mining the structure may now be seen clearly. The HIO₃ molecule contains essentially covalent bonds, the pyramidal shape of the IO₃ group being determined by the type of iodine orbitals used for the single bonds (p-orbitals with some s character). The hydrogen atom of the hyroxyl group might form either one strong hydrogen bond to one of the two remaining oxygen atoms (of another iodate group) or two weaker bonds, one to each of them; it actually forms the bifurcated bond. The iodine atom has less stable orbitals available to form additional octahedral bonds which it now can do partially by forming weak bonds with three oxygen atoms of other iodate groups. Since the hydroxyl oxygen (O_{II}) is not available for these bonds the iodine atom must form the three weak bonds with the remaining two oxygen atoms and it does this by forming one weak bond with one of them (O'_{I}) and two weaker bonds with the other $(O'_{III}$ and $O''_{III})$.

Considering the relation of the structure of HIO₃ to that reported for the iodates it seems likely that in those crystals the oxygen atoms are displaced from the symmetry positions of the perovskite structure in such a manner as to form iodate groups. An investigation of one of the pseudocubic iodates using the proper monoclinic

hemihedral space group and unit cell would settle this question.

The authors are indebted to Professor Linus Pauling for detailed discussion of this work and many helpful suggestions.

Summary

The structure of the α-modification of crystalline iodic acid has been determined. Laue and oscillation photographs show that the orthorhombic unit cell with $a_0 = 5.520 \pm 0.005$, $b_0 = 5.855 \pm 0.005$, $c_0 = 7.715 \pm 0.005$ contains four molecules of HIO₃. The space group is $D_2^4 - P_{2_12_12_1}$. Patterson and Fourier projections on the three axial planes calculated from visually observed intensity data gave the twelve parameters for the oxygen and iodine atoms (Table II). The structure is an aggregate of HIO₃ molecules held together by hydrogen bonds of the bifurcated type and weak iodine oxygen bonds. Iodine atoms are surrounded by distorted octahedra of oxygen atoms and the oxygen atoms are in a nearly closest packed arrangement. The influence of the different types of bond on the structure has been discussed and its relation to the perovskite structure shown.

Dissolution and Diffusion Rates in Alcohol–Water Mixtures

BY E. J. ROEHL,[1] CECIL V. KING AND SOL KIPNESS

Numerous studies have been made of the rate of dissolution of magnesium in aqueous acid solutions, and a thorough study of the rate in absolute ethyl alcohol has been reported by Sclar and Kilpatrick.[1a] Only a few experiments have been carried out in solutions of acids in alcohol–water mixtures. These have indicated that, in relatively dilute alcohol, the rate is inversely proportional to the viscosity of the mixture.[2] The comparatively low rates in absolute alcohol[1a] indicate that this proportionality does not hold over the entire range of alcohol concentration; the fluidity of pure ethyl alcohol is only 20% less than that of water, while the dissolution rate is 70%

less, and there is evidence that part of this rate is due to reaction with the solvent itself.[1a]

Diffusion coefficients have been found in general to be nearly proportional to the fluidity of the medium (for example, measurements of Arrhenius on hydrochloric acid in dilute ethyl alcohol[3]). However, few measurements have been made in water–alcohol mixtures, and many of the measurements in concentrated or "absolute" ethyl and methyl alcohol are of doubtful accuracy.

While the diffusion rates of non-solvated non-electrolytes might be expected to follow the fluidity in mixed solvents, this could hardly be true of solvated electrolytes. In order to clarify the relations between dissolution rate, viscosity, and diffusion rate of acids, we have measured dissolution and diffusion rates in ethyl alcohol–water

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(1a) Sclar and Kilpatrick, THIS JOURNAL, 59, 584 (1937).

(2) King and Braverman, ibid., 54, 1744 (1932); Van Name and Hill, Am. J. Sci., (4) 36, 543 (1913).

(3) Arrhenius, Z. physik. Chem., 10, 51 (1892).

mixtures over a wide range of alcohol concentration. Hydrochloric and acetic acids were chosen because the first is highly ionized and highly solvated, while the latter is weakly ionized in water, even weaker in alcohol, and comparatively little solvated. The diffusion rate of potassium chloride was also measured for comparison, since it is as highly ionized as hydrochloric acid but much less solvated.

Experimental.—Dissolution rates were determined as described in previous papers,[2,4] by rotating metal cylinders (magnesium and zinc) 1.8–1.9 cm. in diameter and about 2.5 cm. long, in 200 cc. of solution at 25° (±0.5°). The amount dissolved was determined by weighing the cylinders. Rate constants k were calculated from the unimolecular equation (2). The adequacy of this equation to represent the process was tested thoroughly, especially in solutions of high alcohol content, both by replacing cylinders in the same solutions after weighing, and by running for various lengths of time in fresh solutions of duplicate concentration. No significant deviations were found except in the case of acetic acid in "absolute" alcohol (99%+) where the rate curve for magnesium was found to be of the autocatalytic type, in agreement with the finding of Sclar and Kilpatrick[1a] for hydrochloric acid.

Diffusion rates were determined using a porous glass disk cell, samples from the lower or both compartments being titrated after twenty-four to ninety-six hours in the thermostat at 25° (±0.02°). Diffusion coefficients were calculated from the equation[5]

$$D = \frac{V_A V_B}{(V_A + V_B)kt} \ln \frac{C_A}{C_A - (1 + V_B/V_A)C_A''}$$

where V_A, V_B are the cell compartment volumes in cc., k the "cell disk constant," t the time in days, C_A the solute concentration in the upper compartment at the start and C_A'' the concentration in the lower compartment at the time t.

The acids were titrated with standard base; the potassium chloride with silver nitrate by the Mohr method. The weight per cent. of alcohol given is for the pure solvent; the solutions contained the same amount of alcohol per cc. The composition was determined from density measurements and is given to the nearest 0.5%.

Dissolution Rate Measurements.—In Table II are given average rate constants for magnesium

(4) King and Cathcart, THIS JOURNAL, 59, 63 (1937).
(5) King and Cathcart, ibid., 58, 1639 (1936).

and zinc in hydrochloric acid. Since the measurements with zinc must be made with some depolarizer present, the magnesium was rotated in solutions containing potassium nitrate and hydrogen peroxide, as well as in solutions of acid alone. The nitrate reduces the rate about 15%, as shown also in Table I, the peroxide rather less. Magnesium dissolves several per cent. faster than zinc, as has been found previously for aqueous solutions. Perhaps magnesium reacts to some extent with the solvent, especially when its surface is kept clean and the reaction products are dissolved by the acid. In water and dilute alcohol containing hydrogen peroxide the magnesium acquired a dense black coating, which disappeared after ten to fifteen minutes, leaving the surface quite bright. In 78% alcohol no such coating was formed, and the metal became very bright. In 65% alcohol a less dense gray-black film appeared and disappeared at intervals of a few minutes.[6]

TABLE I

THE EFFECT OF POTASSIUM NITRATE ON THE DISSOLUTION RATE OF MAGNESIUM. CYLINDERS 1.8–1.9 CM. IN DIAMETER ROTATED AT 2000 R. P. M. IN 0.05 M AQUEOUS HCl, 25°, 5 MINUTE RUNS

C_{KNO_3}, M	0	0.005	0.0125	0.025	0.05	0.10	0.15	0.20
k	2.05	1.73	1.73	1.70	1.70	1.80	1.79	1.74

TABLE II

THE DISSOLUTION RATE OF MAGNESIUM AND ZINC IN 0.05 M HCl IN ETHYL ALCOHOL–WATER MIXTURES AT 25°. CYLINDERS 1.8–1.9 CM. IN DIAMETER, 2000 R. P. M.

Wt. % alcohol	Magnesium			Zinc	
	k	k 0.10 M KNO₃	k 0.08 M H₂O₂	k 0.10 M KNO₃	k 0.08 M H₂O₂
0	2.08	1.74	1.98	1.67	1.76
21	1.20	0.96	1.06	0.80	0.77
32	0.83	.68	..	..	..
43	.63	.54	0.59	.51	.48
55.5	.49	.42	..	..	..
65	.42	.35	.39	.36	.33
78	.33	..	.35	.30	.29
100	.30[a]	..	..	..	..

[a] Rough estimate from maximum rates found by Sclar and Kilpatrick.

Table III gives the rate constants in acetic acid.

Diffusion Rate Measurements.—Table IV gives details of the cell constant determination. Approximately 0.05 M hydrochloric acid diffusing into pure water was used, and the diffusion coefficient was assumed to be 2.71 cm./day, the value found for 0.1 M hydrochloric acid by Mc-

(6) For studies of black magnesium oxide see Mellor, "Comprehensive Treatise," IV, 280, Longmans, Green and Co., New York, N. Y., 1923.

TABLE III

THE DISSOLUTION RATE OF MAGNESIUM IN 0.05 M ACETIC ACID IN ALCOHOL–WATER MIXTURES AT 25°. CYLINDERS
1.8–1.9 CM. IN DIAMETER, 2000 R. P. M.

Wt. % alcohol	0	14	26.5	41.5	57	70.5	85	92	"100"
k	0.70	0.42	0.32	0.253	0.232	0.226	0.176	0.111	[a]

[a] "Autocatalytic," but slower after 85 minutes than at the start in 92% alcohol.

Bain and Dawson.[7] Since samples of equal volume were titrated before and after the diffusion period, cc. of base used may be substituted for C_A and C_A'' in the diffusion equation, and these values are given in Table IV as $cc._A$ and $cc._A''$.

TABLE IV

CELL CONSTANT DETERMINATION, USING APPROXIMATELY
0.05 M HCl (D = 2.71 AT 25°). V_a = 68.1 Cc.; V_b = 71.2 Cc.

Time, days	$cc._A$	$cc._A''$	k
2.083	42.48	8.90	3.45
2.042	42.46	8.88	3.52
1.882	39.40	7.72	3.50
2.951	39.40	10.72	3.54
			Average 3.50

Table V gives values of D determined for approximately 0.05 M hydrochloric acid, acetic acid and potassium chloride in alcohol–water mixtures.

TABLE V

THE DIFFUSION COEFFICIENTS OF HYDROCHLORIC ACID, ACETIC ACID AND POTASSIUM CHLORIDE, APPROXIMATELY 0.05 M, IN ALCOHOL–WATER MIXTURES AT 25°

Wt. % alcohol	D(HCl)	D(CH₃COOH)	D(KCl)
0	(2.71)	1.11	1.63
19	1.49	0.62	1.00
	1.51	.62	1.00
41	0.90	.44	0.63
	.94	.42	.61
62.5	.70	.39	
	.69	.40	..
63.5	..	..	.37
			.43
71	.60	..	..
	.64		
84.5	..	.54	.50[a]
		.56	.46[a]
89	.61	..	..
	.60		
92.5	..	..	.57[b]
100	.59	.85	.65[c]

[a] 0.03 M KCl.   [b] 0.01 M KCl.   [c] 0.003 M KCl.

Temperature Coefficients.—With 0.05 M acetic acid in 92% alcohol, a few measurements were made of the dissolution rate of magnesium at 15 and 35°, in addition to those at 25°. The

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

coefficients are as follows: k_{25}/k_{15} = 1.32, k_{35}/k_{25} = 1.35.

Discussion.—In Figs. 1 and 2 the relative rate constants and diffusion coefficients (k/k_0 and D/D_0, where the subscript $_0$ refers to 0% alcohol) are compared with the relative fluidity (reciprocal viscosity) of the solvent mixtures ("International Critical Tables"). It is evident from Fig. 1 that, up to about 35% alcohol, the rates and diffusion coefficients follow the fluidity closely, in spite of observed discrepancies in the values for magnesium and zinc, with and without oxidizing agents. It was suggested above that magnesium may react with the solvent to some extent, thus accounting for its higher rate. The visible films formed with hydrogen peroxide probably decrease the rate, and the nitrate may assist the formation of invisible films. The commercial c. p. zinc contains impurities which accumulate on the surface and have been found to decrease the rate unless the specimen is polished with an abrasive frequently.

Above 35% alcohol the relative rate and diffusion coefficients parallel each other closely enough to suggest that the rate is essentially diffusion-controlled, though other factors (slow chemical rate or film formation) are not negligible. The plotted point for 100% alcohol is a rough estimate from the maximum rates found by Sclar and Kilpatrick; as they have shown, the rates ordinarily are much smaller and apparently not diffusion controlled.

The great departure of the diffusion and rate curves from the fluidity curve above 35% alcohol is undoubtedly caused by change in character of the diffusing ions. Hydration is replaced by alcoholation and there may be some ion-pair formation in solutions of high alcohol content.

Figure 2 shows that in the case of acetic acid there is similar close agreement between relative rate constants, diffusion coefficients and fluidity to about 40% alcohol. Above this point the diffusion coefficient parallels the fluidity although the relative values are somewhat smaller. This is to be ascribed to the smaller degree of hydration of acetic acid and its replacement by alcoholation;
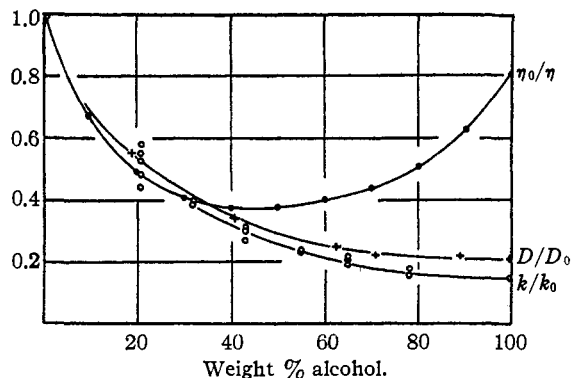
Fig. 1.—The relative rate constants (magnesium and zinc in hydrochloric acid), diffusion coefficients (hydrochloric acid) and fluidity (alcohol–water solvent mixtures).

Fig. 2.—The relative rate constants (magnesium in acetic acid), diffusion coefficients (acetic acid) and fluidity.

there may be some influence from a change in degree of association of the acid molecules.

The divergence between rate constant and diffusion coefficient curves for acetic acid above 40% alcohol indicates profound modification of the normal "diffusion layer." In alcohol-rich solutions the acid concentration gradient must be small, and indications are that in absolute alcohol it would disappear.

Nevertheless the low temperature coefficient in 92% alcohol is typical of diffusion rates and not of normal chemical rates. Two possibilities present themselves: the rate may be partly or entirely controlled by a chemical process having an unusually low temperature coefficient, or it may be controlled by a different type of diffusion process such as slow penetration through a non-reactive surface film.

Table V shows that the diffusion rate curve for potassium chloride lies between those for the weak and strong acids. As the alcohol content of the solutions increases, one would expect the character of the diffusing particles to change less than in the case of hydrochloric acid, more than in the case of acetic acid.

Conclusions.—We may conclude that the dissolution rate of these metals in hydrochloric
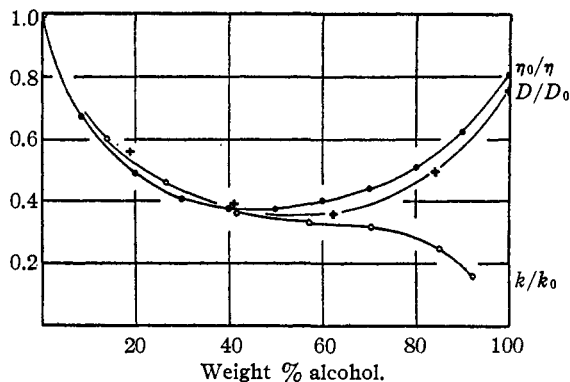
acid is largely, if not entirely, controlled by diffusion of acid through a layer in which a concentration gradient is set up because of the rapid reaction of metal with acid, except in solutions containing practically no water. In acetic acid, however, the normal diffusion layer begins to disappear when more than 45% alcohol is present, and the rate is partly or entirely controlled by some other than the normal diffusion process.

The authors wish to thank Dr. Morris B. Abramson for his assistance.

Summary

Dissolution rates of magnesium and zinc in hydrochloric acid, and of magnesium in acetic acid, have been measured in ethyl alcohol–water mixtures. Diffusion coefficients of these acids and of potassium chloride have been measured in the same mixed solvents. The values obtained have been compared with each other and with the relative fluidity of the solvents.

The mechanism of the dissolution process has been discussed from the viewpoint of the data obtained.