

1937

# The electrometric determination of the solubility of some hydroxides

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THE ELECTROMETRIC DETERMINATION OF THE  
SOLUBILITY OF SOME HYDROXIDES

By

George Childs Bauer

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Inorganic Chemistry

Approved

Signature was redacted for privacy.

In charge of Major work

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1937

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#### GENERAL INTRODUCTION

The present problem, the determination of the solubility of some hydroxides electrometrically, developed in an attempt to learn if magnesium chloride and ammonium chloride formed a double or complex salt in the more dilute solutions. As the two problems differ so much, it almost necessitates dividing the discussion into two parts. The first consists of the work done on the study of the complex formation, and the second of the work done on the solubility of the hydroxides.

IN A FEW SALT MIXTURES  
A STUDY OF COMPLEX FORMATION  
Part I

A STUDY OF COMPLEX FORMATION  
IN A FEW SALT MIXTURES

INTRODUCTION

Prior to the work of Loven (12), the failure of magnesium hydroxide to precipitate in the presence of ammonium salts was explained by the assumption that complex salts of the type  $\text{NH}_4\text{MgCl}_3$  and  $(\text{NH}_4)_2\text{MgCl}_4$  were formed. In case no ammonium salts were present, it was claimed that one half of the magnesium present was precipitated by ammonium hydroxide. This phenomenon could have been explained by the reaction



but the mono ammonium complex was the one generally accepted.

## HISTORICAL

Loven (12), using the ionization constant for ammonium hydroxide and his determination of the concentrations of magnesium and of ammonium hydroxide in a solution made by mixing magnesium chloride and ammonium hydroxide, determined the solubility of magnesium hydroxide and found it to be of the same order of magnitude as that reported by Kohlrausch and Rose (10). Loven's (12) value varied from 3.01 to 4.38 x 10<sup>-4</sup> assuming one hundred per cent ionization of the ammonium salt; while Kohlrausch and Rose (10) found 2.08 x 10<sup>-4</sup> using conductivity methods.

Treadwell (21), by using an excess of ammonium hydroxide, showed that up to eighty-seven per cent of the magnesium present could be precipitated by ammonium hydroxide. He also determined the molecular weight of a mixture, of one mole of magnesium chloride to two moles of ammonium chloride in solution, by the cryoscopic method, and found the results to agree with the presence of simple salts in the solution rather than of complex salts.

Herz and Muhs (5) repeated the work of Loven (12) with the exception that they approached the equilibrium from the other direction, that is through the solubility of magnesium

hydroxide in solutions of ammonium salts. They calculated the ratio  $(Mg)^{1.5} / (NH_4)$  and found it to be nearly constant and approximately equal to 0.15. This ratio was independent of the concentration of the ammonium chloride solution. This value agrees fairly closely with the value calculated from the ionization constant of ammonium hydroxide and the solubility product of magnesium hydroxide. The calculated value is 0.162 at 25°C but at the temperature at which they worked, 29°C, it should be slightly higher as the ionization constant of ammonium hydroxide should decrease slightly with the temperature, and the solubility product of magnesium hydroxide would remain practically the same.

Jones and Knight (9) determined the conductivity of various solutions containing two salts and compared this conductivity with the sum of the conductivities of salt solutions of the same concentrations determined separately. In order to eliminate the change in conductivity due to repression of ionization, because of the common ion effect, they also ran similar experiments on mixtures of salts for which no complex salts were known, even in the solid state. They found that the difference between the observed and calculated values dropped off much more rapidly and disappeared completely at much higher concentrations in the solutions for which no complex salts were known. They concluded

that magnesium chloride and potassium chloride, and magnesium chloride and ammonium chloride formed complexes even in the more dilute solutions.

The work of Jones and Knight (9) cast some doubt upon the conclusions drawn from the previous works cited, and hence this problem was undertaken in an attempt to prove or disprove the formation of complexes by magnesium chloride and ammonium chloride in the dilute solutions.

A STUDY OF THE VISCOSITIES OF SALT  
MIXTURES OF VARYING CONCENTRATION

Dunstan and Langston (2) used the rate of flow of salt solutions at varying temperatures, with rather striking success, in the determination of the transition temperatures of hydrates and hence it was reasoned that the same method might be used to determine the concentrations, in solutions of salt mixtures, at which complex salts form.

Ammonium Chloride and Magnesium Chloride Mixtures

The first attempt was made by determining the viscosities of solutions containing a fixed amount of magnesium chloride and varying amounts of ammonium chloride. The viscosities were run with an ordinary Ostwald viscosimeter. Solutions of 3.879 molar magnesium chloride and 5.060 molar ammonium chloride were made up approximately, and their strengths determined by the volumetric determination of the chloride ion by Mohr's method. Twenty-five milliliter portions of the magnesium chloride solution were introduced by means of a pipette into twelve one hundred milliliter volumetric flasks, and portions of the ammonium chloride solution, varying by

five milliliters, from five to sixty milliliters were introduced into the flasks and the solutions diluted almost to the mark with water. The flasks were well shaken and then placed in a large constant temperature bath, with the thermostat set at 20°C. The solutions were allowed to remain in the bath for about twenty-four hours with occasional shaking and were then diluted to the mark with water that had been in the bath. An attempt was made to vary the amount of ammonium chloride by one milliliter rather than five, but the difference in time of flow was so small that the error in taking the time proved to be larger than the difference caused by the slight change in concentration. The time of flow was run in triplicate and as a rule these checked within one or two-tenths of a second. When the variance was more, reruns were made until three values checked within this limit. Even with these precautions the results will be noted to be somewhat erratic. Some difficulty was encountered in the temperature control and about 0.2°C variance was the best that could be maintained, as the work was done below room temperature and it was necessary to run cooling water through the bath at all times. The viscosimeters were placed in the bath and the samples were introduced, using a pipette so as to give a constant head, and were then allowed to come to the temperature of the bath. The determinations were run viewing them through the glass of the bath and this undoubtedly added to the inaccuracy of the readings.



The densities of the solutions were determined and the products of time multiplied by density calculated. The curve, obtained by plotting these products against concentrations of ammonium chloride, approached so closely to a straight line at the lower concentrations that it was thought more could be learned from the time against concentration curve. For this reason in all of the curves this procedure was followed. This is the same scheme used by Dunstan and Langston (2).

The data in Table I were obtained in the manner outlined above. The time in each of the two columns represents the mean of three determinations agreeing within 0.2 second and the two columns present the time thus obtained using two separate viscosimeters.

Table I

Time of Flow of  $\text{NH}_4\text{Cl}$ - $\text{MgCl}_2$  Mixtures

Volume of : $\text{MgCl}_2$	Volume of : $\text{NH}_4\text{Cl}$	Total : Volume	Time : A	Time : B
25 ml	5 ml	100 ml	1'34.0''	1'30.5''
25 ml	10 ml	100 ml	1'33.5''	1'29.4''
25 ml	15 ml	100 ml	1'33.1''	1'28.8''
25 ml	20 ml	100 ml	1'33.1''	1'28.1''
25 ml	25 ml	100 ml	1'33.2''	1'27.9''
25 ml	30 ml	100 ml	1'32.1''	1'27.9''
25 ml	35 ml	100 ml	1'32.4''	1'28.0''
25 ml	40 ml	100 ml	1'31.8''	1'28.9''
25 ml	45 ml	100 ml	1'31.8''	1'27.0''
25 ml	50 ml	100 ml	1'32.0''	1'26.9''
25 ml	55 ml	100 ml	1'32.3''	1'27.7''
25 ml	60 ml	100 ml	1'32.4''	1'27.2''

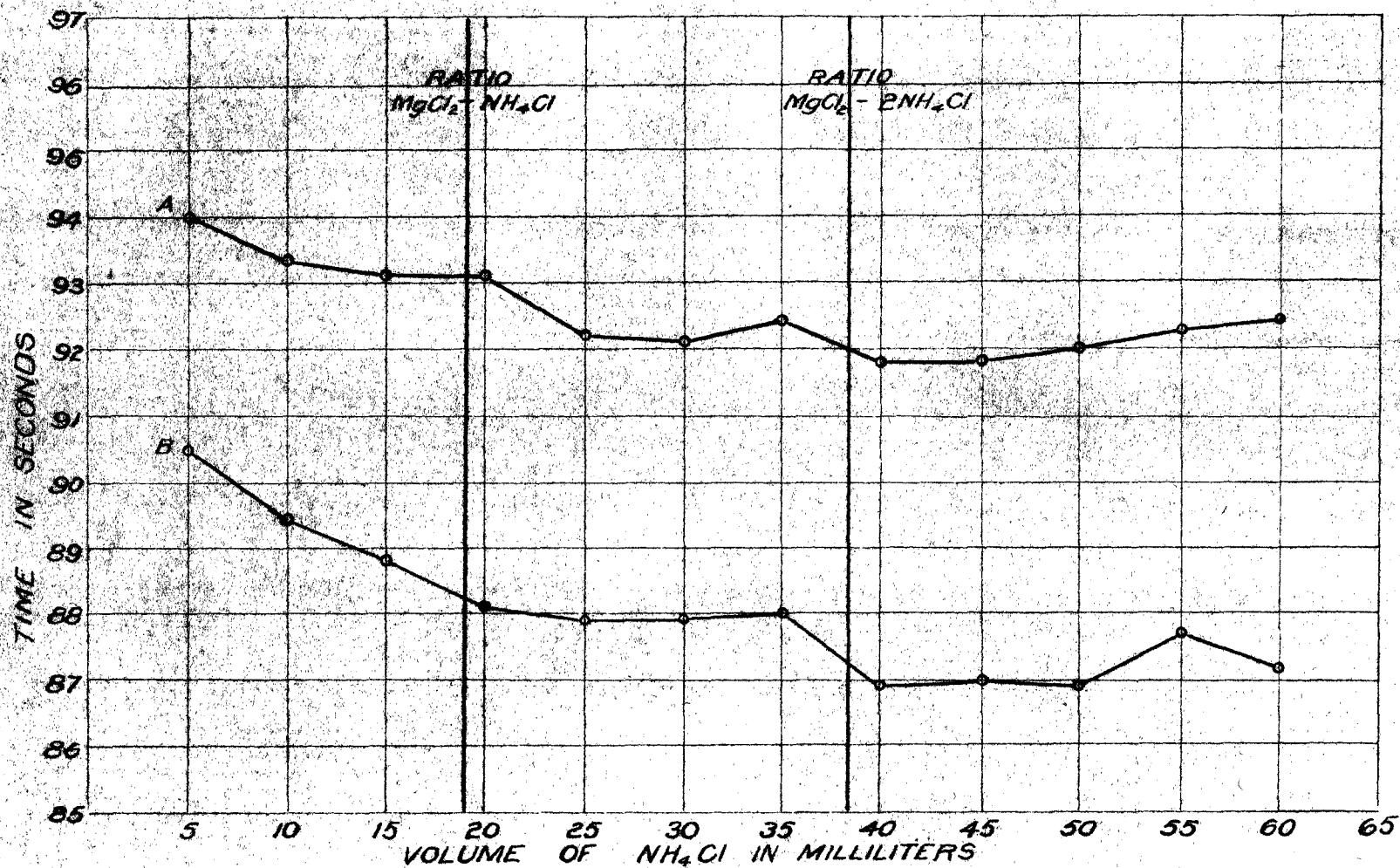


FIG. I. TIME OF FLOW OF MIXTURES OF NH<sub>4</sub>Cl - MgCl<sub>2</sub>

From the erratic variations in time the error in reading the time is evidently comparatively large but when the time is plotted against concentration very similar curves are obtained. These data are presented graphically in Figure I.

#### Potassium Chloride and Magnesium Chloride Mixtures

Using the same procedure as outlined for the ammonium chloride and magnesium chloride mixtures, determinations were made for mixtures of potassium chloride and magnesium chloride. These two salts are known to form the mineral carnallite, the formula of which is  $KMgCl_3 \cdot 6H_2O$ . The strengths of the solutions used in this experiment were 3.923 molar for the magnesium chloride and 4.235 molar for the potassium chloride. These concentrations were determined in the same manner as described before for the other solutions.

Table II

Time of Flow of KCl-MgCl<sub>2</sub> Mixtures

Volume of MgCl <sub>2</sub>	Volume of KCl	Total Volume	Time A	Time B
25 ml	0 ml	100 ml	1'34.6''	1'29.7''
25 ml	5 ml	100 ml	1'33.5''	1'28.7''
25 ml	10 ml	100 ml	1'33.0''	1'28.1''
25 ml	15 ml	100 ml	1'32.6''	1'27.7''
25 ml	20 ml	100 ml	1'32.2''	1'27.1''
25 ml	25 ml	100 ml	1'31.7''	1'26.7''
25 ml	30 ml	100 ml	1'31.4''	1'26.3''
25 ml	35 ml	100 ml	1'31.0''	1'26.0''
25 ml	40 ml	100 ml	1'31.0''	1'25.9''
25 ml	45 ml	100 ml	1'31.0''	1'25.9''
25 ml	50 ml	100 ml	1'30.9''	1'25.9''
25 ml	55 ml	100 ml	1'30.9''	1'26.0''
25 ml	60 ml	100 ml	1'31.0''	1'26.0''
25 ml	65 ml	100 ml	1'31.6''	1'26.5''

These data are presented graphically in Figure II.

Potassium Chloride and Zinc Chloride Mixtures

Again using the same procedure as outlined for the other salt mixtures, determinations were made for mixtures of potassium chloride and zinc chloride. The potassium chloride was the same as that used in the previous experiment and the zinc chloride was made up by weighing a definite weight of the so-called chemically pure salt but the solution was not standardized. The zinc chloride solution was approximately four molar.

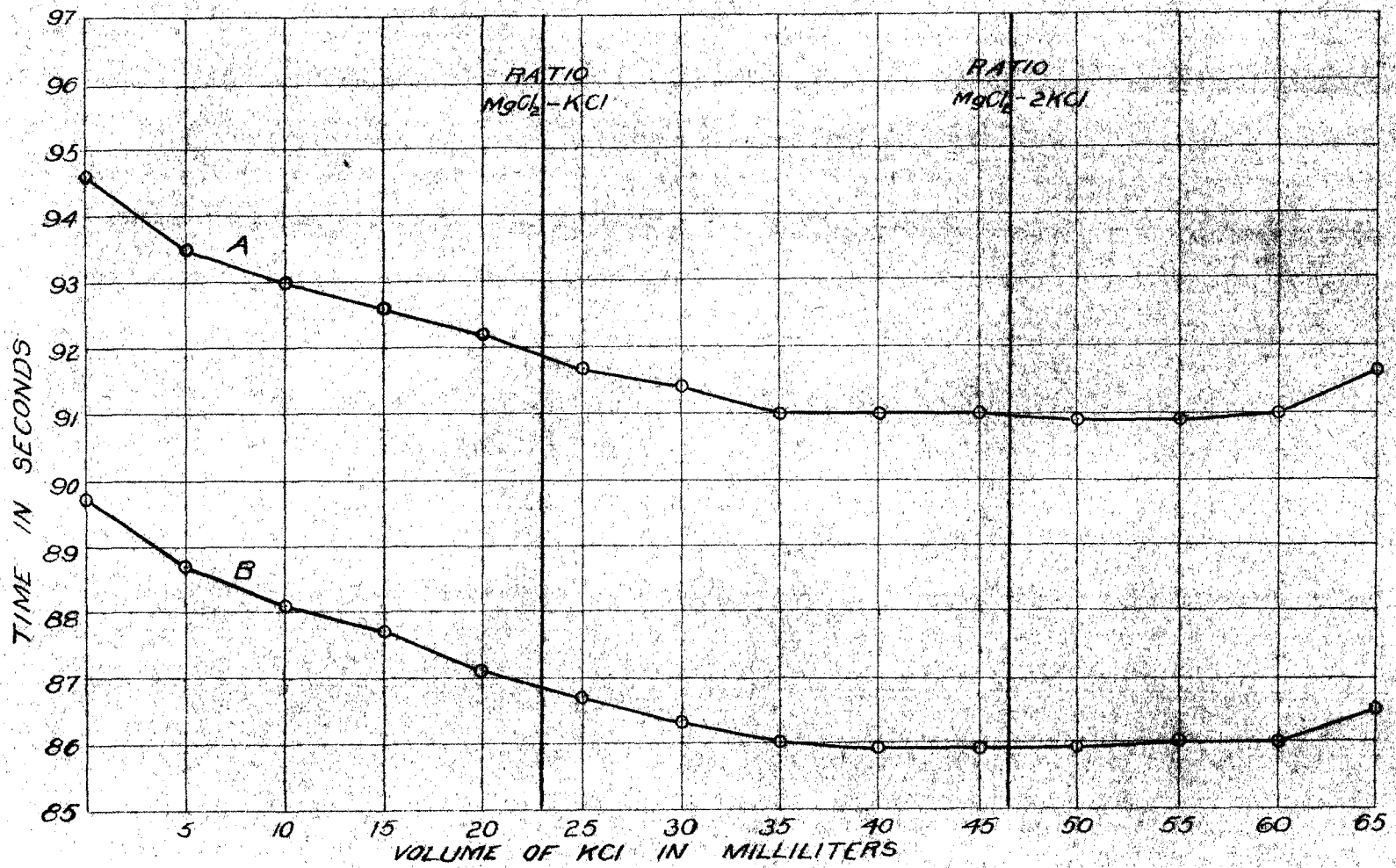


FIG. II. TIME OF FLOW OF  $KCl-MgCl_2$  MIXTURES.

Table III

Time of Flow of KCl-ZnCl<sub>2</sub> Mixtures

Volume of ZnCl <sub>2</sub>	Volume of KCl	Total Volume	Time A	Time B
25 ml	0 ml	100 ml	1'22.3''	1'18.2''
25 ml	5 ml	100 ml	1'20.8''	1'16.4''
25 ml	10 ml	100 ml	1'19.4''	1'14.9''
25 ml	15 ml	100 ml	1'17.9''	1'13.7''
25 ml	20 ml	100 ml	1'16.6''	1'12.2''
25 ml	25 ml	100 ml	1'15.5''	1'11.1''
25 ml	30 ml	100 ml	1'14.1''	1'10.1''
25 ml	35 ml	100 ml	1'13.3''	1' 9.0''
25 ml	40 ml	100 ml	1'12.0''	1' 8.2''
25 ml	45 ml	100 ml	1'11.2''	1' 7.0''
25 ml	50 ml	100 ml	1'10.2''	1' 6.4''
25 ml	55 ml	100 ml	1' 9.4''	1' 5.5''
25 ml	60 ml	100 ml	1' 8.8''	1' 4.8''

These data are presented graphically in Figure III.

Potassium Chloride Solutions

In order to have some means of judging the effect of the potassium chloride, determinations were made using varying concentrations of potassium chloride with no other salt present. The potassium chloride solution used in this experiment was 3.8815 molar.

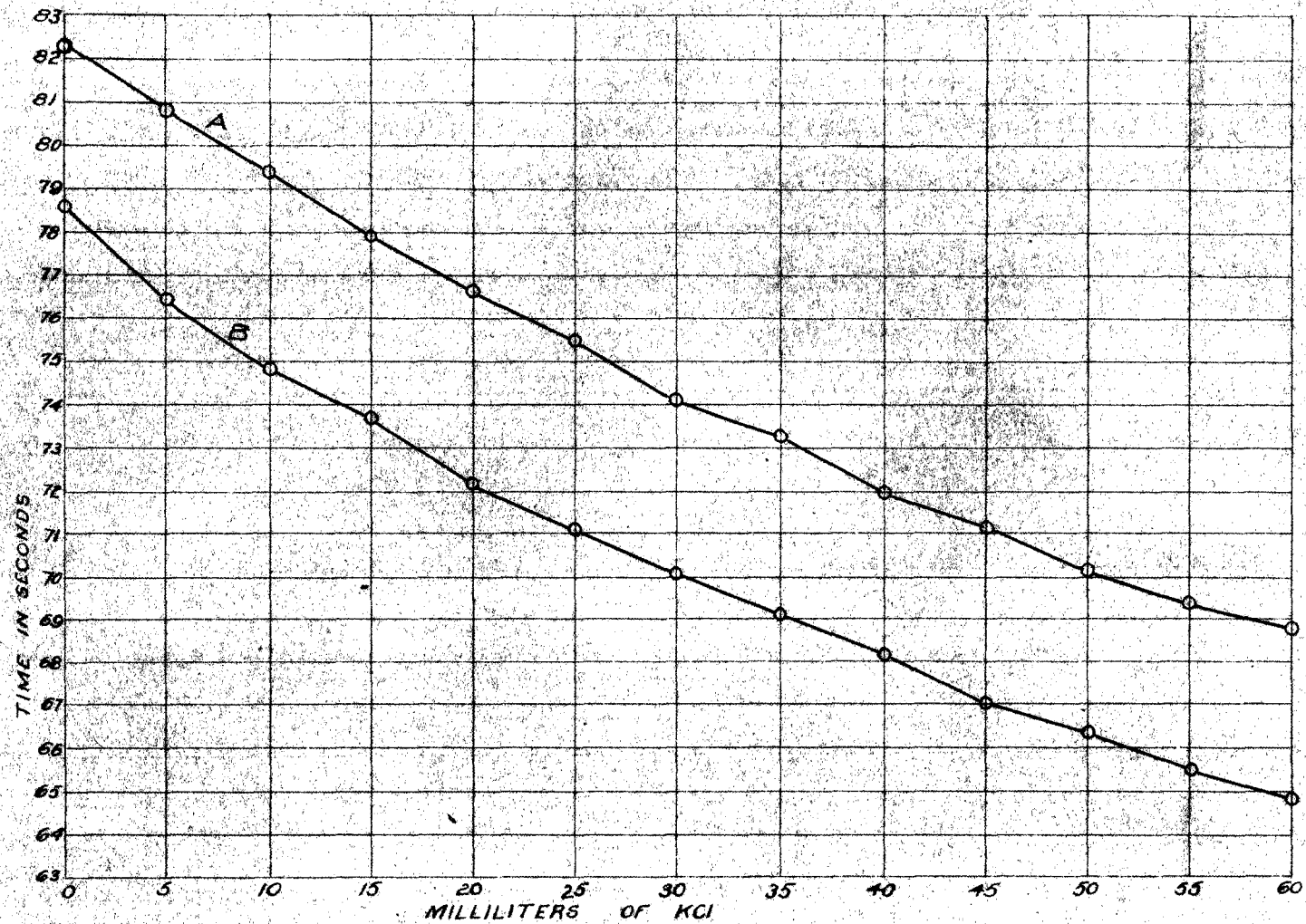


FIG. III. TIME OF FLOW OF KCl-ZnCl<sub>2</sub> MIXTURES

Table IV  
Time of Flow of KCl Solutions

Volume of KCl	Total Volume	Time A	Time B
0 ml	100 ml	1' 10.5''	1' 6.5''
10 ml	100 ml	1' 9.1''	1' 5.1''
20 ml	100 ml	1' 7.9''	1' 4.1''
30 ml	100 ml	1' 6.8''	1' 3.2''
40 ml	100 ml	1' 6.3''	1' 2.8''
50 ml	100 ml	1' 5.5''	1' 1.9''
60 ml	100 ml	1' 5.0''	1' 1.6''
75 ml	100 ml	1' 4.7''	1' 1.3''
80 ml	100 ml	1' 4.6''	1' 1.1''
85 ml	100 ml	1' 4.8''	1' 1.2''
90 ml	100 ml	1' 4.8''	1' 1.1''
100 ml	100 ml	1' 4.9''	1' 1.5''

These data are presented graphically in Figure IV.

#### Discussion of Results and Conclusions

An inspection of the results in Tables I, II and III and the graphic presentation of these results in Figures I, II and III shows that the only sign of a break is on the ammonium chloride and magnesium chloride mixture at the ratio corresponding to the compound  $(\text{NH}_4)_2\text{MgCl}_4$ . This break is so very slight that one is almost forced to conclude that it is due to an error in manipulation rather than to the formation of a complex, although it is of about the same magnitude in the two curves in Figure I. With the precision attained in these experiments it might have been possible for a break, if it



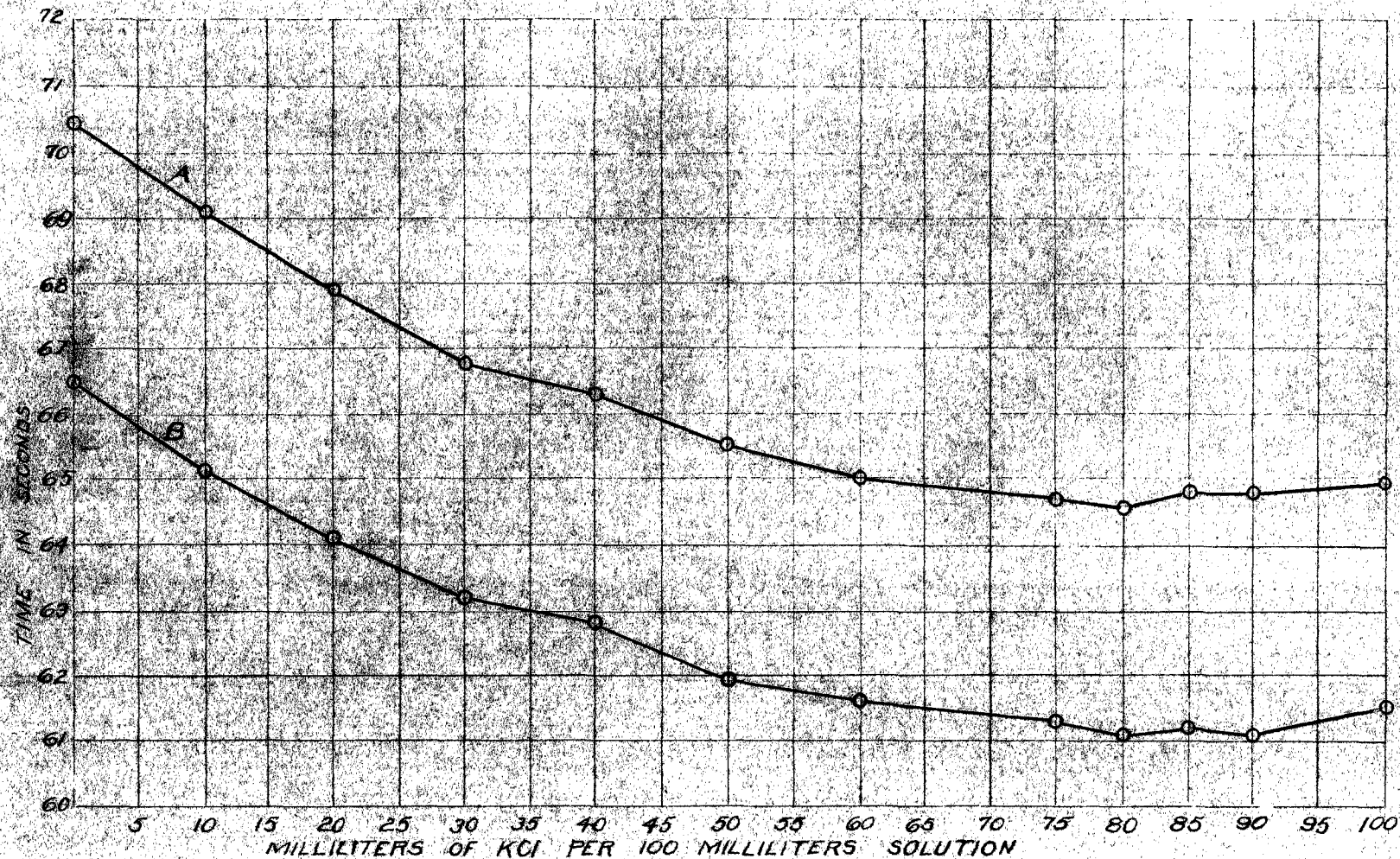


FIG. IV. TIME OF FLOW OF KCl SOLUTIONS

were not very sharp, to have escaped detection. From the work of Dunstan and Langston (2) one would expect the break to be definite enough to have been detected. The viscosity determinations offer fair evidence that at the concentrations used in these experiments complex salts do not exist in the solutions studied.

A STUDY OF THE INDICES OF REFRACTION OF MIXTURES OF  
AMMONIUM CHLORIDE AND MAGNESIUM CHLORIDE SOLUTIONS

The refractive index, being an additive property except when a difference of combination is effected, was resorted to in order to determine if a complex was formed in the case of mixtures of ammonium chloride and magnesium chloride solutions. The ammonium chloride used in this experiment was 5.002 molar and the magnesium chloride was 4.746 molar. The concentrations were determined as in the previous experiments. It was found necessary to reduce the concentrations used in order to keep the reading on the scale of the immersion type refractometer which was used in the experiment. Hence the solutions used in this determination are approximately four-tenths as strong as those used in the viscosity determinations.

Table V

Refractometer Reading for  $\text{NH}_4\text{Cl}$ - $\text{MgCl}_2$  Mixtures

Volume of $\text{MgCl}_2$	:	Volume of $\text{NH}_4\text{Cl}$	:	Total Volume	:	Refractometer Reading
10 ml	:	0.0 ml	:	100 ml	:	37.1
10 ml	:	2.5 ml	:	100 ml	:	40.5
10 ml	:	5.0 ml	:	100 ml	:	43.9
10 ml	:	7.5 ml	:	100 ml	:	47.1
10 ml	:	10.0 ml	:	100 ml	:	50.2
10 ml	:	12.5 ml	:	100 ml	:	53.4
10 ml	:	15.0 ml	:	100 ml	:	56.8
10 ml	:	17.5 ml	:	100 ml	:	59.9
10 ml	:	20.0 ml	:	100 ml	:	63.1
10 ml	:	22.7 ml	:	100 ml	:	66.9
10 ml	:	25.0 ml	:	100 ml	:	70.0

These data are presented graphically in Figure V. The refractometer readings are plotted against the milliliters of the ammonium chloride solution per one hundred milliliters of the final solution.

#### Discussion of Results and Conclusions

In order to determine whether the refractive index curve could be used as a criterion for complex formation, determinations were made in the same manner using mercuric chloride and ammonium chloride. These salts had been reported by Shibata (17) and his co-workers, to form a complex of the type  $\text{NH}_4\text{HgCl}_3$ . Upon plotting the concentration of the ammonium chloride against refractometer readings, as was done for the

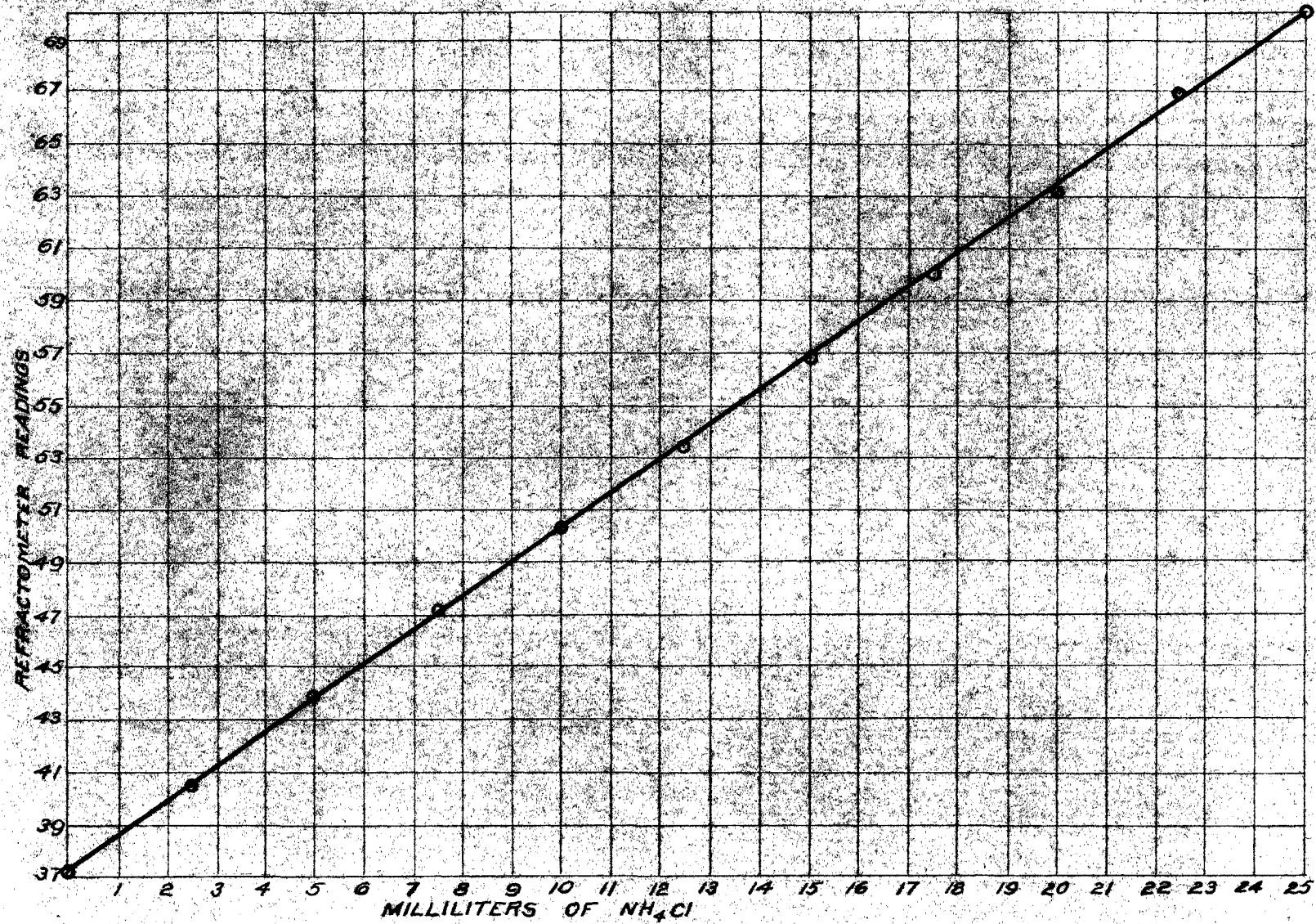


FIG. V. REFRACTOMETER READINGS FOR  $\text{NH}_4\text{Cl}$ - $\text{MgCl}$  MIXTURES.

previous mixture, a straight line was again obtained. One is thus forced to conclude that complex formation does not have large enough effect upon the refractive index to be detected by the immersion type refractometer.

#### ABSORPTION SPECTRA

The work of Shibata (17) and his co-workers shows that absorption ends, in the shorter wave length region, are shifted toward the longer wave lengths by complex formation. This effect is very definite and could scarcely escape detection if one works in the correct region. Their results were duplicated, in this laboratory, for a mixture of ammonium chloride and mercuric chloride in the ratio of one mole to one mole. The transmission extended much farther into the ultra-violet region for the mixture than for either of the salts alone. The observations were made between 2300 and 3000<sup>o</sup> Angstrom units using an iron spark. Observations were made on solutions of one molar magnesium chloride and one molar ammonium chloride and a mixture containing equal volumes of these solutions. No change in the absorption was noted. The absorption ends could not be noted due to the fact that the transmission had been extended beyond this region. The extension of the transmission was probably due to the hydrochloric acid which was added to the solutions in order to prevent hydrolysis of the magnesium chloride. Shibata (17), using the same method, found no evidence of complex formation between magnesium chloride and potassium chloride. He did not mention in what region he worked in this experiment.

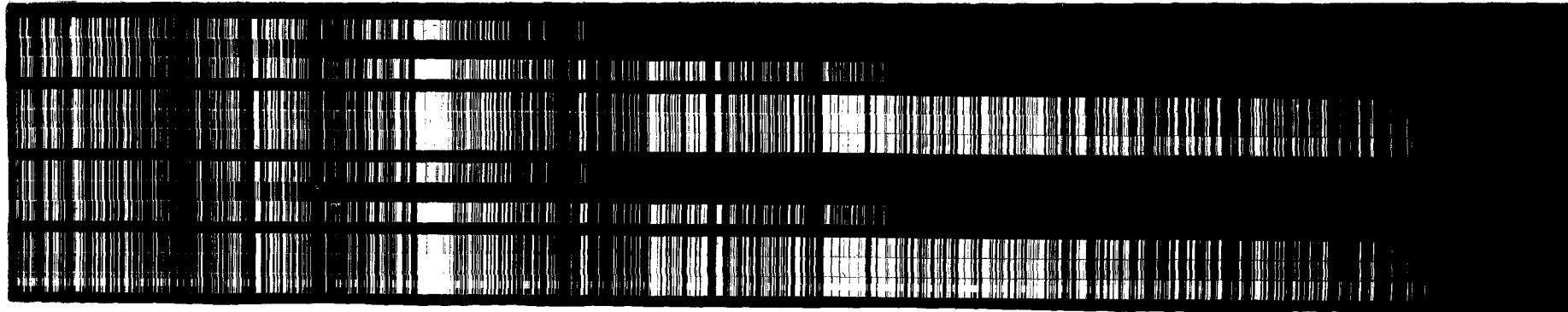


Plate I Absorption Spectra

- 1 - Top -  $\text{HgCl}_2$  0.1 M  
Center -  $\text{HgCl}_2$  0.05 M and  $\text{NH}_4\text{Cl}$  0.05 M  
Bottom -  $\text{NH}_4\text{Cl}$  0.1 M
- 2 - Top -  $\text{MgCl}_2$  1.0 M and  $\text{HCl}$  1.0 M  
Center -  $\text{MgCl}_2$  0.5 M,  $\text{NH}_4\text{Cl}$  0.5 M and  $\text{HCl}$  1.0 M  
Bottom -  $\text{NH}_4\text{Cl}$  1.0 M and  $\text{HCl}$  1.0 M
- 3 - Duplicate of 1
- 4 - Duplicate of 2



## GENERAL DISCUSSION OF RESULTS AND CONCLUSIONS

It must be admitted that the interpretation of the time of flow - concentration curves is open to the serious objection that there is not sufficient agreement in the literature on viscosity at present for one to draw a very firmly established conclusion. Since the experimental work was completed, Ishikawa (8) and his co-workers have done some work in an attempt to calculate the viscosities of solutions of electrolytes by means of a formula which has already been used successfully on solutions of nonelectrolytes. The observations of refractive indices should be given no weight in conclusions drawn as to complex formation, in view of the fact that a mixture reported, using absorption spectra data, to contain a complex gave negative results using this method. The absorption spectra study, which probably offers the surest method of attack, was very limited due to the inavailability of the proper apparatus.

Although no evidence of complex formation in the mixtures of ammonium chloride and magnesium chloride solutions was found, this lack of evidence is not necessarily proof that no complex is formed. This lack of evidence might well be attributed to the unsuitableness of these methods for detecting the presence of a complex in these mixtures.

Part II

THE ELECTROMETRIC DETERMINATION OF THE  
SOLUBILITY OF SOME HYDROXIDES

ELECTROMETRIC DETERMINATION OF THE  
SOLUBILITY OF SOME HYDROXIDES

INTRODUCTION

This part of the problem was undertaken in an attempt to ascertain the pH at which magnesium hydroxide precipitated and also to determine, if possible, whether this critical pH varied due to the presence of ammonium salts. If it were found that the presence of ammonium salts caused no variation in the pH at which magnesium hydroxide precipitated, then the question as to whether magnesium forms a complex with ammonium salts in dilute solution would be answered.

## HISTORICAL

Hildebrand (6), with more or less success, titrated calcium hydroxide and magnesium hydroxide in the presence of each other electrometrically. Britton (1) did considerable work on the precipitation of hydroxides and the determination of the pH at which these precipitations began. Britton (1) plotted potential against volume of sodium hydroxide added and in order to eliminate the error due to the rounding of the curve where precipitation first began, he projected the curves as straight lines and considered the point of intersection of these two lines as the point at which precipitation actually began. He assumed the equivalents of sodium hydroxide added to be the minimum amount of metal ion which could be present, and calculated the hydroxyl ion concentration from the potential in the usual manner. By this method he calculated the solubility products for five metallic hydroxides, magnesium, cobalt, nickel, manganese and ferrous iron with a very satisfactory agreement with the generally accepted values.

## EXPERIMENTAL

The determination of the solubility of some hydroxides electrometrically was tried by three distinct methods.

1. The determination of the pH at which precipitation began using ammonium hydroxide rather than sodium hydroxide as used by Britton (1).

2. The determination of the pH at which the hydroxide dissolved in a solution of ammonium chloride.

3. The determination of the pH of a saturated solution of the hydroxide.

No originality can be claimed for the first method as it embodies only a change in the precipitating agent used in the method suggested and used by Britton (1).

### Precipitation of Magnesium Hydroxide by Means of Sodium Hydroxide

Using the student type potentiometer set-up, an attempt was made to duplicate Britton's (1) work. Difficulty was encountered in noting the appearance of the precipitate but this was immaterial in the method used since the intersection of the two projections was taken as the point where

precipitation began. The potential of the original solution of magnesium chloride varied considerably and as this affected the slope of one of the lines, it caused the point of intersection to shift considerably, thus rendering it difficult to obtain consistent results. However as long as one used approximately the same strength base and the same strength magnesium chloride as Britton (1) used, the results were of the same order as that generally accepted for the solubility product of magnesium hydroxide. Using 0.5 normal instead of 0.1 normal sodium hydroxide and 0.1 molar magnesium chloride instead of 0.025 molar the potential, at which precipitation started, dropped considerably and hence the solubility product also dropped. This drop in potential is as one would expect from the law of mass action, that the higher the concentration of the metal the lower the pH that would be necessary to start precipitation, but is directly in opposition to Britton's (1) work in which he found that the pH at which precipitation took place was practically independent of the original concentration of the thorium salt.

Three determinations using the stronger solutions showed precipitates between a potential of 0.795 and 0.800 and between 0.25 and 0.30 of a milliliter of sodium hydroxide. Data for one titration are recorded in Table VI and the same data are presented graphically in Figure VI. Points

beyond twenty milliliters were not plotted as they do not enter into the calculations.

Table VI

Electrometric Titration at 20°C of 125 ml of 0.1M Magnesium Chloride with 0.5N Sodium Hydroxide

ml of NaOH	E.M.F.	ml of NaOH	E.M.F.	ml of NaOH	E.M.F.
0.0	0.5317	10.0	0.8100	43.0	0.8565
0.2	0.7876	15.0	0.8145	44.0	0.8620
0.4	0.7930	20.0	0.8185	45.0	0.8760
0.6	0.7995	25.0	0.8222	46.0	0.9054
0.8	0.8000	30.0	0.8275	47.0	0.9300
1.0	0.8000	35.0	0.8315	48.0	0.9420
1.2	0.8000	40.0	0.8472	49.0	0.9520
1.4	0.8000	41.0	0.8490	50.0	0.9585
5.0	0.8050	42.0	0.8497		

Calculation of results:

This determination was run at 20°C using a saturated calomel half cell. The calculation of the solubility product of magnesium hydroxide is shown below. The potential of the solution and the volume of sodium hydroxide at which precipitation started being read from the intersection of the two projections in Figure VI.

$$PH = (0.8000 - 0.2492) / 0.0581 = 9.48$$

$$POH = 14.07 - 9.48 = 4.59$$

$$4.59 = 1 / \log C_{OH} \text{ hence } C_{OH} = 2.57 \times 10^{-5}$$

$$C_{Mg} = (0.25 / 50) \times 0.1 = 5 \times 10^{-4}$$

$$K_{sp} \text{ of } Mg(OH)_2 = (5 \times 10^{-4}) (2.57 \times 10^{-5})^2 = 3.38 \times 10^{-12}$$

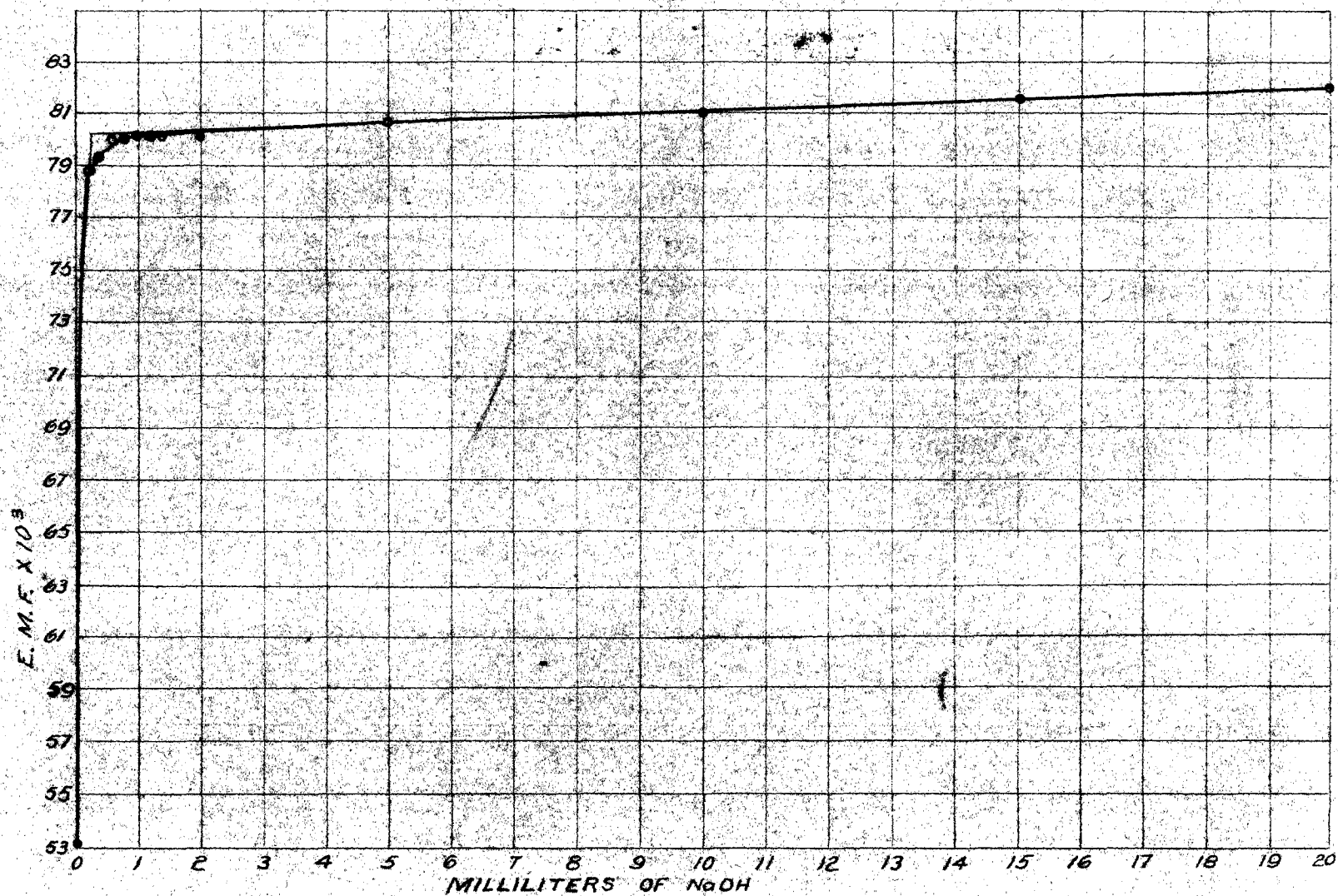


FIG. VI. PRECIPITATION OF  $Mg(OH)_2$



In the titration of one hundred milliliters of 0.025 molar magnesium chloride with 0.1 normal sodium hydroxide, the potential at which precipitation began was 0.855 and the volume of the sodium hydroxide necessary to start precipitation was 0.6 of a milliliter. The data for this titration are recorded in Table VII and are presented graphically in Figure VII. The temperature during the titration reported was 27.5°C.

Table VII

Electrometric Titration at 27.5°C of 100 ml of 0.025 M Magnesium Chloride with 0.1 N - Sodium Hydroxide

ml of NaOH	E.M.F.	ml of NaOH	E.M.F.	ml of NaOH	E.M.F.
0.0	0.575	0.9	0.841	20.0	0.858
0.2	0.772	1.0	0.844	25.0	0.861
0.4	0.825	1.1	0.845	30.0	0.876
0.5	0.829	3.0	0.855	35.0	0.873
0.6	0.831	5.0	0.855	40.0	0.884
0.7	0.836	10.0	0.854	45.0	0.912
0.8	0.839	15.0	0.855	50.0	0.943

Calculation of results:

$$P_H = (0.855 - 0.345) / 0.0596 = 10.24$$

$$P_{OH} = 13.81 - 10.34 = 3.57$$

$$3.57 = \log (1 / C_{OH}) \text{ hence } C_{OH} = 2.7 \times 10^{-4}$$

$$C_{Mg} = (0.6 / 50) \times 0.025 = 3 \times 10^{-4}$$

$$K_{SP} \text{ of } Mg(OH)_2 = (3 \times 10^{-4})(2.7 \times 10^{-4})^2 = 2.19 \times 10^{-11}$$

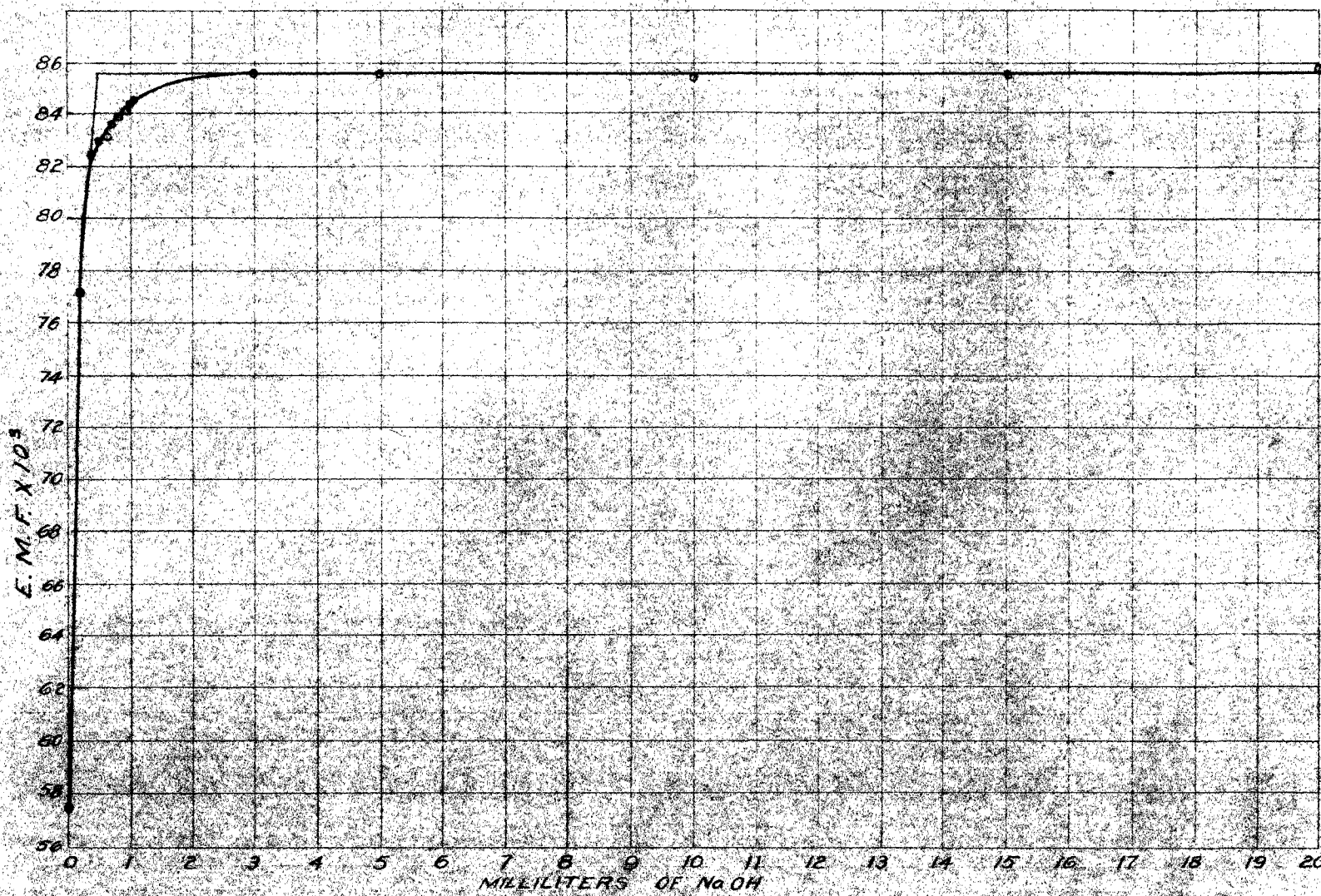


FIG. VII. PRECIPITATION OF  $Mg(OH)_2$

This result compares favorably with Britton's (1) value of  $2.3 \times 10^{-11}$  and Kohlrausch and Rose's (10) value of  $3.4 \times 10^{-11}$ . Gjaldbaek (3) attributes the variance in solubility reported, by different workers, to the existence of two forms of magnesium hydroxide, a stable and an unstable variety. The values for the potential of the solution and the volume of sodium hydroxide necessary to start precipitation were taken from the intersection of the two projections on Figure VII.

#### Precipitation of Magnesium Hydroxide by Means of Ammonium Hydroxide

It was thought that a more constant potential would be obtained if ammonium hydroxide were used instead of sodium hydroxide, as one would then be reading the potential of a buffered solution. The potential was found to be even more constant than had been expected as the hydrogen swept the excess of ammonia out of the solution. In seven experiments the potential never rose above 0.86 although in some of these 0.5 normal ammonium hydroxide was used and twice the amount necessary to precipitate the magnesium was added. In an experiment designed to check on this phenomenon however, the potential rose steadily upon the addition of 0.5 normal ammonium hydroxide to a saturated solution of magnesium hydroxide.

One hundred milliliters of a 0.05 molar solution of magnesium chloride was titrated with 0.25 normal ammonium hydroxide. The experiment was run at 27.5°C. The data are recorded in Table VIII and are presented graphically in Figure VIII.

Table VIII

Electrometric Titration at 27.5°C of 100 ml of 0.05 M Magnesium Chloride with 0.25 N - Ammonium Hydroxide

ml of NH <sub>4</sub> OH	:	E.M.F.	:	ml of NH <sub>4</sub> OH	:	E.M.F.	:	ml of NH <sub>4</sub> OH	:	E.M.F.
0.0	:	0.580	:	1.0	:	0.840	:	25.0	:	0.855
0.2	:	0.807	:	5.0	:	0.857	:	30.0	:	0.855
0.4	:	0.825	:	10.0	:	0.861	:	35.0	:	0.855
0.6	:	0.833	:	15.0	:	0.859	:	40.0	:	0.855
0.8	:	0.836	:	20.0	:	0.855	:	50.0	:	0.859

Calculation of results:

From Figure VIII the potential of the solution and the volume of ammonium hydroxide at which precipitation began are taken as 0.853 and 0.3 of a milliliter respectively.

$$PH = (0.835 - 0.245) / 0.0596 = 10.19$$

$$POH = 13.81 - 10.19 = 3.62$$

$$COH = 2.4 \times 10^{-4}$$

$$CMG = (0.3 / 40) \times 0.05 = 3.75 \times 10^{-4}$$

$$K_{sp} \text{ of } Mg(OH)_2 = (3.75 \times 10^{-4})(2.5 \times 10^{-4})^2 = 2.34 \times 10^{-11}$$

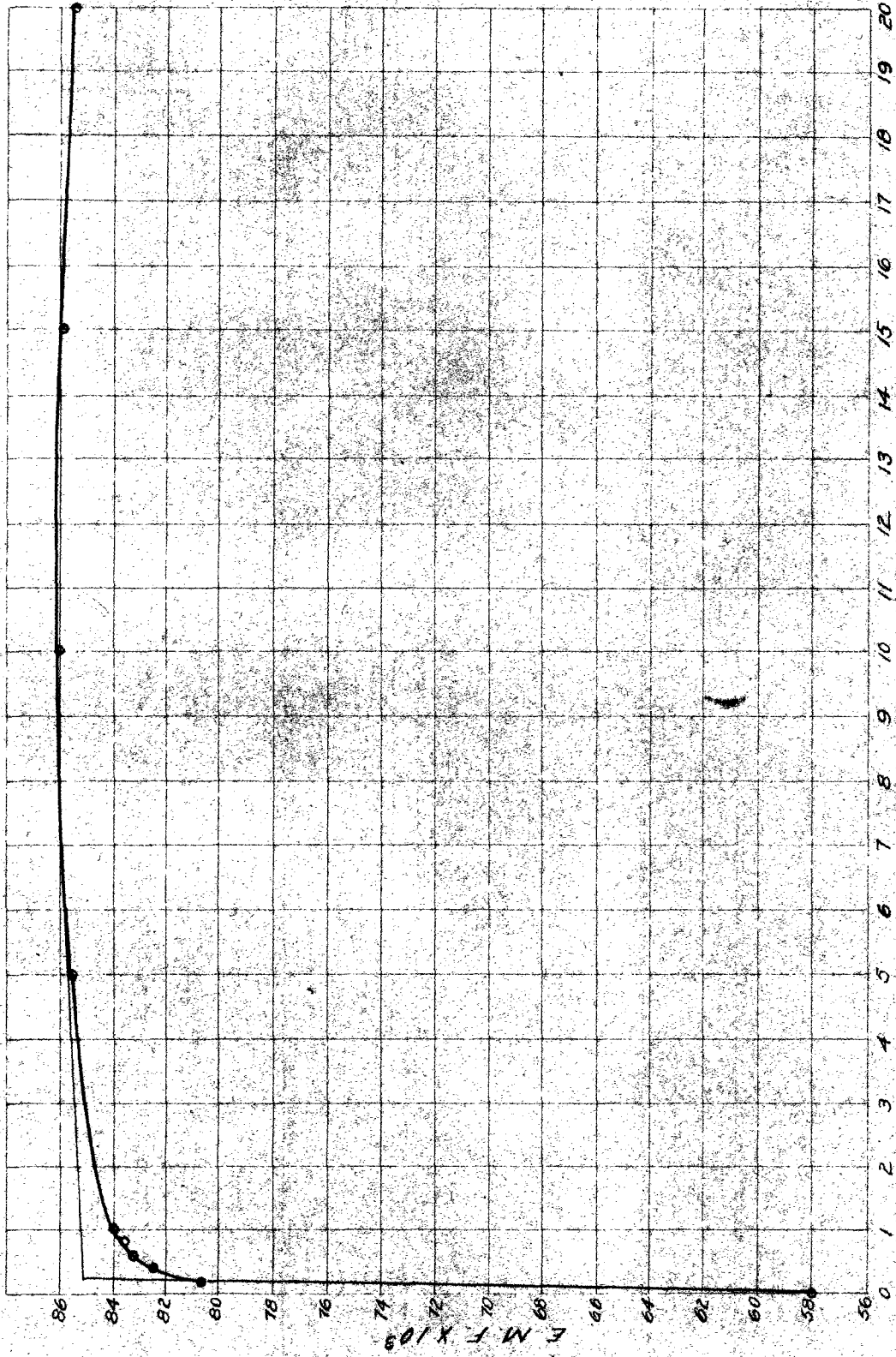


FIG. VIII. PRECIPITATION OF  $\text{Mg}(\text{OH})_2$

Attention should be called to the fact that all the results with ammonium hydroxide do not check this value. The value found for the solubility product in the seven experiments varied from  $1.7 \times 10^{-11}$  to  $4 \times 10^{-11}$ . One can, however, determine the order of magnitude of the solubility product for magnesium hydroxide by this method.

#### Precipitation of Other Hydroxides by Means of Ammonium Hydroxide

Zinc and nickel, as was to be expected, gave no results with this method due to complex formation with the ammonia. Ferrous iron, although run in a closed cell, showed signs of oxidation and gave results that varied widely. Cadmium, due probably to its reduction to the univalent state, could not even be read. Using one hundred milliliters of tenth normal cadmium chloride, the potential rose on the addition of three normal ammonium hydroxide, from 0.350 to 0.450 upon the gradual addition of five milliliters of the hydroxide. At this point the potential dropped rapidly and the polarity reversed. The addition of sufficient ammonium hydroxide to almost clear up the solution had no effect. The electrode had the appearance of one poisoned by mercury and acted similarly in that it was restored by treatment with concentrated nitric acid. The potential obtained using the reconditioned electrode was 0.721

but again rapidly dropped off. Upon repeating the experiment with a new solution and a different electrode, similar results were obtained. Britton (1) states that the hydrogen electrode is inapplicable to cadmium salts and resorts to the oxygen electrode.

#### Dissolving Magnesium Hydroxide in Ammonium Chloride

It was attempted to approach the equilibrium from the other side, that is, by dissolving the precipitates formed in the experiments above in approximately one molar ammonium chloride solution and noting the pH at which the precipitate disappeared. In this method there would be no question as to the correct value of the magnesium concentration, if one knew the volume of the standard magnesium chloride added and the final volume at which the precipitate disappeared. Difficulty was encountered in telling exactly when the precipitate disappeared, and it is doubtful if these values are closer than five milliliters. This discrepancy would make no appreciable difference in the values of the magnesium concentration, but it made, in some cases, as much as four millivolts difference in the potential, and this does make an appreciable difference in the solubility product calculated. A decrease of four millivolts will decrease the solubility product approximately thirty-five per cent. Evidently even this precision

was not attained since the values found in six determinations varied from  $1.1 \times 10^{-11}$  to  $9.2 \times 10^{-11}$ . In one experiment two hundred milliliters of 0.025 molar magnesium chloride, to which had been added twenty-five milliliters of 0.5 normal ammonium hydroxide, were titrated with one molar ammonium chloride solution. It required fifty milliliters of the ammonium chloride to clear up the solution. This experiment was run at  $30^{\circ}\text{C}$ . The potential noted when the solution cleared up was 0.8016.

Calculation of results:

$$C_{\text{Mg}} = (200 \times 0.025) / (200 + 25 + 50) = 1.8 \times 10^{-2} \text{ if complete ionization of the } \text{MgCl}_2 \text{ is assumed.}$$

$$p_{\text{H}} = (0.8016 - 0.2437) / 0.0601 = 9.30$$

$$p_{\text{OH}} = (13.73 - 9.30) = 4.43 \text{ hence } C_{\text{OH}} = 3.7 \times 10^{-5}$$

$$K_{\text{sp}} = (1.8 \times 10^{-2})(3.7 \times 10^{-5})^2 = 2.5 \times 10^{-11}$$

The same objection can be offered to this method as to the previous one, that one is able to obtain the solubility product only accurate as to the order of magnitude.

Saturated Solution of Magnesium Hydroxide

The next experiment was an attempt to determine the pH of a saturated solution of magnesium hydroxide and from this, calculating the solubility product of the hydroxide. The solutions were made in four different ways:



1. Magnesium hydroxide was precipitated by means of a base and washed free of the anion. The precipitated magnesium hydroxide was then suspended in water. An excess of salt was used to render the removal of the base easier.

2. The solution was prepared in exactly the same manner as in the first method except that an excess of base was used and the precipitate was allowed to stand in contact with the excess base for several hours in order to prevent the formation of basic salts.

3. The chemically pure grade of magnesium oxide was washed thoroughly with hot water and then suspended in water.

4. Magnesium oxide was prepared by calcining magnesium carbonate. The oxide was then suspended in water.

The values obtained in this manner varied from  $2.45 \times 10^{-12}$  to  $8.3 \times 10^{-11}$ , the higher values being obtained using the magnesium oxide. The explanation of this difference is probably the precipitation of basic salts rather than the pure hydroxide. The precision of these experiments is slightly less than that obtained in the other two methods, but the manipulation is simpler. The temperature varied from  $18^{\circ}\text{C}$  to  $29^{\circ}\text{C}$  and did not seem to affect the solubility product appreciably. In some of the experiments both the hydrogen electrode and calomel half cell were in a constant temperature bath, in others both were out of the bath, and

in some the hydrogen electrode was in the bath and the calomel half cell outside. These variations seemed to have no consistent effect on the results obtained. Sample calculations on two of these determinations are given below.

Calculation of results:

A. This solution was prepared from calcined magnesium carbonate. The solution containing the hydrogen electrode was in the constant temperature bath at 19°C and the temperature of the saturated calomel half cell above the bath was 28°C. The observed potential was 0.866, which was constant within 0.5 of a millivolt.

$$p_H = (0.866 - 0.2503 + 9 \times 0.0002) / 0.0579 = 10.61$$

$$p_{OH} = 14.10 - 10.61 = 3.49$$

$$C_{OH} = 3.2 \times 10^{-4}$$

$$C_{Mg} = 1.6 \times 10^{-4}$$

$$K_{SP} = (1.6 \times 10^{-4})(3.2 \times 10^{-4})^2 = 1.6 \times 10^{-11}$$

B. This solution was prepared from magnesium hydroxide which had been precipitated with an excess of ammonium hydroxide from a magnesium chloride solution and then washed free of chloride. Both the hydrogen electrode and the calomel half cell were in the air at 29°C. The potential was 0.843, constant within two millivolts.

$$P_H = (0.843 - 0.244) / 0.0599 = 10.00$$

$$P_{OH} = 13.76 - 10.00 = 3.76$$

$$P_{OH} = \log (1 / C_{OH}) \text{ hence } C_{OH} = 1.7 \times 10^{-4}$$

$$C_{Mg} = 0.85 \times 10^{-4}$$

$$K_{SP} = (0.85 \times 10^{-4})(1.7 \times 10^{-4})^2 = 2.45 \times 10^{-12}$$

#### Saturated Solution of Calcium Hydroxide

A solution made by suspending calcium oxide, which had been prepared by calcining calcium carbonate, in water recently boiled, gave potentials of 1.0165 and 1.0183 at 25°C using a one normal calomel half cell and 0.9810 at the same temperature using a saturated calomel half cell. In these three determinations the calomel half cell was not in the bath and was at 30°C. These values when calculated to grams of calcium oxide per hundred milliliters of solution, allowance being made for the ionization of this concentration of calcium hydroxide, gave values of 0.1115, 0.1147 and 0.1141 respectively. These values compare very favorably with the calculated value of 0.1148 g. per hundred milliliters of water from Moody and Leyson's (13) work on the solubility of calcium oxide. The calculation of the last value is given below.

Calculation of results:

$$p_H = (0.9810 - 0.2464 + 0.002 \times 5) / 0.0591 = 12.45$$

$$p_{OH} = 13.90 - 12.45 = 1.45 \text{ hence } C_{OH} = 3.55 \times 10^{-2}$$

$$\text{Solubility} = \left( \frac{455}{406} \right) \times \left( \frac{3.55 \times 10^{-2}}{30} \right) \times 56.07 = 0.1141 \text{ g. per hundred milliliters.}$$

The factor 455 / 406 is made up of the molar conductivity at infinite dilution and the molar conductivity at this dilution as found by Ostwald (14).

Saturated Solution of Zinc Hydroxide

Zinc hydroxide prepared by precipitation, by means of an excess of ammonium hydroxide, from a hot solution of zinc chloride and washing free of the chloride ion gave values varying from 0.706 to 0.735 for the potential. The solution which gave a potential of 0.726 or a pH of 7.63 was checked colormetrically using phenol red and standard boric acid - borax buffers and found to be between 7.36 and 7.60 and much closer to the 7.60. Zinc oxide, that had been well washed, was suspended in water and gave potentials varying between 0.7055 and 0.7070. Zinc hydroxide prepared by adding zinc chloride to a solution of sodium zincate and washing the precipitate free from the chloride ion gave a potential of 0.7045. All of these determinations were run between 18°C and 20°C using a one molar calomel half cell. Using the value

0.707 for the potential found at 20°C one calculates the solubility product to be  $1.69 \times 10^{-21}$  which is completely out of line with the generally accepted value of  $1.8 \times 10^{-14}$  reported by Herz (4), but agrees fairly well with Britton's (1) value of approximately  $10^{-21}$ . The amphoteric nature of zinc hydroxide, however, renders the calculations by the above method somewhat questionable.

#### Saturated Solution of Lanthanum Hydroxide

The value of the potential, given by freshly precipitated lanthanum hydroxide varied widely but, after thoroughly washing the precipitate, several solutions gave results between 0.776 and 0.784 at 25°C. Using the mean value 0.780 and calculating the solubility in terms of grams of lanthanum sesquioxide one obtains 0.0080 g. per liter. A careful search of the literature failed to reveal any work on the solubility of lanthanum sesquioxide in water but a value of 0.004 g. per hundred milliliters of water is reported in the Handbook of Chemistry and Physics (7).

#### Saturated Solution of Thorium Hydroxide

The thorium hydroxide was prepared in four ways:

1. By suspending thorium dioxide, prepared by igniting thorium oxalate, in water.

2. By precipitating thorium hydroxide from thorium sulphate by means of sodium hydroxide. The thorium sulphate was made by heating thorium oxalate with concentrated sulphuric acid.

3. By precipitating thorium hydroxide by means of ammonium hydroxide, from a solution of thorium oxalate in ammonium oxalate.

4. By precipitating thorium nitrate by means of ammonium hydroxide.

The solution prepared from the thorium dioxide gave the most nearly reproducible potential but even this varied by as much as ten millivolts from 0.728 to 0.738 at 24°C. In an unbuffered solution of this concentration some variation should be expected. Taking the mean of these two values the solubility of thorium hydroxide was calculated.

Calculation of results:

$$p_H = (0.733 - 0.285) / (0.0589) = 7.43$$

$$p_{OH} = 13.93 - 7.43 = 6.50 \text{ hence } C_{OH} = 3.2 \times 10^{-7}$$

$$\text{Solubility of Th(OH)}_4 = (3.2 \times 10^{-7}) / (4) = 8 \times 10^{-8}$$

of a mole per liter

$$8 \times 10^{-8} \times 300.5 = 2.4 \times 10^{-5} \text{ g. per liter}$$

This value agrees in order of magnitude with the solubility of  $\text{Th(OH)}_4$  reported by Spitzin (20) of  $2 \times 10^{-5}$  g. per liter.

The other solutions gave values for the potential which varied widely from a low of 0.496 to 0.8695. The higher values are probably due to the difficulty encountered in washing the precipitate free of the base used in the precipitation, and the lower values due to basic salts being present rather than the hydroxide. Britton (1) reports that basic salts are precipitated in all cases for thorium and that their composition varies with the anion present and with the base used as the precipitating agent.

#### Saturated Solution of Strontium Hydroxide

The strontium hydroxide solutions used in this experiment were prepared in two ways. The first method was to saturate a solution with strontium oxide, formed by calcining strontium carbonate in a high temperature gas furnace, using a fire clay crucible to hold the material. The size of the furnace necessitated the preparing of small batches of the oxide and although checks were obtained on the potential determinations, solubility data by other methods varied so that it was thought the product might not be uniform, although recrystallization was resorted to in order to assure the purity of the product. Some strontium hydroxide octahydrate was secured and this was run both with and without recrystallization.

Four solutions prepared from the calcined strontium carbonate and two prepared from the octahydrate when run at

25°C gave potentials which checked within three millivolts. One of these solutions was run using both a saturated and a normal calomel half cell and the results, when the pH of the solution was calculated, checked within 0.005 pH. This check was probably by chance as the accuracy of the method is not thought to be this high, as it would necessitate a checking in potential of 0.3 millivolts and this cannot be done consistently. The observed potentials on the six solutions were 1.0070, 1.0079, 1.0087, 1.0094, 1.0061, and 1.0084 with a saturated calomel half cell. The solution, giving the last reading, when checked with a normal calomel half cell gave 1.0463. The pH's calculated from the above results, using barometric corrections, were 12.89, 12.90, 12.91, 12.92, 12.86, 12.902, and 12.897. The last results were reported to three decimals as they are the same solution run against the two half cells. Using the conductivity data of Ostwald (14) and the solubility data reported later in this problem, the fraction ionized was calculated and used in the calculation of the solubility of strontium oxide from the electrometric data. Sample calculations using the highest and lowest pH found are given below. A saturated solution of strontium oxide contains approximately 8.55 grams per liter at 25°C and this is approximately one twelfth molar. The molar conductivity of strontium hydroxide at infinite dilution is 452 and the extrapolated value for one twelfth molar is 381.



Calculation of results:

(A)  $p_{OH} = 13.90 - 12.92 = 0.98$

$C_{OH} = 0.105$

Solubility =  $(0.105 / 20) \times (452 / 381) \times 103.63 =$   
0.644 g. per 100 ml

(B)  $p_{OH} = 13.90 - 12.86 = 1.04$

$C_{OH} = 0.0912$

Solubility =  $(0.0912 \times 2) \times (452 / 381) \times (103.63 \times 10) =$   
0.561 g. per 100 ml

Solubility of Strontium Oxide

The values found for the solubility of strontium oxide were at such variance from those found in the literature it was deemed advisable to determine the solubility by ordinary analytical methods. Sidersky (16,18), by plotting values actually found and reading the other values from the curve, reported 0.82 g. per hundred grams or 0.83 g. per hundred milliliters of solution as the solubility at 25°C. Riedel (15) reported one isolated determination at 25°C of 0.1639 of an equivalent weight per liter which calculated to grams per hundred milliliters gives 0.849 as the solubility.

The solubility was determined by three different methods, namely volumetric, precipitation and evaporation. In the volumetric method both direct titration, using methyl orange

as the indicator, and back titration after an excess of standard acid had been added and the solution heated to boiling were tried. The back titration method gave results more nearly in agreement with the other methods. The precipitation method used was the ordinary precipitation of strontium sulphate in an alcoholic solution. In the evaporation method five milliliters of approximately six normal sulphuric acid were added to twenty-five milliliters of the strontium hydroxide in a tared platinum dish and the solution evaporated to dryness and fumed in an air bath. The residue was then ignited for thirty minutes over a Bunsen flame.

Difficulty was encountered in getting solutions made from different batches of strontium oxide to give consistent results. This was at first attributed to impurities in the material but later was found to be due to the fact that strontium hydroxide has a tendency to form supersaturated solutions which take considerable time to come to equilibrium. For this reason in the later determinations the solutions were placed in the constant temperature bath and allowed to remain there several days, with frequent shaking, before the samples were taken out. Another difficulty encountered was the formation of some strontium carbonate in the solution, in spite of the fact that the water used in preparing the solutions was boiled and added hot to the recrystallized

hydroxide. This difficulty was overcome by filtering while hot into a flask from which boiling water had just been poured. Solutions made in this way were very clear and if allowed to cool slowly, so as to insure large crystals, were easy to sample by means of a pipette.

Some difficulty was encountered in getting results by the three methods to check closer than two or three parts per thousand on the same solution. Twenty-five milliliter samples of the strontium hydroxide prepared by combining strontium carbonate yielded the following weights of strontium sulphate 0.3787, 0.3790, 0.3781, 0.3788, 0.3788, 0.3793, 0.3788, 0.3805, 0.3785, 0.3779, 0.3780, 0.3808, 0.3780, and 0.3788 or a mean value of 0.3788 for the fourteen determinations. The same size samples when run by the evaporation method yielded 0.3787, 0.3788, 0.3789, 0.3790, 0.3784, and 0.3785 g. of strontium sulphate, or a mean value of 0.3789. For some unknown reason the volumetric determinations did not check with these values and it was attributed to impurities in the strontium oxide. Part of the trouble was probably due to attempting to run the volumetric determinations by direct titration. The strontium hydroxide absorbed carbon dioxide from the air and the precipitated strontium carbonate dissolved very slowly, hence a false end point was obtained and the results ran low. Three sets of checks by the volumetric

method gave 0.8482, 0.8482, and 0.8486 g. of strontium oxide per hundred milliliters. The values given above for the precipitation and evaporation method when calculated to grams of strontium oxide per hundred milliliters give 0.8548 and 0.8550 respectively.

Due to the fact that several values, which later were thrown out as being supersaturated, were considerably higher it was thought that the product formed by calcining strontium carbonate was not uniform. To remedy this some strontium hydroxide octahydrate, of the chemically pure grade, was secured and the solutions made from the crystals formed from this by recrystallization. It was found that the concentration of these solutions gradually dropped for as long as twenty-four hours after coming to the temperature of the bath. The time required for reaching equilibrium was prolonged, no doubt, by the fact that it was necessary to allow the solutions to stand unshaken for about four hours before sampling in order to obtain samples free from the precipitate. The solutions, after that, were allowed to stay in the bath for two or three days with frequent shaking before sampling. The results obtained on four solutions prepared in this manner are given in Table IX. The columns headed A and B under evaporation and precipitation are grams of strontium sulphate obtained from twenty-five milliliters of solution

and grams of strontium oxide per hundred milliliters respectively.

Table IX  
Solubility of Strontium Oxide at 25°C

No.	Solution : Volumetric:		Evaporation		Precipitation	
	A	B	A	B	A	B
1	0.8557	0.3787	0.8548	0.3793	0.8559	0.8510
1	0.8539	0.3785	0.8541	0.3771	0.8548	0.8570
1	0.8549	0.3780	0.8530	0.3798	0.8533	0.8562
1	0.8555			0.3798	0.8375	0.8577
2	0.8539			0.3790	0.8571	0.8593
2	0.8541			0.3794	0.8575	0.8553
3	0.8541	0.3782	0.8535	0.3800	0.8559	0.8559
3	0.8553	0.3780	0.8530	0.3801	0.3808	0.8505
3	0.8545	0.3793	0.8559	0.3798	0.3790	0.8553
3	0.8541	0.3794	0.8562	0.3808	0.3793	0.8559
3		0.3781	0.8532	0.3880		
4	0.8547	0.3786	0.8544	0.3790		
4	0.8547	0.3781	0.8532			
4	0.8541	0.3805	0.8587			
4	0.8530	0.3798	0.8550	0.3769		
4	0.8533					
Mean	0.8544	0.3787	0.8546	0.3792		

Although the checks on the individual determinations are not very close it seems reasonable to conclude that the solubility of strontium oxide at 25°C is 0.855 g. per hundred milliliters of solution.

In order to compare the solubility found with that reported by Sidersky, it was converted to grams per hundred grams. The density of the strontium hydroxide solution was determined by weighing twenty-five milliliters of the solution. Duplicate determinations gave the density to be

1.0065. The solubility of strontium oxide, expressed in grams per hundred grams of solution is found to be 0.855 / 1.0065 or 0.850. The value thus determined and checked by three methods exceeds the solubility of 0.82, reported by Sidersky (16, 18) much more than could be attributed to experimental error.

## DISCUSSION OF RESULTS AND CONCLUSIONS

With our present lack of knowledge of even the correct potentials of our standard calomel half cell, one would be very bold to claim an accuracy greater than just the order of magnitude of any mass action constant determined electrometrically. Results obtained using Lewis, Brighton, and Sebastian's (11) value for their standard normal calomel electrode, and results obtained using Sorensen's (19) value for his standard tenth normal electrode vary by about two millivolts. This difference in ordinary electrometric titrations is immaterial, but in determining mass action constants it becomes very significant. A drop of two millivolts in potential will cause the solubility product of the hydroxide of a divalent metal to be reduced approximately twenty per cent, and will cause the solubility in moles or grams to be reduced about eight per cent.

Activity coefficients should have been brought into the calculations for the more soluble hydroxides, but sufficient data were not available in the literature to make use of activity.

From a comparison of the results obtained in the titration of magnesium chloride with 0.1 molar sodium hydroxide

and those obtained using 0.1 molar ammonium hydroxide, one is justified in the conclusion that in dilute solutions magnesium chloride and ammonium chloride do not form a complex salt, and the failure of magnesium to precipitate as a hydroxide in the presence of ammonium salts is due entirely to the repression of the ionization of the ammonium hydroxide by the common ion.

The use of ammonium hydroxide in precipitating hydroxides is not considered preferable to sodium hydroxide although it gives a more constant potential, during the precipitation, as it has the disadvantage of forming complexes with a number of metallic ions and thus limits the use of the method in determining the solubility of hydroxides.

The determination of pH's at which hydroxides dissolve in ammonium chloride did not prove very satisfactory. The difficulty in observing the exact point at which the hydroxide dissolves renders this method somewhat inaccurate. The use of a photoelectric cell might eliminate or reduce this difficulty.

The determination of the pH's of saturated solutions of hydroxides of magnesium, thorium, calcium, and strontium gave results, when calculated to solubility or to solubility product, at least of the same order of magnitude as those generally accepted. No doubt the use of this method could be extended by the substitution of a nonreducing electrode for



the hydrogen electrode. The results obtained by this method for amphoteric elements are questionable.

The solubility of strontium oxide as reported by Riedel (15) at 35°C is much closer to the correct value than that reported by Sidersky (16,18) for this temperature from his curve. The error in Sidersky's (16,18) determinations might be expected to be large, due to the fact that one normal hydrochloric acid was used in his titrations.

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