[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Rate of Dissolution of Magnesium and Zinc in Acids

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It is obvious that when a metal dissolves in dilute aqueous acid two processes must operate: (a) the acid must reach the metal surface, and (b) the chemical reaction must take place. If one of these processes is much slower than the other it will control the observed dissolution rate. In much of the published work on solid–liquid interaction rates it is evident that transport to or from the solid surface is rate controlling. Numerous attempts have been made to find conditions under which the chemical reaction is the rate controlling process. For instance it is supposed that if at sufficiently great stirring speeds the rate becomes independent of stirring speed, such conditions would be present. Unfortunately in most such cases studied the stirring speed has not been varied sufficiently and the observed rate has only become "constant" within the experimental error over a very small range of speeds. Two such cases have been discussed in previous papers from this Laboratory.[1,2]

The rate of solution of magnesium in the form of fine shavings has been measured by T. H. James,[3] by a method involving shaking the acid solution with the metal shavings. Over a range of 220 to 500 vigorous shakes per minute, the rate was found sensibly constant and the conclusion was reached that the chemical process was rate controlling. James, however, made the following reservation: "Because of the low specific gravity of the magnesium particles, the possibility exists that the metal will to a certain extent share the motion of the adjacent portion of the liquid Hence, an increase in shaking speed may not produce a correspondingly great increase in the relative motion of the liquid and solid."

The present work was undertaken to extend the stirring speeds used by James to higher values, if possible; to compare magnesium chips, whose effective density is made even less by adhering hydrogen bubbles, with similar zinc chips which have a greater density and which with a depolarizer present evolve no hydrogen; and to compare both rates with those obtained with rotating metal cylinders and with stationary metal strips located near a stirring cylinder.

Experimental

In all cases 1500 ml. of dilute hydrochloric or acetic acid was placed in a 2000-ml. vessel, and the stirring was accomplished with a $^1/_4$ h. p. motor with built-in 10 to 1 gear box. The steel shaft was coated with varnish, and on its lower end could be mounted the 2 × 2 cm. magnesium cylinder or the 3.4 × 2.5 cm. grooved bakelite stirring cylinder. Two bakelite baffle plates were mounted in the solution to prevent cavitation. The rate with the magnesium cylinder was measured by weighing the cylinder, which was polished with very fine emery paper before each run. With the strips and the chips, a portion of the solution was withdrawn rapidly after a fixed time (three, four or five minutes), through a large tube with a glass wool strainer. An aliquot portion was then titrated with standard sodium hydroxide, using phenolphthalein in the experiments with magnesium, methyl red for the solutions containing zinc.

Magnesium chips were prepared by cutting ribbon (3 × 0.15 mm.) into short pieces. Zinc chips of similar size were cut from sheet zinc 0.25 mm. thick. The magnesium chips swirled freely with the solution at all stirring speeds used, but the zinc chips did not all leave the bottom of the vessel until approximately 11000 r. p. m. was reached.

Rate constants were calculated from the equation

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

where V is the volume of the solution in ml., A the area of metal in sq. cm., and a and $a - x$ are the amounts of acid initially and at time t.

Results

More details of the experiments, and the rate constants found are given in Tables I–IV.

TABLE I

MAGNESIUM CHIPS IN HYDROCHLORIC ACID AT 25°

R. p. m.	A, sq. cm.	C_{HCl}, N	t, min.	k
7100	386	0.0526	3	1.03
8800	395	.0526	3	1.21
9200	416	.0526	3	0.99
9300	409	.0526	3	1.01
9900	177	.0371	4	1.04
11850	402	.0526	3	1.02
12400	394	.0526	3	1.04
13500	178	.0371	4	1.01
15400	178	.0371	4	1.01
16800	401	.0526	3	1.33

TABLE II

MAGNESIUM AND ZINC CHIPS

Magnesium, 0.0348 M $HC_2H_3O_2$, 177 sq. cm., 5 min., 25°		Zinc, 0.050 M HCl, 0.050 M KNO_3, 139 sq. cm., 26°			
		3 min.		5 min.	
R. p. m.		R. p. m.		R. p. m.	
4950	0.299	9250	1.98	9300	1.29
6000	.300	10200	2.14	10050	1.73
7200	.298	11000	2.18	11050	2.15
8350	.299	12200	2.24	12050	2.20
10350	.300	13350	2.24	12850	2.22
12200	.300	47000	2.27	14150	2.24
14000	.300				
16000	.300				

Other experiments were run at 15 and 40° with zinc chips, and the temperature coefficient was found to be approximately 1.2 per 10° throughout this range. Experiments with zinc cylinders

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[1] King and Burger, *Trans. Electrochem. Soc.*, **65**, 403 (1934).

[2] King and Brodie, THIS JOURNAL, **59**, 1375 (1937).

[3] James, *ibid.*, **65**, 39 (1943).

TABLE III

MAGNESIUM AND ZINC SHEET IN HYDROCHLORIC ACID

Magnesium, 0.0445 M HCl, 59.3 sq. cm., 3 min., 25°		Zinc, 0.050 M HCl, 0.050 M KNO_3, 80 sq. cm., 3 min., 25°	
R. p. m.		R. p. m.	
7650	0.466	6200	0.364
8600	.507	7500	.383
9800	.669	8800	.457
11400	.711	9850	.474
13050	.824	10850	.492
14900	.940	12600	.563
		14250	.648

TABLE IV

MAGNESIUM CYLINDER IN HYDROCHLORIC ACID

0.050 M HCl, *ca.* 15 sq. cm., 5 min., 25°

R. p. m.	
3750	3.34
6700	5.31
7800	6.38
8800	6.68
10250	7.25
11750	8.18
14100	8.37
14900	9.82

rotating in hydrochloric and acetic acids have been carried out previously.[4,5]

Discussion

In agreement with the results obtained by James,[3] the rate of solution of magnesium chips is independent of the stirring speed in both acids. The highest stirring speeds probably agitate the liquid much more than the shaking used by James. A steady rate is approached by the zinc chips at the higher speeds, but only when they leave the bottom of the vessel and swirl with the solution. It is significant that the maximum rate reached with zinc is more than twice as great as with magnesium.

It was found previously that under identical conditions (a depolarizer being necessary with zinc though not with magnesium), the two metals dissolve at almost the same rate.[4] The fact that the zinc chips dissolve much faster than the magnesium would seem to be explained by the higher density and greater inertia of the zinc particles, which allows the solution to flow past their surface faster. In Table III it is seen that the rate with the metal sheets is considerably lower than from the chips, indicating that this type of stirring is not so effective, although the rate continually increases with stirring speed. The two metals do not dissolve at the same rate, and this is explained by the fact that the strips were mounted differently. The zinc strip replaced one of the bakelite baffle plates, while the magnesium strip was mounted separately in a position closer to the stirring cylinder. (The top portions of both strips were coated with varnish to leave a definite area exposed under the solution.)

More conclusive evidence that the steady rates of Tables I and II are not chemical rates is provided by the fact that the rotating cylinders dissolve at much higher rates (Table IV and refs. 4, 5). The rotating cylinder method apparently brings fresh solution in contact with the metal more effectively than any of the other methods. It has been suggested that frictional heating effects in the film at the surface of the cylinder may account for the high solution rates. This seems highly improbable in view of the low temperature coefficients. The lowest rate of Table IV, at 3750 r. p. m., is already 3.3 times the steady rate with magnesium chips.

The rate of solution of magnesium chips in hydrochloric acid is about 3.3 times the rate in acetic acid. It has been shown that, in magnesium salt solutions, the ratio of the diffusion coefficients of the acids is somewhat higher than this,[6] but it was shown that dissolution rates are proportional to a fractional power of diffusion coefficients rather than to the first power.

Summary

It has been shown that the rates of solution of magnesium and zinc chips in acids are independent of the stirring speed up to very high speeds. These rates have been compared with the rates obtained with sheets of the metals suspended in similar acid solutions and with rotating metal cylinders.

The conclusion is reached that the constant rates of the floating chips are not true chemical rates, but that the chips acquire the motion of the liquid to such an extent that higher speeds are ineffective in increasing the relative motion of metal and solution.

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(4) King and Braverman, THIS JOURNAL, **54**, 1744 (1932).

(5) King and Schack, *ibid.*, **57**, 1212 (1935).

(6) King and Cathcart, *ibid.*, **59**, 63 (1937).