closely together.[9] The excess volume introduced by the tetrahedral arrangement is therefore approximately 45% of the total volume. The expansion coefficient of water at 25° is 25.7×10^{-5} ml. per gram per degree. If it behaved as a normal liquid it would have an expansion coefficient of approximately 85×10^{-5} ml. per gram per degree. This difference may be accounted for if we assume that a rise of one degree introduces a randomness which corresponds to a loss of about 0.1% of the excess volume, a very reasonable amount.

Summary

We have measured the specific volumes at 25° and the expansion coefficients in the neighborhood of this temperature of solutions of some salts in methanol and glycol. A comparison of the apparent and partial volumes of lithium bromide in water, glycol and methanol gives strong evidence that this salt influences the structure of water by promoting the tetrahedral arrangement of the molecules.

Unlike the same quantities for salts in aqueous solution, the apparent molal expansibilities of the salts in glycol and methanol are negative and increase with the concentration of salt, thereby agreeing qualitatively with the predictions of the interionic attraction theory and the effective pressure hypothesis. A comparison of the behavior of the salts in water on the one hand and in glycol and methanol on the other indicates that the structural changes in water play a predominant role in determining the thermal expansions of aqueous solutions.

WASHINGTON, D. C. RECEIVED DECEMBER 26, 1936

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Rate of Reaction of Magnesium with Acids in Ethyl Alcohol[1,2]

BY MARTIN SCLAR[3] AND MARTIN KILPATRICK

The rate of reaction of metals with acids in aqueous solution has been the subject of many investigations. A summary of the work up to 1929 has been given by Centnerszwer.[4] In non-aqueous solvents two quantitative studies have appeared. Zecchini[5] measured the rates of reaction of zinc with hydrogen chloride in water, ethyl alcohol, methyl alcohol and acetone. Brönsted and Kane[6] sought to show that sodium amalgam reacted with molecules of carboxylic acids in benzene, and that the rate of the reaction increased with the ease with which the acid gave up its proton. In addition, several partially quantitative observations have been made, especially by Kahlenberg and his co-workers in connection with their criticism of the Arrhenius theory of electrolytic dissociation. Smith[7] gives a summary of this work. Additional investigations are desirable because comparison of the results in aqueous and non-aqueous solutions may lead to a better understanding of the problem.

In the present work ethyl alcohol was selected as the solvent and magnesium as the metal for the general study. After describing the procedure and some orientating experiments, we shall proceed to demonstrate that magnesium can displace hydrogen from the molecules of ethyl alcohol without the intermediate formation of solvated proton. We shall also show that this reaction predominates when magnesium dissolves in alcoholic solutions of acids. It will be seen that the observed rate of this reaction shows great variations. Experiments with solutions of acids containing chloride ion, organic chlorine compounds and small amounts of water, respectively, will be described, which indicate that the variations in the observed rates probably are due to differences in the amount of metal surface available for reaction. The results of experiments to determine the effect of temperature and the rate at which the magnesium cylinder is rotated will then be presented. Finally some miscellaneous experiments will be described.

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(1) Abstracted from the dissertation of Martin Sclar presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1935.

(2) An abstract of this paper was presented at the eighty-ninth meeting of the American Chemical Society held at New York, April, 1935.

(3) George Leib Harrison Fellow in Chemistry, 1934–1935.

(4) Centnerszwer, *Z. physik. Chem.*, **141A**, 297 (1929).

(5) Zecchini, *Gazz. chim. ital.*, **27**, 466 (1897).

(6) Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

(7) Smith, "The Effects of Moisture on Chemical and Physical Changes," Longmans, Green and Co., London, 1929, Chap. 14.

Experimental

1.—The experimental procedure is essentially a modification and improvement of that of Kilpatrick and Rushton.[8] Figure 1 is a diagram of the apparatus. The reaction vessel was located in an air thermostat regulated at 30 ± 0.05°. The cylinder of magnesium was rotated at 980 r. p. m. by a small synchronous motor. Other speeds were obtained by the use of gears. A piece of Bakelite was inserted between the steel shaft and the magnesium, and the latter was completely immersed. The solution was added from a fast delivering 50-cc. pipet to the reaction vessel through the side-arm extending through the top of the thermostat. The gas evolved was collected over anhydrous ethyl alcohol in a water-jacketed double-armed buret.

The ethyl alcohol was dried by the method of Bjerrum and Lund.[9] Density measurements on various batches showed that the water content did not exceed 0.025%. Dried nitrogen was bubbled through the alcohol to remove oxygen.

The solutions of hydrogen chloride were freshly prepared, and precautions were taken to exclude moisture. The carboxylic acids were purified where necessary. All acid solutions were diluted to the desired concentration and standardized against 0.1 *M* sodium hydroxide one-half hour before use. Solutions of lithium chloride were prepared from Kahlbaum fused lithium chloride, which was found to contain a negligibly small amount of alkali.

Kahlbaum magnesium was used in the form of cylinders about 0.9 cm. in diameter and 5.5 cm. in length. Zinc cylinders of the same dimensions were cast in vacuum from a supply of very pure zinc.[10] Before use a skin was removed from each cylinder by turning on a lathe. Then the metal was washed with carbon tetrachloride and ethyl alcohol, polished with emery paper and wiped with a dry cloth.

Each experiment was carried out in duplicate, and at least 3 runs were made when the reproducibility was unsatisfactory. The reproducibility varied with the acid used, hydrochloric and the chloro acids yielding much better results than acetic acid. Different batches of alcohol gave the same results. It made no difference whether or not the magnesium was polished with emery paper. Table I shows the reproducibility of the results with hydrochloric and chloroacetic acids.

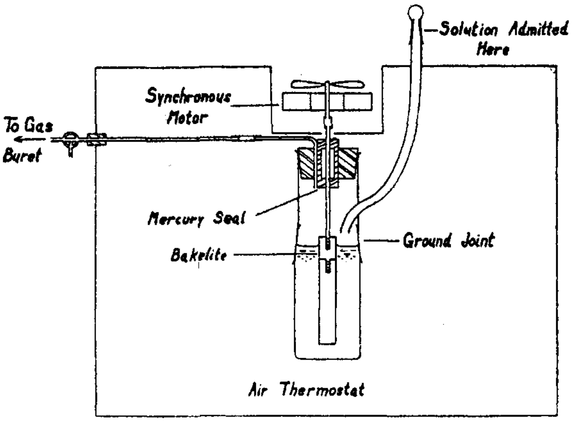

Fig. 1.—Apparatus.

2.—Whitby[11] and Kilpatrick and Rushton[8] found that no oxygen was consumed when magnesium dissolved in aqueous solutions of sodium chloride and acids, respectively. When ethyl alcohol is the solvent, however, considerable quantities of hydrogen are lost as a result of its combination with oxygen. This can be seen from the data in the last three rows of Table II. The difference in the results in water and in alcohol may be due to the fact that oxygen is 8.6 times more soluble in alcohol than in water[12] at 76 cm. of oxygen. However, when oxygen is removed from both the alcohol and the reaction vessel, the hydrogen evolved, the magnesium dissolved and the acid consumed are equivalent to within a few per cent. The results of some of the experiments which were carried out to determine this are given in Table II. Therefore, unless otherwise noted, oxygen was excluded in the experiments. Additional reasons for excluding oxygen were: first, in some cases oxygen increases the rate of the reaction in the initial stages, and, second, the formation of water inhibits the reaction.

TABLE I

REPRODUCIBILITY OF THE DISSOLUTION OF MAGNESIUM IN ACIDS AT 30°

0.065 *M* Hydrochloric Acid[a,b]

Minutes				
2	5	11	18	25
Equivalents hydrogen evolved × 10^4/cm.^{2}				
0.258	0.825	1.47	1.98	2.36
.255	.811	1.47	1.98	2.35
.222	.818	1.51	1.98	2.37
.297	.795	1.46	1.96	2.34

[a] The first and last two experiments, respectively, were carried out with different batches of alcohol. [b] In the last experiment the metal was not polished with emery.

0.059 *M* Monochloroacetic Acid

5	12	18	25	32
Equivalents hydrogen evolved × 10^4/cm.^{2}				
0.122	0.480	0.965	1.44	1.93
.122	.464	.952	1.42	1.85

The equivalence of the gas evolved, metal dissolved and acid consumed indicated that the chlorine-substituted acids which were used were only

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(8) Kilpatrick and Rushton, *J. Phys. Chem.*, **38**, 269 (1934).

(9) Bjerrum and Lund, *Ber.*, **64B**, 210 (1931).

(10) The authors take this opportunity to thank the New Jersey Zinc Co. for the zinc.

(11) Whitby, *Trans. Faraday Soc.*, **28**, 474 (1932).

(12) Calculated from data in the "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VIII, 1928, pp. 257 and 262.

TABLE II

EQUIVALENCE OF GAS EVOLVED, METAL DISSOLVED AND ACID CONSUMED

Acid and initial molarity[a]	Hydrogen, cc. at N. T. P. Expected from wt. loss	Expected from acid consumed	Obtained
0.148 acetic	81.0	84.5	82.0
.122 chloroacetic	84.5	85.0	85.0
.117 α-chloropropionic		95.3[b]	96.5
.119 *o*-chlorobenzoic	80.5	82.6	83.8
.117 dichloroacetic	87.5	85.3	84.9
.112 dichloroacetic	123[b]		126[c]
.0646 hydrochloric	34.4	35.8	36.4
.0512 hydrochloric[d]	26.4		20.4
.144 acetic[d]	78.5		70.3
.0588 chloroacetic[d]		30.1	22.9

[a] Salts present not noted. [b] Solution alkaline at end of experiment. [c] Experiment at 50°. [d] Oxygen not excluded.

slightly reduced. Lund[13] heated 1 g. of magnesium with 30 cc. of alcohol containing 1 cc. of carbon tetrachloride until the metal dissolved completely, and found that the amount of chloride ion in the resultant solution corresponded to only 8% of the total. In that experiment the volume of hydrogen evolved was about 1000 cc. or 10 times the volume evolved in our experiments. In the latter, therefore, where the maximum concentration of chlorine compound was about one-half of that used by Lund and the maximum temperature 50°, the amount of reduction was probably slight. Kilpatrick and Rushton[8] working with aqueous solutions found that the chloro acids used by them were not reduced. However, Tarle,[14] Bodforss and Kajmer[15] and Dunning and Fletcher,[16] the latter working with sodium and lithium amalgams, observed reduction.

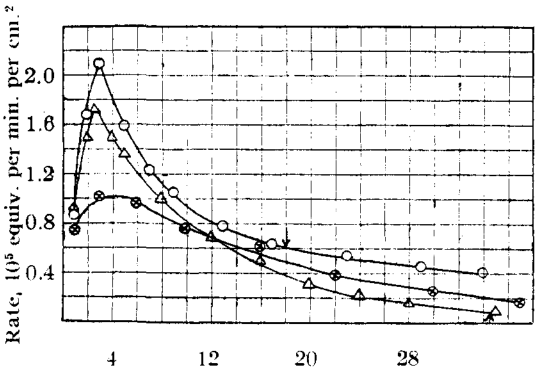

Fig. 2.—Effect of water on the reaction of magnesium with 0.064 *M* hydrochloric acid. The arrow indicates when all the acid has been consumed. The circles, triangles and crossed circles show the rates obtained with solutions which were 0.011, 0.050 and 0.102 *M* in water, respectively.

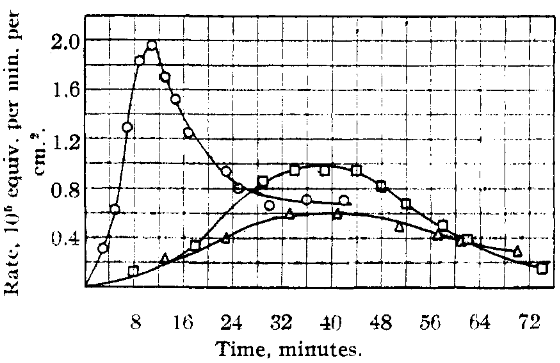

Fig. 3.—Effect of water on the reaction of magnesium with 0.12 *M* chloroacetic acid. The circles, squares and triangles show the rates obtained with solutions which were 0.011, 0.024 and 0.05 *M* in water, respectively.

3.—Data for some typical experiments are presented graphically in Figs. 2, 3 and 4. From them it may be observed that, in contrast to the behavior in aqueous solutions of acids, induction periods are observed in alcohol. After the induction period the reaction rate decreases, and the magnesium continues to liberate hydrogen from the alcohol after a volume of hydrogen equivalent to the acid originally present has been evolved, despite the fact that magnesium does not react with pure boiling ethyl alcohol. We have been

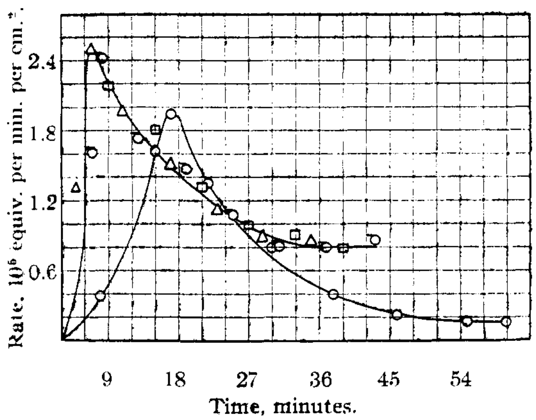

Fig. 4.—The effect of lithium chloride on the solution of magnesium in 0.12 *M* acetic acid. The circles, triangles, squares and tailed-circles show the rates for solutions which were 0.0, 0.025, 0.05 and 0.10 *M* in lithium chloride, respectively.

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[13] Lund, *Ber.*, **67B**, 935 (1934).

[14] Tarle, Dissertation, Leipzig, 1911.

[15] Bodforss and Kajmer, *Z. physik. Chem.*, **A171**, 190 (1934).

[16] Dunning and Fletcher, unpublished results, this Laboratory.

unable to fit a reaction rate equation to any portion of the reaction for experiments of this type. Since the "alcohol reaction" after the "equivalence point" is not complicated by the presence of acid, we shall deal with it first.

The velocity of this reaction is too great to be accounted for on the basis of the number of collisions of hydrogen ion, $C_2H_5OH_2^+$, with the surface of the metal. Therefore, alcohol molecules must react with magnesium. A simple calculation will demonstrate this.

From Table X, in which some data on the effects of stirring are presented, it can be seen that at 30° a reaction velocity as high as 0.705×10^{-5} equivalent per min. per sq. cm. has been observed in 0.05 *M* magnesium ethylate. This rate would require $0.705 \times 10^{-5} \times 6.06 \times 10^{23} = 4.27 \times 10^{18}$ collisions of hydrogen ion per minute with one sq. cm. of the magnesium cylinder, if every colliding ion gave up its proton. Now, the ionic product of ethyl alcohol is[17] about 10^{-20}, so that the concentration of solvated proton in 0.05 *M* ethylate is 10^{-22} mole per cc. For this concentration of solvated proton, the number[18] of collisions of the protons per minute with one sq. cm. of the magnesium cylinder is 3.36×10^7. Therefore, the ratio of the number of collisions which occur to the minimum number required is 7.87×10^{-12}, or collisions of hydrogen ion with the surface of the metal could account for only $7.87 \times 10^{-10}\%$ of the observed reaction. The answer for a similar calculation, which was made for an observed reaction velocity of 2.72×10^{-5} equivalent per min. per sq. cm. at the equivalence point, is 0.20%. These calculations constitute a definite proof that metals can displace hydrogen from the molecules of acids without the intermediate formation of solvated proton.

4.—We shall now try to determine what portion of the reaction rates which are observed when acid is present is due to the reaction of the alcohol molecules with magnesium. In order to do this it will be necessary to compare the reaction rates obtained with magnesium and zinc, respectively, with hydrochloric acid.

Detailed data for the experiments with magnesium are to be found in Table III. As previously stated we have been unable to fit a reaction rate law to individual experiments of this type. However, we have found that a fairly straight line is obtained on plotting the maximum rate of reaction, that is, the rate at the end of the induction period, *versus* the concentration of acid at the time of maximum rate. The plots for hydrochloric and the other acids are given in Fig. 5. From these plots we can find the maximum rate of reaction for any corresponding concentration of acid.

TABLE III

EXPERIMENTS AT 30° WITH MAGNESIUM AND HYDROCHLORIC ACID

N_i = initial molarity of acid. N_m = molarity of acid at point of maximum rate. *M* = maximum rate of reaction. *R* = equivalents per sq. cm. reacted during induction period. *T* = minutes elapsed during induction period. *F* = equivalents of magnesium dissolved per min. per sq. cm. at the equivalence point.

N_i, mole/l.	N_m, mole/l.	*M*, 10^5 equiv./min./cm.^{2}	*R*, 10^5 equiv. per cm.^{2}	*T*, min.	*F*, 10^5 equiv./min./cm.^{2}
0.0285	0.0191	0.960	2.75	4.5	0.371
.0407	.0288	1.25	3.20	3.8	.312
.0654	.0534	2.21	3.68	2.5	.598
.0969	.0844	3.16	4.02	1.5	.645
.101	.0828	3.22	5.35	2.3	.625
.112	.0975	3.78	4.31	1.8	.705

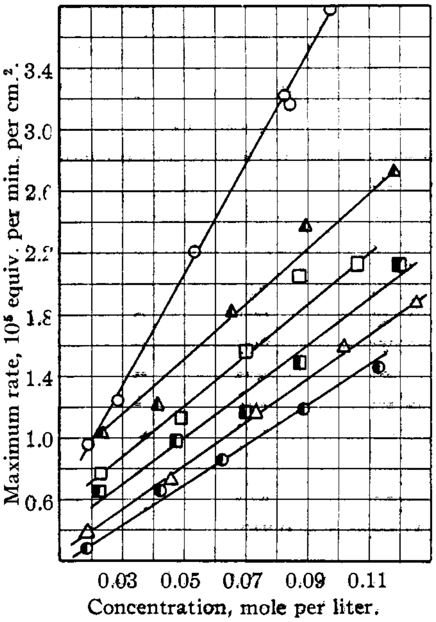

Fig. 5.—Maximum rate of reaction *versus* the concentration of acid at the time of maximum rate. Circles, hydrochloric acid. Shaded triangles, chloroacetic (up 0.4). Squares, acetic (up 0.4). Shaded squares, dichloroacetic (down 0.1). Triangles, *o*-chlorobenzoic (down 0.1). Shaded circles, α-chloropropionic (down 0.5). In parentheses is given the number of units the line is displaced. A point has been omitted for acetic acid at concentration = 0.074, rate = 1.04.

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(17) MacFarlane and Hartley, *Phil. Mag.*, **13**, 425 (1932).

(18) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, Oxford, 1933, p. 281.

The results of the experiments with zinc and alcoholic hydrochloric acid are summarized in Table IV. We have found that zinc dissolves in alcoholic hydrochloric acid in accordance with the unimolecular reaction rate law. The zinc reacts only with hydrogen ion, $C_2H_5OH_2^+$. The average unimolecular velocity constant, $k = (2.3\ V/Si) \log a/(a - x)$, is 0.217 cm. per min. V is the volume of the solution in cc., S the area of the metal cylinder in sq. cm. and t the minutes elapsed since the start of the experiment. a is the concentration of acid at the start of the experiment and $a - x$ the concentration at the time t.

Sometimes a short induction period was observed, and the reaction velocity decreased too rapidly at the end of the experiment for the reaction rate law to be obeyed. The extent of these deviations is also given in Table IV. The addition of lithium nitrate as a depolarizer did not speed up the reaction. When lithium nitrate was present very little hydrogen was evolved, which shows that it was an efficient depolarizer.

Table IV

Experiments at 30° with Zinc and Hydrochloric Acid

Molarity of acid, mole/l.	k, cm./min.	Induction period, min.	% law obeyed
0.1203	0.213	0	91
.1153	.195	2	88
.1159	.281	0	94
.1140	.231	0	90
.1123	.200	0	81
.1128	.224	6	88
.0635	.157	4	78
.0636	.210	1	75
.0615	.214	1	46
.0288	.245	4	94
.0296	.213	10	37

Average k = 0.217

King and his co-workers[19,20] have found that magnesium and zinc dissolve in aqueous hydrochloric acid with very nearly the same velocity. If the reaction of the magnesium were with the $C_2H_5OH_2^+$ alone, we should expect the same result for the two metals with alcoholic hydrochloric acid. When different solids dissolve in identical solutions with the same velocity, it is generally conceded that the rates of the reactions are governed by the speed with which the dissolved reactant is transported to the surface of the solid. Therefore, a comparison of the results obtained with magnesium and zinc, respectively, and hydrochloric acid should enable us to determine what portion of the maximum reaction rate is due to the reaction of the magnesium with alcohol.

Using the velocity constant k = 0.217 cm. per min. for the dissolution of zinc in alcoholic hydrochloric acid, reaction rates have been calculated for three concentrations of acid, which would also be correct for magnesium if it reacted only with the acid. These rates are compared in Table V with those taken from the plots of maximum rate of reaction *versus* the concentration of acid at the time of maximum rate in Fig. 5. From the data in the table it would appear that ethylate ion was being generated at the surface of the metal about as fast as hydrogen ion was scheduled to arrive. On this basis most of the acid would be neutralized before it reached the magnesium. Then to account for the observed rates we would have to raise the estimate of the portion of the reaction due to the reaction of the metal with the alcohol molecules considerably. The ethylate would then be produced much more rapidly than the hydrogen ion was scheduled to arrive. This would mean that practically no hydrogen ion reaches the surface, so that the observed reaction rate must be almost entirely an alcohol reaction and the region immediately adjacent to the surface of the metal must be alkaline. The same picture applies to the carboxylic acids. In brief, the alcohol reaction predominates, and the rapid production of ethylate ion prevents any reaction with acids other than the solvent.

Table V

Comparison of the Rates of Solution of Magnesium and Zinc in Hydrochloric Acid at 30°

N_m, mole/liter	M (for Mg) 10^5 equiv./min./cm.^{2}	Rate for Zn (Z) 10^5 equiv./min./cm.^{2}	M − Z, 10^5 equiv./min./cm.^{2}	(M − Z)/M
0.03	1.35	0.65	0.70	0.52
.06	2.44	1.30	1.14	.47
.09	3.52	1.95	1.57	.45

5.—It is apparent from the tables and graphs that the observed rate of the reaction after the induction period varies considerably. Now if the reaction is always one of magnesium with alcohol, the concentration of which is practically constant, some explanation must be found for this variation. The results of experiments with solutions of acids containing chloride ion and small amounts of water, respectively, indicate that the variation is due to differences in the amount of metal surface available for reaction. Small traces of water retard the reaction and chloride ion speeds it up.

The water content of the dehydrated alcohol

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(19) King and Braverman, This Journal, 54, 4774 (1932).

(20) King, *ibid.*, 57, 828 (1935).

was 0.025%, corresponding to a molarity of 0.011. The effect of adding small amounts of water to solutions of hydrochloric and chloroacetic acids made from the dehydrated alcohol can be seen from Figs. 2 and 3, respectively. From the plots of rate *versus* time we note that the addition of water depresses the rate. Seligman and Williams[21] and Zecchini[5] observed a similar result for the solution of aluminum in phenol and glacial acetic acid and zinc in alcoholic hydrochloric acid, respectively. The inhibitory effect of water is usually attributed to the formation of a difficultly soluble coating of hydroxide on the surface of the metal. This coating is supposed to result from the reaction of the metal with the water. That we can vary the rate of reaction by causing a portion of the surface of the metal to become covered with a coating during the course of an experiment indicates that the original variations in rate are due to differences in the amount of surface available for reaction. It also shows that the amount of clean surface varies in the same experiment.

It should be pointed out that the addition of water to the dehydrated alcohol did not destroy the reproducibility of the experiments with hydrochloric acid, but did destroy it for the experiments with chloroacetic acid. In the latter case, therefore, the faster of two duplicate experiments was used for comparison.

6.—From Fig. 4 it may be seen that the addition of lithium chloride to acetic acid solutions speeds up the reaction during the induction period and at the equivalence point. The fact that chloride ion hastens corrosion has been observed by many investigators, and the effect is generally ascribed to the ability of that ion to penetrate coatings. The results of these experiments, in conjunction with the fact that induction periods were observed, are evidence, therefore, that the magnesium cylinders contain an invisible coating before being placed in the acid solutions. This coating must be removed before the alcohol can react with the metal, and the magnitude of the observed reaction depends on the extent to which the coating is removed. From Fig. 4 it also may be seen that the effects due to chloride ion were independent of its concentration between 0.025 and 0.1 M.

7.—With certain organic chlorine compounds results were obtained which were similar to those observed with chloride ion. Thus from Table VI it may be seen that solutions of acetic acid which are 0.12 M in ethyl dichloroacetate, chloroform or carbon tetrachloride dissolve magnesium more rapidly than solutions of acetic acid alone. This happens despite the fact that magnesium does not dissolve in 0.12 M solutions of these substances in alcohol at 30°. From the data it is also seen that the compound with the greatest number of chlorine atoms in the molecule speeds up the reaction most. The effects were found to decrease with the concentration of chlorine compound, but in no regular manner. Similar results were observed in a few experiments with *o*-toluic and phenylacetic acids. They could not be used alone to any considerable extent, because with them the metal bore scattered deep pits at the conclusion of an experiment, and because the reproducibility was exceedingly poor. This pitting and poor reproducibility, which were observed with acetic acid alone to a smaller extent, are further evidence that the surface of the metal is not entirely available for reaction.

TABLE VI

THE EFFECT OF CHLORINE COMPOUNDS ON THE RATE OF SOLUTION OF MAGNESIUM IN 0.125 M ACETIC ACID

Concentration of chlorine compound = 0.12 M

Chlorine compd.	N_m, mole/liter	M, 10^5 equiv./min./cm.^{2}	M/N_m	F, 10^5 equiv./min./cm.^{2}	Induction, pd., min.
None	0.0699	1.11	15.9	0.15	29.0
Ethyl dichloroacetate	.1107	3.21	29.0	1.35	2.5
Chloroform	.0947	3.26	34.4	1.55	5.5
Carbon tetrachloride	.101	4.30	42.6	1.69	3.5

TABLE VII

EXPERIMENTS AT 30° WITH MAGNESIUM AND CHLOROACETIC ACID

N_i, mole/liter	N_m, mole/liter	M, 10^5 equiv./min./cm.^{2}	R, 10^5 equiv. per cm.^{2}	T, min.	F, 10^5 equiv./min./cm.^{2}
0.0297	0.0232	0.635	2.00	5.5	0.368
.0588	.0419	.823	5.14	12.5	.594
.0909	.0654	1.42	7.75	9.5	.776
.121	.0894	1.97	9.25	9.5	.629
.150	.118	2.32	9.55	9.3	.689

From the similarity of the results with chloride ion and the chlorine compounds it appears that the latter also clean the surface of the metal. We cannot say how they do this. However, it is not probable that the similarity is due either to the formation of chloride ion resulting from the reduction of the chlorine compounds or to those compounds acting as depolarizers. We have al-

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(21) Seligman and Williams, *J. Soc. Chem. Ind.*, **35**, 188 (1916); **37**, 159 (1918).

ready shown that the amount of reduction is very small.

TABLE VIII

COMPARISON OF THE MAXIMUM RATES OF SOLUTION AT 30° OF MAGNESIUM IN DIFFERENT ACIDS[a]

N_m, mole/liter	Maximum rates (M) in 10^5 equivalents per min. per cm.^{2} Acetic	Chloro-acetic	α-Chloro-propionic	o-Chloro-benzoic	Dichloro-acetic
0.03	0.50	0.74	0.94	0.62	0.78
.06	1,00	1.28	1.34	1.06	1.24
.09	1.49	1.82	1.73	1.50	1.71

[a] For hydrochloric acid see Table V.

The curves in Fig. 5 enable one to obtain the maximum rates of reaction for the same concentration of different acids. (The data used to construct the curve for chloroacetic acid are contained in Table VII.) Maximum rates obtained in this manner are compared in Table VIII. With the exception of o-chlorobenzoic acid, the rates for the chloro acids are greater than those for acetic acid. While we should have predicted this from the results of the experiments with acetic acid and the chlorine compounds, we should also have expected greater rates with dichloroacetic acid than with monochloroacetic and α-chloropropionic acids. However, the rates at 30° of the alcohol reaction at the equivalence point, which were obtained with 0.12 M solutions of the five carboxylic acids, may be divided into three distinct groups, according to the number of chlorine atoms to the molecule. For the acids in the order in which they are given in Table VIII the rates are 0.145, 0.660, 0.885, 0.715 and 1.13 × 10^{-5} equivalents per min. per sq. cm., respectively.

8.—The rate at which the magnesium cylinder rotates and the temperature also affect the maximum rates of reaction and the alcohol reaction. The results of experiments to determine the extent of these influences are presented in Tables IX to XII.

TABLE IX

INFLUENCE OF STIRRING AT 30° ON THE MAXIMUM RATES OF SOLUTION OF MAGNESIUM IN ACIDS

Acid	N_m, mole/liter	Max. rate in 10^5 equiv./min./cm.^{2} 520 r. p. m.	980 r. p. m.	1980 r. p. m.
Hydrochloric	0.06	1.45	2.42	3.23
Hydrochloric	.09	2.23	3.50	4.58
Chloroacetic	.06	1.06	1.31	1.73
Chloroacetic	,09	1.51	1.87	2.38

TABLE X

INFLUENCE OF STIRRING ON THE ALCOHOL REACTION AT 30° REACTION STARTED WITH 0.115 M DICHLOROACETIC ACID

R. p. m.	Rate of alc. react. in 10^5 equiv./min./cm.^{2} At 0.0	0.025	0.05 M magnesium ethylate
520	0.976	0.653	0.452
980	1.23	.932	.561
1980	2.72	1.72	.705

TABLE XI

INFLUENCE OF TEMPERATURE ON THE MAXIMUM RATES OF SOLUTION OF MAGNESIUM IN ACIDS

N_m, mole/liter	Max. rate (M) in 10^5 equiv./min./cm.^{2} 30°	40°	50°	M_{40}/M_{30}	M_{50}/M_{40}
Hydrochloric Acid					
0.03	1.35	1.23	2.05	0.9	1.7
.09	3.50	3.04	3.82	.9	1.3
Chloroacetic Acid					
0.03	0.757	1.18	1.60	1.6	1.4
.09	1.87	2.70	3.15	1.4	1.2

TABLE XII

INFLUENCE OF TEMPERATURE ON THE ALCOHOL REACTION[a] REACTION STARTED WITH 0.115 M ACID

Average rate (A) in 10^4 equiv./min./cm.^{2}

Acid	Average rate (A) in 10^5 equiv./min./cm.^{2} 30°	40°	50°	A_{40}/A_{30}	A_{50}/A_{40}
From 0.0 to 0.025 M magnesium ethylate					
Dichloroacetic	1.11	1.34	1.69	1.2	1.3
α-Chloropropionic	0.88	1.36	1.76	1.5	1.3
From 0.025 to 0.05 M magnesium ethylate					
Dichloroacetic	0.73	0.86	1.02	1.2	1.2
α-Chloropropionic acid	.622	.88	1.06	1.4	1.2

[a] Approximate solubility of magnesium ethylate = 0.1 M at 30°.

The maximum rates were taken from plots of maximum rate *versus* concentration of acid at the time of maximum rate. They are given for only two concentrations of acid because the fractional changes did not differ to any considerable extent for the other concentrations. The stirring effects are not sufficiently[20,22] great and the temperature effects not sufficiently small to indicate that the observed rates of reaction are controlled solely by diffusion processes. However, the diffusion of solutes must be a contributing factor. Because the reproducibility of the experiments at 40 and 50° was not good, and it was difficult to draw a curve through the points obtained on plotting maximum rate *versus* concentration of acid at the time of maximum rate, too much weight should not be given to the negative temperature coefficients for hydrochloric acid in Table XI. Moreover, at 40 and 50° it was difficult to select the points of maximum reaction for the higher concentrations of acid, because the induction periods were exceedingly short and the reaction velocities inconveniently rapid.

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[22] Roller, *J. Phys. Chem.*, **39**, 221 (1935).

In connection with the results for the alcohol reaction, we have found that the solubility of magnesium ethylate is approximately 0.1 *M* at 30°. Consequently the progressive decrease in the reaction rate after the equivalence point could not be due to the insolubility of that substance.

9.—A description of some miscellaneous experiments concludes the presentation of the experimental results.

The presence of oxygen in the alcohol and reaction vessel was found to affect the rates of solution of magnesium in acid solutions. In experiments in which oxygen was not excluded, the progress of the reaction was followed by determining the loss in weight of different cylinders of metal after they had dissolved in solutions of the same initial composition for successively longer periods of time.

In Table XIII the results of such experiments with acetic and chloroacetic acids are compared with those obtained in the absence of oxygen. In the initial stages of the experiment the reaction rates were more rapid when oxygen was not excluded. But as the reaction proceeded it slowed down more rapidly due to the formation of water. The greater initial velocity was probably due to depolarization on the surface of the metal. This is the first time depolarization has been observed for magnesium.

TABLE XIII

EFFECT OF OXYGEN ON THE DISSOLUTION OF MAGNESIUM IN ACIDS AT 30°

Atmosphere, and gas in alcohol	10^5 equiv. per min. per sq. cm. Metal dissolved Minutes 5	12	19	27
	0.12 *M* Acetic Acid			
Nitrogen	1.17	8.07	19.8	28.6
Air	4.25	12.8	17.0	23.0
	Minutes 5	12	18	25
	0.059 *M* Chloroacetic Acid			
Nitrogen	1.29	6.28	11.1	15.8
Air	1.48	8.69	10.1	15.0

Experiments were also carried out with mixtures of hydrochloric acid and lithium chloride, in which oxygen was not excluded. The results of these experiments are summarized in Table XIV. Most of the acid was consumed in accordance with the unimolecular reaction rate law. The unimolecular velocity constant is 0.242 cm. per min. The straight lines in Fig. 6, which were obtained by plotting log $a - x$ *versus* time, illustrate how well the law was obeyed. In these experiments the amount of acid consumed always was found to be equivalent to the weight of metal which had been dissolved.

TABLE XIV

EXPERIMENTS AT 30° WITH MAGNESIUM AND HYDROCHLORIC ACID WITH OXYGEN NOT EXCLUDED

Concn. of acid, mole/l.	Concn. of lithium chloride, mole/l.	Slope of log $a - x$ *vs.* time	% Acid consd. via law
0.0275	0.0725	0.0430	78
.0388	.0612	.0473	76
.0408	.0000	.0427	59
.0626	.0374	.0511	88
.0636	.0864	.0421	55
.0679	.0000	.0430	82
.0926	.0000	.0524	82

Average slope = 0.0459.

k = 0.242 cm. per min.

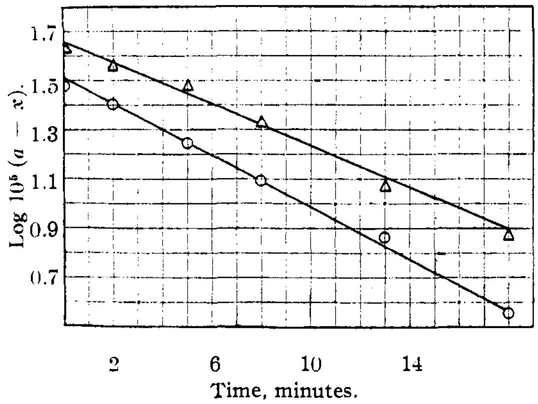

Fig. 6.—Relationship between log $a - x$ and time for the solution of magnesium in hydrochloric acid when oxygen is not excluded. The circles and triangles show the points obtained with 0.0626 and 0.0679 *M* acid, respectively. The line for the latter solution is displaced upward 0.1 unit.

Short induction periods were expected here as in the experiments in which oxygen was excluded. That they were not detected was probably due to the method which had to be used to follow the progress of the reaction. After most of the acid had been consumed, the reaction velocity decreased too rapidly to obey the rate law, and no reaction with the solvent was detected. The apparent absence of this reaction is peculiar, when we consider that it occurred when magnesium dissolved in a solution of acetic acid containing lithium chloride in the presence of oxygen. However, the velocity constant is very similar to that for the solution of zinc in alcoholic hydrochloric acid, which is 0.217. And as we explained previously, this is exactly what we should expect if magnesium reacted only with the hydrochloric acid and if the observed reaction rate was governed by the rate at which the acid was transported to the surface of the metal.

We have already described how a very pure sample of zinc dissolved readily in alcoholic hydrochloric acid without the aid of a depolarizer. In contrast to this, it is commonly known that pure zinc scarcely dissolves in aqueous acids unless a depolarizer such as potassium nitrate is present.[23] From these results it appears that the discharge potential of hydrogen on zinc is smaller in alcohol than in water. For magnesium the reverse seems to be true, since we have already shown that oxygen hastens the solution of magnesium in alcoholic solutions, whereas depolarizers,[8,19] do not increase the velocities of solution of magnesium in aqueous acids.

In connection with these experiments, it might well be pointed out that one should be careful in the use of depolarizers, when measuring the rates of solution of metals in acids. Thus the data in Table XV show that lithium nitrate lowers the rates of solution of magnesium and zinc in aqueous acetic acid. In order to show this for zinc it was necessary to determine the effect of increasing the duration of different experiments with solutions of the same initial composition since the reaction scarcely proceeded in the absence of nitrate.

A more striking example of the effect may be observed in the behavior of zinc with alcoholic dichloroacetic acid solutions. Although zinc scarcely dissolved in solutions of acetic and chloroacetic acids, it did dissolve readily in 0.1 *M* dichloroacetic acid. No hydrogen was evolved, no titratable acid was consumed and considerable chloride ion was formed. This reaction, which seems to be similar to the Wurtz reaction, did not occur when the solution was 0.05 *M* in lithium nitrate. We consider these results evidence that nitrate ion can oxidize the surfaces of magnesium and zinc.

Data for similar experiments with aqueous mixtures of hydrochloric acid and lithium nitrate are also reported in Table XV. From this it is plainly seen that with hydrochloric acid a considerable side reaction occurs.

TABLE XV

EXPERIMENTS AT 30° WITH AQUEOUS MIXTURES OF ACIDS AND LITHIUM NITRATE

Concn. of acid, mole/liter	Concn. of nitrate, mole/liter	Length of expt., min.	Vel. const., *k*, cm./min.
Magnesium and Acetic Acid			
0.0353	0.00	20	0.368
.0785	.00	16	.369
.0785	.05	6	.315
Zinc and Acetic Acid			
0.0322	0.05	9	0.258
.0322	.05	27	.237
.103	.10	9	.236
.103	.10	27	.228
Magnesium and Hydrochloric Acid			
0.0298	0.00	12	1.058
.0500	.00	14	0.978
.0298	.05	3	.894
.0298	.05	7	.648
Zinc and Hydrochloric Acid			
0.0312	0.05	3	0.875
.0312	.05	6	.875
.0312	.05	9	.730
.0312	.05	12	.651
.0312	.10	3	.884
.0312	.10	12	.544
.103	.10	3	.592
.103	.10	12	.459

Although experiments of this type with alcoholic solutions are not reported in detail, because water was formed, we did find that lithium nitrate retarded the solution of magnesium in alcoholic hydrochloric and acetic acids.

Discussion

The following description of what occurs when a cylinder of magnesium is rotated in a solution of an acid in ethyl alcohol is based on the preceding experimental results.

The induction period probably starts with acid reacting and removing a coating from the surface of the metal. The acid is aided by chloride ion or chlorine compound if present. Chloroacetate ion (and like ions) aids also, when produced in the reaction. On those areas which have been cleaned the alcohol reacts. Ethylate ion is formed faster than acid approaches the surface of the metal. As a result the acid is neutralized before it reaches the metal, and the region adjacent to the metal is alkaline. The clean portions of the metal tend to become covered again with a coating of magnesium hydroxide, due to the water present, more rapidly than they can be cleaned by chloride ion, etc., as we have seen from the fact that the reaction rate decreases after the acid has been con-

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[23] This opportunity is taken to correct a statement by Kilpatrick and Rushton,[8] that potassium nitrate causes zinc to dissolve in aqueous acids more rapidly than magnesium. Our results agree more nearly, though not completely, with those of King and Braverman,[19] who found that the addition of nitrate raised the rates of solution of zinc to those of magnesium.

sumed. Since the region adjacent to the surface of the metal is alkaline, the acid cannot aid in this cleaning. Meanwhile, the rate of cleaning of surface with which alcohol is not reacting decreases, due to the decrease in the concentration of acid. When equal areas of the metal are being cleaned and covered in the same period of time, the clean area will have reached a maximum, and the maximum rate of reaction will be observed. The higher the initial concentration of an acid, the larger will be the quantity of acid consumed during the induction period and consequently the area of clean surface. This is what happens, as can be seen from the data in Tables III and VII. From the point of maximum reaction onward surface is covered more rapidly than cleaned.

The observed rate of reaction at any time depends on the area of clean surface. This, in turn, appears to be related to the concentration of ethylate ion adjacent to it. We should expect this to be so, since the concentration of ethylate ion next to the surface should be an important factor in determining the amount of magnesium hydroxide which forms on the metal due to the reaction with water. From the results of the experiments to determine the influence of temperature and the rate of stirring we should conclude as was pointed out previously, that the rate of disappearance of ethylate ion from the surface by transport of acid and ethylate ion only partially determines the concentration of ethylate at the reaction interface. It also depends on the actual rate of the chemical reaction between the magnesium and the alcohol molecules. That is, the two rates do not differ sufficiently in magnitude for one to be the sole rate-determining factor.

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Summary

1. It was found that magnesium can displace hydrogen from the molecules of ethyl alcohol without the intermediate formation of solvated proton.

2. When magnesium dissolves in solutions of acids in ethyl alcohol the predominant reaction is between the metal and the alcohol. The production of ethylate ion is sufficiently rapid to prevent other acids from reaching the metal.

3. The observed rate of reaction depends directly on what portion of the measured surface of the metal is available for reaction. This is related to the concentration of ethylate ion at the reaction interface, which is determined by two processes whose velocities do not differ sufficiently for either of them to be the sole rate-controlling factor. They are the actual rate of the chemical reaction between the metal and alcohol and the rate of removal of ethylate ion from the reaction interface by neutralization and transport.

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NOTES

Ultramicroscopic Examination of Mixed Films

BY FREDERICK M. FOWKES, ROBERT J. MYERS AND WILLIAM D. HARKINS

The presence of a paraffin oil, such as nujol, in an expanded film formed by a fatty acid, such as myristic or pentadecylic acid, has a surprisingly great effect upon the pressure–area relations, as found by Myers and Harkins [R. J. Myers and W. D. Harkins, *J. Phys. Chem.*, **40**, 959 (1936); W. D. Harkins and R. J. Myers, THIS JOURNAL, **58**, 1817 (1936)]. This fact suggests that even if some of the paraffin oil is present in the form of lenses, a part remains mixed with the monomolecular film of acid. Myers and Harkins were unable to find any lenses visible to the naked eye in most of the mixed films investigated by them. In order to determine whether microscopic lenses are present, somewhat similar work has been done in which the pressure–area relations were determined by the Wilhelmy method and simultaneous observations of the structure of the film were made by the use of a dark field condenser and a micro-