Summary.

1. Observations have been made of the changes in the electrical resistance and in the cathode potential of palladium wires, both during their occlusion of hydrogen electrolytically evolved, and after the interruption of electrolysis.
2. The proportional increase of resistance at apparent saturation has been found to vary widely, even with wires from the same lot of carefully purified palladium.
3. The resistance of saturated wire of 0.1 mm. diameter or less, observed during momentary interruptions of electrolysis, has been found to vary in a well-defined manner with the polarizing current; and the resistance after the interruption of electrolysis has been shown to undergo changes which are reversible and reproducible.
4. Saturated wire of 0.32 mm. diameter has been found not to exhibit these changes.
5. Considerations are given which make it probable that the changes of resistance in the smaller wires are due to processes occurring within the metal, and not far removed from its surface.
6. The tentative conclusion is suggested that hydrogen occluded at the cathode surface exists for some time in a transitional state in which it possesses an electrical conductance of its own, and passes gradually into another form which has much less conductance, or none.
7. Characteristic changes have been observed, after the interruption of electrolysis, in the cathode potential of saturated palladium wire, and certain connections have been noted between the manner and magnitude of these changes and the conditions of electrolysis.
8. A few observations have been made upon copper wires which show that this metal does not suffer any measurable alteration of electrical resistance, under the same conditions which produce a high degree of occlusion in the case of palladium.
9. A single experiment has been made upon nickel wire, which appears to show that it too is unable to occlude sufficient hydrogen, under the conditions of these experiments, to produce any perceptible alteration of its electrical resistance.

PRINCETON, N. J.

THE ACTION OF MAGNESIUM ON SOLUTIONS OF POTASSIUM CHLORIDE.

By Frederick H. Getman.

Received September 18, 1916.

It has long been known that metallic magnesium reacts very slowly with distilled water at ordinary temperatures, the products of the reaction being magnesium hydroxide and hydrogen. An apparently similar, though more energetic, reaction has been shown to occur when magnesium is introduced into an aqueous salt solution. On the other hand, when magnesium is introduced into a solution of one of the caustic alkalies no reaction takes place.

In an attempt to determine the difference of potential between metallic magnesium and various magnesium salts, the attention of the author was directed for the first time to the unusual reaction between magnesium and saline solutions. After reviewing the literature of the subject,[1] it became evident that none of the explanations of the phenomenon which have been advanced is wholly satisfactory. Undoubtedly the best explanation is that suggested by Kahlenberg based upon the assumption that solutions are chemical combinations of solvent and solute in varying proportions. While this assumption offers a ready explanation of all of the phenomena described and consequently is superior to the explanations advanced by earlier investigators in this field, it is open to the objection that it involves a step backward to the older theories of solutions. The modern theory of solutions has proven to be so comprehensive a generalization that it does not seem unreasonable to assume that it can be invoked to explain the action of metallic magnesium on saline solutions.

With this end in view, the present investigation was undertaken.

Theoretical.—The reaction between magnesium and water may be represented by the following equation:

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

or writing the reaction in terms of ions, we have

$$2H^{\cdot} + Mg \longrightarrow Mg^{\cdot\cdot} + H_2.$$

Since, for a definite temperature, the ionic product of water is constant, $c_{H^{\cdot}} \times c_{OH'} = \text{const.}$, it follows that the rate of the reaction should decrease owing to the increase in the concentration of hydroxyl ions furnished by the dissolved magnesium hydroxide. When the solubility product of magnesium hydroxide is exceeded, then the reaction should proceed at a uniform rate, provided that the effective surface of the metal is not reduced by the accumulation of precipitated magnesium hydroxide. In general, aqueous solutions react more energetically with magnesium than pure water alone. This suggests that the dissolved substance may function as a catalyst in the reaction. The possibility that the solute might function as a catalyst was suggested by Tommasi[2] in connection with his experiments on the action of magnesium on solutions of potassium chloride. In commenting on this suggestion, Kahlenberg[2] says: "It would scarcely be helpful to dismiss the matter by saying that in these

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[1] Tommasi, *Bull. soc. chim.*, [3] **21**, 885 (1899); Lemoine, *Compt. rend.*, **29**, 291 (1899); Mouraour, *Ibid.*, **130**, 140 (1900); Kahlenberg, THIS JOURNAL. **25**, 380 (1903); Roberts and Brown, *Ibid.*, **25**, 801 (1903).

[2] *Loc. cit.*

diverse solutions the rate of evolution of hydrogen is increased by the catalytic action of the solute when hydrogen is liberated more rapidly than from water, and that the rate is diminished by the negative catalytic action of the solute, when the formation of hydrogen takes place less rapidly than from water." As a matter of fact, Kahlenberg's experiments with a wide variety of solutes, failed to reveal but three cases where the rate of the reaction between magnesium and water was lessened. Glycerol, mannite and cane sugar each produced a distinct retardation of the reaction, but it is conceivable that this effect may be traceable to the presence of several hydroxyl groups in each of these compounds. Whatever the cause of the retarding action of these substances, the fact seems to be well established that dissolved substances, as a rule, tend to promote rather than to retard the reaction between magnesium and water. A further consequence of the catalytic theory is, that the dissolved substance should remain unaltered throughout the reaction and be recoverable in its original amount at the end of the reaction.

Materials.—The magnesium used in this investigation was obtained in the form of wire 3.3 mm. in diameter. Analysis showed it to contain 99.66% of magnesium, together with a residue consisting of aluminium and iron. Spectroscopic examination of the wire with a grating spectroscope confirmed the results of chemical analysis. The potassium chloride was obtained from a reliable source and, after recrystallization, was found to be of a high degree of purity. In addition to ordinary distilled water, so-called "conductance water" was used. This was prepared in the usual manner by successive redistillation of ordinary distilled water, first from chromic acid and then from alkaline potassium permanganate, the final distillate being condensed in block tin and stored in a receiver of Jena glass. The water obtained by this process was found to possess a specific conductance of about 3×10^{-6} reciprocal ohms.

Experimental.

The present investigation is limited to the study of the action of metallic magnesium on aqueous solutions of a single solute, potassium chloride. The experimental work may be conveniently considered in the following order: (*a*) measurement of the volume of hydrogen obtained from water under varying conditions, (*b*) measurement of the volume of hydrogen obtained from solutions of potassium chloride of different concentrations, (*c*) determination of the difference of potential between magnesium and solutions of potassium chloride, (*d*) study of the concentration of the hydrogen ion in the presence of magnesium in both pure water and solutions of potassium chloride, and (*e*) determination of the concentration of potassium chloride in a solution before and after the action of magnesium.

(*a*) **Volume of Hydrogen from Water.**—A form of apparatus similar to that shown in Fig. 1 was used in measuring the volume of hydrogen resulting from the action of metallic magnesium on water alone or on aqueous solutions of potassium chloride. It consisted of a graduated gas-measuring tube, B, of 50 cc. capacity and a leveling tube, A, the two tubes being connected by means of a piece of rubber tubing fitted with a pinchcock, E. In carrying out an experiment with this apparatus, E was closed and, after removing the rubber stopper and tubing at D, A was filled with water or with the solution to be studied. The pinchcock E was then opened and the liquid in A was allowed to flow out until any air bubbles which might be present in the tubing were removed. After again closing E, the tube B was filled full of the liquid to be studied, a piece of magnesium wire of known dimensions was dropped in, and the stopper D was quickly inserted, taking care to avoid the inclusion of air. On inverting the tube B, the piece of magnesium wire could be readily caused to fall into place at C, the end of the glass tubing projecting through the stopper serving to hold it in a vertical position as shown in the illustration. The pinchcock E was then opened and the tubes A and B clamped in such relative positions that the level of the liquid in the former was slightly higher than that in the latter. Readings of the volume of gas disengaged were made with the liquids in the two tubes at the same level. The pieces of magnesium wire used were exactly 50 mm. in length and were carefully polished in a lathe to an average diameter of 3.25 mm. before introducing into the liquid in the tube B. It was assumed that the effective surface of the wire was its total superficial area minus the area of the end in contact with the rubber stopper. That this assumption was justifiable was proven by the fact that only a slight tarnish was observed on the ends of wires which had been immersed for several days. The effective surface of magnesium in each of the following experiments may thus be taken to be 518.9 sq. mm. In the subjoined tables, t denotes the interval of time in hours from the beginning of the experiment, v denotes the volume of gas evolved in cubic centimeters and reduced to 0° and 760 mm., and $\Delta v/\Delta t$ gives the rate at which gas is evolved, Δt being reckoned from the initial time as zero.

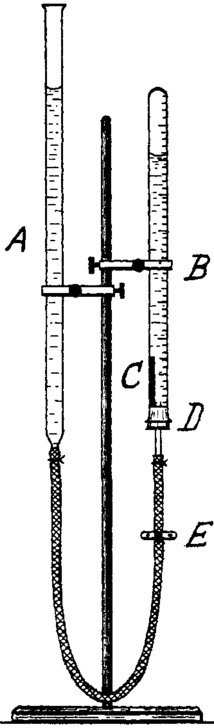

Fig. 1.

TABLE I.
Distilled Water.

t.	v.	$\Delta v/\Delta t$.
6	0.26	0.043
21	0.44	0.021
45	0.55	0.011
69	0.60	0.009
213	0.80	0.004
261	0.89	0.004
405	1.44	0.004
501	1.79	0.004

TABLE II.
Conductance Water.

t.	v.	$\Delta v/\Delta t$.
48	0.35	0.007
120	0.54	0.005
360	1.37	0.004
384	1.48	0.004
408	1.59	0.004
432	1.68	0.004
624	2.57	0.004

TABLE III.
Distilled Water Saturated with Air Freed from Carbon Dioxide.

t.	v.	$\Delta v/\Delta t$.
48	1.15	0.024
72	1.38	0.019
120	1.59	0.013
168	1.77	0.011
216	1.86	0.009
240	1.95	0.008
336	2.34	0.007
384	2.48	0.006

The water used in the first two experiments was freed from dissolved air, while that used in the last experiment was saturated with air from which the carbon dioxide had been removed by passing it successively through a solution of potassium hydroxide and a column of soda lime. The data recorded in Tables I and II indicates that magnesium reacts initially at nearly identical rates with ordinary distilled water and with that which has been freed from dissolved gases, and that ultimately the two rates become equal. On the other hand, the data of Table III shows that the presence of dissolved air augments the volume of hydrogen liberated in a given interval of time. The results obtained with distilled water confirm the results of Kahlenberg[1] and Bryant,[2] the latter of whom states that magnesium reacts equally well with both boiled and unboiled water. The experiments of Roberts and Brown,[1] however, led to the conclusion that magnesium is without action on distilled water, boiled free from dissolved gases, and cooled out of contact with air. A further deduction drawn by the last-mentioned authors from their experiments was that magnesium reacts with water which has been boiled and subsequently charged with oxygen. This conclusion is fully confirmed by the data recorded in Table III. From the evidence at hand, it seems justifiable to conclude that metallic magnesium reacts slowly with the purest distilled water and that the rate of reaction is augmented by the presence of neutral dissolved gases.

(*b*) **Volume of Hydrogen from Solutions of Potassium Chloride.**—In view of the fact that magnesium reacts at approximately the same rate with ordinary distilled water as with conductance water, the former was used in preparing the solutions of potassium chloride.

Two distinct series of experiments were carried out and the agreement between the results was as close as could be expected when the inherent defects of the method are taken into consideration. The solubility of the evolved hydrogen in the solution and the difficulty of removing the last

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[1] *Loc. cit.*

[2] Bryant, *Chem. News*, 80, 211 (1899).

adhering bubbles of gas from the surface of the magnesium wire constituted the chief defect in the method and introduced an appreciable error for which no correction was attempted. The curves shown in Fig. 2 are plotted from the experimental data, with the exception of that for *N* KCl, which is calculated from Kahlenberg's data, on the assumption that the amount of hydrogen evolved is proportional to the surface of magnesium exposed in the solution. The full line curves show the relation between time and the volume of hydrogen disengaged, while the dotted curves represent the variation in the rate of gas evolution with time. It will be observed that the rate of reaction between magnesium and water is greatly accelerated by the presence of potassium chloride. Furthermore, it is evident that the increase in gas evolution is not proportional to the increase in concentration of the solution. All of the curves show a tendency to become rectilinear with time, indicating that the reaction has attained a constant rate. None of the curves show the inflection which is characteristic of the curves of Roberts and Brown,[1] notwithstanding the fact that readings were taken every twenty minutes during the earlier stages of the reaction where this effect was observed. Direct comparisons with the data of the above investigators could not be made because of the insufficient information as to the dimensions of the magnesium used in their experiments.

(*c*) **Difference of Potential between Magnesium and Potassium Chloride Solutions.**—Determinations of the difference of potential between magnesium and solutions of several electrolytes were made by Kahlenberg.[1] The measurements were made at 20° against the normal calomel electrode, the potential of which was assumed to be 0.56 volt. The following table summarizes the results obtained, the value of each difference of potential representing the mean of four determinations in which different bars of magnesium were used:

TABLE IV.

Electrolyte.	Concentration.	Diff. of potential.
NaCl	2 (mols per liter)	1.163 (volts)
NaOH	1	1.111
KOH	1	1.140
KOH	0.1	1.105
$MgSO_4$	1	1.366

It was observed that in the solution of sodium chloride, the e. m. f. changed but slightly with time; in the caustic alkali solutions the e. m. f. slowly diminished on standing, while in the solution of magnesium sulfate it showed a tendency to increase. In discussing these results, Kahlenberg says: "The difference of potential between magnesium and the solutions would be expected to be higher in the case of solutions that are vigor-

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[1] *Loc. cit.*

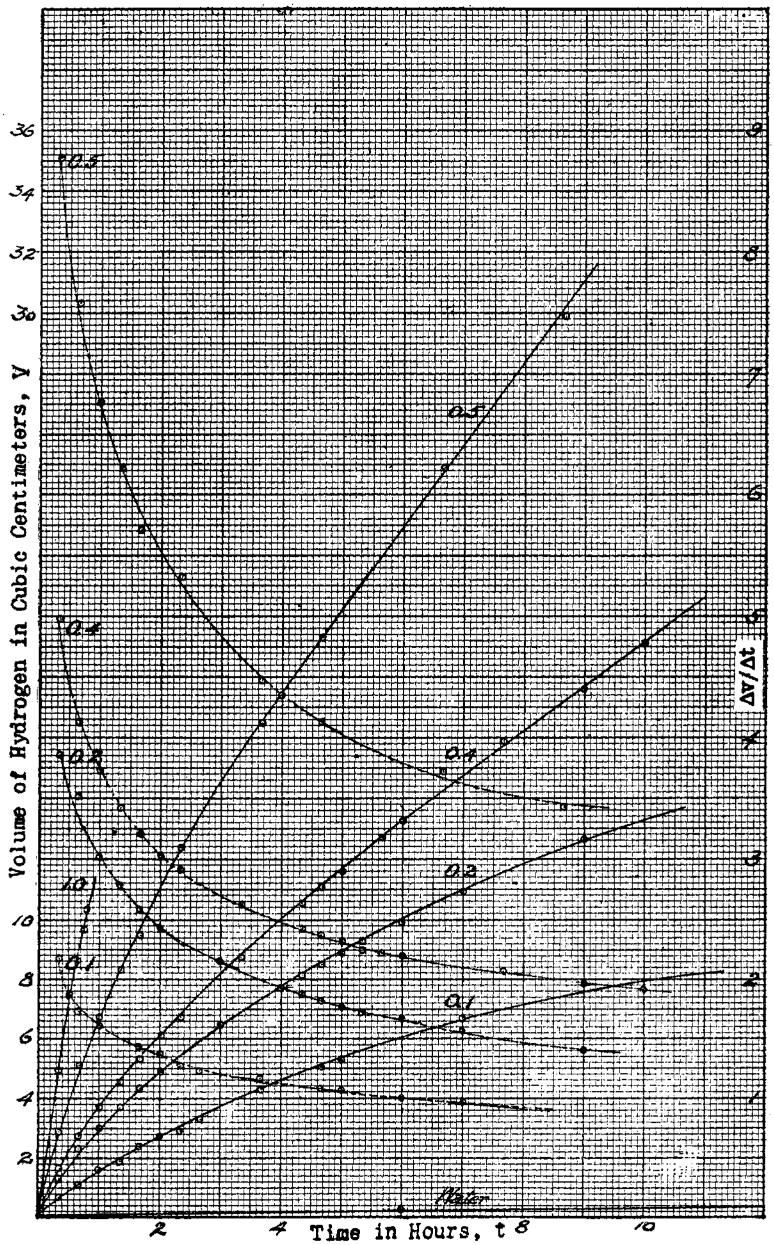
Volume of Hydrogen in Cubic Centimeters, V
36
34
32
30
10
8
6
4
2
0.5
0.4
0.2
1.0
0.1
0.5
0.4
0.2
0.1
Water
2
4
Time in Hours, t
8
10
Δv/Δt
9
8
7
6
5
4
3
2
1

Fig. 2.

ously attacked than in solutions in which the action is slight. The experimental data are in accord with this." Similar determinations of differences of potential between magnesium and solutions of potassium chloride were made in the present investigation. The data given in this subjoined tables were obtained from measurements of the e. m. f. of cells of the following type:

$$\mathrm{Mg}^{-} — \mathrm{KCl\ solution}\ \|\ \overset{\longleftarrow}{0.1}\ N\ \mathrm{KCl,HgCl} — \mathrm{Hg}^{+},$$

the current flowing outside of the cell in the direction of the arrow. The cell was immersed in a thermostat maintained at 25° C. ± 0.05°, at which temperature the potential of the calomel electrode was taken to be 0.6186 volt. Two different magnesium electrodes were used in these experiments, care being taken to remove all traces of oxidation by polishing with emery cloth immediately before immersing in the solution. The results tabulated represent the mean of several determinations with each of the two electrodes:

TABLE V.—0.1 *N* KCl.

Time.	Diff. of potential
0 (min.)	1.1007 (volts)
10	1.0948
20	1.0920
30	1.0893
40	1.0868
50	1.0860
120	1.0840
250	1.0690
450	1.0638
1200	1.0589

TABLE VI.

Concentration.	Diff. of potential.
0.1 (mol. per liter)	1.0962 (volts)
0.05	1.0760
0.02	1.0517
0.01	1.0199
0.005	1.0069
0.001	0.9870
0.0005	0.9170
0.0001	0.8856

It will be seen from Table V that when magnesium is immersed in 0.1 *N* KCl, the difference of potential between the metal and the solution decreases with the time. This effect is undoubtedly caused by the gradual accumulation of the products of the reaction upon the surface of the electrode and a consequent lessening of its rate of solution. When the difference of potential is plotted against the time, a curve is obtained which is similar to that expressing the relation between the rate of evolution of hydrogen and the time as shown in Fig. 2. The values of the differences of potential given in Table VI are based upon measurements of electromotive force which were made as soon as possible after introducing the magnesium electrodes into the respective potassium chloride solutions. They may, for all practical purposes, be regarded as the differences of potential between an untarnished surface of magnesium and the different solutions of potassium chloride given in the table. As will be seen, the difference of potential decreases with decreasing concentration, a result which is not unexpected, when it is remembered that the rate of solution of magnesium is conditioned by the amount of salt present.

An interesting phenomenon was noted in connection with the study of the electromotive behavior of magnesium in solutions of potassium chloride. When the surface of the electrode was cleaned by immersion in acid, it was found that the difference of potential between it and the solution was invariably lower than when the surface was cleaned by means of emery cloth. The influence of the preliminary treatment on the subsequent behavior of the electrode is clearly shown by the data of Table VII.

TABLE VII.—0.1 *N* KCl.

	Potential after treatment with		
Electrode.	Emery.	Acid.	Difference.
I	1.0957	1.0666	0.0291
I	1.0958	1.0423	0.0535
II	1.0935	1.0524	0.0411
II	1.1000	1.0530	0.0470

While the value of the difference of potential established between a freshly polished magnesium electrode and 0.1 *N* KCl was practically constant and reproducible, the corresponding values obtained with electrodes previously immersed in acid were always numerically smaller and varied considerably. It will be observed that the differences of potential established by electrodes which have been treated with acids are comparable with the final values of Table V. This tends to confirm the suspicion that the surface of an electrode which has been immersed in acid is enveloped by an adsorbed film of hydrogen which cannot be removed by prolonged washing.

(*d*) **Concentration of the Hydrogen Ion.**—Attention has already been called to the fact that when magnesium is immersed in water, or in a solution of potassium chloride, an alkaline reaction ensues almost immediately. It is evident that any satisfactory explanation in this reaction must take into account the changes which occur in the concentration of the hydrogen ion as the reaction proceeds. With this end in view, determinations of the concentration of the hydrogen ion were made at definite intervals of time in reacting mixtures of water and magnesium and of potassium chloride solutions and magnesium. A hydrogen electrode consisting of a strip of platinum foil coated with platinum black and saturated with hydrogen under a definite pressure was used to determine the concentration of the hydrogen ion. When such an electrode is immersed in a solution which is normal with respect to the hydrogen ion, and is connected with a similar electrode, immersed in a solution of unknown hydrogen-ion concentration, c, the resulting e. m. f., E, can be calculated by means of the well-known formula of Nernst, *viz.*,

$$E = RT/nF \log_e 1/c.$$

Since it is more convenient to use the calomel electrode than the normal hydrogen electrode, the above expression may be written

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

where δ denotes the difference between the potential of the normal hydrogen electrode and that of the calomel electrode.

At a temperature of 25°, using a calomel electrode containing 0.1 N KCl, the formula becomes, on transforming to Briggsian logarithms,

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

the value of δ being 0.33 volt under these conditions.

A hydrogen electrode similar to that described by Hildebrand[1] was prepared and was found to attain equilibrium quickly and also to be both constant and reproducible. The hydrogen used was prepared by the action of granulated zinc on hydrochloric acid, and was washed by passing successively through solutions of potassium hydroxide and potassium permanganate. As in the foregoing experiments, the magnesium used was in the form of wire polished to an average diameter of 3.15 mm. and cut in 40 mm. lengths, thus giving a total surface of 411.6 sq. mm. Owing to the fact that in these experiments the solution was stirred before taking each reading, it may be assumed that the entire surface of the wire represents the effective surface. An enclosed type of Lippmann electrometer, sensitive to 0.0001 volt, was employed to determine the point of balance on the bridge wire, according to the familiar method of Poggendorff. Before beginning a series of measurements, care was taken to insure the complete saturation of the hydrogen electrode at atmospheric pressure. By passing a current of hydrogen through the electrode at such a rate that about one bubble per second escaped from the immersed end of the electrode, it was found that complete saturation could be secured in ten minutes, and that by continuing the passage of gas at the same rate, the constancy of the electrode could be maintained indefinitely. The volume of water or of solution used in all of the experiments was 25 cc. and care was taken not to immerse the hydrogen electrode to a greater depth than was necessary to prevent the free escape of hydrogen. Having secured a completely saturated electrode, connection with the calomel electrode was established by dipping the siphon tube of the latter into the contents of the beaker. Having measured the e. m. f. of the combination as quickly as possible, the freshly polished magnesium wire was introduced and, after an interval of five or ten minutes, the e. m. f. was again determined. As soon as the point of balance on the bridge wire was obtained, connection with calomel electrode was broken by closing the stopcock in the siphon tube and then removing the latter from the

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[1] Hildebrand and Harned, *Eighth Intern. Congr. Appl. Chem.*, 1, 217; THIS JOURNAL, 35, 847 (1913).

solution in the beaker. This procedure minimizes errors due to diffusion at the liquid junction. No attempt was made to introduce a correction for liquid potentials since such a correction would in every case be negligible in comparison with the experimental error. The solution in the siphon tube of the calomel electrode was renewed before the beginning of each experiment, thus insuring a connecting solution which was strictly 0.1 *N* with respect to potassium chloride. The experimental data are

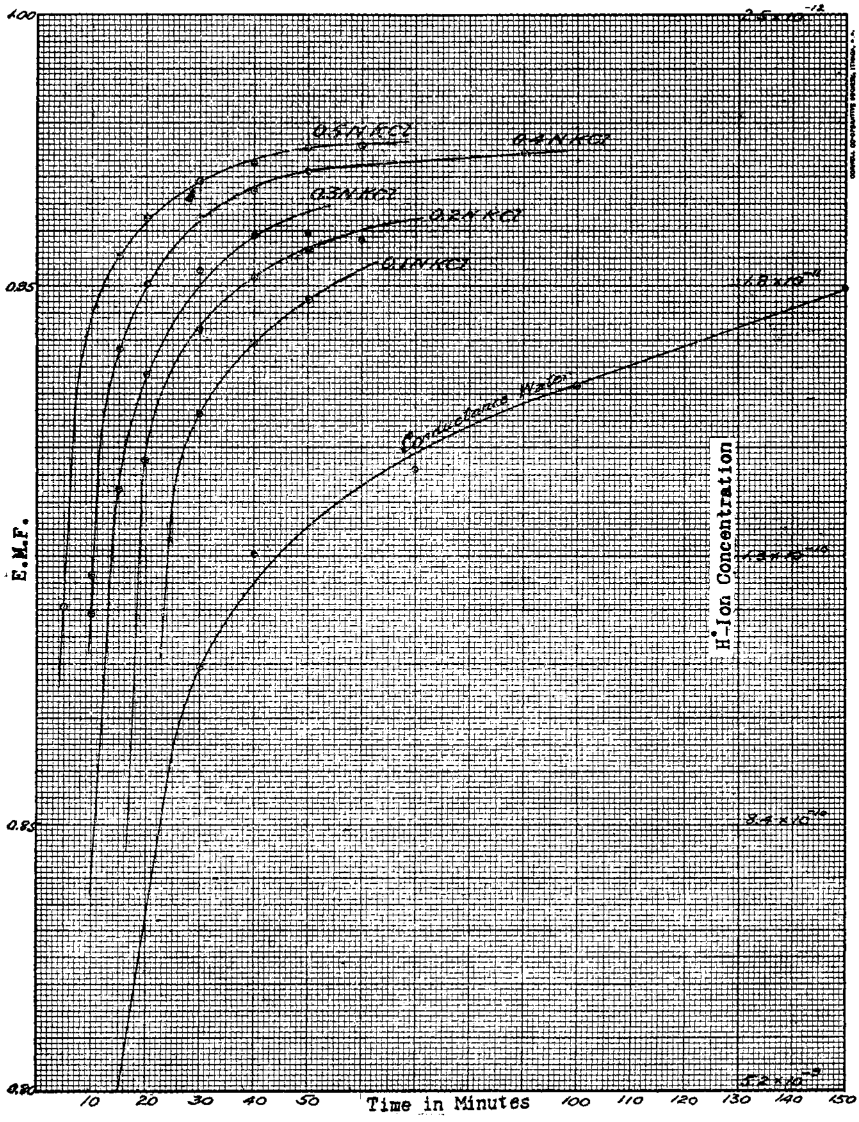

Fig. 3.

represented by the curves shown in Fig. 3. The influence of increasing amounts of potassium chloride in accelerating the reaction between magnesium and water with a consequent diminution of the hydrogen-ion concentration, is clearly shown. The rapidity with which the e. m. f. changes in the early stages of the reaction rendered it extremely difficult to secure satisfactory readings during the first five or ten minutes of an experiment. It will be observed that the curves of Fig. 3 all show a tendency to become horizontal with increasing time and that this tendency becomes more pronounced as the amount of potassium chloride is increased. This result furnishes weighty evidence in favor of the proposed explanation of the reaction between magnesium and water and the function of potassium chloride therein. According to this explanation, magnesium is assumed to dissolve in water by virtue of its high solution pressure, forming magnesium hydroxide. This latter substance undergoes ionization, thereby increasing the concentration of hydroxyl ions in the water and causing a corresponding decrease in the concentration of the hydrogen ions. The process will continue until the water becomes saturated with magnesium hydroxide, after which the concentrations of the hydroxyl and hydrogen ions will remain constant. The addition of increasing amounts of potassium chloride should not only accelerate the velocity of the reaction but also should increase the solubility of the magnesium hydroxide formed, with a consequent further depression of the limiting concentration of the hydrogen ion.

(*e*) **Concentration of Potassium Chloride before and after Reaction.**—If the action of potassium chloride in the reaction between magnesium and water is purely catalytic, its amount should remain unaltered. As has already been stated, Tommasi[1] found this to be the case in his investigation of the action of magnesium on solutions of potassium chloride and, as a result, he suggested that the potassium chloride should be considered as a catalyst promoting the reaction between magnesium and water. With a view to verifying the statement of Tommasi that the initial weight of potassium chloride remains unchanged throughout the reaction, the following experiment was performed. A piece of freshly polished magnesium wire was immersed in distilled water containing a known weight of potassium chloride. The reaction was allowed to proceed for several days until the rate of evolution of hydrogen became very slow. Then, after scraping off the accumulated magnesium hydroxide from the wire as completely as possible, the entire reaction mixture was filtered and the wire and residue washed repeatedly with boiling water. The object of this last operation was to remove the last traces of adhering potassium chloride from the wire and the residual magnesium hydroxide. The filtrate was then treated with a solution of barium

[1] *Loc. cit.*

hydroxide and the precipitated magnesium hydroxide was removed by filtration. The excess of barium was next removed by means of a solution of ammonium carbonate and the resulting filtrate carefully evaporated to dryness. After freeing the residue from ammonium salts by cautious heating, it was raised to the temperature of.a full Bunsen burner for twenty minutes. The weight of the ignited residue was then determined, after allowing it to cool in a desiccator. The amount of potassium chloride present initially was 0.1868 g. while the weight of the residue at the conclusion of the experiment was 0.1886 g. While it may be conceded that the experiment established the fact that there is negligible adsorption of potassium chloride by the surface of the magnesium wire and the magnesium hydroxide produced by the reaction, it is evident that the various steps involved in the recovery of the salt would in all probability bring about the decomposition of any compound which it might have formed with the products of the reaction. So far as the writer is aware, however, no compounds of potassium chloride and magnesium hydroxide are known.

Discussion of Results.—The proposed explanation of the reaction between magnesium and water and of the role of potassium chloride in accelerating this reaction has been confirmed by several distinct lines of experimentation of which perhaps the most satisfactory is that involving the determination of the change in concentration of the hydrogen ion as the reaction progressed. The function of potassium chloride in the reaction may be likened to other well-established cases of so-called "salt-action." For example, Ostwald[1] showed that when a 0.4 *N* solution of potassium nitrate was added to a solution of cane sugar containing a 0.05 *N* solution of nitric acid, the coefficient of velocity of inversion of the sugar was raised from 29.9 to 33.9. From this and similar experiments he was led to the conclusion that while the presence of a neutral salt containing an ion in common with the inverting acid lowers the concentration of the hydrogen ions of the latter, it also exerts a marked stimulating influence on the remaining hydrogen ions. Quite another type of salt action is that described by Van Name and Edgar.[2] They showed that the rate of solution of a number of different metals in aqueous solutions of iodine is greatly increased by the presence of potassium iodide. In the Silliman lectures delivered at Yale University in 1911 by Arrhenius,[3] he says: "It has been proved that salts exert a certain influence which is sometimes very great, especially on the velocity of reaction." While in the present investigation the influence of only one salt on the reaction has been studied,

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[1] Ostwald, *J. prakt. Chem.*, [2] **31**, 307 (1885).

[2] Van Name and Edgar, *Am. J. Sci.*, [4] 237 (1910).

[3] "Theories of Solutions," p. 165, Yale Univ. Press, 1912.

it is believed that the explanation here given is of general application and that it is not necessary to invoke the assistance of the older chemical compound theory of solution.

Summary.

In this paper the action of magnesium on solutions of potassium chloride has been investigated. The experimental work has involved (*a*) the measurement of the volume of hydrogen obtained by the action of magnesium on water prepared in a variety of ways, (*b*) the measurement of the volume of hydrogen obtained from solutions of potassium chloride of different concentrations, (*c*) the determination of the differences of potential between magnesium and solutions of potassium chloride, (*d*) the determination of the concentration of the hydrogen ion in both pure water and solutions of potassium chloride, and (*e*) the determination of the concentration of potassium chloride in a solution before and after the action of magnesium. The evidence furnished by these several lines of experimentation has led to the conclusion that the reaction between magnesium and water may be represented by the equation

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

and that the presence of the dissolved salt merely accelerates the reaction catalytically.

HILLSIDE LABORATORY, STAMFORD, CONN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

OXIDATION-REDUCTION REACTIONS WITHOUT THE ADDITION OF ACID.

III. FERROUS CHLORIDE AND POTASSIUM PERMANGANATE.

A New Method for the Preparation of Colloidal Hydrous Ferric Oxide.

BY MARKS NEIDLE AND JOHN N. CROMBIE.

Received October 6, 1916.

The most familiar reaction involving the oxidation of ferrous ion by permanganate ion, is that between potassium permanganate and ferrous sulfate in the presence of an excess of sulfuric acid, and may be formulated by either of the following equations:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightleftarrows 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$5Fe^{++} + MnO_4^- + 8H^+ \rightleftarrows 5Fe^{+++} + Mn^{++} + 4H_2O$$

The data necessary for predicting whether a mixture of aqueous solutions of ferrous chloride and potassium permanganate contains a sufficient concentration of hydrogen ion to render the normal reaction possible, and to make it go practically to completion are not available. Nor was it possible to gain this information from the results of the oxidation-