

THE ACTION OF METALLIC MAGNESIUM UPON AQUEOUS SOLUTIONS.

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Received May 27, 1903.

The paper read by Mr. Kahlenberg on the above subject, at the Washington meeting of the American Chemical Society, interested us so much that we undertook a few simple experiments in the same line for ourselves. Since his paper has appeared in print¹ we find that in a few particulars our results differ from his and that our experiments have been carried on along somewhat different lines, and it has therefore seemed possible that our results also might be of interest to others.

In all of our experiments the *modus operandi* was the same. A 100 cc. gas-measuring tube was filled with the solution to be employed. In the mouth of this tube a one-holed rubber stopper was inserted, and a piece of magnesium ribbon was held in place in the solution by fastening it to the stopper with a bit of cheesecloth and some thread. The whole was then set up, in most cases in a tall jacket containing more of the same solution, for convenience in measuring, frequently, the volume of the gas under atmospheric pressure. The magnesium used was the magnesium ribbon manufactured by Schuchardt, and in our experiments the *solution* was always in excess. We used in most of our experiments an amount of magnesium equivalent to about 50 cc. of gas, or a piece about 8 cm. in length.

The most important particular in which our results differed from those of Mr. Kahlenberg was in the action of magnesium on distilled water. We found that if we used ammonia-free water, freshly boiled to drive out dissolved gases, no gas collected in the tube. The experiment was tried first with a short strip of magnesium ribbon and left standing for a week. It was then repeated with a strip of magnesium ribbon 50 cm. in length and left standing for four weeks. The magnesium appeared slightly tarnished, but no trace of gas was visible at the end of that time. When *unboiled* distilled water was used, in the same length of time, with much smaller amounts of magnesium, varying amounts

¹ This Journal, 25, 380.

of gas, from 2 to 3 cc., were collected. These results are apparently in opposition to those obtained by Bryant, who states that boiled and unboiled water have the same effect on magnesium.¹

The experiment was tried of taking some of the pure boiled distilled water and passing a current of oxygen through it before setting up the apparatus. In this case gas began to collect after standing twenty-four hours, and in the course of two weeks, 2.7 cc. of gas had collected from a strip of magnesium about 8 cm. in length. When a similar experiment was tried, using carbon dioxide instead of oxygen, the escape of gas was, as might have been expected, very rapid, the rate being greatest at first and decreasing with the time, as with other acids.

The principal facts indicated by our experiments seem to be:

(1) That magnesium is without action on distilled water, boiled to free it from gases and carefully cooled out of contact with air.

(2) That magnesium acts on undistilled water and on unboiled distilled water, setting free varying amounts of gas; also on water boiled and afterward charged with oxygen or carbon dioxide.

(3) That the hydrogen equivalent of magnesium can be obtained from aqueous solutions of varying strengths of the chlorides of sodium, potassium, magnesium, barium, calcium and strontium; also very slowly from the sulphate of magnesium (probably also of sodium and potassium); also from such dilute solutions of hydrochloric and sulphuric acids as contain in themselves but a small proportion of the hydrogen liberated.

(4) That with the same surface of magnesium the action of the chlorides is much more rapid than that of the corresponding sulphates. With chlorides of the same metal, the rate is dependent upon the concentration, though no strict proportionality can be traced. The maximum rate is more quickly attained in the stronger solution than in the weaker and is greater in amount, but the length of time for completing the reaction does not differ very much in the two cases.

(5) With equimolecular solutions of chlorides of sodium, potassium, magnesium, calcium, strontium and barium, the order of rapidity of action upon magnesium ribbon in our experiments was as follows: Magnesium, barium, strontium, calcium, sodium and potassium.

¹ *Chem. News*, Nov. 3, 1899.

In such experiments as these it is, of course, impossible to determine exactly the end-point of the reaction or to measure with any accuracy the rate of the reaction as it approaches completion. Occasional tapping of the tube is necessary to liberate the last portions of gas, and there is always the possibility that some magnesium may be covered by the precipitate and left unacted upon. We observed, however, what was mentioned by Mr. Kahlenberg, *viz.*, that the coating of precipitate over the magnesium did not retard the action as much as might have been expected. Even when the magnesium ribbon appeared to be entirely crusted over, the reaction went on until approximately the hydrogen equivalent of the magnesium had been collected. It is true that the results as shown in the following tables run a little low, but considering the possible sources of error, they seem near enough to justify the statement that the hydrogen equivalent may be set free in all cases.

TABLE I.

(Solutions contained $\frac{1}{10}$ gram-mol. per liter.)

	Weight of magnesium calculated from gas.	Weight of magnesium taken.
MgCl ₂	0.0538	0.0539
KCl	0.0535	0.0539
NaCl	0.0525	0.0539
BaCl ₂	0.05345	0.0540
CaCl ₂	0.05276	0.0534
SrCl ₂	0.0526	0.0534
MgSO ₄	0.0530	0.0539

Although but one result is given, confirmatory experiments were made in almost every case.

The time required for the completion of the reaction, with the amounts above given, was from twenty-four to forty-eight hours in the case of the chlorides, but in the case of the sulphates was much greater. The sulphates of sodium, potassium and magnesium were all tried, and the one which acted most rapidly was magnesium. With this it took nearly four weeks to get the result above given. With the sulphates of sodium and potassium the action was so slow that the experiment was discontinued before the reaction was completed.

That very dilute solutions of the chloride of magnesium are adequate to set free the hydrogen equivalent of the magnesium is indicated by our experiments with very dilute hydrochloric

acid. The acid used was of such strength that from 100 cc. only 8.1 cc. of hydrogen could be set free. The tube was inverted in a small dish containing more of the same liquid, and this might increase the possible yield of hydrogen by a small amount. The apparatus was left standing for a week, although the operation was probably completed a little before that time. At the end of a week, the volume of hydrogen was 52.5 cc. at a temperature of 19° C. and pressure of 765 mm. This corresponds to 0.0540 gram of magnesium, and the weight of magnesium taken was 0.0539 gram. A study of the rate of this reaction per twenty-four hours is interesting.

TABLE II.

	Volume of gas collected.	Volume increment per hour.
1st 24 hours	5.2	0.22
2nd 24 hours.....	7.8	0.1
3rd 24 hours	17.6	0.4
4th 24 hours	29.8	0.5
8 hours later.....	35.1	0.66
6th 24 hours	48.0	0.32
7th 24 hours	52.5	0.19

The relation between the time and the amount of gas collected is therefore represented by the following curve :

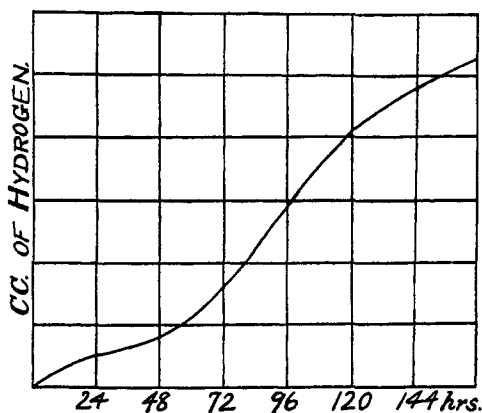


Fig. 1.

It will be noticed that the *rate* of the reaction at first decreases with the time, as is usual with the action of an acid on a metal; then, when an amount of gas has been collected nearly equal

to the amount calculated as contained in the hydrochloric acid used, the rate increases until it reaches a maximum and then decreases in about the same way as has been observed when the metal was put directly into a solution of magnesium chloride. In this case, when the rate began to increase, the amount of magnesium which had gone into solution as magnesium chloride can not have been greater than 10 milligrams.

As has just been indicated, we observed that the curve showing the relation between the *time* and the *volume increment* in a given time was distinctly different in the case of the action of acid in excess upon magnesium, and the action of aqueous solutions of chlorides. This is shown in the following table:

TABLE III.

	HCl. (Weight magnesium taken = 0.0536.)		MgCl ₂ , 1/6 molecule per liter. (Weight magnesium taken = 0.0539.)	
	Volume of gas.	Rate per hour.	Volume of gas.	Rate per hour.
1 hour	11.6	11.6	0.9	0.9
2 hours.....	18.2	6.6	3.9	3.0
3 "	21.8	3.6	8.7	4.8
4 "	24.1	2.3	13.3	4.6
5 "	26.1	2.0	17.6	4.3
6 "	27.7	1.6	21.3	3.7
7 "	24.8	3.5
8 "	28.3	3.5
9 "	31.6	3.3
10 "	34.2	2.6
11 "	36.4	2.2

These data and corresponding ones in regard to certain other solutions are represented in the following curves, which show how the volume increment per hour changes as time advances. It will be observed that the acid-rate curve is a rapidly descending one, according to the law of mass action, whereas in the case of the chlorides, the curve ascends in each case until it reaches a maximum and then descends slowly.

The maximum rate depends upon the particular chloride employed and upon the strength of the solution. With different concentrations of the same salt, the maximum rate is higher in the case of a strong solution than with a weak one and is, in general, more quickly attained. The curves also show that after the maximum rate has been reached, there is a tendency for the rates to approach one another, so that after four or five hours, the volume

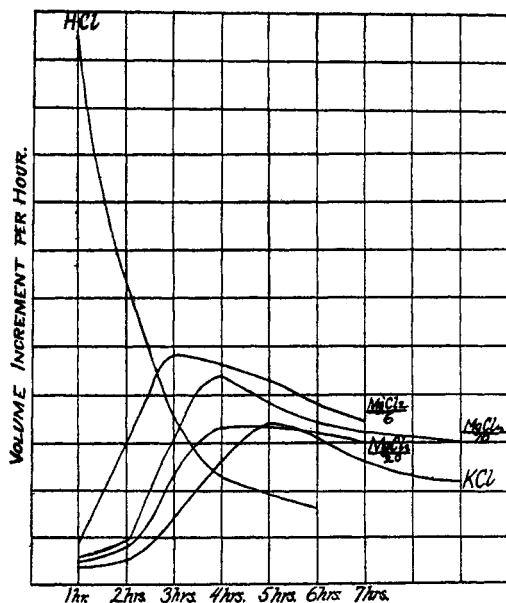


Fig. 2.

increments per hour do not vary much with the different concentrations.

Although Mouraour and others have stated that the action of magnesium on solutions of the alkaline earth metals is feeble, it was not our experience that the rate of the reaction with these substances fell so very far behind that on solutions of the same strength of magnesium chloride. In order to compare the rates of action of the chlorides of the alkali and alkaline earth metals, solutions containing $\frac{1}{10}$ gram-mol. per liter were set up as nearly as possible at the same time; pieces of magnesium ribbon 33 cm. long were used and observations taken every half hour. A solution of magnesium chloride containing $\frac{8}{10}$ gram-mol. per liter was also used. The results of these experiments are expressed in the following table:

TABLE IV.
Volume of gas collected.

	KCl.	NaCl.	CaCl ₂ .	SrCl ₂ .	BaCl ₂ .	MgCl ₂ .	$\frac{8}{10}$ MgCl ₂ .
1 hour.....	0.7	1.7	2.2	2.3	3.0	3.3	3.2
2 hours.....	3.5	5.6	6.6	7.0	9.9	11.6	13.8
3 ".....	9.0	11.8	13.2	14.3	21.2	24.6	29.8
4 ".....	16.6	19.5	22.7	24.1	34.4	37.5	42.4

	KCl.	NaCl.	CaCl ₂ .	SrCl ₂ .	BaCl ₂ .	MgCl ₂ .	⁸ / ₁₀ MgCl ₂ .
5 hours.....	25.0	27.4	32.1	33.8	45.5	48.7	54.0
6 ".....	33.8	35.3	41.0	43.0	55.3	59.3	64.8
7 ".....	41.6	42.6	48.8	51.6	64.3	69.6	74.6
8 ".....	..	49.4	56.0	59.8	72.5	78.4	83.4

Volume increment per hour.

	KCl.	NaCl.	CaCl ₂ .	SrCl ₂ .	BaCl ₂ .	MgCl ₂ .	⁸ / ₁₀ MgCl ₂ .
1 hour.....	0.7	1.7	2.2	2.3	3.0	3.3	3.2
2 hours.....	2.8	3.9	4.4	4.7	6.9	8.3	10.6
3 ".....	5.5	6.2	6.6	7.3	11.3	13.0	16.0
4 ".....	7.6	7.7	9.5	9.8	13.2	12.9	12.6
5 ".....	8.4	7.9	9.4	9.7	11.1	11.2	11.6
6 ".....	8.8	7.8	8.9	9.2	9.8	10.6	10.8
7 ".....	7.8	7.3	7.8	8.6	9.0	10.3	9.8
8 ".....	..	6.8	7.2	8.2	8.2	8.8	8.8

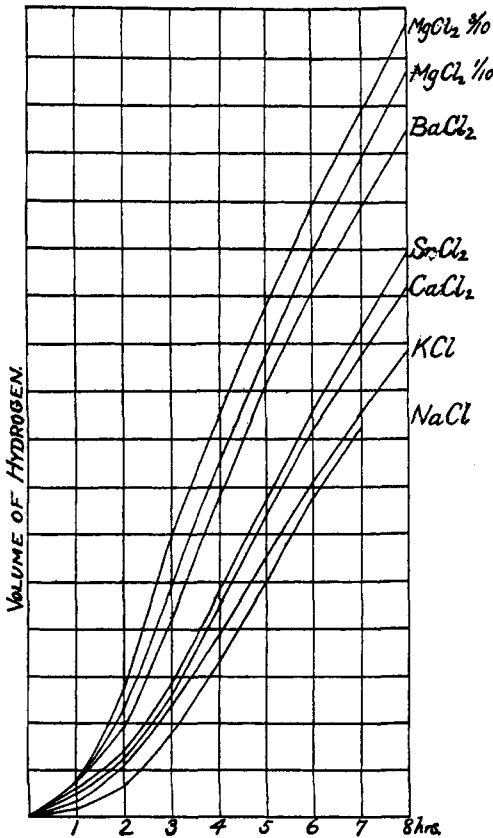


Fig. 3.

The curves representing the relation between the time and the volume of gas collected show at a glance the similarity in action of the sodium and potassium chlorides, and also of the chlorides

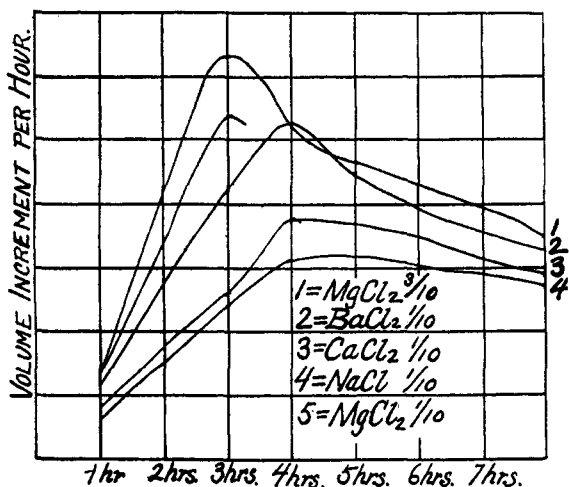


Fig. 4.

of calcium and strontium, but that the action of the barium salt is more nearly like that of the magnesium chloride than like that of the other alkaline earth chlorides. It will be noticed that the chloride of magnesium attains its maximum rate in the third hour, the salts of the alkaline earth metals in the fourth hour, and of sodium and potassium in the fifth and sixth hours; also that the sodium begins more rapidly than the potassium, but that the potassium gradually gains upon the sodium. In all cases, the rate of the reaction at first increases and then decreases, as is shown in the accompanying graphic representation of the relation between the time and the volume increments per hour. The potassium and strontium curves are omitted because they correspond so nearly with the sodium and calcium, and the curve of the weaker magnesium chloride solution is only given in part, because, after passing the maximum, it coincides in various parts with the barium chloride and the stronger magnesium chloride. It is noteworthy that the curves, which reach the highest maxima, descend the most rapidly, and therefore there is a tendency to approach a uniform rate. It should perhaps be mentioned that the hydrogen equivalent of the magnesium used would be about 200 cc., so that these observations were made only during the first part of the reaction.

The persistency of type of the rate curve in all these salts, consisting as it does of an ascending and then a descending portion, seems to us of sufficient importance to be taken into account in any explanation of the phenomenon.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF CINCINNATI, No. 59.]

A METHOD FOR THE DETECTION OF CHLORIDES, BROMIDES AND IODIDES.¹

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Received June 5, 1903.

THE problem of the detection of chlorides, bromides and iodides in presence of each other is one to which a great deal of attention has been devoted, and the present proposal of a new method is justified only by the conviction of the authors that in simplicity of execution, in reliability and in delicacy this method is superior to any hitherto proposed.

Like many of the methods proposed in the past, the one here presented is based upon the varying ease of oxidation of the halogen acids. It arose from a reasonably successful attempt to use dilute nitric acid as the oxidizing agent. Concentrated nitric acid, added dropwise, was employed for this purpose by Kebler,² who states that during a five years' trial by students it gave very satisfactory results. We have found that if nitric acid of suitable dilution is used, it is indeed possible to boil a mixture of the halogen salts with it long enough to liberate and expel all the iodine and bromine without any noticeable loss of chlorine. We may cite here two out of about twenty-five experiments. The acid was of five times molar strength and the quantity used was about half the volume of the solution to be tested:

1. Cl detected in a mixture of 49.9 cc. N KBr and 0.1 cc. N NaCl.
2. Cl detected in a mixture of 10 cc. N/100 KI, 9.8 cc. N/100 KBr, and 0.3 cc. N/100 NaCl.

The substitution of dilute for concentrated nitric acid obviates one defect in Kebler's method, *viz.*, that the concentration of the

¹ Read before the Cincinnati Section of the American Chemical Society, May 13, 1903.

² *J. Anal. Appl. Chem.*, 6, 569 (1892).