the preceding paper[1] should be consulted for other important principles in regard to molecular orientation in surfaces as related to solubility.

CHICAGO, ILL.

THE ACTION OF MAGNESIUM ON AQUEOUS SOLUTIONS.

BY FREDERICK H. GETMAN.

Received February 3, 1917.

Action of Chemically Pure Magnesium.

In a previous communication[2] on the action of metallic magnesium on solutions of potassium chloride, experimental evidence was adduced in favor of the view that the dissolved salt functions merely as a catalyst in the reaction represented by the equation

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2.$$

The magnesium used in these experiments was found to be 99.66% pure. Notwithstanding this high degree of purity, it is conceivable that the presence of even so small an amount of residual impurity might be sufficient to account for the reactivity of the metal when immersed in a saline solution. In other words, just as there is scarcely any reaction between chemically pure zinc and dilute hydrochloric or sulphuric acids, so also there may be a marked diminution in the rate of reaction between magnesium and a solution of potassium chloride if special precautions are taken to secure a chemically pure sample of the metal.[3] In order to determine the possible influence of small amounts of impurities on the reactivity of magnesium when placed in saline solutions, some experiments were carried out with magnesium which had been purified by distillation.

A sample of magnesium wire, known to contain less than 0.5% of impurity, was cut into short lengths and distilled *in vacuo*. The resulting crystalline deposit of presumably pure magnesium was allowed to cool and then transferred immediately to a 0.1 M[4] solution of potassium chloride. Hydrogen began to be evolved at once, but owing to uncertainty as to the extent of surface of metal in contact with the solution it was impossible to make any quantitative comparison with the volume of gas obtained under similar conditions with magnesium wires of known superficial area.

The reaction between distilled magnesium and a 0.1 M solution of potassium chloride was also studied, as in our previous paper, by means of the hydrogen electrode.

A cell was prepared as indicated by the following scheme:

$$Hg^+\text{–}Hg_2Cl_2,\ \overrightarrow{0.1\ M\ KCl\ ||\ 0.1\ M\ KCl}\text{–}Pt\text{–}H_2^-$$

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[1] THIS JOURNAL, 39, 354 (1917).

[2] Getman, THIS JOURNAL, 38, 2594 (1916).

[3] The suggestion to test this point experimentally was very kindly made to the author by the Editor of THIS JOURNAL.

[4] The term M is used in this article to express molar concentration.

the current flowing outside of the cell from the calomel electrode to the hydrogen electrode as indicated by the arrow.

After having the measured electromotive force of the cell as represented by the above scheme, a piece of magnesium was introduced into the solution of potassium chloride and the change in electromotive force resulting from the reaction of the magnesium with the solution was observed.

The relation between the electromotive force of the cell and the hydrogen-ion concentration in the potassium chloride solution is given by the familiar formula of Nernst,

$$E = RT/nF \log_e 1/c + \delta$$

where δ denotes the difference between the potential of the normal hydrogen electrode and that of the calomel electrode. In this case where a 0.1 *M* solution of potassium chloride is used in the calomel electrode the value of δ is 0.33 volt. At a temperature of 25° the above formula becomes on transformation to Briggsian logarithms

$$E = 0.0595 \log 1/c + 0.33.$$

Redistilled mercury and carefully purified mercurous chloride were used in making up the calomel electrode. The potassium chloride used in preparing the solutions had been twice recrystallized from a specimen of high purity and had remained in a desiccator over phosphorus pentoxide for more than a year. The water used in making up the solutions was distilled according to the method of Kendall[1] using a small amount of Nessler's reagent to eliminate carbon dioxide and ammonia. The distillate so obtained possessed a specific conductance less than 1×10^{-6} reciprocal ohms. The hydrogen electrode was supplied with hydrogen which in addition to being purified in the usual manner was bubbled through a 0.1 *M* solution of potassium chloride before entering the electrode.

The experimental data are shown in the form of curves in Fig. 1. Curve B represents the results obtained with distilled magnesium, while Curve A shows the results of a similar experiment in which a piece of magnesium wire having a surface of 411.6 sq. mm. was used. It will be observed that while the initial hydrogen-ion concentrations were practically identical in the two solutions of potassium chloride, the hydrogen-ion concentration in the solution in which the distilled magnesium was immersed increased more rapidly than in the solution which contained the wire. This result, however, was to be expected since the surface of the distilled magnesium was known to be at least twice that of the magnesium wire. An inspection of the Curves A and B shows that they both tend to approach the same limiting hydrogen-ion concentration.

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[1] Kendall, This Journal, 38, 2463 (1916).

The foregoing experimental facts apparently justify the conclusion that the small amount of impurity present in the magnesium wire used in the previous experiments did not exert any appreciable influence on the reaction between the metal and a saline solution.

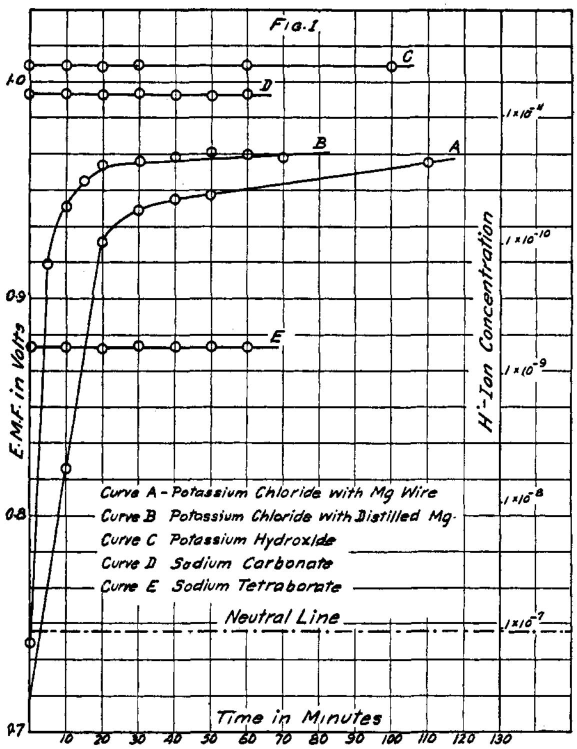

FIG. I

If the proposed explanation of the function of potassium chloride in promoting the reaction between magnesium and water be correct, other salts should exert a similar action.

In order to test the validity of the hypothesis of the catalytic action of a dissolved substance on this reaction, the behavior of magnesium with a number of typical solutions was investigated.

Action of Magnesium in Different Solutions.

In all of the subsequent experiments, magnesium wire containing less than 0.5% of impurity was used, the wire being cut into 40 mm. lengths and thus exposing a total surface of 411.6 sq. mm. to the solution. The wires were polished with emery cloth immediately before introducing into the solutions.

All of the solutes employed were carefully purified before using. The solutions were prepared with ordinary distilled water and were made up either by direct weighing or by titration. A uniform concentration was used in all of the experiments, 0.1 *M* solutions being adopted.

No intermediary solution was employed to minimize or eliminate any potential which might be developed at the junction of the solution with the 0.1 *M* KCl of the calomel electrode. While in some cases this liquid potential was undoubtedly appreciable, its value in all cases was considered to be hardly greater than the experimental error.

In each experiment the hydrogen supplied to the electrode was bubbled through several Drechsel bottles containing the solution under investigation. This precaution was taken after having encountered great difficulty in duplicating results with 0.1 *M* NH_4Cl. After considerable experimentation, the source of the trouble was traced to the fact that the passage of hydrogen through the solution of ammonium chloride liberated some ammonia, thus leaving the solution slightly acid.[1] By allowing hydrogen to bubble through two Drechsel bottles containing 0.1 *M* NH_4Cl before entering the hydrogen electrode, equilibrium with the displaced ammonia was established and a steady electromotive force obtained.

The experimental data are summarized in the curves shown in Figs. 1 to 5. Each plate of curves gives the observed electromotive force and the corresponding hydrogen-ion concentration. The dotted line, termed the "neutral line," is drawn through 0.7465 volt, the electromotive force corresponding to 1×10^{-7}, the accepted concentration of the $H^{\cdot}$– and OH'– ions in pure water. With ordinary distilled water, such as was used in these experiments, and where the solutions were exposed to the air, it is certain that absorbed carbon dioxide caused an increase in the concentration of the $H^{\cdot}$– ion and a consequent lowering of the neutral line.[2]

The following table gives the total gas evolution in 24 hours due to the immersion of pieces of magnesium wire of approximately 412 sq. mm. surface in the respective solutions:

HYDROGEN EVOLVED IN 24 HOURS.

Dissolved substance.	Volume of gas in cc.
$NaCl$	24.5
$NaBr$	10.9
KCl	15.5
KI	2.7
NH_4Cl	18.3[3]
$CaCl_2$	24.4
$SrCl_2$	29.7
$BaCl_2$	42.6
$MgCl_2$	28.3
K_2SO_4	20.5
$MgSO_4$	8.4
$AlCl_3$	33.7
Na_2CO_3	0.4
$Na_2B_4O_7$	18.2
KOH	0.0
HCl	36.4[4]
H_3BO_3	18.6
$CO(NH_2)_2$	0.2
$C_6H_8(OH)_6$	0.4
$C_{12}H_{22}O_{11}$	0.8

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[1] Denham, *J. Chem. Soc.*, **93**, 49 (1908).

[2] Kendall, *Loc. cit.*

[3] Volume of hydrogen evolved in 6 hrs.

[4] Volume of hydrogen evolved in 3 hrs.

Discussion of Results.—With the exception of ammonium chloride, which gives in twenty-four hours about four times as much hydrogen as the other alkali halides, all of the uni-univalent electrolytes investigated were found to behave alike. The concentration of the hydrogen ion in the solution of ammonium chloride is also larger than in the solutions of the other uni-univalent salts. The exceptional behavior of ammonium chloride is caused by the slight hydrolysis of this salt in aqueous solution.

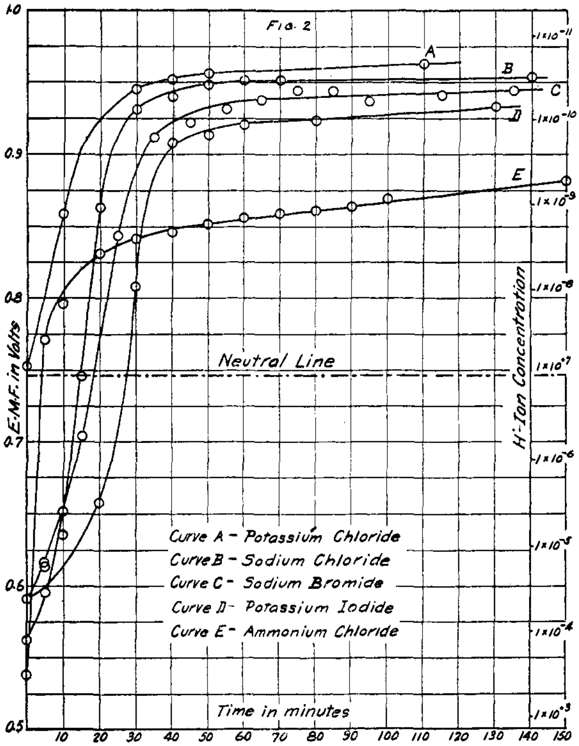
Fig. 2

The absence of any appreciable liquid potential in this case permits of the calculation of the percentage of hydrolysis of ammonium chloride in a 0.1 *M* solution. Thus, the mean electromotive force at 25° C. of the cell

$$\overrightarrow{\mathrm{Hg^{+}–Hg_2Cl_2,\ 0.1}\ M\ \mathrm{KCl}\ \|\ 0.1\ M\ \mathrm{NH_4Cl–Pt–H_2^{-}}}$$

was found to be 0.5376 volt; on substituting this value for E in the equation

$$E = 0.0595 \log 1/c + 0.33$$

and solving for c, we obtain $c = 3.2 \times 10^{-4}$.

If x represents the fraction of a molecule of ammonium chloride which is hydrolyzed in 0.1 *M* solution, then $x/0.1$ is the concentration of the resulting hydrochloric acid which, in turn, must be equal to c. Hence the percentage hydrolysis must be $(3.2 \times 10^{-4}/10^{-1})0.10^{2} = 0.32\%$. The mean value given by Denham[1] for the percentage hydrolysis of ammonium chloride at the same dilution is 0.30%.

The presence of this small amount of hydrochloric acid together with the normal catalytic activity of the unhydrolyzed salt is probably the cause of the increased volume of hydrogen evolved. The curves for solu-

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[1] Denham, *Loc. cit.*

tions of the uni- and bi-bivalent salts plotted in Fig. 3 are very similar in form to the curve for potassium chloride in Figs. 1 and 2. The hydrogen-ion concentration in the solution of potassium sulfate is less than in the solution of potassium chloride, while the volume of gas disengaged in twenty-four hours by the action of magnesium on the former is greater than that liberated from the latter by the same agent. This suggests the existence of some connection between the catalytic action of the salt on the one hand and the electrical charge carried by its ions on the other.

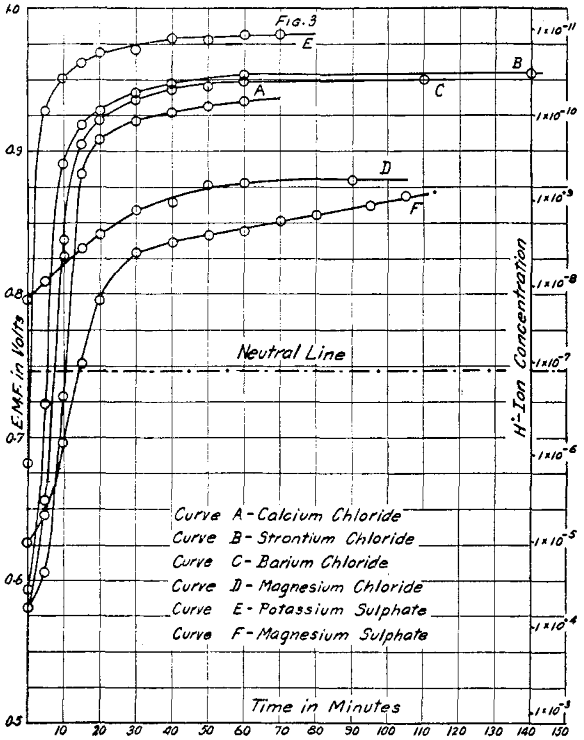
Fig. 3

Aluminium chloride was selected as a typical uni-trivalent electrolyte. As is well known, this salt is very appreciably hydrolyzed in 0.1 *M* solution and the resulting hydrochloric acid gives rise to a copious evolution of hydrogen. It was observed that the evolution of hydrogen was initially much greater than after the reaction had proceeded for several hours. The gradual accumulation of basic compounds on the surface of the metal caused a rapid diminution in the rate of gas evolution.

There was relatively little change in the hydrogen-ion concentration in the solution of aluminium chloride during the first day, owing to the fact that as fast as the hydrogen ions of the hydrochloric acid were discharged, fresh acid was formed by further hydrolysis of the salt. It is for this reason that complete neutralization did not occur until four-and-a-half days after the magnesium was introduced into the solution.

Curve A of Fig. 4 furnishes an example of the action of magnesium on an acid. Here, it will be observed, complete neutralization was attained in less than four hours and thereafter the curve follows the normal course; the process of neutralization is not retarded by the production of fresh acid as in the case of aluminium chloride and the limiting concentration of the hydrogen ion is reached more quickly.

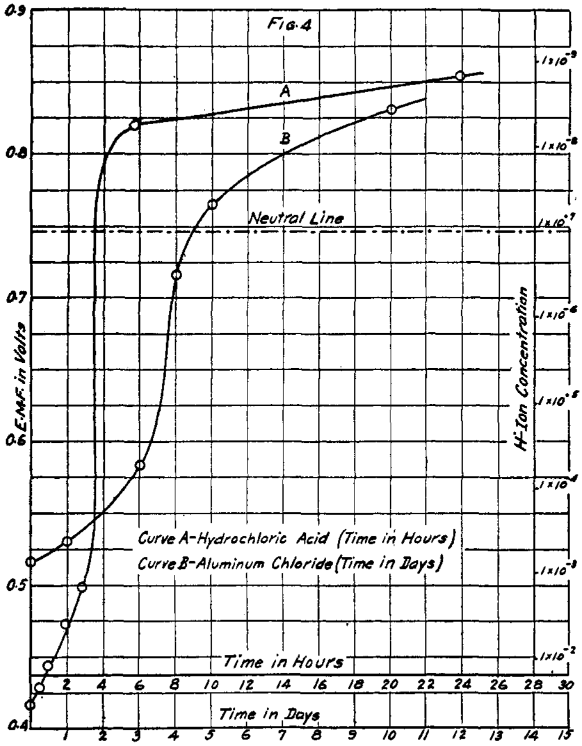
Fig. 4

Sodium carbonate and sodium tetraborate were chosen as typical salts of weak acids. Since these salts, when dissolved, undergo hydrolysis giving alkaline solutions, we should naturally expect a marked depression of the hydrogen-ion concentration. That this actually occurs is shown by the curves for these salts as plotted in Fig. 1. There is no progressive decrease in the hydrogen-ion concentration with time nor does the introduction of the magnesium alter the initial concentration.

Solutions of potassium hydroxide behave similarly, the only difference being that the hydrogen-ion concentration is depressed to a greater extent. This is just what we should expect with a highly ionized base such as potassium hydroxide.

Notwithstanding the fact that no gas is evolved when magnesium is introduced into 0.1 M potassium hydroxide and that only a very slight evolution occurs in a solution of 0.1 M sodium carbonate, a surprisingly large volume of gas is liberated when magnesium is immersed in a 0.1 M solution of borax. Because of this somewhat anomalous behavior of borax it seemed of interest to try a few experiments with boric acid. To our disappointment, it was almost impossible to secure steady and reproducible electromotive forces when the hydrogen electrode was immersed in a 0.1 M solution of boric acid and we were forced to content ourselves with a determination of the volume of gas evolved in twenty-four hours. Though probably nothing more than a coincidence, one's attention is arrested by the fact that in 0.1 M solutions of borax and boric acid, magnesium liberates practically equal volumes of hydrogen.

The behavior of magnesium with solutions of urea, mannite and cane sugar was studied with a view to determining, if possible, whether the catalytic influence of the solute in accelerating the reaction between magnesium and water is confined to electrolytes. While the concentration of the hydrogen ion in these solutions is depressed in the presence of magnesium to nearly the same extent as in solutions of many of the neutral salts, as is shown by the curves plotted in Fig. 5, yet the evolution of hydrogen is decidedly less. In fact, the volume of gas liberated is hardly greater than the volume set free when magnesium is immersed in pure water alone. This fact makes it appear highly probable that the accelerating influence of a dissolved salt on the reaction between magnesium and water is to be ascribed to the ions of the salt rather than to the un-ionized molecules.

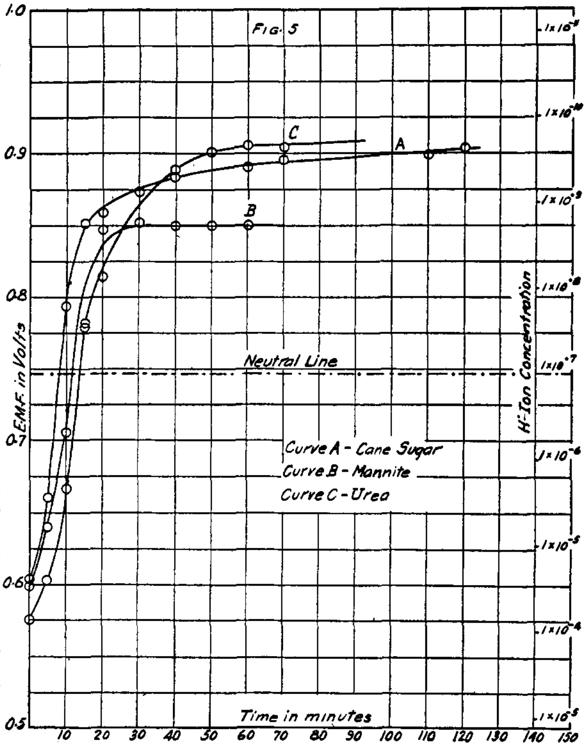
FIG. 5

The different ways in which magnesium may react when introduced into an aqueous solution of a salt may be conveniently summarized as follows:

(1) When the metal is immersed in a solution of a neutral salt it reacts with the solvent, liberating hydrogen and forming magnesium hydroxide or a basic salt. The neutral salt functions solely as a catalyst in the reaction.

(2) When the metal is immersed in a solution of a salt of a weak base it reacts primarily with the acid produced by the hydrolysis of the salt and ultimately with the solvent. In the latter reaction the saline constituents of the solution function catalytically.

(3) When the metal is immersed in a solution of a salt of a weak acid, owing to the depression of the hydrogen-ion concentration by the hydroxyl ions of the hydrolytically-formed base, it reacts with the solvent very slowly, if at all.

(4) When the metal is immersed in a solution of a salt, the cation of which is less electro-positive than magnesium, the metal of the salt is displaced by the magnesium. Solutions of such salts generally have an acid reaction, in which case the hydrogen of the acid is also displaced by the magnesium.

Summary of Results.

(1) A 0.1 *M* solution of potassium chloride was found to react quite as readily with chemically pure magnesium prepared by distillation *in vacuo* as with a sample of the metal containing less than 0.5% of impurity.

(2) The behavior of magnesium when immersed in 0.1 *M* solutions of a variety of typical electrolytes was found to be similar to its behavior in solutions of potassium chloride previously investigated. This is considered as additional evidence in favor of the hypothesis already advanced that in the reaction represented by the equation

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2,$$

the solute acts catalytically.

(3) In solutions of salts which undergo hydrolysis, the evolution of hydrogen was found to be accelerated if the base of the salt was weak and retarded if the base of the salt was strong.

(4) Non-electrolytes appear to exert no appreciable influence on the rate of the reaction. This suggests that the effective catalytic agency is ionic.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

DIFFERENTIAL IODIMETRY.

II. THE TITRATION OF CHROMIC ACID IN THE PRESENCE OF FERRIC IRON AND THE ANALYSIS OF CHROMITE FOR ITS CHROMIUM CONTENT.[1]

BY O. L. BARNEBEY.

Received January 15, 1917.

In a previous paper[2] the rate of reaction of ferric iron and iodide in phosphoric acid solution was shown to be a very slow one. The reaction is so slow indeed that interaction of iodic acid and iodide could be allowed to proceed and the liberated iodine titrated with thiosulfate without the ferric iron present causing interference. The principle of utilizing regulated acidities with iodide to determine various oxidizing agents has also been applied in the determination of periodates, iodates, bromates and chlorates in the presence of each other.[3]

When potassium iodide is added in excess to chromic acid the amount

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[1] Read at the Urbana meeting of the American Chemical Society.

[2] THIS JOURNAL, 37, 1503 (1915).

[3] *Ibid.*, 38, 330 (1916).