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Rate of Solution of Magnesium in Acids

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Previous studies on the kinetics of solution of magnesium in acids have given measured rates which depend upon the stirring speed, and hence involve diffusion effects. The rates measured by Brunner¹ and Centnerszwer² were largely or wholly controlled by diffusion. King and his co-workers have made an extensive comparison under various conditions of the rates of diffusion with the rates of solution of a rotating magnesium cylinder.^{3,4,5} The two rates frequently ran parallel courses. However, the parallel was not complete, and some results even showed the inverse of the expected relationship. Thus, the measured diffusion coefficient of chloroacetic acid was smaller than that of acetic, whereas the solution rate was appreciably greater.

The most important criterion for a diffusion-controlled rate is the dependence of measured rate upon stirring. All of the investigations cited previously showed a marked dependence of measured rate upon stirring speed. The least dependence of any results reported to date was obtained by Kilpatrick and Rushton,⁶ using the rotating cylinder method. Their data fit the equation

$$k = aR^{0.36} \quad (1)$$

where R is the surface velocity and a is a constant. The small value of the coefficient, 0.36, implies that a mixture of reaction and diffusion rates was actually measured.⁷

The true kinetics of the chemical reaction evidently cannot be determined unless diffusion effects are eliminated experimentally or corrected for by suitable means.⁷ In the present investigation, rates were obtained which were independent of agitation above a certain critical value. The measured rates, therefore, are probably the true reaction rates. The experimental results were, in general, reproducible to within $\pm 2\%$.

Experimental Procedure

Magnesium metal was employed in the form of finely divided shavings (60–80 mesh) and was always used in

excess of the acid. The apparatus⁸ was essentially that employed in previous work on solution–solid reactions.⁹ Initially, the magnesium shavings were placed in the lower chamber of the reaction vessel, together with water. The acid and any salt solution used were placed in the upper chamber. The delivery stopcock of the upper chamber had a large bore and delivery of acid into the lower chamber was complete within two seconds. In the shaking apparatus, the propeller rod was very loosely connected with the shaker rod, so that a sharp kick was imparted to the reaction vessel at the end of each swing. This markedly increased the efficacy of the agitation and gave an appreciably lower critical shaking speed than when the propeller rod was more tightly connected. A shaking speed of 400 cycles per minute normally was employed.

Reaction was carried out at $20 \pm 0.02^\circ$, unless otherwise specified. One millimole of magnesium was used in each experiment, and the total solvent volume was 50 ml. No attempt was made in the present investigation to determine accurately the specific surface of the magnesium samples used, but this could probably be done by the adsorption method of Emmett and Brunauer.¹⁰ The reaction rates were determined by following the evolution of hydrogen. Hence, the method is dependent upon the absence of any substances which react with the hydrogen. All runs were carried out in an atmosphere of nitrogen.

The reaction followed the first-order equation over most of the total course when the magnesium was in considerable excess, and the rates reported subsequently are "first-order constants" calculated on the basis of the total hydrogen available. The water reaction was measurable at 20° , but was insignificant in comparison with the rate of the acid reaction.

Experimental Results

The measured rate became independent of the shaking speed above 220 cycles per minute. Data are given in Table I. In general, deviation from the first-order relation occurred somewhat sooner at the lower shaking speeds than at the higher, suggesting some effect of rates of diffusion of the reaction products away from the surface during the later stages of the reaction. This effect, if real, is quite small and does not influence the values of the rate constants determined from the first third of the reaction course.

Because of the low specific gravity of the magnesium particles, the possibility exists that the metal will to a certain extent share the motion

- (1) E. Brunner, *Z. physik. Chem.*, **47**, 100 (1904).
- (2) M. Centnerszwer, *Rec. trav. chim.*, **42**, 579 (1923); *Ann. X^o Congr. int. chim.*, **3**, 555 (1939).
- (3) C. V. King, *THIS JOURNAL*, **57**, 828 (1935).
- (4) C. V. King and W. H. Cathcart, *ibid.*, **59**, 63 (1937).
- (5) E. J. Roehl, C. V. King and S. Kipness, *ibid.*, **63**, 284 (1941).
- (6) M. Kilpatrick and J. H. Rushton, *J. Phys. Chem.*, **38**, 269 (1934).
- (7) P. S. Roller, *ibid.*, **39**, 221 (1935).

(8) A. Weissberger, H. Mainz and E. Strasser, *Ber.*, **62**, 1942 (1929).

(9) T. H. James, *THIS JOURNAL*, **62**, 536 (1940).

(10) P. H. Emmett and S. Brunauer, *THIS JOURNAL*, **57**, 1754 (1935); "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

of the adjacent portions 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 possibility that no relative change at all occurs cannot be eliminated definitely with the data at hand. However, the agitation at the higher shaking speeds used is quite violent. It appears improbable that no effect exceeding the 2% experimental error limits would be observed upon doubling the shaking speed if diffusion played a significant part in controlling the measured reaction rate. Furthermore, in some of the subsequent measurements, significant divergence occurs between the reaction rates and the diffusion rates measured by King and his co-workers.

TABLE I

EFFECT OF SHAKING SPEED ON MEASURED REACTION RATE

Shaking speed, cycles/min.	k , HAc	k , HCl
220	0.131	...
240	...	0.375
280	.136	...
300	.136	...
400	.138 .136	.370
500	.140 .136	.383

Table II gives the effect of change in the composition of the reacting solution. Data on the temperature dependence of the reactions of acetic acid and hydrochloric acid are given in Table III. The figures given are the averages of triplicate runs at each temperature. Table IV lists the rates obtained with a series of acids.

TABLE II

EFFECT OF VARIATION IN SOLUTION COMPOSITION

Addition	Concn.	Acid concn.	k (HAc)	k_u	k (HCl)
...	...	0.004	0.145	0.130	0.350
		.010	.137	.128	.375
		.020	.135	.128	.400
NaAc	0.020	.010	.130	.129	...
NaCl	.010	.010	.138	.127	.402
	.040	.010	.140	.126	.488
	.400	.010	.139	.125	.492
MgCl ₂	.33	.010	.128460
Sucrose	.295	.010	.127	.118	.347
	.441	.010	.093

TABLE III

TEMPERATURE DEPENDENCE OF SOLUTION OF Mg IN ACIDS

Temp., °C.	k (HAc)	k (HAc) 0.4 M NaCl	k (HCl)
20.0	0.137	0.138	0.376
29.8	.183	.182	.506
40.1	.239	.239	.637
E (cal.)	5100	5060	4920

TABLE IV
REACTION RATES OF VARIOUS ACIDS

Acid	pK_a^a	Salt of acid, M	k measured	k_u	$k_u M^{1/2}$
Formic	3.75	..	0.170	0.143	0.97
Acetic	4.76	..	.137	.128	.98
		0.02	.130	.130	1.01
Valeric	4.79	..	.110	.100	1.01
		.01	.094	.094	0.95
Glycolic	3.83	..	.141	.114	.99
		.01	.115	.112	.98
HSO ₄ ⁻379
HCl377
		Na ₂ SO ₄	.01 .389

^a Values for 25°.

Discussion

The constant for the reaction of hydrogen ion (H₃O⁺) with magnesium should be that of the completely dissociated hydrochloric acid after correction is made for the accelerating effect of chloride ion. Extrapolation to zero chloride-ion concentration of the data in Table II for the variation of k with initial hydrochloric acid concentration and the variation with added sodium chloride leads to the value of 0.34–0.35 for the hydrogen-ion reaction.

In the reactions of the weak organic acids, the hydrogen-ion concentrations are too small to account for the observed rates. The measured rates are largely those of the undissociated acids. The true constants for the reactions of the undissociated acids can be evaluated readily after the contribution of the hydrogen-ion reaction has been corrected for. Such constants, designated as k_u , are listed in Column 5 of Tables II and IV. The calculated constants are in good agreement with those obtained from buffered solutions, where the hydrogen-ion concentrations are almost negligible.

The reaction of the undissociated acetic acid is clearly first order with respect to acid concentration. The rate is likewise proportional to the available magnesium surface. Thus, an increase of threefold in the magnesium surface increased the reaction rate from 0.137 to 0.398.

Sodium chloride has little or no effect upon the acetic acid reaction. The observed change is within the limit of experimental error, whereas the diffusion coefficient is increased from 0.77 to 0.82 by the addition of 0.1–0.2 M sodium chloride.⁴ On the other hand, the salt markedly increased the rate of solution in hydrochloric acid. Magnesium chloride exerted a similar effect. However, the increase due to 0.33 M magnesium salt amounted

to only 1.23-fold in contrast to an increase in diffusion rate of 1.78-fold. Further data are required before an explanation of the salt effect upon the hydrogen-ion reaction can be given.

The activation energies of the acetic and hydrochloric acid reactions are low, being 5100 and 4920 cal., respectively. Such low activation energy values have been taken by some writers as good evidence for a diffusion-controlled process. However, the criterion that a so-called "normal" chemical reaction should have a temperature coefficient of 2 or greater is not valid evidence, since numerous reactions are known with markedly lower coefficients.¹¹ Several heterogeneous reactions which have been studied under conditions where the measured rates are controlled by diffusion probably have low true energies of activation. For example, it would be difficult to explain the high rate of solution of zinc in hydrochloric acid measured by King and Braverman,¹² unless the actual chemical reaction possessed a low activation energy. If a "normal" activation energy of 14,000 cal. or above were assumed, the rate of the chemical reaction should be sufficiently low to control the over-all rate. It may be noted that the temperature coefficient obtained in the present work with acetic acid checks well with that which Roehl, King, and Kipness found for acetic acid in 92% ethanol solution,⁵ where the reaction rates showed a marked departure from the diffusion rates.

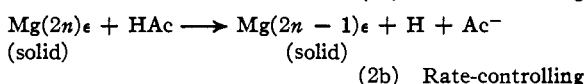
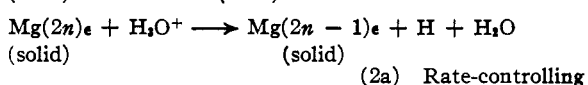
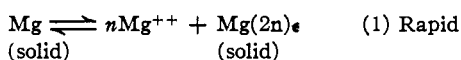
The rates of reaction of the various acids listed in Table IV show remarkably little variation. If the calculated rates for the undissociated acids are further corrected to allow for differences in

(11) Cf. E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Press, New York, N. Y., 1933, p. 278.

(12) C. V. King and M. M. Braverman, *THIS JOURNAL*, **54**, 1744 (1932).

collision frequencies, the resulting rates ($k_{11}M^{1/2}$) are substantially constant. Even the value for the hydrogen ion (H_3O^+) becomes nearly equal to that for acetic acid, when correction is made for the small difference in activation energies. The values are 1.17 and 0.98, respectively.

Schematically, the reactions involved in the solution of magnesium in acids under the conditions employed may be represented as follows



The rate-controlling reaction is that of the acid with electrons at the metal surface.

Summary

1. The rate of solution of magnesium in various acids was studied by a method which gave results independent of the agitation rate. The measured rates are apparently those of the chemical reaction.

2. Undissociated formic, acetic, valeric, and glycolic acids react with magnesium at a smaller rate than H_3O^+ , but the rates of all five are of the same order of magnitude. Sodium chloride has little or no effect upon the rates of the undissociated acids, but accelerates the hydrogen-ion rate.

3. The apparent energy of activation of the acetic acid reaction is 5100 cal.; that of the hydrogen-ion reaction is 4900 cal.

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