

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

## The Rate of Solution of Copper in Dilute Aqueous Reagents

BY CECIL V. KING AND LILLIAN WEIDENHAMMER

Recent studies of the solution rate of copper in dilute acids containing dissolved oxygen, hydrogen peroxide or other oxidizing agents<sup>1,2,3</sup> indicate that this metal dissolves at a much lower rate than magnesium, zinc or cadmium in the same solutions. The temperature coefficient of the rate is said to be high, the effect of changed stirring speed low and various faces of single crystals dissolve at far different rates. All these factors indicate that in such solutions the observed rate may be controlled by the chemical process at the surface rather than by the diffusion rate of one or more of the reactants to the surface. Copper differs from the other metals mentioned in that, under ordinary conditions, it cannot be oxidized by hydrogen ion if an appreciable concentration of copper ion is present; various oxygen-containing reagents such as hydrogen peroxide can oxidize the copper if acids are present to provide the necessary hydrogen ion.

In the work reported below, the rate of solution from a rotating cylinder of polycrystalline copper was studied in solutions of hydrogen peroxide and acetic acid over a wider range of concentrations and stirring speeds than used by Glauner and Glocker. For comparison the rate was also studied in solutions of ferric salts where it seems to be largely diffusion-controlled.

### Experimental

A cylinder of electrolytic copper, 5 cm. long and 2 cm. in diameter, was rotated in 500 cc. of solution, at 4000  $\pm$  200 r. p. m. and 25  $\pm$  0.5° unless otherwise stated. The cylinder was polished with rouge paper before each run; washed, dried and weighed after the run. The experimental reproducibility varied from 1 to 20%, the latter value applying to a few solutions only; usually it was 5 to 6%. A single copper cylinder was used for most of this work; it decreased in diameter about 10% during the entire set of experiments, and this decrease was partly corrected for by using the actual area in all calculations of velocity constants. A number of check runs with a second cylinder differed by about 10%.

(1) Glauner and Glocker, *Z. Metallkunde*, **20**, 244 (1928).

(2) Glauner, *Z. physik. Chem.*, **142A**, 67 (1929).

(3) Glauner and Glocker, *Z. Kryst.*, **80**, 377 (1931).

The reagents used were C. P.; ferric chloride and nitrate were recrystallized once and the stock solutions standardized gravimetrically. Hydrogen peroxide solutions were made up from 30% "Superoxol" and standardized by titration with permanganate.

Where possible, rates are compared merely by reporting the number of milligrams of copper dissolved in a given time interval. When this method is inadequate, unimolecular "constants" are calculated from the equation

$$k = \frac{2.3 V}{At} \log \frac{a}{a-x}$$

where the symbols have the usual meaning.

1. The rate of solution was measured in 0.1 molar acetic acid and 0.1 molar hydrogen peroxide, at 25 and 35°. The cylinder was weighed at the end of each hour and replaced in the same solution, which is similar in composition to some of those used by Glauner and Glocker. The reaction is auto-catalytic as found by these authors, since the dissolved cupric ion reacts with the copper. The results are given in Table I. The temperature coefficient is 2.1 per 10°.

TABLE I  
RATE OF SOLUTION IN 0.1 M ACETIC ACID, 0.1 M HYDROGEN PEROXIDE

Time (hours)	1	2	3	4
Mg. diss. (25°)	24.0	54.5	87.0	124
Mg. diss. (35°)	51.0	117	..	...

2. With fixed acetic acid concentrations (0.02 and 0.1 molar) the hydrogen peroxide concentration was varied up to 2 molar. The results are shown in Fig. 1. The behavior is quite different from that of zinc in the same solutions.<sup>4</sup> Maximum rates are reached at far higher peroxide concentrations and are not proportional to the acid concentration. The rates are not highly reproducible, especially in the stronger acid solution and with the higher peroxide concentrations; this is probably due to heavy brown films (probably of oxide) which appear on the surface of the copper. In the more dilute peroxide solutions where acid is present in excess no films are noticeable, but they appear at intermediate concentra-

(4) King and Schack, *THIS JOURNAL*, **57**, 1212 (1935).

tions as thin red coatings. The peroxide decomposes noticeably with evolution of oxygen after a few minutes, in the stronger solutions. The maximum rate, in 0.02 molar acetic acid, is

speeds, twenty and ten minutes at the higher speeds. The velocity constants for the twenty and ten minute intervals were empirically corrected, with the aid of the data of Table II, to

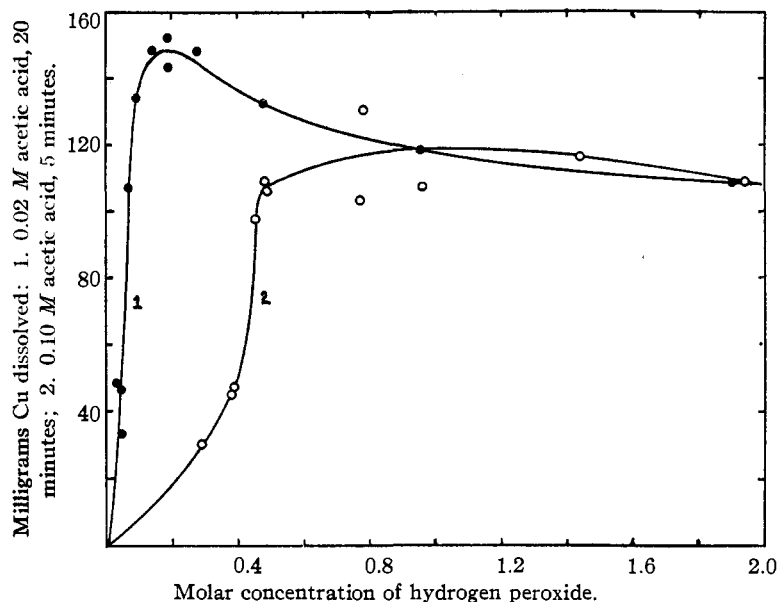


Fig. 1.—Effect of hydrogen peroxide on the solution rate in acetic acid.

one-third to one-half the maximum for zinc in similar solutions (in terms of equivalents per sq. cm. per min.).

3. The temperature coefficient was measured in 0.02 molar acetic acid containing 0.2 molar hydrogen peroxide to ensure the maximum rate. The same solution was used throughout each run as in section 1, the cylinder being removed and weighed at ten-minute intervals. The results are given in Table II. It will be seen that the rate "constants" *k* fall off with time; the dissolved copper ion does not show the same autocatalytic effect as before. The temperature coefficient, only 1.2 per 10° during the first ten minutes, also falls with time, apparently becoming negative.

TABLE II  
RATE OF SOLUTION IN 0.02 M ACETIC ACID, 0.2 M HYDROGEN PEROXIDE

Time, min.	10	20	30	40
Mg. diss. (25°)	87.0	145	182	204
Mg. diss. (35°)	103	156	179	180
<i>k</i> (25°)	0.52	0.50		
<i>k</i> (35°)	.64	.55		

4. The effect of varying the speed of rotation of the cylinder was studied, in 0.02 molar acetic acid with 0.20 molar hydrogen peroxide. The cylinder was rotated thirty minutes at the lower

compare with the values for the thirty-minute runs. Fresh solution was used for each rotational speed. The results are shown in Fig. 2 along with similar experiments in 0.02 molar ferric chloride solutions. In the latter solutions the rate is nearly unimolecular (see below); the cylinder was rotated for ten, five and three minutes since the rate is much higher than in the other solution.

The rate in the acid-peroxide solution is by no means independent of the speed of rotation; Glauner<sup>2</sup> found little dependence on the stirring speed in more concentrated acetic acid solutions with less peroxide, but he varied the speed over a much smaller range (150 to 359 r. p. m. with a different experimental arrangement). This curve is, however, fundamentally different from the curve obtained in ferric nitrate solution and from

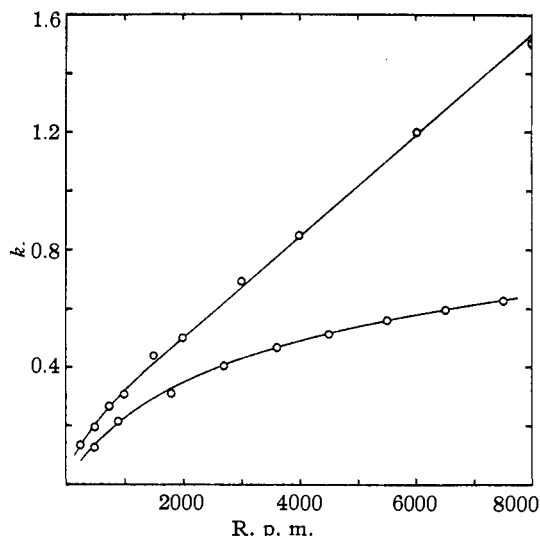


Fig. 2.—The effect of rotational speed on the rate of solution: lower curve, 0.02 M acetic acid + 0.20 M hydrogen peroxide; upper, 0.02 M ferric chloride.

the curve for zinc in acetic acid with hydrogen peroxide or potassium nitrate as an oxidizing agent.<sup>4</sup> While the curve for ferric nitrate is

typical of a diffusion controlled process, that for the acid-peroxide system would seem to indicate a process intermediate between one controlled by the speed of transport to the surface and one controlled by the chemical process (in which stirring should have no effect). If this is true, the method of analysis of the data devised by Roller<sup>5</sup> should be applicable. We have not attempted this analysis since data obtained with lower peroxide, higher acid concentrations would be preferable for the purpose; there would be less chance of mechanical obstruction by surface films in such solutions.

5. A number of other oxidizing agents were investigated including nitrate, nitrite, permanganate, dichromate, *p*-nitrophenol, nitrobenzene and nitromethane. With 0.1 molar acetic acid none of these, in concentrations up to 0.1 molar (or saturation if less soluble), dissolve more than 1 mg. of copper from this cylinder of some 30 sq. cm. area, in five minutes at 25° and 4000 r. p. m. Possibly in some of these cases a slow, chemically-controlled rate might be found. Quinone is intermediate in effectiveness; as shown in Fig. 3 the rate is proportional to the quinone concentration at low values of the latter, reaches a maximum and falls off at higher concentrations. Two experiments at 35° gave temperature coefficients of 1.9 and 1.4 per 10°.

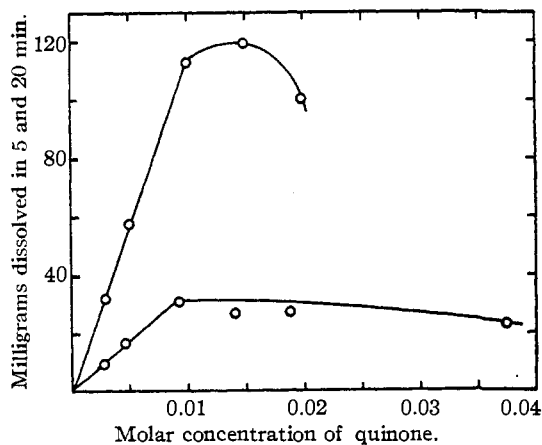


Fig. 3.—The effect of quinone as an oxidizing agent on the solution rate in 0.02 *M* acetic acid: lower curve, 5 min. runs; upper curve, 20 min. runs.

6. The rate was now studied more thoroughly in solutions of ferric chloride and nitrate. For short periods of rotation at 4000 r. p. m. the highly polished copper remains bright in these solutions,

(5) Roller, *J. Phys. Chem.*, **39**, 221 (1935).

with no visible film formation. At lower speeds a red film resembling cuprous oxide appears after some time, perhaps because of reaction with dissolved oxygen. This is true even with considerable hydrochloric acid present. The rate constant decreases about 7% between 0.008 and 0.08 molar ferric nitrate concentrations, and somewhat more at higher concentrations, as shown in Table III.

TABLE III  
RATE OF SOLUTION IN FERRIC NITRATE AT 25°, 4000 R. P. M., 500 CC. SOLUTION

$C_{Fe(NO_3)_3}$ , <i>M</i>	Mg. diss. in 15 min.	<i>k</i>	Mg. diss. in 5 min.	<i>k</i>
0.008	45.5	0.500	22.0	0.646
.012	81.5	.633	32.5	.643
.020	134	.617	53.5	.631
.040	270	.620	106	.616
.080	528	.599	208	.602
.160	1014	.565	...	...
.320	...	...	742	.530

The rate in 0.02 molar ferric nitrate was also followed at five-minute intervals for twenty minutes, at 25 and 35°. These results are given in Table IV. The temperature coefficient is 1.3 per 10°.

TABLE IV  
THE RATE IN 0.02 *M* FERRIC NITRATE SOLUTION

Time, min.	5	10	15	20
Mg. diss. (25°)	53.5	99.0	137	168
Mg. diss. (35°)	68.0	123	167	201
<i>k</i> (25°)	0.636	0.636	0.644	0.640
<i>k</i> (35°)	.818	.832	.849	.852

7. A comparison of the rate constants for ferric chloride and nitrate (Table IV and Fig. 2, 4000 r. p. m.) shows that the former is some 30% higher than the latter. Now ferric ion forms complexes to an unknown extent with chloride ion, and the dissociation of these into oxonium ion and hydroxy-ferric ion is probably less than that of hexa-aquo ferric ion.<sup>6</sup> The ferric nitrate thus contains more basic ferric ion and perhaps an appreciable amount of colloidal basic salt. Experiments were run in both ferric chloride and ferric nitrate solutions with added hydrochloric acid up to a concentration which almost completely prevents dissociation (or hydrolysis). Comparison experiments were made with added potassium chloride. These experiments are recorded in Tables V and VI and shown graphically in Fig. 4. In a few experiments sodium hydroxide was added to the ferric salt solutions, since half the ferric ion can be converted to hydroxy ion

(6) Brönsted and Volqvartz, *Z. physik. Chem.*, **134**, 127 (1928).

without visible precipitation of ferric hydroxide or basic salt, at least for several hours. Brönsted and Volqvartz give the dissociation constant of the hexa-aquo ferric ion at 15° with an expression for its change with ionic strength;<sup>7</sup> using a value twice as large we have calculated approximate values for the aquo-ferric ion in these solutions at 25°. There is evidently no simple proportionality between this concentration or the hydrogen-ion concentration and the rate; as shown below there is also no simple proportionality between the rate and the diffusion coefficients.

TABLE V

THE RATE IN 0.0125 M FERRIC NITRATE WITH ADDED SODIUM HYDROXIDE, HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

$C_{NaOH}, M$	Mg. diss. in 5 min.	$k$	$CKCl, M$	$k$
0.00669	26.0		0	0.666
.00401	30.0	...	0.0091	.761
.00268	30.5		.0182	.827
.00134	31.5		.0364	.875
			.0455	.916
$C_{HCl}, M$			.0910	.988
0	34.5	0.666	.182	1.04
0.0095	41.0	.792	.364	1.08
.0190	44.0	.861		
.0285	46.5	.927		
.0570	51.5	1.05		
.0950	57.0	1.16		
.190	63.0	1.31		
.380	68.0	1.44		

The hydrochloric acid has a much greater effect on the rate in ferric nitrate than in ferric chloride;

TABLE VI

THE RATE IN 0.0150 M FERRIC CHLORIDE WITH ADDED SODIUM HYDROXIDE, HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

$C_{NaOH}, M$	Mg. diss. in 5 min.	$k$	$CKCl, M$	$k$
0.00770	36.0		0	0.829
.00402	37.0	...	0.0182	.819
.00268	39.0		.0455	.782
.00134	42.5		.0910	.875
			.182	.875
$C_{HCl}, M$			.364	.875
0	50.5	0.829		
0.00950	52.5	.869		
.0190	54.0	.885		
.0285	55.0	.909		
.0544	57.0	.941		
.0570	60.5	1.02		
.0950	64.5	1.10		
.109	63.5	1.08		
.190	67.5	1.16		
.218	63.0	1.06		
.380	70.5	1.22		
.436	67.0	1.14		

(7) Brönsted and Volqvartz, *Z. physik. Chem.*, **155**, 214 (1931).

the same is true of potassium chloride, although the effect of the latter is less than that of hydrochloric acid. Part of the effect of these additions must be due to the chloride ion, perhaps through formation of complex chlorido-ferric ion; but part of it is due to the hydrogen ion, since the effect of the acid is greater than that of the salt.

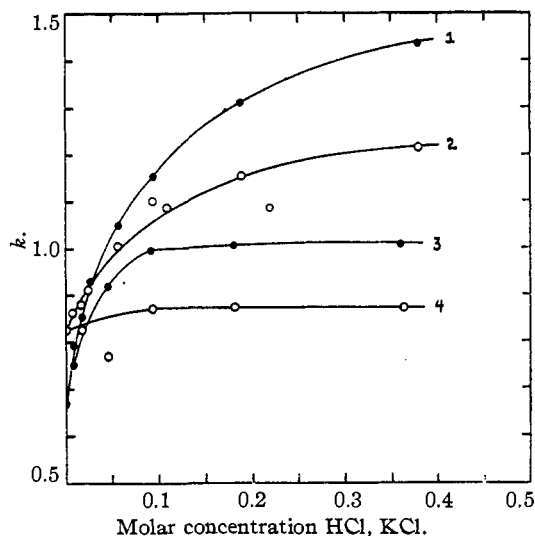


Fig. 4.—Effect of additions of (1) HCl to 0.0125 M  $Fe(NO_3)_3$ ; (2) HCl to 0.0150 M  $FeCl_3$ ; (3) KCl to the same  $Fe(NO_3)_3$ ; (4) KCl to the same  $FeCl_3$ .

In Table VII are given measurements of the diffusion coefficients of ferric chloride and nitrate, with added hydrochloric acid and potassium chloride. These coefficients were measured<sup>8</sup> in cells of the type described by McBain and Dawson.<sup>9</sup> The diffusion coefficient of ferric nitrate with no acid added appears to be higher than that of the chloride, but too much dependence should not be placed on these values, since hydrolysis of both salts occurs when they diffuse into water; brown stains appeared on the under side of the porous glass disks of the diffusion cells. This did not occur when a small amount of acid was present, but persisted with all additions of potassium chloride. Nevertheless, the curves with added acid parallel each other, but reach a maximum and decrease, while the solution rates continue to increase, possibly reaching a maximum at much higher acid concentrations.

Diffusion coefficients determined with ferrous salts present, which would more nearly simulate conditions at the copper surface, are not available; but it does not seem probable that a quanti-

(8) By W. H. Cathcart.

(9) McBain and Dawson, *THIS JOURNAL*, **56**, 52 (1934).

tative explanation of all these rates could be made in any case. There are other complications; one is the auto-catalytic effect of the dissolved copper ion, which becomes of more importance in acid solutions.

TABLE VII

THE DIFFUSION COEFFICIENTS OF FERRIC CHLORIDE AND NITRATE, 0.02 MOLAR, 25°, WITH ADDED HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

$C_{HCl}, M$	$D_{FeCl_3}$ $cm.^2/min. \times 10^4$	$D_{Fe(NO_3)_3}$ $cm.^2/min. \times 10^4$	$C_{KCl}, M$	$D_{FeCl_3}$ $\times 10^4$	$D_{Fe(NO_3)_3}$ $\times 10^4$
0	2.15	2.77	0	2.15	2.77
0.01	3.25	4.03	0.05	2.13	3.85
.05	4.44	5.47	.10	2.29	3.15
.10	4.03	4.81	.20	3.20	1.75
.20	3.14	3.92			

8. In Table IV it is seen that there may be a slight auto-catalytic effect due to the dissolved copper ion. Further experiments with 0.0150 molar ferric chloride showed a 7% increase in  $k$  over a period of twelve minutes, the copper cylinder being weighed at three-minute intervals. Similar experiments in 0.0125 molar ferric nitrate and 0.0150 molar ferric chloride with 0.190 molar hydrochloric acid added gave a 20–23% increase in the velocity "constant" during twelve minutes.

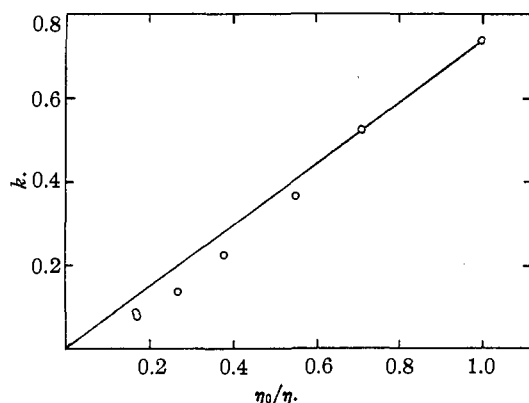


Fig. 5.—The effect of added cane sugar on the rate in ferric nitrate: 25°, 4000 r. p. m.

The experiments of Table VIII, in which copper nitrate was added to the solutions, show that its effect is much greater in the more acid solutions. It is evident that a portion of the increase in rate on addition of hydrochloric acid, Tables V and VI, is due to the enhanced effect of cupric ion formed during the experiment. The effect would not be large, since the cupric ion did not reach a concentration much above 0.002 molar in solutions containing the most hydrochloric acid.

TABLE VIII

THE EFFECT OF CUPRIC ION ON THE RATE IN FERRIC CHLORIDE SOLUTIONS

$C_{FeCl_3}, M$	$C_{HCl}, M$	$C_{Cu(NO_3)_2}, M$	Mg. diss. in 5 min.
0.0150	...	...	56.0
.0150	...	0.005	58.0
.0150	...	.050	62.5
.0150	0.272	...	78.0
.0150	.272	.005	124
.0150	.272	.050	154
....	.272	...	0
....	.272	.005	55.0
....	.272	.050	90.5

9. The effect of increased viscosity is shown in Fig. 5. Cane sugar up to 1.5 molar was added to 0.0209 molar ferric nitrate; rate constants are plotted *vs.* reciprocal of relative viscosity. The copper cylinder used dissolved about 11% faster than the one used in previous experiments. The significance of the small departure from linearity is not known.

### Discussion

Four factors indicate that the rate in ferric salt solutions is largely controlled by the rate of diffusion of the ferric ion to the surface of the copper. (1) The temperature coefficient is low; (2) the rate increases linearly with the speed of rotation above 1000 or 1500 r. p. m.; (3) the rate is almost inversely proportional to the viscosity when cane sugar is added up to 1.5 molar; (4) the calculated thickness of the diffusion layer agrees closely with the value expected by comparison with similar experiments with zinc in acetic acid and oxidizing agent. For example, taking the values for the ferric salts in 0.05 molar hydrochloric acid, at which concentration the diffusion coefficients should be dependable and the auto-catalysis by dissolved copper ion small: from the Nernst relation  $\delta = D/k$  we have, for ferric chloride,  $4.44 \times 10^{-4}/0.96 = 4.6 \mu$ ; for ferric nitrate,  $5.47 \times 10^{-4}/1.03 = 5.3 \mu$ . The rate constant for a zinc cylinder rotating with the same peripheral speed in 0.01 molar acetic acid, 0.05 molar potassium nitrate, is about 1.3 (4);  $D$ -(acetic acid) =  $7.64 \times 10^{-4} cm.^2/min.$ , whence  $\delta = 5.9 \mu$ .

Further experiments are in progress in this Laboratory on the rate of solution of copper from various faces of single crystals. If the rate in ferric salts is largely diffusion controlled, as it appears from the present data, all faces should dissolve at the same rate. It seems possible that the rate with very low hydrogen peroxide con-

centrations and excess of acid present may be entirely or almost entirely controlled by the chemical rate; in such solutions the copper surface remains very bright with no trace of oxide film. On the other hand, in solutions of low acid and high peroxide concentration, the rate may have an entirely new significance because of surface coatings which partly prevent access of reagents to the copper itself.

### Summary

The rate of solution of polycrystalline copper from a rotating cylinder has been measured, in solutions of acetic acid and various oxidizing agents, especially hydrogen peroxide and quinone;

and in solutions of ferric chloride and nitrate, with the addition of hydrochloric acid.

From the temperature coefficient, variation in rate with rotational speed, effect of changed viscosity and a comparison of the rate with that of other metals dissolving in acid solutions, it has been concluded that the rate in the ferric salt solutions is largely diffusion-controlled. In the acetic acid solutions, the rate may be entirely or partly controlled by the rate of the chemical reaction; in some of these solutions surface coatings may mechanically prevent access of reagent to the copper surface or otherwise change the character of the reaction.

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## The Mechanism of the Decomposition of Ethylene Iodide

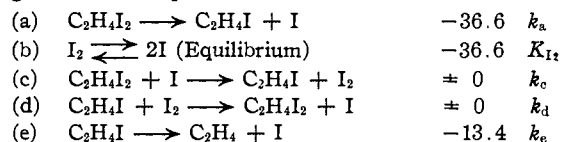
BY RICHARD A. OGG, JR.

The thermal homogeneous decomposition of gaseous ethylene iodide was found by Arnold and Kistiakowsky<sup>1</sup> to obey the rate expression

$$-d(\text{C}_2\text{H}_4\text{I}_2)/dt = k_1(\text{C}_2\text{H}_4\text{I}_2) + k_2(\text{I}_2)^{1/2}(\text{C}_2\text{H}_4\text{I}_2)$$

The first term on the right was interpreted by these investigators to indicate a dissociation in one act (into ethylene and iodine) of the ethylene iodide molecule. The author wishes to show that this is not necessarily the case, and that the chain mechanism postulated to account for the second term may be extended to account entirely for the whole rate expression.

The following steps are considered, with corresponding rate constants. The heat effects, whose estimation is described below, are given in kilocalories per mole



This set of processes is very similar to that proposed for the decomposition of *s*-butyl iodide.<sup>2</sup>

The rate expression derived from the above steps is

$$\frac{-d(\text{C}_2\text{H}_4\text{I}_2)}{dt} = \frac{k_a(\text{C}_2\text{H}_4\text{I}_2) + K_{I_2}^{1/2}k_c(\text{I}_2)^{1/2}(\text{C}_2\text{H}_4\text{I}_2)}{k_d/k_e(\text{I}_2) + 1}$$

(1) L. Arnold and G. B. Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

(2) R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).

This reduces to the experimental expression, with  $k_a = k_1$  and  $K_{I_2}^{1/2}k_c = k_2$  if the quantity  $k_d/k_e(\text{I}_2)$  is negligible in comparison with unity. Estimation of the absolute magnitudes of  $k_d$  and  $k_e$  shows this to be the case.

The heat effect of reaction (a) is taken as the activation energy for the unimolecular dissociation<sup>2,3</sup> which is identified with the activation energy found by Arnold and Kistiakowsky for the rate constant  $k_1$  (since  $k_1 = k_a$ ). The value 36.6 kilocalories per mole is about that to be expected, since the carbon-iodine bond strength in methyl, ethyl and *n*-propyl iodides<sup>3</sup> is some 43 kilocalories per mole, and that in *s*-butyl iodide<sup>2</sup> 39.5 kilocalories per mole.

The heat of dissociation of gaseous iodine in the temperature region concerned (some 200°) is obtained from the data of Bodenstein and Starck.<sup>4</sup> The remaining heats of reaction are obtained by Hess's law, using in addition the value -13.4 kilocalories per mole found by Cuthbertson and Kistiakowsky<sup>5</sup> for the gas phase reaction  $\text{C}_2\text{H}_4\text{I}_2 \longrightarrow \text{C}_2\text{H}_4 + \text{I}_2$ .

At the highest temperature in their study (230°) Arnold and Kistiakowsky found that the rate constant  $k_2$  to have the value 12.75 (mole/cc.)<sup>-1/2</sup> sec.<sup>-1</sup>. At this temperature  $K_{I_2}$  (the dissociation

(3) R. A. Ogg, Jr., *THIS JOURNAL*, **56**, 526 (1934).

(4) M. Bodenstein and H. Starck, *Z. Elektrochem.*, **16**, 961 (1910).

(5) G. R. Cuthbertson and G. B. Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).