixed position in the iodine solution with the plane of the disk vertical and close to the path of the blades of a propeller-shaped glass stirrer revolving at a known rate. The velocity of the reaction was measured by removing samples of the liquid from time to time and titrating with 0.02 normal thiosulphate.

Two points in which the procedure differed from that of Van Name and Edgar are worthy of mention; first, the special precautions, described below, which were employed to insure uniformity in the size of the metal disks, and second, the use of a holder for the disks made entirely of platinum. The latter eliminated a source of trouble and uncertainty present in the earlier work owing to the occasional breakage of the glass holder, since it was necessary, and by no means easy, to repair the holder without appreciably altering its dimensions. This new holder, which was identical in shape with the glass ones, was constructed of stiff heavy platinum wire. To prevent

* Van Name and Edgar, this Journal, xxix, 237, 1910.

metallic contact between disk and holder, the three horizontal projecting arms which grasped the disk at three points on its circumference were coated with a heavy layer, renewed from time to time, of a commercial pyroxylin preparation known as "New Skin." The slight spring of the platinum wire sufficed to hold the disk firmly in place.

Variations in the diameter of the disks, since they affect the surface area to a relatively large extent, were avoided in the following way. The metals used were carefully rolled out to a uniform thickness of 0.5^{mm} and cut into pieces slightly larger than desired. A pair of specially prepared patterns in the form of thick circular disks of hardened steel were then clamped in concentric position on opposite sides of the metal sheet, and the edges of the latter carefully trimmed and filed away to exact coincidence with the circumference of the patterns. The diameter of the disks so prepared was 38.3^{mm} with a maximum variation of about 0.05^{mm}. Before using, the disks were always cleaned with hot caustic alkali and then slightly etched with acid to insure uniform action over the whole surface.

The velocity constant was calculated from the expression $K = 2.3 \frac{v}{t_2 - t_1} \log \frac{c_1}{c_2}$, in which v is the total volume of the liquid, and c_1 and c_2 are the amounts of thiosulphate needed to titrate a 20^{°c} sample at times t_1 and t_2 .

The rate of stirring was the same in all the experiments here recorded, 170 revolutions per minute. Variations in the rate seldom exceeded ± 1 per cent, and as great care was taken to adjust the *mean rate* to 170 revolutions, the fluctuations affected chiefly the single values of the constant, and must have had an almost negligible effect upon the final result, i. e., upon the average value of the velocity constant for the given experiment.

In many of the experiments a further precaution was taken. With the aid of a stop-watch, and of a bell connected with the speed indicator so as to ring after every 100 revolutions, it was possible without interfering with the experiment to accurately determine the mean rate of stirring for the whole of each separate reaction period. The corresponding values of the velocity constant were then corrected to 170 revolutions on the assumption that the value of the constant is proportional to the $4/5$ power of the rate of stirring.* Although this procedure gave greater security against possible variations in the stirring, the effect of the corrections upon the final result

* This relation was shown to hold approximately by the work of Van Name and Edgar.

proved in many cases to be wholly negligible, and in only one experiment out of about thirty did it amount to five units in the second decimal place (about 0·7 per cent), thus showing that for most purposes the simpler method was sufficiently accurate.

Experiments with Cadmium.

A preliminary series of experiments showed that cadmium would be a more suitable metal for the purposes in view than mercury, the metal used by Van Name and Edgar in the majority of their experiments. It is worthy of mention that the rates of solution of these two metals were found to be the same within the error of experiment, thus confirming the conclusion reached in the earlier paper.* The values obtained were as follows:

Mercury (Disk of gold, heavily amalgamated)					
with $n/1$ KI, (4 exps.)	7·41	7·36	7·46	7·47	Mean, 7·43
“ $n/1$ NaI, (3 exps.)	6·86	6·56	6·72		Mean, 6·71
Cadmium					
with $n/1$ KI, (2 exps.)	7·46	7·54			Mean, 7·50
“ $n/1$ NaI, (1 exp.)					6·83

Substitution of sodium for potassium iodide lowers the rate of solution of both metals, and by the same amount. Details of these experiments are omitted both because the results are inferior in accuracy to those later obtained with the improved apparatus and method, and because the constants are not directly comparable with the later ones on account of subsequent changes in the dimensions of the apparatus.

Except in the above preliminary work, the iodide solutions used were invariably 0·5 equivalent normal with respect to iodide ($1/2$ KI, $1/4$ BaI₂, etc.). The change to a more dilute iodide solution brought with it the same phenomenon observed with zinc in the earlier work,†—a tendency for the metal disk to become coated with hydroxide owing to hydrolysis of its iodide. To avoid this the solutions were in all cases made slightly acid, generally 0·02 equivalent normal, with sulphuric or hydrochloric acid. It will be shown later that up to over 0·1 normal the degree of acidity has no appreciable effect upon the reaction velocity. The fact that hydrolysis of the cadmium iodide did not occur when the concentration of alkali iodide was normal or above is no doubt due to the extensive formation of the double salt of the type K_2CdI_4 in the stronger solutions.

The metallic cadmium used was of Kahlbaum's preparation. To ascertain whether possible impurities in the metal were

*-This Journal, xxix, 237.

† This Journal, xxix, 245.

affecting the results a portion of about 200 grams was subjected to two successive distillations in a current of hydrogen, but the redistilled metal showed on trial no perceptible difference in behavior from the original sample. Thereafter the Kahlbaum cadmium was used without further attempt at purification.

In Table I are the results of sixteen duplicate experiments with cadmium, the first six recorded in detail. No corrections for variations in the rate of stirring have been applied in this series. The volumes of the solution are given for experiment 1 only, but the same values apply to all the experiments of

TABLE I.

	Metal: CADMIUM.		Stirring, 170 revs.		Temperature 25°.		
	580	560	540	520	500	480 ^{cc}	
	KI 0.5 normal.		H ₂ SO ₄ 0.02 normal.				
1. $v =$	580	560	540	520	500	480 ^{cc}	
$\Delta t =$	10	10	10	12	11	10 ^{min}	
$c =$	19.76	17.58	15.58	13.74	11.79	10.11	8.78
$K =$	6.78	6.75	6.78	6.63	6.97	6.77	Average, 6.78
2. $\Delta t =$	11	10	11	10	10	10	
$c =$	20.01	17.70	15.76	13.77	12.21	10.68	9.33
$K =$	6.45	6.49	6.63	(6.24)	6.68	6.48	Av. 6.55
3. $\Delta t =$	10	10	10	10	10	10	
$c =$	20.13	17.92	15.93	14.05	12.39	10.80	9.36
$K =$	6.74	6.58	6.77	6.53	6.87	6.86	Av. 6.73
4. $\Delta t =$	10	10	10	10	10	10	
$c =$	21.46	19.11	16.90	14.94	13.13	11.45	9.92
$K =$	6.71	6.88	6.64	6.71	6.84	6.88	Av. 6.78
5. $\Delta t =$	10	10	11	11	10	10	
$c =$	19.52	17.34	15.37	13.33	11.42	10.00	8.68
$K =$	6.87	6.74	6.99	(7.29)	6.63	6.79	Av. 6.80
6. $\Delta t =$	10	10	10	10	10	10	
$c =$	18.81	16.73	14.81	13.11	11.53	10.10	8.80
$K =$	6.79	6.81	6.58	6.67	6.61	6.61	Av. 6.68
7. $K =$	6.80	6.81	6.68	6.59	6.79	6.62	Av. 6.72
8. $K =$	6.66	6.90	6.76	6.77	6.79	6.66	Av. 6.76
9. $K =$	6.56	6.70	6.72	6.52	6.88	6.52	Av. 6.65
10. $K =$	6.46	6.44	6.48	6.49	6.52	6.64	Av. 6.51
11. $K =$	6.80	6.77	6.72	6.85	7.01	6.79	Av. 6.82
12. $K =$	6.59	6.85	6.88	6.65	7.04	6.64	Av. 6.78
13. $K =$	6.52	6.69	6.73	6.53	6.79	6.67	Av. 6.66
14. $K =$	6.64	6.98	6.85	6.76	6.88	6.70	Av. 6.80
15. $K =$	6.71	6.68	6.78	6.67	7.00	6.68	Av. 6.75
16. $K =$	6.56	6.77	6.82	6.49	6.90	6.57	Av. 6.69
							Average of all, 6.72

this paper; 580^{cc} for the first reaction period, and 20^{cc} less for each succeeding one. Values of *c*, the iodine concentration, are expressed in cubic centimeters of an approximately 0.02 normal thiosulphate solution required by 20^{cc} of the liquid. Δt is the time interval ($t_2 - t_1$, page 208) in minutes. A few abnormal constants, indicated by parentheses, have been omitted in calculating the averages.

Table II shows the effect of varying acidity. Corrections for fluctuations in the stirring have been applied by the method described above, *r* being the mean rate of stirring during the given reaction period. In experiments 4 to 11 the correction data have been omitted for the sake of brevity, but the average given in each case is that of the corrected constants.

A necessary readjustment of the apparatus between this series and that of Table I has slightly altered the value of the constant. A proper comparison is obtained by comparing experiments 2, 3, and 4, which are closely concordant, and whose average is $K = 6.86$, with the 6.72 of Table I.

The close agreement between the first five experiments of Table II shows that a change in acidity between the limits of 0.002 and 0.1 normal has no appreciable effect upon the results. Further increase in the acidity diminishes the rate of solution by an amount which increases with the concentration of the acid. A comparison of experiments 3 and 4 shows that the substitution of hydrochloric for sulphuric acid does not appreciably alter the constant.* A similar agreement between the effect of hydriodic acid and of sulphuric acid at 0.5 normal concentration will appear later.

TABLE II.

Metal: CADMIUM. KI 0.5 normal. Temperature 25°.

1. H ₂ SO ₄ 0.002 normal.									
<i>v</i> =	580	560	540	520	500	480	460		
Δt =	10	10	10	10	10	10	10	10	
<i>c</i> =	19.65	17.51	15.50	13.61	lost	10.41	9.05	7.80	
<i>K</i> =	6.68	6.83	6.78			6.83	6.72	6.82	
<i>r</i> =	170.5	170.0	169.3	169.5	171.1	168.9	169.5		
<i>K</i> (corr.) =	6.67	6.83	6.80			6.82	6.75	6.84	
									Av. 6.79
2. H ₂ SO ₄ 0.02 normal.									
Δt =	10	10	10	10	10	10			
<i>c</i> =	19.92	17.71	15.68	13.74	12.09	10.51	9.09		
<i>K</i> =	6.82	6.81	7.12	6.65	6.99	6.96			
<i>r</i> =	171.3	170.1	171.0	170.2	170.9	168.8			
<i>K</i> (corr.) =	6.78	6.81	7.09	6.64	6.96	7.00			Av. 6.88

* Compare also, in Table III, experiments 1 and 2, and in Table VI, experiments 8 and 9.

TABLE II.—Continued.

Metal: CADMIUM. KI 0.5 normal. Temperature 25°.							
3. H ₂ SO ₄ 0.02 normal.	$\Delta t =$	10	10	10	10	10	10
	$c =$	39.62	35.19	31.13	27.37	24.00	20.96
	K =	6.87	6.85	6.94	6.83	6.76	6.90
	$r =$	170.5	170.6	170.3	169.5	169.3	169.5
	K (corr.) =	6.85	6.83	6.93	6.85	6.78	6.92
							Av. 6.86
4. HCl 0.02 normal.	$\Delta t =$	10	10	10	10	11	10
	$c =$	39.79	35.43	31.50	27.72	24.27	21.13
	K =	6.72	6.58	6.89	6.90	6.92	6.96
							6.90
							K (corr.) av. 6.83
5. H ₂ SO ₄ 0.1 normal.	$\Delta t =$	10	10	10	10	10	10
	$c =$	19.93	17.70	15.68	13.79	12.09	10.50
	K =	6.87	6.79	6.92	6.84	7.04	6.70
							9.13
							K (corr.) av. 6.86
6. H ₂ SO ₄ 0.33 normal.	$\Delta t =$	10	10	11	10	12	10
	$c =$	20.01	17.88	15.90	13.90	12.28	10.47
	K =	6.51	6.57	6.59	6.43	6.64	6.67
							9.11
							K (corr.) av. 6.64
7. H ₂ SO ₄ 0.5 normal.	$\Delta t =$	10	10	10	11	10	10
	$c =$	20.20	18.10	16.11	14.30	12.50	10.98
	K =	6.36	6.52	6.43	6.35	6.47	6.29
							9.63
							K (corr.) av. 6.40
8. H ₂ SO ₄ 0.9 normal.	$\Delta t =$	10	10	11	10	12	13
	$c =$	19.27	17.32	15.49	13.64	12.11	10.35
	K =	6.19	6.23	6.24	6.18	6.54	6.45
							8.69
							K (corr.) av. 6.31
9. H ₂ SO ₄ 1. normal.	$\Delta t =$	10.05	10	10	10	10	10
	$c =$	20.46	18.34	16.34	14.57	12.89	11.30
	K =	6.29	6.45	6.19	6.36	6.58	6.54
							9.86
							K (corr.) av. 6.39
10. H ₂ SO ₄ 1. normal.	$\Delta t =$	10	10	10	10	10	10
	$c =$	21.11	18.97	16.97	15.08	13.36	11.80
	K =	6.19	6.23	6.37	6.29	6.20	6.47
							10.31
							K (corr.) av. 6.34
11. H ₂ SO ₄ 1. normal.	$\Delta t =$	10	10	10	10	10	10
	$c =$	20.54	18.48	16.56	14.72	13.08	11.57
	K =	6.12	6.13	6.36	6.14	6.13	6.33
							10.14
							K (corr.) av. 6.17

With the more strongly acid solutions it is necessary to prevent oxidation of the iodide by the air. All experiments of the present investigation in which the acidity of the solution was greater than 0.1 normal were therefore carried out in an

TABLE III.

Metal: IRON. KI 0.5 normal. Temperature 25°. $r = 170$.
 H_2SO_4 0.02 normal (except in experiments 1, 10, and 11).

Common Wrought Iron.

*1.	$v =$	580	560	540	520	500	480	
	$\Delta t =$	10	10	11	10	11	10	
	$c =$	19.96	17.67	15.67	13.50	11.83	10.12	8.77
	$K =$	7.07	6.71	7.32	6.85	7.09	6.87	Average, 6.99
2.	$K =$	6.82	7.01	6.89	7.01	7.15	7.02	Av. 6.98

Swedish Iron.

3.	$K =$	6.75	6.76	7.08	6.58	6.93	6.82	Av. 6.82
4.	$K =$	6.68	6.90	7.19	6.64	7.00	7.08	Av. 6.92

"American Ingot Iron."

5.	$\Delta t =$	10	10	10	10	10	10	
	$c =$	20.18	17.95	15.91	14.02	12.38	10.81	9.44
	$K =$	6.78	6.75	6.83	6.46	6.77	6.49	Av. 6.68
6.	$\Delta t =$	10	10	10	10	10	10	
	$c =$	18.97	16.83	14.92	13.18	11.57	10.10	8.79
	$K =$	6.94	6.74	6.69	6.77	6.79	6.66	Av. 6.77
7.	$\Delta t =$	10	11	13	13	17	20	
	$c =$	17.95	16.03	14.04	11.99	10.17	8.14	6.18
	$K =$	6.56	6.73	6.55	6.58	6.54	6.50	Av. 6.59
8.	$\Delta t =$	14	10	10	13	12	24	
	$c =$	20.54	17.40	15.43	13.59	11.54	9.77	6.98
	$K =$	6.87	6.71	6.86	6.53	6.93	6.72	Av. 6.77
9.	$\Delta t =$	10	10	12	10	10	5	13
	$c =$	19.40	17.25	15.25	13.04	11.45	lost	9.29 7.68
	$K =$	6.80	6.89	7.04	6.76		6.87	6.72
								Av. 6.85
10.	H_2SO_4 0.1 normal.							
	$\Delta t =$	10	10	10	10	10	10	
	$c =$	19.55	17.40	15.39	13.55	11.93	10.48	9.00
	$K =$	6.75	6.86	6.87	6.61	6.46	(7.31)	Av. 6.71
11.	H_2SO_4 0.1 normal.							
	$\Delta t =$	10	10	11	10	10	10	
	$c =$	19.35	17.25	15.30	13.28	11.74	10.24	8.91
	$K =$	6.66	6.71	6.94	6.40	6.83	6.67	Av. 6.70

* HCl 0.02 normal, instead of H_2SO_4 .

atmosphere of carbon dioxide, obtained by conducting a rapid current of the gas into the upper part of the reaction vessel throughout the experiment. Blank tests showed that this method, when properly carried out, reduced the oxidation to a negligible amount. In one case, however, experiment 6, a failure of the generating apparatus allowed some oxidation to occur, the amount of which was roughly estimated, and a calculated correction of 0.07 added to the final result. The value of "K (corr.," for experiment 6 as given in the table includes this correction.

Experiments with Iron.

The disturbing effect of impurities in the metal used is well illustrated by the experiments with iron recorded in Table III. In experiments 1 and 2 the disks were of common sheet iron, which in dissolving set free a considerable quantity of carbon. Swedish iron, supposed to be of fairly high purity, was used in experiments 3 and 4. The rest were carried out with "American Ingot Iron,"* which, according to the advertised analysis, is about 99.9 per cent pure. That this last material was comparatively free from carbon was evident from the bright surface which it maintained in dissolving, and the clear solution produced.

It is seen in the table that the common and Swedish iron gave higher constants than the purer metal. A possible effect of the presence of carbon in the iron is illustrated by the results of certain experiments in which metallic contact existed between the disk and its platinum holder. This occasionally happened owing to the wearing through of the layer of pyroxlin on one of the arms supporting the disk, and was indicated by an abnormally high rate of solution as shown by the two following experiments with cadmium in the presence of barium iodide:

A.	9.22	9.13	9.20	9.04	9.05	9.25	Av. 9.15
B.	8.73	8.49	8.82	8.21	8.27		Av. 8.50

The normal value of the constant under the prevailing conditions was 6.45. In both cases a plainly visible point of contact between the cadmium and platinum was found.

It is easy to account for the high constants in such cases. Contact between the two metals establishes a short-circuited cell of which platinum is the cathode. This affects the results in two ways: first, the nascent hydrogen evolved on the platinum reduces iodine, thus causing an apparent increase in the reaction velocity; second, the rate of movement of the iodine diffusing toward the disk in the form of I_3^- ions is accelerated by the superposition of an electrical force upon the osmotic

* From the American Rolling Mill Co., Middletown, Ohio.

force, thus actually increasing* the rate of solution of the disk. In view of these facts it seems reasonable to conclude that a particle of carbon or of a more negative metal adhering to the disk might have a similar effect, so that in many cases (not necessarily in all) an impure metal would give a higher constant than a pure one, as in the present instance.

In comparing these results with those obtained with cadmium, only those experiments need be considered in which the purest iron was used. Experiments 5, 6, 7, 8, and 9 carried out at 0.02 normal acidity, give an average value of K of 6.74; experiments 10 and 11, at 0.1 normal acidity, an average of 6.71, thus again proving that the rate of solution is independent of the acidity when the latter is not too high. Since these experiments were carried out before the readjustment of the apparatus† they are to be compared with the value 6.72 for cadmium. The agreement is excellent.

TABLE IV.

	KI 0.5 normal.	H ₂ SO ₄ 0.02 normal.				Temperature 25°. $r = 170$	
		<i>Nickel.</i>					
1. $v =$	580	560	540	520	500	480	
$\Delta t =$	10	10	15	10	10	10	
$c =$	20.03	17.82	15.81	13.12	11.55	10.09	8.77
$K =$	6.78	6.70	6.71	6.61	6.75	6.72	Average, 6.71
2. $\Delta t =$	10	10	10	10	10	10	
$c =$	19.84	17.69	15.69	13.84	12.17	10.59	9.18
$K =$	6.64	6.71	6.77	6.67	6.95	6.86	Av. 6.77
		<i>Cobalt (Impure).</i>					
3. $K =$	6.24	6.00	6.15	5.72	5.83	5.73	Av. 5.95
4. $K =$	6.47	6.25	6.33	6.05	6.37	6.18	Av. 6.28
		<i>Cobalt (Electrolytic).</i>					
5. Disk 38.76×0.075 mm							
$\Delta t =$	10	10	11	11	10	11	
$c =$	39.40	34.68	30.38	26.26	22.59	19.64	16.70
$K =$	7.39	7.41	7.15	7.11	6.99	7.07	
		K (corrected for stirring) av. 7.15					
		K, with further correction for size of disk, 6.90					
6. Disk 38.64×0.068 mm							
$\Delta t =$	10	10	11	10	10	10	
$c =$	39.54	34.92	30.58	26.70	23.39	20.37	17.48
$K =$	7.19	7.43	6.65	6.88	6.90	7.34	
		K (corrected for stirring) av. 7.01					
		K, with further correction for size of disk, 6.83					

* A greater increase would be produced by the discharge of the much more numerous I⁻ ions, but as this would not directly affect the free iodine concentration it would not appear in the results.

† See page 211.

Experiments with Nickel and Cobalt.

No special tests for purity were applied to the sample of nickel used, but the fact that in dissolving in acid or iodine solution it retained a bright surface and gave no residue may be accepted as an indication that it contained very little carbon. The velocity constants obtained agree very closely with those for iron and cadmium.

The first two experiments with cobalt, Nos. 3 and 4 in the table, were carried out with a comparatively impure sample of the metal, which on treatment with acids or iodine solution soon acquired a black, closely adherent coating. This cobalt was proved by chemical tests to contain a good deal of nickel and iron together with traces of copper. The results obtained with this sample of cobalt are much lower than with iron or nickel.

For experiments 5 and 6 disks of pure electrolytic cobalt were used, obtained by depositing the metal on a disk of platinum of the standard diameter from a solution of carefully purified cobalt chloride containing sodium formate and a slight excess of formic acid. Very smooth and compact deposits of ample thickness were thus obtained, using a current density of 0.4 amp. per sq. dm. The purification of the cobalt chloride was based on two successive precipitations as potassium cobaltinitrite.

These disks retained a perfectly clean surface in dissolving. Before using they were measured with a micrometer and the constants obtained were corrected for the difference in surface area from that of the standard size (38.3^{mm} diam. and 0.5^{mm} thick).

Since experiments 5 and 6 were performed after the readjustment of the apparatus they are to be compared with the value 6.86 of Table II. The agreement is evidently all that could be desired.

Experiments with Tin, Magnesium, and Aluminum.

The results obtained with tin are of particular interest since they show the nature of the disturbances to be expected in the case of a metal which may give two different soluble iodides. As compared with the metals previously considered the velocity constants for tin were found to be, on the average, about 15 per cent higher. This can not be attributed to impurities, for the sample of tin used was of the highest purity which could be purchased, and was further purified for this special purpose by decomposing it with nitric acid, washing the metastannic acid, and finally reducing with cane sugar. The probable explanation is as follows: Iodine reacts with a stannous salt according to the equation

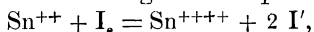


TABLE V.

Metal : TIN.		KI 0.5 normal.			Temperature 25°.			$r = 170.$
HCl		1. normal in experiments 1, 2, 3, and 4.						
1.	$v =$	580	560	540	520	500	480	
	$\Delta t =$	10	10	10	10	10	10	
	$c =$	20.52	18.16	15.92	13.67	11.71	9.93	8.05
	$K =$	7.08	7.37	8.21	8.04	8.25	(10.06)	Av. 7.79
2.	$\Delta t =$	6	6	5	7	10	7	
	$c =$	20.79	19.22	17.74	16.51	14.95	12.69	11.36
	$K =$	7.58	7.47	7.77	7.36	8.18	7.59	Av. 7.66
3.	$\Delta t =$	10	14	11	14	15	21	
	$c =$	20.95	18.60	15.60	13.54	11.04	8.76	5.71
	$K =$	6.90	7.03	6.94	7.57	7.70	(9.77)	Av. 7.27
4.	$K =$	7.07	6.99	6.99	7.50	8.11	(9.56)	Av. 7.33
5.	HCl 0.33 normal.							
	$K =$	7.87	6.83	7.30	7.52	7.08	7.39	Av. 7.33
6.	HCl 0.25 normal.							
	$K =$	7.43	7.49	7.71	8.18	7.69	8.67	Av. 7.86

the change from left to right being nearly complete.* At the actual surface of the metal the iodine concentration is practically zero, and the tin will therefore dissolve as stannous iodide. As this diffuses through the "unstirred" layer it will encounter an ever increasing concentration of iodine, and will therefore soon be converted into stannic salt. The diffusion path for the iodine so used will be less than the thickness of the diffusion layer, thus causing a more rapid consumption of iodine than in a normal case and giving the high velocity constants actually observed.

To prevent hydrolysis of the tin salt and the resulting accumulation of hydroxide on the disk, the solutions were made at least 0.25 normal with hydrochloric acid. Oxidation was prevented by the use of carbon dioxide as described above.

In the experiments with metallic magnesium, hydrogen was always evolved from the disk, thus introducing a disturbing factor of a new kind. None of the metals discussed above had evolved hydrogen in visible amounts even at the highest acidity employed, but with magnesium hydrogen was produced to some extent even in neutral solution, and when enough acid was present to keep the disk free from hydroxide, the gas evolution became very marked.

There are two obvious ways in which the gas evolution would affect the results; first, the adhering gas bubbles would

*The use of this reaction as a quantitative method of estimating iodine has been proposed by Spring, Jour. Am. Chem. Soc., xix, 809.

TABLE VI.

Metal:—CADMIUM. Iodides all 0.5 normal. Temp. 25°. $r = 170$.*Hydrogen Iodide.*

1. HI 0.5 normal. No other acid.

$v =$	580	560	540	520	500	480	460	
$\Delta t =$	11	11	13	13	11	12	18	
$c =$	36.75	32.55	28.73	24.80	21.16	18.34	15.59	12.00
$K =$	6.39	6.36	6.09	6.35	6.50	6.49	6.68	
							K (corr.) av. 6.45	

Sodium Iodide.

2. H
- ₂
- SO
- ₄
- 0.02 normal.

$\Delta t =$	10	10	10	10	11	10	
$c =$	38.59	34.46	30.63	27.09	23.87	20.69	18.01
$K =$	6.56	6.59	6.62	6.56	6.49	6.67	
							K (corr.) av. 6.59

3. H
- ₂
- SO
- ₄
- 0.02 normal.

$\Delta t =$	12	11	10	11	10	12	
$c =$	51.78	45.31	39.84	35.32	30.77	26.98	22.91
$K =$	6.45	6.54	6.50	6.51	6.57	6.53	
							K (corr.) av. 6.53

Lithium Iodide.

4. H
- ₂
- SO
- ₄
- 0.02 normal.

$\Delta t =$	10	12	11	11	10	10	10	
$c =$	39.91	35.34	30.83	27.07	23.65	20.80	18.18	15.81
$K =$	(7.04)	6.36	6.38	6.38	6.41	6.46	6.42	
							K (corr.) av. 6.40	

5. H
- ₂
- SO
- ₄
- 0.02 normal.

$\Delta t =$	10	11	12	11	10	11	
$c =$	39.97	35.79	31.56	27.39	23.91	21.04	18.10
$K =$	6.39	6.40	6.37	6.41	6.39	6.55	
							K (corr.) av. 6.41

Barium Iodide.

6. HCl 0.02 normal.

$\Delta t =$	10	10	10	12	11	11	11	
$c =$	39.32	35.19	31.30	27.78	23.92	20.79	17.86	15.31
$K =$	6.43	6.56	6.43	6.47	6.37	6.62	6.43	
							K (corr.) av. 6.47	

7. HCl 0.02 normal.

$\Delta t =$	10	10	10	10	11	12	10	
$c =$	39.16	35.09	31.29	27.81	24.61	21.36	18.18	15.74
$K =$	6.35	6.41	6.36	6.35	6.43	6.44	6.62	
							K (corr.) av. 6.42	

TABLE VI.—*Continued.*

Metal :—CADMIUM. Iodides all 0.5 normal. Temp. 25°. $r = 170$.

Magnesium Iodide.

8. H₂SO₄ 0.02 normal.

$v =$	580	560	540	520	500	480	460	
$\Delta t =$	11	12	11	10	11	10	11	
$c =$	39.71	35.47	30.95	27.21	24.13	21.03	18.39	15.83
$K =$	5.95	6.35	6.32	6.23	6.25	6.43	6.26	

K (corr.) av. **6.25**

9. HCl 0.02 normal.

$\Delta t =$	10	10	10	10	10	10	
$c =$	40.35	36.27	32.42	28.92	25.62	22.61	19.79
$K =$	6.18	6.27	6.16	6.29	6.24	6.39	

K (corr.) av. **6.25**

10. HCl 0.02 normal.

$\Delta t =$	10	10	10	10	10	10	
$c =$	40.96	36.81	32.90	29.32	26.00	22.94	20.11
$K =$	6.19	6.29	6.21	6.24	6.26	6.31	

K (corr.) av. **6.25**

Calcium Iodide.

11. HCl 0.02 normal.

$\Delta t =$	10	10	10	10	12	10	
$c =$	39.70	35.67	31.90	28.40	25.18	21.67	18.99
$K =$	6.20	6.25	6.27	6.24	6.25	6.34	

K (corr.) av. **6.25**

12. HCl 0.02 normal.

$\Delta t =$	10	10	10	10	10	10	
$c =$	40.19	36.19	32.38	28.81	25.57	22.56	19.79
$K =$	6.07	6.22	6.31	6.20	6.26	6.28	

K (corr.) av. **6.21**

Cadmium Iodide.

13. HCl 0.02 normal.

$\Delta t =$	10	10	10	11	15	10	
$c =$	22.17	19.64	17.47	15.40	13.41	10.66	9.34
$K =$	7.03	6.54	6.81	6.53	7.64	6.35	

K (corr.) av. **6.80**

14. HCl 0.02 normal.

$\Delta t =$	10	10	10	10	4	10	11	
$c =$	14.82	13.18	11.70	10.36	lost	8.56	7.42	6.29
$K =$	6.79	6.66	6.56		7.00	6.86	6.89	

K (corr.) av. **6.78**

15. HCl 0.02 normal.

$\Delta t =$	10	10	10	10	10	10	
$c =$	14.15	12.59	11.17	9.85	8.59	7.50	6.46
$K =$	6.78	6.68	6.79	7.10	6.78	7.16	

K (corr.) av. **6.87**

reduce the available surface of the disk, and second, the breaking off of the bubbles would stir the diffusion layer, thus bringing the strong outside solution into direct contact with the metal. These two effects would act in opposite directions, but apparently the second predominates, for the constants obtained are high.

An experiment in the presence of 0.1 normal sulphuric acid, giving a brisk hydrogen evolution, resulted as follows:

A. 8.72 9.28 8.50 8.43 Average 8.73

In neutral solutions the disk remains free from hydroxide if a little ammonium chloride is present, but even under these conditions there is a very marked evolution of hydrogen. The two following experiments were performed in neutral solutions which were about 0.025 normal with respect to ammonium chloride:

B. 9.31 10.71 11.85 12.75 9.50 Av. 10.82
C. 9.19 9.76 10.06 13.12 7.50 8.90 Av. 9.76

The conspicuous irregularity of the constants is only what would be expected when we consider the large effect which would be produced by variations in the rate of formation or in the size of the gas bubbles, factors which it is very difficult to control.

A number of experiments were carried out with aluminum disks, but in every case the metal was so irregularly attacked by the iodine that no confidence can be placed in the results. The disk after use was always found to be pitted with small holes, with intervening spaces which appeared to have been attacked but little if at all by the iodine. The single experiments gave fairly regular constants but duplicate experiments did not agree at all closely. The values of the constants were low in every case except one, this being an experiment in the presence of normal hydrochloric acid which gave an evolution of hydrogen and a high constant, no doubt on account of the hydrogen. In the other cases the acidity was 0.25 normal or less. All of the results, however, were entirely compatible with the conclusion drawn from the inspection of the disks; namely, that a part of the surface of the metal was not attacked.

Cadmium in the Presence of Various Iodides.

It has been shown by Jakowkin* that iodine dissolved in a large excess of an iodide of an alkali or alkali earth metal in water solution is almost completely combined in the form of triiodide. We should expect, therefore, that the diffusion of iodine in such a solution would be determined chiefly by the

* Zeitschr. phys. Chem., xx, 19.

rate of diffusion of the triiodide molecules, which in turn must vary with the nature of the positive ion. Hence the rate of solution of a metal in the liquid should be different in the presence of different iodides.

These differences in the rate of solution furnish the basis for an interesting and valuable test of the validity of the diffusion theory, and we have therefore carried out a series of parallel experiments with cadmium in the presence of a number of different iodides in equivalent concentration. These experiments were very carefully performed, and the results, given in detail in Table VI, are very concordant. The greatest fluctuation in the constants occurred with cadmium iodide, and is probably due to the low iodine concentrations which had to be employed, which magnified the errors of titration. Corrections for rate of stirring were applied in the manner already described. The magnesium iodide used contained a small amount, perhaps one or two per cent, of calcium iodide, but the effect of this impurity must have been negligible as the constants for these two iodides are practically equal. Values for potassium iodide, comparable with Table VI, are furnished by experiments 2, 3, and 4 of Table II. The agreement between experiment 1 of Table VI and experiment 7 of Table II shows that hydriodic acid alone has practically the same effect as sulphuric acid of the same concentration in the presence of an equivalent amount of potassium iodide.

Discussion.

A summary of all the results of previous tables with the exception of those obtained with impure metals is given in Table VII. Most of the values represent the mean of two or more experiments under the stated conditions.

Under A, are the mean values of the velocity constants for different metals in the presence of potassium iodide, for each degree of acidity tested. To facilitate comparison results obtained before the readjustment of the apparatus referred to on page 211 have been multiplied by the factor $6.86/6.72$, thus reducing them to the later standard. Such values are indicated by stars.

The agreement between the metals cadmium, iron, nickel, and cobalt is very striking, and clearly proves that under like conditions these metals dissolve in iodine at the same rate. In the earlier investigation a like result was obtained with the five metals, mercury, copper, silver, zinc and cadmium. Eight metals in all have, therefore, been shown to possess the same rate of solution in iodine, a result for which there seems to be no satisfactory explanation other than that furnished by the diffusion theory.

Under B in Table VII are given the mean values of the velocity constants for the experiments with cadmium in the presence of different iodides. Considered from the standpoint of the diffusion theory, these figures must represent, at least roughly, the relative magnitudes of the rates of diffusion of iodine in the different solutions. An exact parallelism would not be expected, since this could only exist if the thickness of the diffusion layer were the same in each case, while in reality the thickness would vary somewhat with the properties of the liquid, especially its viscosity.

It would be extremely interesting to compare these velocity constants with the directly measured diffusion coefficients of iodine in the different solutions, but as yet none of the necessary diffusion coefficients have ever been determined, though it is likely that this deficiency will be remedied before long.* It is possible, however, by making certain assumptions, to obtain a rough estimate of the relative values of these rates of diffusion. For reasons already given (p. 221), they would be expected to depend chiefly upon the diffusion velocities of the triiodide molecule. As a first approximation we may assume that the rates of diffusion of the different triiodides would follow the same order as the corresponding iodides. Inspection of the existing data on the rates of diffusion of iodides shows clearly that potassium, sodium, and lithium iodides stand in the order named, while hydrogen iodide, by analogy with hydrogen chloride, should be highest of all. With the divalent iodides it is necessary to base the estimate chiefly upon the migration velocities of the positive ions, which are given in the third column of Table VII, B. The difference in the ionization of divalent and univalent iodides makes it unsafe to base any comparison between the two groups upon the ionic velocities. The diffusion data seem to show that the alkali earth halides diffuse slower than the alkali halides.

On referring to the values of the velocity constants for cadmium in the presence of different iodides, as given in Table VII, B, we find the alkali iodides in the order, potassium; sodium; lithium; as would be expected from the above considerations. Barium stands above both magnesium and calcium, as would be anticipated, but calcium is slightly below magnesium, thus deviating from the order of the ionic velocities.

There are two values, however, for which the above analysis gives no explanation. One is the high velocity constant for cadmium iodide, which in view of its abnormally low ionization and its tendency to form complex anions would be

* Dr. Graham Edgar has kindly undertaken to carry out these measurements in connection with other experiments on diffusion which he is conducting at the University of Virginia.

TABLE VII.

Summary of Velocity Constants.

A.									
Acidity	N/500	N/50	N/10	N/4	N/3	N/2	9N/10	N/1	NH ₄ Cl N/40
Cadmium	6.79	6.86	6.86	----	6.64	6.40	6.31	6.30	
Iron		*6.88	*6.85	----	----	----	----	----	
Nickel		*6.88	----	----	----	----	----	----	
Cobalt		6.87	----	----	----	----	----	----	
Tin		----	----	*8.02	*7.48	----	----	*7.67	
Magnesium		----	8.73	----	----	----	----	----	10.29

B.				
Cadmium in presence of	K	Migration velocity of cation.		Viscosities of chlorides in N/2 sol. at 25°.
Potassium Iodide	6.86	K ⁺	64.9	0.987
Cadmium Iodide	6.82	1/2 Cd ⁺⁺	47.4	1.063
Sodium Iodide	6.56	Na ⁺	43.6	1.047
Hydrogen Iodide	6.45	H ⁺	318.	1.034
Barium Iodide	6.45	1/2 Ba ⁺⁺	55.1	1.057
Lithium Iodide	6.41	Li ⁺	33.4	1.067
Magnesium Iodide	6.25	1/2 Mg ⁺⁺	45.9	1.094
Calcium Iodide	6.23	1/2 Ca ⁺⁺	51.5	1.076

* Starred values have been multiplied by 6.86/6.72.

expected to stand at the bottom of the list or near it; the other is the value for hydrogen iodide, which is surprisingly low considering the high mobility of the hydrogen ion. It is evidently this peculiarity in the behavior of hydriodic acid which accounts for the observed effect of acidity in lowering the velocity constant.

Another factor besides the rate of diffusion, which would affect the rate of solution of a metal, is the viscosity, an increase in which would tend to increase the thickness of the diffusion layer and thus retard the reaction. In the absence of published data on the iodides, the viscosities of the corresponding 0.5-normal chloride solutions at 25°, referred to water at the same temperature as unity, are given for comparison in the last column of the table.† The order of increasing viscosity is K, H, Na, Ba, Cd, Li, Ca, Mg, which is nearer the order of the velocity constants than was the case with the ionic velocities, and explains in part the unexpected values observed with cadmium and hydrogen iodides. The inference to be drawn from the two anomalous velocity constants is that

† According to measurements by J. Wagner, *Zeitschr. phys. Chem.*, v, 31, and by Reyher, *Zeitschr. phys. Chem.*, ii, 744.

iodine will probably prove to diffuse in cadmium iodide faster, and in hydrogen iodide slower, than the above considerations have led us to expect.

There is obviously nothing in the results of this investigation, as judged by the evidence at present available, which is incompatible with the diffusion theory. On the other hand, the results are in most respects in striking agreement with the predictions of that theory. A study of the temperature coefficient of the reaction between iodine and a metal has already been begun.

Summary.

1. The rates of solution of cadmium, iron, nickel, and cobalt in similar iodine solutions have been measured and found to be equal. This result extends the list of metals, which by the former article were shown to dissolve at the same rate, from five to eight: viz. Hg, Cu, Ag, Zn, Cd, Fe, Ni, and Co.

2. Tin gives a higher velocity constant than the above metals. This is what would be expected if the formation of the stannic iodide took place in two stages, as is probably the case.

3. Magnesium dissolves abnormally fast owing to the stirring action of the bubbles of hydrogen set free from its surface.

4. An increase in the acidity of the solution above 0.1 normal lowers the value of the velocity constant.

5. The rates of solution of cadmium in the presence of eight different iodides have been determined. Except in the cases of cadmium iodide and of hydriodic acid the relative values of the velocity constants roughly correspond with what would be expected from the probable rates of diffusion of the corresponding triiodides as estimated from the available data. Since the diffusion coefficients of iodine in the different solutions are still unknown, it is not yet possible to base a satisfactory test of the diffusion hypothesis upon these constants.

6. The results as a whole support the validity of the diffusion theory.