number of very fine quartz capillaries, prepared by the method of Patrick and Shereshesky.[7] The theory predicts that hysteresis should occur to a degree approximating that indicated by equation III. The larger the capillaries the more exact should equation III become. Of course, such an artificial system if closely examined would show discontinuities in both adsorption and desorption. However, in connection with experimental reports of discontinuous isotherms it is of interest to note that if capillaries could be obtained with a slight taper, say, from $r = a$ to $r = 2a$, discontinuities should disappear in the desorption but not in the adsorption isotherm. For the latter, the theory would still predict discontinuities since as soon as the pressure reaches $P_0e^{-\sigma V/aRT}$ the capillary will become blocked at the point $r = a$ and a meniscus will form. The vapor pressure will then be supersaturated with respect to a spherical surface of radius up to $2a$; hence, the entire capillary will fill. Another experiment, suggested by Prof. J. C. W. Frazer of the John Hopkins University Chemistry Department, is the measurement of the sorption isotherm on two parallel optically plane plates. The plates should be adjustable so that their distance apart could be varied. Such experiments as these present considerable but not insurmountable experimental difficulties. However, they would be of great value not only in testing the views expressed in this paper but also in interpreting sorption phenomena in general.

The author wishes to thank Professor J. C. W. Frazer of the Johns Hopkins University for his interest and helpful criticism.

Summary

1. The vapor pressure in equilibrium with the interior of a cylindrical shell of liquid is $P_r = P_0e^{-\sigma V/rRT}$ where r is the internal radius.
2. The above equation is used to show that in certain sorption systems hysteresis must be expected.
3. In the light of these new considerations an explanation of various experimental results is given.
4. Experiments to further test the views presented are suggested.

BALTIMORE, MD. RECEIVED NOVEMBER 23, 1937

[COMMUNICATION NO. 61 OF THE PHYSICAL CHEMISTRY DEPARTMENT, J. PILSUDSKI UNIVERSITY]

The Influence of Small Percentages of Certain Metals on the Solution Rate of Cadmium

BY M. CENTNERSZWER AND F. GONET[1]

The theory of local elements, published in 1830 by de la Rive, with the aim of explaining the fact that chemically pure zinc dissolves much more slowly in acids than zinc containing "admixtures" of foreign metals (*e. g.*, copper, lead, iron), postulates that the "foreign" metal particles form small "local elements" with the zinc particles. The latter become the anode, whereas the admixture forms the cathode, from which the hydrogen is evolved.[2]

In 1902, Palmaer formulated an equation by the aid of which it was thought possible to estimate quantitatively the rate of solution of metals containing certain admixed metals.[3] In the case of zinc, containing a small percentage of lead, Palmaer's equation takes the form

$$\rho = 0.217K/C\ (A + 2 \log C_{\mathrm{H}^+} - \log C_{\mathrm{Zn}^{++}})$$

where ρ is the reaction velocity, K the specific electrical conductivity of the solution, A the acting e. m. f. of the local element, C_{H^+} and $C_{\mathrm{Zn}^{++}}$ the concentration of the hydrogen and zinc ions in solution. The equation was proved experimentally by Ericson-Aurén and Palmaer, who found it to agree well with the experimental results.[4] Above all they showed that the influence of admixtures on the solution rate of zinc is the greater the smaller the hydrogen overvoltage on the positive metals (compare this with M. Centnerszwer and Is. Sachs[5]).

In 1914 Centnerszwer and Sachs[6] investigated

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(1) Kościuszko Foundation Scholar.

(2) De la Rive, *Ann. chim. phys.*, **43**, 425 (1830).

(3) T. Ericson-Aurén and Wh. Palmaer, *Z. physik. Chem.*, **39**, 1 (1902).

(4) T. Ericson-Aurén and Wh. Palmaer, *Z. anorg. allgem. Chem.*, **18**, 83 (1898); **27**, 209 (1901); *Z. physik. Chem.*, **39**, 1 (1902); **45**, 182 (1903); **56**, 689 (1906); Wh. Palmaer, "The Corrosion of Metals," Vol. I, Handlingar 93, Stockholm, 1929; Vol. II, Handlingar 108, Stockholm, 1931.

(5) M. Centnerszwer and Is. Sachs, *Z. physik. Chem.*, **87**, 692 (1914).

(6) M. Centnerszwer and Is. Sachs, *ibid.*, **89**, 213 (1914).

the solution rate of zinc alloyed with copper in hydrochloric acid, and showed that the rate initially increased very rapidly, but after the completion of the "period of induction" it slowly fell away. The reaction constant calculated according to Boguski's equation[7]

$$K_1 = dv/dt \times 1/F \times C \quad (1)$$

was the smaller the greater the copper content in the alloy. They also showed that slowly cooled alloys dissolved faster than alloys which were suddenly quenched. They showed further that lead, cadmium and arsenic did not increase the rate of solution of zinc, contrary to the theory of Aurén and Palmaer, and that, on the other hand, gold, nickel and platinum caused a very large increase in the solution rate even when added in very small amounts (about 0.01%).

In 1925 Centnerszwer and Straumanis[8] investigated the influence of layers of different metals, precipitated on the surface of zinc plates from solutions of their salts, on the solution rate of zinc. Their experiments show that there is no direct relation between the solution rate of zinc coated with a given metal and the hydrogen overvoltage on that metal. For example, adhering particles of tin and lead do not influence the solution rate of zinc, although their hydrogen overvoltage is smaller than that of zinc. Even iron increases the solution rate of zinc (though in a very small degree) and the hydrogen overvoltage on iron (0.28 v.) is much smaller than that of copper (0.40 v.) which accelerates this process to a very marked degree.

Cadmium was chosen for this investigation of the theory of local elements because it is easily obtained in a chemically pure form and as such does not dissolve in dilute acids. Hence one can ascertain more accurately what admixtures influence the solution rate of cadmium and to what degree. From the former research published by one of us jointly with M. Straumanis[9] it appears that cadmium dissolves easily when in contact with platinum or metals in the platinum group, and to a lesser degree in galvanic elements formed by cadmium with copper or cobalt. In the present investigation we would like to show the influence that some of the above metals have on the solution rate of cadmium when used as admixtures in cadmium alloys. We would like to mention that chemically pure cadmium only dissolves in very strong acids of high concentrations,[10] and that the alloys investigated by us at present dissolve very little, if at all, in dilute hydrochloric and sulfuric acids. On the other hand, a cadmium–platinum element immersed in 1 *N* sulfuric acid begins to dissolve rather quickly, while the same elements alloyed require 4 *N* hydrochloric or 8 *N* sulfuric acid before the alloy will dissolve.

Preparation and Analysis of the Alloys.—The method of preparing the samples differs little from that given by Straumanis.[9] Weighed amounts of metal and admixture were melted together in a sealed Pyrex tube rolled up in asbestos. The molten alloy was shaken until it began to solidify and then remelted. This operation was repeated from three to five times to make sure that the alloy was really homogeneous. Then it was allowed to cool slowly. When thoroughly cooled the metal was taken out of the glass and the thin oxide layer on the surface was removed with sandpaper. The clean cylindrical sample was then rolled into a sheet from 0.5 to 2.0 mm. thick, depending on the concentration of acid in which it was to be dissolved. Small disks (diameters from 12 to 20 mm.) were next turned from the sheets, the shavings and clippings being used for analysis.

The analysis of the alloys was carried out according to Treadwell and Hall.[11] The platinum in the platinum–cadmium alloy was determined by cupelling[11a] and gave 0.485 atomic per cent. platinum in the first alloy, and 0.98 atomic per cent. platinum in the second alloy. The gold in the cadmium–gold alloy was determined by Vanino and Seeman's method[11b] and was found to amount to 0.975 atomic per cent. The copper in the third alloy was separated electrolytically[11c] and the cadmium–copper alloy contained 0.795 atomic per cent. copper.

Procedure.—The solution rate of the cadmium and cadmium alloys in hydrochloric and sulfuric acids was investigated volumetrically,[12] *i. e.*, by using the hydrogen liberated by the metal as a measure of the rate of solution. The acids and the cadmium used were Kahlbaum "chemically pure" chemicals. The samples were dissolved in the reaction flask shown in Fig. 1. It consists of a bulb (A) with a capacity approximately equal to 300 cc. The slanting arm (B), which is used for the introduction of the preheated acid, is fitted with a ground stopper (E); (C), which is of a larger diameter, serves as a holder for the mechanical stirring device. The latter is made from a long glass rod, 0.7 cm. in diameter. The lower end of the rod is flattened into a "paddle" (F) bent (approx.) 35° from the plane of the axis of the rod. This angle has been developed by long practice, as the hydrogen formed on the surface of the sample does not slip off the surface easily, and thus causing an enlargement of the reacting

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[7] J. J. Boguski, *Kosmos*, **1**, 538 (1876); *Ber.*, **9**, 1646 (1876).

[8] M. Centnerszwer and M. Straumanis, *Z. physik. Chem.*, **118**, 415 (1925).

[9] M. Centnerszwer and M. Straumanis, *ibid.*, **128**, 388 (1927); M. Straumanis, *Acta Univ. Latviensis*, **20**, 393 (1929).

[10] M. Centnerszwer, *Z. physik. Chem.*, **A137**, 352 (1928).

[11] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 6th ed., 1924: (a) p. 249, (b) p. 240, (c) p. 199.

[12] M. Centnerszwer, *Z. physik. Chem.*, **A141**, 297 (1929).

surface (and hence an increase in the reaction velocity). The upper part of the stirrer is sealed off by a gas-tight mercury seal (G). A pulley wheel (H), rotated by a motor, sets the paddle (F) in motion. This type of stirrer has been found to work well at speeds not exceeding 400 r. p. m. The remaining side-arm (D) leads to a (50 cc./0.1 cc.) buret (which is not shown in the diagram), which was used to measure the volume of the hydrogen evolved. The metal disks are attached to the paddle (F) by means of beeswax, and before the run is made the whole apparatus is tested for possible leaks. All connections shown are glass ground and sealed by means of Ramsey fat, which is removed and applied anew before every run. As all runs are made in pairs, two such flasks are kept in a thermostat, electrically heated and regulated to within 0.05° of 25 and 40°.

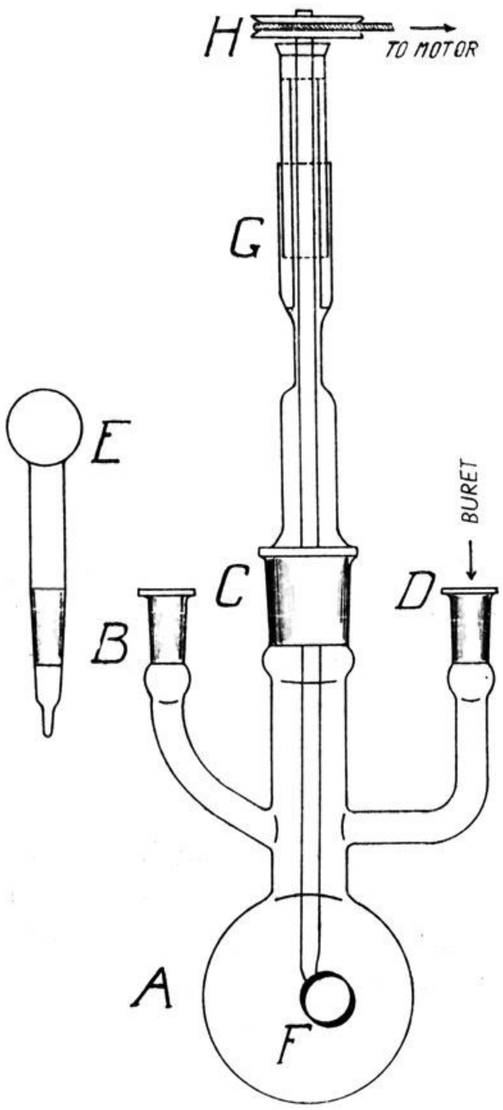

Fig. 1.—The reaction flask.

The following notation is used in the tables and formulas: t_0, the period of induction in minutes; v_0, volume of hydrogen evolved during t_0 at N. T. P.; dv/dt, the solution rate of the metal, calculated from the experimental results by dividing the amount of hydrogen evolved in cc. by the time of evolution and by the area, or cc. H_2/min./sq. cm. surface. K_1, the solution rate constant calculated according to Boguski's equation[7]

$$K_1 = 1/FC \times v_n - v_0/t_n - t_0 \qquad (2)$$

where F is the area of the exposed metal surface, C the concentration of the acid in mole equivalents/cc., t_n the time from the beginning of the experiment, v_n the volume of hydrogen evolved in time t_n.

Solution Rate of Cadmium Alloys in Hydrochloric Acid.—Practically, cadmium alloyed with platinum, gold or copper does not dissolve in dilute hydrochloric acid, although the hydrogen overvoltage on these metals is very small; hence the measurements of the solution rate were begun in 5 N hydrochloric acid. Here, as in the case of zinc alloyed with the noble metals,[5] the rate of solution of the alloy increased very quickly at first, reaching a maximum after a certain time, and then slowly fell away (Fig. 2). This period of initial growth, up to the maximum solution rate, is called the "period of induction." In the experiments with hydrochloric acid this period lasts from forty-five to three thousand minutes, depending on the nature of the admixture and on the concentration of the acid. The shortest period was obtained in the cadmium–platinum alloy; the longest in the cadmium–copper alloy. The experimental results at 25° and without mechanical stirring are given in Table I. During the dissolution of the cadmium alloy the disk became covered with a black, granular deposit, a

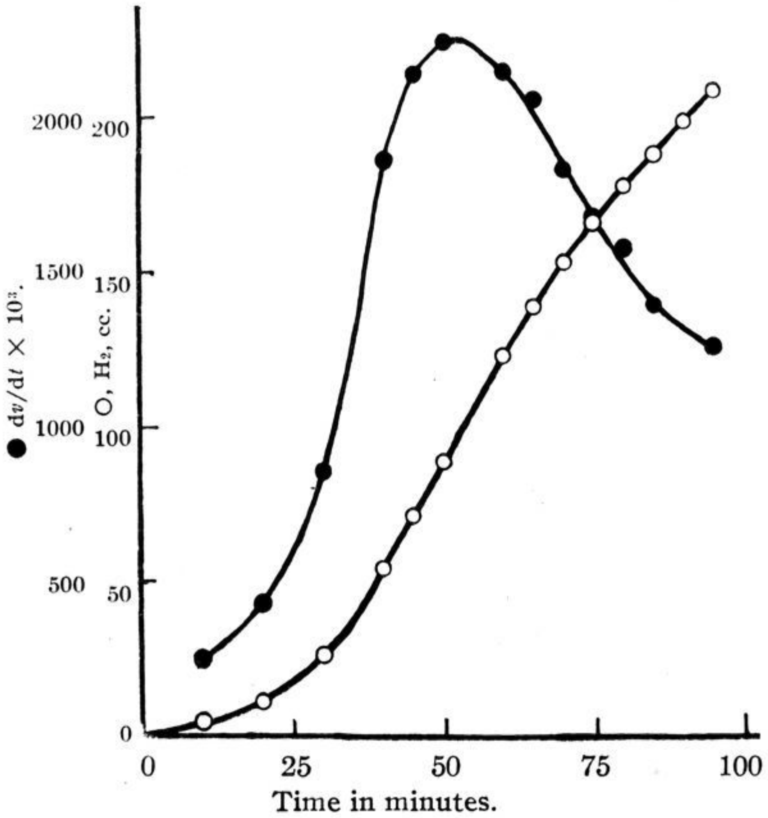

Fig. 2.—The solution rate of Cd + 0.98 at. % Pt in 6 N HCl, at 40°, without mechanical stirring. The upper curve shows the solution rate with time, the lower, the amount of hydrogen evolved in the same time.

TABLE I

SOLUTION RATE OF CADMIUM ALLOYED WITH Pt, Au, Cu IN HCl

Temp., 25°; vol. acid, 250 cc.; without mechanical stirring.

Alloy, Cd with	*N* HCl	t_0	v_0	$(dv/dt) \times 10^3$	K_1	$K^2 \times 10^{-3}$		$C_0 \times 10^3$
0.48 at. % Pt	5	250	85.3	375	70.6	70.6	60.4	4.0
	6	68	74.1	722	103.5	51.7		
	7	75	186.7	1484	177.2	59.0		
.98 at. % Pt	5	175	47.3	399	78	78.0	82.9	4.0
	6	90	65.8	1123	165	82.2		
	7	45	110.3	2261	266	88.8		
.97 at. % Au	5	722	72.0	123	24.2	30.3	29.1	4.2
	6	370	114.0	344	51.8	28.7		
	7	130	96.2	582	78.9	28.2		
.79 at. % Cu	6	2680	116.3	22.8	3.3	6.6	5.6	5.5
	8	1410	121.4	49.3	5.8	2.3		
	10	277	124.0	239	21.4	4.8		
	12	107	147.2	772	54.6	8.9		

part of which fell to the bottom of the reaction vessel. A jet of water easily removed it from the disk, leaving a rough, pitted surface.

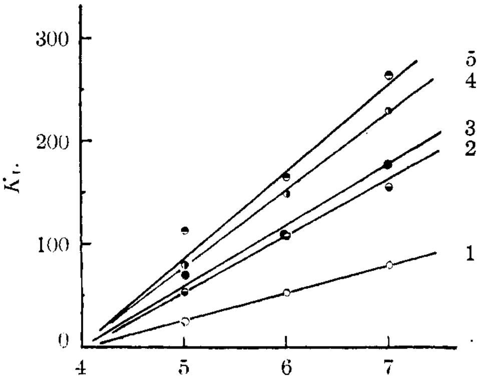

Fig. 3.—Relation between Boguski's constant and the concn. of hydrochloric acid used. (1) Cd + 0.79 at. % Au, 25°; (2) Cd + 0.79 at. % Au, 40°; (3) Cd + 0.48 at. % Pt, 25°; (4) Cd + 0.48 at. % Pt, 40°; (5) Cd + 0.98 at. % Pt, 25°.

From the experimental results given in Table I it appears that

(1) The period of induction (t_0) is the shorter the higher the concentration of the hydrochloric acid used and, conversely, the volume of hydrogen evolved during the period t_0 is greater the greater the concentration of the hydrochloric acid used.

(2) The maximum rate of solution of the alloys is reached at the end of the period of induction, and dv/dt increases with increased hydrochloric acid concentration.

(3) The period is shorter and the maximum rate of solution greater as the platinum content in the alloy is increased.

(4) Of the admixtures investigated, platinum increases the rate of solution of cadmium the most, gold somewhat less, and copper very little.

(5) The value of the smallest concentration in which the solution process of cadmium alloys still takes place (C_0) lies between 4 and 6 *N* hydrochloric acid.

It is possible to calculate Boguski's constant K_1 (equation 1) from the solution process of cadmium alloys in hydrochloric acid in various concentrations. The results of this calculation show that the constant increases with an increase in the hydrochloric acid concentration, which relation is shown in Fig. 3. The above-mentioned relation between Boguski's constant and the concentration of the hydrochloric acid used can be expressed by means of a first degree equation

$$K_1 = K_2 (C - C_0) \qquad (3)$$

where K_1 is Boguski's constant calculated according to equation (1), C_0 the smallest concentration of hydrochloric acid in which the given alloy is soluble, C the concentration of hydrochloric acid used in the experiment, and K_2 a constant (given in Table I, column 7) calculated according to the equation

$$K_2 = dv/dt \times 1/FC(C - C_0) \qquad (4)$$

From the curves shown in Fig. 3 it appears that the cadmium solution process begins when the concentration of the hydrochloric acid used is greater than a certain minimum concentration (C_0), whose value depends on the character of the admixture. In the case of the cadmium-platinum alloys in Table I, it is equal to 4 *N* hydrochloric acid. For other admixtures C_0 is still larger, as Table I, column 8, shows.

Solution Rate of Cadmium Alloys in Sulfuric Acid.—Cadmium alloyed with platinum, gold and copper dissolves much more slowly in sulfuric acid than in hydrochloric acid of the same concentration. To get a measurable rate of solution 8 N sulfuric acid had to be used, but even in these conditions the rate of solution was much smaller than in hydrochloric acid and the cadmium–copper alloy was found almost insoluble in sulfuric acid. The results are shown in Table II. The behavior of the alloys in sulfuric acid was found to be completely different from that in hydrochloric acid. In the latter, the solution rate increased nearly proportionally to the increase of the hydrochloric acid concentration. In sulfuric acid, on the other hand, the rate of solution of the alloy decreased with increased sulfuric acid concentration. It seems as though the sulfuric acid (or some product as hydrogen sulfide) had a poisonous effect on the solution process of cadmium alloys, as was shown recently by K. Jabłczyński.[13] In general the solution rate of even the cadmium–platinum alloy is so small that there is no possibility of speaking of the influence of the local elements in this case.

TABLE II

SOLUTION OF CADMIUM ALLOYED WITH Pt, Au, Cu IN H_2SO_4. TEMP., 25°. VOL. ACID, 250 CC.; WITHOUT ROTATION

Alloy, Cd with	N H_9SO_4	t_0	v_0	$(dv/dt) \times 10^3$	K_1
0.48 at. % Pt	8	..	..	128.0	13.5
	10	645	91.5	97.7	9.2
	12	330	31.4	57.0	4.8
	14	90	6.7	41.5	0.9
.98 at. % Pt	8	..	..	259.7	16.3
	10	540	66.2	165.0	15.8
	12	270	19.6	87.0	3.7
	14	30	2.2	47.0	1.4
.97 at. % Au	10	3290	46.1	30.7	2.2
	12	1260	61.0	82.9	2.7
	14	960	21.8	38.1	1.7
.79 at. % Cu	14	165	1.1	7.8	0.3

The Influence of Stirring.—Rotation of the sample (see Fig. 1) has no influence on the rate of solution of the cadmium alloys, as is seen from the results gathered in Table III, at 25 and 40° and 150 r. p. m. However, if we compare the lengths of the induction periods during solution (with and without stirring), we see that stirring cuts the period. In some cases it is shortened by as much as 50%. In general, however, stirring has a smaller effect on the period of induction than does the concentration of the acid.

TABLE III

SOLUTION RATE OF CADMIUM ALLOYED WITH Pt, Au, Cu IN HCl AND H_2SO_4, WITH AND WITHOUT ROTATION. VOL. ACID, 250 CC.; 25 AND 40°

Alloy, Cd with	Acid, N	Temp., °C.	R. p. m.	t_0	$(dv/dt) \times 10^3$	K_1
0.48 at. % Pt	5 HCl	25	150	160	422	77.6
	5 HCl	25	0	250	375	70.6
	6 HCl	25	150	60	623	100
	6 HCl	25	0	68	722	103.5
	7 HCl	25	150	60	1281	167
	7 HCl	25	0	75	1484	177.2
	5 HCl	40	150	107	827	152
	5 HCl	40	0	180	642	115.3
	6 HCl	40	150	50	1096	173
	6 HCl	40	0	47	967	148.1
	7 HCl	40	150	12	1728	231
	7 HCl	40	0	50	1849	230
	10 H_2SO_4	25	150	330	96.6	9.2
	10 H_2SO_4	25	0	645	97.7	9.2
.98 at. % Pt	6 HCl	25	150	55	962	151
	6 HCl	25	0	90	1123	165
.97 at. % Au	10 H_2SO_4	25	150	2145	140	8.6
	10 H_2SO_4	25	0	3290	30.7	2.2
.79 at. % Cu	6 HCl	25	250	895	16.4	1.8
	6 HCl	25	0	2680	22.8	3.3
	8 HCl	25	250	665	161	13.7
	8 HCl	25	0	1410	49.3	5.8
	10 HCl	25	250	225	342	30.4
	10 HCl	25	0	277	239	21.4
	12 HCl	25	250	90	645	42
	12 HCl	25	0	107	772	54.6
	14 H_2SO_4	25	150	210	9.2	0.4
	14 H_2SO_4	25	0	165	7.8	0.3

Influence of the Temperature.—A series of experiments was carried out at 40° with the aim of determining the influence of the temperature on the solution rate of the cadmium alloys. The results obtained for K_1, calculated according to Boguski's equation, are shown in Table IV. From the results one sees that the values are typical of "mixed processes," *i. e.*, those whose rate depends both on the chemical reaction rate and on the diffusion rate. In the cases where the rate of solution is relatively fast, diffusion is a measure of the solution rate. To such may be included the solution of the cadmium–platinum alloy in 7 N hydrochloric acid whose temperature coefficient, $K_t - 10/K_t = 1.2$, *i, e.*, equal to the value for the temperature coefficient of a diffusion process. As the concentration of the hydrochloric acid is lowered the solution rate constant decreases, while the temperature coefficient of the reaction increases. In 5 N hydrochloric acid it attains a value of 2.2. This value is typical of chemical reaction rates. On the other hand, the temperature coefficient of the reaction rate constants for

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[13] K. Jabłczyński and Mączkowska, *Rocz. Chem.*, **11**, 139 (1931); K. Jabłczyński and J. Kulesza, *ibid.*, **12**, 676 (1932); *Z. anorg. allgem. Chem.*, **207**, 157 (1932).

cadmium alloyed with gold and copper show intermediate values.

TABLE IV

BOGUSKI'S CONSTANT K_1 CALCD. AT 25 AND 40° AND THE TEMPERATURE COEFFICIENT

Alloy, Cd with	Acid, N	Soln. rate const. K_1 25°	40°	Temp. coeff. K_t-10/K_t
Cd, chem. pure[10]	6 HCl	1.74	[a]	1.74
	8 HCl	7.27	[a]	1.86
	10 HCl	19.2	[a]	1.4
	14 H_2SO_4	0.2	0.5	1.7
0.48 at. % Pt	5 HCl	70.6	115.3	1.4
	6 HCl	103.5	148.1	1.3
	7 HCl	177.2	230.0	1.2
	8 H_2SO_4	13.5	33.1	1.8
	10 H_2SO_4	9.2	22.7	1.8
	12 H_2SO_4	4.8	(10.5)	(1.7)
	14 H_2SO_4	0.9	4.3	2.8
.98 at. % Pt	5 HCl	78	250	2.2
	6 HCl	165	302	1.5
	7 HCl	266	354	1.2
	8 H_2SO_4	16.3	46.4	2.0
	10 H_2SO_4	15.8	32.0	1.6
	12 H_2SO_4	3.7	9.0	1.8
	14 H_2SO_4	1.4	3.5	1.8
.97 at. % Au	5 HCl	24.2	53.0	1.7
	6 HCl	51.8	107.1	1.6
	7 HCl	78.9	153.0	1.6
	10 H_2SO_4	2.2	12.6	3.2
	12 H_2SO_4	2.7	7.8	1.3
	14 H_2SO_4	1.7	3.1	1.5
0.79 at. % Cu	6 HCl	3.3	7.1	1.7
	8 HCl	5.8	13.5	1.8
	10 HCl	21.4	40.3	1.5
	12 HCl	54.6	86.0	1.4
	14 H_2SO_4	0.3	1.12	1.8

[a] Results obtained by M. Centnerszwer[10] for 50°. K_1 at 50° was: 6 *N* HCl, 6.9; 8 *N* HCl, 34.5; 10 *N* HCl, 42.5.

In sulfuric acid the solution rate is much slower and the chemical reaction rate seems to be the governing mechanism, and diffusion plays a minor role in the reaction.

In conclusion, one of us (F. G.) would like to thank the Kościuszko Foundation of New York for a scholarship, which made the above work possible.

Summary

The rate of solution of cadmium and cadmium alloyed with platinum, gold and copper has been measured in sulfuric and hydrochloric acids, with and without stirring. The effects of varying temperature, rotation, concentration of the acids, and amount and kind of admixture on the reaction velocity, solution rate constant, and duration of the period of induction have been studied.

WARSAW, POLAND RECEIVED OCTOBER 25, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Heats of Organic Reactions. VI. Heats of Hydrogenation of Some Oxygen-containing Compounds

BY M. A. DOLLIVER, T. L. GRESHAM, G. B. KISTIAKOWSKY, ELGENE A. SMITH AND W. E. VAUGHAN

In the previous papers of this series[1] we have reported the heats of hydrogenation of a considerable number of unsaturated hydrocarbons and have determined some regularities correlating the thermo quantity and molecular structure. This publication concerns itself with the heats of hydrogenation of some oxygen-containing compounds; in it we shall show some further effects of various substituents on the ethylenic linkage and also give some derived values for other reactions.

Preparation of Compounds

Vinyl Acetate.—A pure grade of vinyl acetate containing an inhibitor was obtained from Shawinigan Chemicals Limited. This was systematically fractionated in column A. Sixty-six per cent. of the distillate boiled at 72.32 ± 0.01° at 765 mm.; n^{20}D 1.3953, f. p. −100.2°.[2]

Methyl Methacrylate.—Inhibitor-free methyl methacrylate of 99.9+% purity was kindly sent us by D. E. Strain of the du Pont Company. While in our possession it was stored in ice in the dark. The refractive index as measured by us was $n^{20.1}$D 1.4149[3] and the f. p. −48.0°.

Crotonaldehyde.—Crotonaldehyde from Carbide and Carbon Chemicals Corporation was distilled through column B giving a fraction boiling at 102.26–102.42° at 765 mm.; this was refractionated through column A. The portion, representing 50% of the material, distilling at 102.29–102.30° at 765 mm. was collected for use in the calorimeter; f. p. −76.6°, n^{20}D 1.4366.[4]

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[1] See, for a summary, Paper V, Dolliver, Gresham, Kistiakowsky and Vaughan, THIS JOURNAL, **59**, 831 (1937).

[2] Morrison and Shaw, *Trans. Electrochem. Soc.*, **63**, 443 (1933), give f. p. below −84°, b. p. 73°, n^{20}D 1.3958.

[3] Contributions from E. I. du Pont de Nemours and Co., *Ind. Eng. Chem.*, **28**, 1160 (1936), give $n^{15.6}$D 1.4168, m. p. −48°.

[4] "I. C. T.," Vol. I, p. 186, gives m. p. −75°, b. p. 104°; p. 276, n^{20}D 1.4373.