

3. In using isohydric indicator solutions and applying the proper salt corrections, the  $P_H$  of pure water has been determined with brom thymol blue and phenol red at 25° with an accuracy of 0.05 in  $P_H$ . With isohydric phenolphthalein or thymol blue solutions, the  $P_H$  of extremely dilute sodium hydroxide solutions has been measured with an accuracy of 0.1 in  $P_H$ .

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## THE HYDROLYSIS OF ZINC SULFATE SOLUTIONS, SOLUBILITY PRODUCT OF HYDROUS ZINC OXIDE AND THE COMPOSITION OF THE LATTER PRECIPITATED FROM ZINC SULFATE SOLUTIONS

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1. **Hydrolysis of Zinc Sulfate.**—For two reasons no reliable data on the hydrolysis of solutions of zinc sulfate are given in the literature; in the first place, no careful attention has been paid to the preparation of pure zinc sulfate, and in the second place the accurate measurement of the hydrogen-ion activity in zinc sulfate solutions is relatively difficult. The latter solutions have an extremely small buffer capacity, and on account of the hydrolytic adsorption by platinized platinum described in a former paper,<sup>2</sup> the ordinary type of platinized hydrogen electrode does not give reliable or reproducible results. The use of the quinhydrone electrode too is rather precarious in slightly buffered solutions. The authors have applied this electrode in all measurements described in this paper, but the readings were reproducible no better than to within 0.04 to 0.05 in  $P_H$ , which was not considered sufficiently accurate for this type of work. Finally, the colorimetric method involves some complications on account of the salt influence upon the color of an indicator at constant activity of the hydrogen ions. In the present work the  $P_H$  has been determined with a hydrogen electrode adapted to measurements in unbuffered solutions and described in a former paper.<sup>3</sup> The platinum wire was coated with a bright layer of platinum; after each set of measurements it was cleaned with aqua regia, ignited and replated. For details regarding manipulation the reader is referred to the former paper.<sup>3</sup>

The measurements were reproducible to within 0.01 to 0.02 of  $P_H$ . In a former study<sup>4</sup> it had been found that the salt error of methyl red is negli-

<sup>1</sup> From the experimental part of a thesis submitted by T. Kameda to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> I. M. Kolthoff and T. Kameda, *THIS JOURNAL*, 51, 2888 (1929).

<sup>3</sup> I. M. Kolthoff and T. Kameda, *ibid.*, 53, 821 (1931).

<sup>4</sup> I. M. Kolthoff, *J. Phys. Chem.*, 32, 1820 (1928).

gibly small in solutions with an ionic strength smaller than 0.5. For this reason the colorimetric method was applied with adjusted methyl red solutions<sup>5</sup> as indicator. At concentrations of zinc sulfate below 0.1 molar the electrometric and colorimetric methods gave exactly identical results.

### Materials Used

**Zinc Sulfate.**—C. p. zinc sulfate was repeatedly recrystallized from conductivity water, until methyl red added to 0.5 g. of salt dissolved in 15 cc. of water indicated within 0.01 in *PH* a constant hydrogen-ion concentration. The products from the sixth, seventh and eighth recrystallization showed the same acidity and the salt after the seventh recrystallization was used in this work.

The recrystallization of the zinc sulfate has to be done very carefully; if the salt is boiled with water for some time a scum of basic sulfate is formed, and the crystals obtained in cooling the filtrate have too acid a reaction. In this work the zinc sulfate was added to conductivity water which was kept at about 70° in a larger bath. After the crystals had been dissolved by mechanical stirring, the solution was cooled in an ice-bath, repeatedly stirred and the salt collected by suction.

**Water.**—The water used as a solvent was obtained from conductivity water by distillation over very dilute sulfuric acid and finally in a quartz apparatus without any further addition. It was protected from atmospheric contamination.<sup>3,5</sup>

**Methyl Red.**—A product which was 99% pure was recrystallized from methyl alcohol. The conductimetric titrations with sodium hydroxide gave the calculated results. A solution of 100 mg. of indicator in 70% alcohol was prepared. A 0.1% solution of the sodium salt in 50% alcohol was obtained by adding the equivalent amount of sodium hydroxide. From these two stock solutions the adjusted mixtures were prepared.<sup>5</sup>

**Buffer Solutions.**—Biphthalate-sodium hydroxide buffers with an interval of 0.1 in *PH* were used. The *PH* values of these were checked with the hydrogen electrode at 25°. The colorimetric determinations were made at the same temperature.

### Results

In Table I the results of the measurements are reported. The first column gives the concentration of zinc sulfate (moles per liter), the second the *PH* measured with the hydrogen electrode, the third the data found colorimetrically. The fourth column gives figures graphically interpolated from measurements made by M. Quintin<sup>6</sup> (using the quinhydrone elec-

TABLE I  
HYDROLYSIS OF ZINC SULFATE AT 25°  
*PH* acc. to K. and K.

| Concn. of ZnSO <sub>4</sub> ,<br>molar | H <sub>2</sub> electrode | Colorim.<br>(m. red) | Quintin | Denham and<br>Marris |
|--|--------------------------|----------------------|---------|----------------------|
| 0.01                                   | 6.00                     | 6.00                 | 5.52    | 5.09                 |
| .02                                    | 5.89                     | 5.90                 | 5.30    | 5.21                 |
| .05                                    | 5.76                     | 5.77                 | 5.03    | 5.3                  |
| .10                                    | 5.67                     | 5.66                 | 4.8     | ..                   |
| .25                                    | 5.26                     | 5.48                 | ..      | ..                   |
| .50                                    | 5.08                     | 5.30                 | 4.28    | ..                   |

<sup>5</sup> I. M. Kolthoff and T. Kameda, *THIS JOURNAL*, 53, 822 (1931).

<sup>6</sup> M. Quintin, *J. chim. phys.*, 24, 712 (1925).

trode), and the last column gives interpolated data of H. G. Denham and N. A. Marris<sup>7</sup> (also obtained with the quinhydrone electrode).

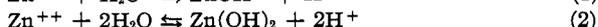
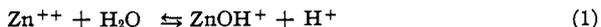
The figures obtained by the writers are quite different from those of Quintin.<sup>6</sup> Apparently he used a preparation containing a trace of free acid. The figures of Denham and Marris<sup>7</sup> are irregular; a study of their paper shows that the measurements are not well reproducible;<sup>8</sup> moreover, according to their report the *P<sub>H</sub>* increases with increasing zinc sulfate concentration, which seems highly improbable.

From the table it will be seen that the electrometric and colorimetric data obtained by the authors agree within 0.01 in *P<sub>H</sub>* up to a concentration of 0.1 molar. At higher concentrations the colorimetric reading gives a higher *P<sub>H</sub>* than the hydrogen electrode indicates. This may be caused by a salt error of the indicator at these high ionic strengths. However, it should be mentioned that at these high concentrations of zinc sulfate the measurements with the hydrogen electrode are not as well reproducible (to about 0.08 *P<sub>H</sub>*) as those in more dilute solutions. In order to test the magnitude of the salt error of methyl red at high ionic strengths, electrometric (hydrogen electrode) and colorimetric (methyl red) measurements have been made in 0.01 *N* acetate buffers in the presence of large amounts of sodium sulfate, magnesium chloride and magnesium sulfate.

TABLE II  
SALT ERROR OF METHYL RED AT HIGH IONIC STRENGTH

| Concn. of salt in 0.01 <i>N</i> acetate buffer, molar |      | <i>P<sub>H</sub></i> , electr. | <i>P<sub>H</sub></i> , color. | Salt error of methyl red |
|---|------|--------------------------------|-------------------------------|--------------------------|
| Na <sub>2</sub> SO <sub>4</sub>                       | 0.25 | 5.48                           | 5.59                          | +0.11                    |
| MgCl <sub>2</sub>                                     | .25  | 5.38                           | 5.50                          | + .12                    |
| MgSO <sub>4</sub>                                     | .25  | 5.39                           | 5.56                          | + .17                    |
| MgSO <sub>4</sub>                                     | .5   | 5.30                           | 5.52                          | + .22                    |

Magnesium sulfate is a salt of the same type as zinc sulfate, and it appears that if added to the acetate buffer the difference between the electrometric and colorimetric reading is of the same order as in pure zinc sulfate solution. On account of the uncertainty in the results obtained with the hydrogen electrode in the latter solutions, no correction has been applied at these higher ionic strengths. Depending upon the strength of zinc hydroxide as a mono-acid or diacid base, the hydrolysis of zinc sulfate can take place according to the reactions



As a matter of fact both reactions can occur simultaneously. From the *P<sub>H</sub>* values obtained in zinc sulfate solutions, it can be calculated according

<sup>7</sup> H. G. Denham and N. A. Marris, *Trans. Faraday Soc.*, **24**, 510 (1928).

<sup>8</sup> See Ref. 7. On p. 512 of their paper they mention that the  $[\text{H}^+]$  at a dilution of 32 is  $1.6 \times 10^{-6}$ ; in the table on p. 514 a value of  $5.05 \times 10^{-6}$  is given.

to which equation the hydrolysis takes place. If it occurs according to (1)

$$\frac{[a\text{ZnOH}^+][a\text{H}^+]}{[a\text{Zn}^{++}]} = K_{1 \text{ hydr.}} \quad (3)$$

$K$  should be constant. In the other case the equation

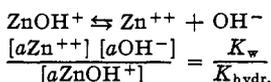
$$\frac{[a\text{Zn}(\text{OH})_2][a\text{H}^+]^2}{[a\text{Zn}^{++}]} = K_{2 \text{ hydr.}} \quad (4)$$

should hold. From the experimental figures it appears that the hydrolysis takes place according to (1) and is quantitatively expressed by (3). In the calculation of  $K_{\text{hydr.}}$  (Eq. 3) it is assumed that the activity of the  $\text{ZnOH}^+$  ions is equal to the hydrogen-ion activity  $[a\text{H}^+]$ . This will be approximately true in the more dilute solutions, at higher ionic strengths the difference between the activity coefficients of both ions probably will be no longer negligibly small. However, we have no means of determining the activity of  $\text{ZnOH}^+$  ions separately, and therefore this assumption must be made. The activity of the zinc ions ( $[a\text{Zn}^{++}]$ ) in zinc sulfate solutions has been taken from an experimental study of U. B. Bray,<sup>9</sup> assuming that the activities of the zinc and sulfate ions are equal at the same ionic strength. The values of the hydrolysis constant are given in the following table.

TABLE III  
HYDROLYSIS CONSTANT (EQ. 3) IN ZINC SULFATE SOLUTIONS AT 25°

| Concn. of zinc sulfate,<br>molar | $[a\text{H}^+] \times 10^8$ | $[a\text{Zn}^+]$      | $K_{\text{hydr.}} \times 10^{10}$ |
|----------------------------------|-----------------------------|-----------------------|-----------------------------------|
| 0.01                             | 1.00                        | $4.2 \times 10^{-3}$  | 2.4                               |
| .02                              | 1.26                        | $6.4 \times 10^{-3}$  | 2.60                              |
| .05                              | 1.70                        | $1.1 \times 10^{-2}$  | 2.76                              |
| .1                               | 2.14                        | $1.61 \times 10^{-2}$ | 2.84                              |
|                                  |                             | Average               | 2.65                              |

As the  $P_{\text{H}}$  values in the more concentrated zinc sulfate solutions are rather uncertain, the figures obtained in these solutions have not been used for the calculation of the hydrolysis constant. From the figures given in the table, it appears that  $K_{\text{hydr.}}$  is constant within 10% at zinc sulfate concentrations between 0.01 and 0.1 molar. Therefore the hydrolysis according to Equation 2 is negligibly small, and it may be inferred that zinc hydroxide with regard to its first step of ionization behaves like a strong base. Considering the similarity between magnesium and zinc hydroxide, this result could be expected. The second ionization constant of zinc hydroxide



has been calculated from the hydrolysis constant and the ionic product of water. At 25°  $K_w = 1.00 \times 10^{-14}$ , and for  $K_{\text{hydr.}}$  an average value of

<sup>9</sup> U. B. Bray, THIS JOURNAL, 49, 2372 (1927).

$2.65 \times 10^{-10}$  has been found. Therefore the second ionization constant of zinc hydroxide at  $25^\circ$  is equal to  $3.8 (\pm 0.3) \times 10^{-5}$ , which is about twice as large as the basic constant of ammonia.

It may be mentioned that all values of  $P_H$  have been calculated by using the standard values originally given by S. P. L. Sørensen,<sup>10</sup> and advocated by W. M. Clark.<sup>11</sup> The Sørensen values do not exactly correspond to the activity exponents of the hydrogen ions. Accepting the relation

$$P_{aH} = P_H + 0.04$$

( $P_{aH}$  is the negative logarithm of the activity of the hydrogen ions and  $P_H$  is the hydrogen-ion exponent according to Sørensen), it is found that  $K_{hydr.} = 2.2 \times 10^{-10}$  and  $K_2$  of zinc hydroxide is  $4.4 (\pm 0.4) \times 10^{-5}$ . Finally it may be mentioned here that the authors have found no indications whatsoever that the  $P_H$  of zinc sulfate solutions changes on standing.<sup>12</sup> If kept in pyrex bottles (or Jena glass) the  $P_H$  is unaltered after a few months' standing.

## 2. Solubility Product of Hydrus Zinc Oxide and the Composition of the Latter Obtained by Precipitation from Zinc Sulfate Solution.—

Solutions of pure zinc sulfate of various strengths were titrated at  $25 \pm 0.1^\circ$  with sodium hydroxide, the latter usually having a concentration about ten times larger than the zinc solution. During the titration the  $P_H$  was measured by means of a hydrogen electrode. The titration cell as shown in Fig. 1 is very suitable for this purpose. Again a platinum wire coated with a bright layer of platinum was used. With an electrode coated with platinum black the results were not quite reproducible, and it is difficult to find the values with an accuracy of 0.1 in  $P_H$ . With the wire coated with a bright layer of platinum the readings were reproducible to within 0.02. Replating is necessary after each set of measurements.

After the addition of 1 to 2% of the equivalent amount of sodium hydroxide, the hydrus zinc oxide begins to precipitate; from this point on the  $P_H$  increases very slightly on further addition of sodium hydroxide. In the following table the  $P_H$  values at which the precipitation of the hydrus zinc oxide starts are indicated. As the zinc concentration was known at this point, the solubility product could be calculated. The activity of the zinc ions again was found from the data

$$[aZn^{++}] [aOH^-]^2 = S_{Zn(OH)_2 \cdot xH_2O}$$

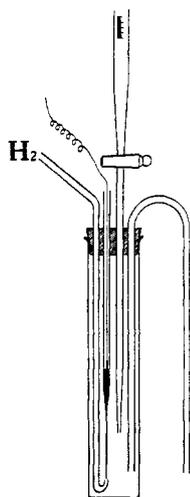


Fig. 1.

<sup>10</sup> S. P. L. Sørensen, *Compt.-rend. trav. lab. Carlsberg*, **8**, 23 (1909).

<sup>11</sup> W. M. Clark, "The Determination of Hydrogen Ions," 3d ed., The Williams and Wilkins Co., Baltimore, Maryland, 1928.

<sup>12</sup> See H. G. Denham, *J. Chem. Soc.*, **93**, 41 (1908).

given by U. B. Bray.<sup>9</sup> At 25°,  $P_{\text{OH}} = 14.00 - P_{\text{H}}$ . If the solubility of the hydrous zinc oxide at 25° is  $s$ , and the saturated solution is completely dissociated into the ions, which practically is the case as may be inferred from the magnitude of the second ionization of zinc hydroxide, then  $s = \sqrt[3]{S/4}$ .

The values of  $s$  expressed in moles per liter are given in the table. It appears that the apparent solubility product is not quite constant, but decreases with increasing zinc concentration in the solution. The product  $[c\text{Zn}^{++}] [a\text{OH}^-]^2$ , in which  $[c\text{Zn}^{++}]$  indicates the total zinc-ion concentration, yields a value which is a much better constant than  $[a\text{Zn}^{++}] [a\text{OH}^-]^2$ . The corresponding values are included in the table. The first column gives the concentration of the zinc sulfate solution titrated, the second the  $P_{\text{H}}$  values computed on the basis of Sørensen's standard values, the third column the solubility product  $[a\text{Zn}^{++}] [a\text{OH}^-]^2$ , the fourth one the corresponding solubility  $s$ , and the last column the product  $[c\text{Zn}^{++}] [a\text{H}^+]$ .<sup>2</sup>

TABLE IV  
SOLUBILITY PRODUCT OF HYDROUS ZINC OXIDE

| Concn. of zinc sulfate, molar | $P_{\text{H}}$ at precipitation of hydrous oxide | $S = [a\text{Zn}^{++}][a\text{OH}^-]^2 \times 10^{18}$ | $s \times 10^6$ | $[c\text{Zn}^{++}][a\text{OH}^-]^2 \times 10^{18}$ |
|-------------------------------|--|--|-----------------|--|
| 0.01                          | 6.49   | 4  | 1.0             | 9.5  |
| .05                           | 6.17   | 2.5  | 0.85            | 10.9   |
| .25                           | 5.80   | 1.0  | .64             | 9.9  |

H. T. S. Britton,<sup>13</sup> who studied the precipitation of hydrous zinc oxide, found that in 0.025 molar zinc sulfate solution the precipitation started at a  $P_{\text{H}}$  of 5.2 (at 18°). This value is more than one unit lower than that found by the authors. Accordingly Britton calculated a solubility product of the order of  $10^{-21}$ , which is about 1000 times smaller than the figure in the above table. Probably some error must have been introduced in Britton's measurements of  $P_{\text{H}}$ . From the curve in his paper (p. 2125) it can be calculated that the  $P_{\text{H}}$  in 0.025 molar solution of pure (?) zinc sulfate is 3.8, whereas this figure according to our measurements is 5.87!

The figures found by the authors are of the same order of magnitude as those reported by H. G. Dietrich and J. Johnston<sup>14</sup> and Miss de Wÿs.<sup>15</sup> The former calculate a solubility of  $2 \times 10^{-6}$  molar, the latter of  $2.7 \times 10^{-6}$ . The value found by the authors is about  $1 \times 10^{-6}$ , whereas other data reported in the literature are much higher.<sup>16</sup>

As will be discussed below, the hydrous zinc oxide precipitated by sodium hydroxide contains some sulfate in a ratio of about  $3\text{ZnO}:1\text{ZnSO}_4$ . Die-

<sup>13</sup> H. T. S. Britton, *J. Chem. Soc.*, **125**, 2124 (1927).

<sup>14</sup> H. G. Dietrich and J. Johnston, *THIS JOURNAL*, **49**, 1419 (1927).

<sup>15</sup> De Wÿs, *Rec. trav. chim.*, **44**, 663 (1925).

<sup>16</sup> Bodländer, *Z. physik. Chem.*, **27**, 66 (1898), gives  $1.25 \times 10^{-6}$  molar; Herz, *Z. anorg. Chem.*, **23**, 222 (1900),  $1.3 \times 10^{-6}$ ; Dupré and Biala, *Z. angew. Chem.*, **16**, 54 (1903),  $5.2 \times 10^{-6}$ ; Remy and Kuhlmann, *Z. anal. Chem.*, **65**, 161 (1924),  $3.7 \times 10^{-6}$ .

trich and Johnston,<sup>14</sup> as well as de Wÿs,<sup>15</sup> used crystalline zinc hydroxide in their work. In order to obtain a better comparison with their data, measurements of  $P_H$  have been made in zinc sulfate solution saturated with different kinds of zinc hydroxide and zinc oxide. In addition the neutralization curve of zinc chloride (instead of zinc sulfate) with sodium hydroxide has been determined at 25°. The hydrous zinc oxide formed in the latter case contains only a small fraction of chloride. The zinc chloride solution was obtained by adding an equivalent amount of barium chloride solution to zinc sulfate.

Crystalline zinc hydroxide (a) was obtained according to the directions of H. G. Dietrich and J. Johnston by crystallization from an ammoniacal solution. The crystals obtained were kept in a desiccator over deliquescent sodium bromide for two years. The water content determined by ignition in an electric furnace at 800° was 18.18% (calcd., 18.11%).

Another crystalline product (b) was obtained by precipitation of zinc sulfate with an excess of ammonia. The product was carefully washed in a mortar with water, during which time it changed into a definite crystalline compound—zinc oxide. Products a and b were heated in an electric furnace for about three hours at 800°.

0.05 Molar zinc sulfate was saturated at 25° in the hydrogen electrode cell adapted for measurements of unbuffered solutions with the different products of zinc hydroxide and zinc oxide. The data are reported in Table V. The figures obtained in the precipitation of zinc sulfate and zinc chloride with sodium hydroxide are also included.

TABLE V  
 $P_H$  OF 0.05 MOLAR ZINC SULFATE SATURATED WITH DIFFERENT KINDS OF ZINC HYDROXIDE OR ZINC OXIDE AT 25°

| Zinc hydroxide or oxide                      | $P_H$ | Remarks   |
|--|-------|---|
| Cryst. $Zn(OH)_2$ (a)                        | 6.13  | All solutions have a colloidal appearance on shaking with the different preparations. |
| Cryst. $Zn(OH)_2$ (b)                        | 6.16  |   |
| ZnO by ignition of (a)                       | 6.22  |   |
| ZnO by ignition of (b)                       | 6.12  |   |
| Freshly pptd. by NaOH                        | 6.17  |   |
| Freshly pptd. by NaOH in 0.05 molar $ZnCl_2$ | 6.19  |   |

In all cases the  $P_H$  measured is the same within 0.05 as in the zinc sulfate solution to which a trace of sodium hydroxide has been added, whereas one would expect individual differences between the different solutions as the solids present in excess have different compositions and crystal structures. However, it seems doubtful whether these different modifications are stable in a zinc sulfate solution; on shaking, all solutions assume a colloidal appearance as in zinc sulfate with a small amount of sodium hydroxide.

In Fig. 2 the change in  $P_H$  during the titration of 0.01 molar and 0.05 molar zinc sulfate with 0.2 *N* sodium hydroxide and of 0.25 molar zinc sul-

fate with 1 *N* sodium hydroxide have been given. The abscissa gives the percentage of the equivalent amount of sodium hydroxide added.

In each case the *P<sub>H</sub>* values have been determined in the hydrogen electrode titration cell usually after addition of 0, 2, 4, 6, 8, 10, 25, 40, 60, 70, 75, 78, 80, 82, 85, 90, 95 and 100% of the equivalent amount of base. Moreover, the curve in the titration of 0.05 molar zinc chloride under similar conditions has been given. A jump in potential occurs at a *P<sub>H</sub>* approximately between 7 and 10, long before an equivalent amount of sodium hydroxide has been added. This indicates that a basic zinc sulfate or

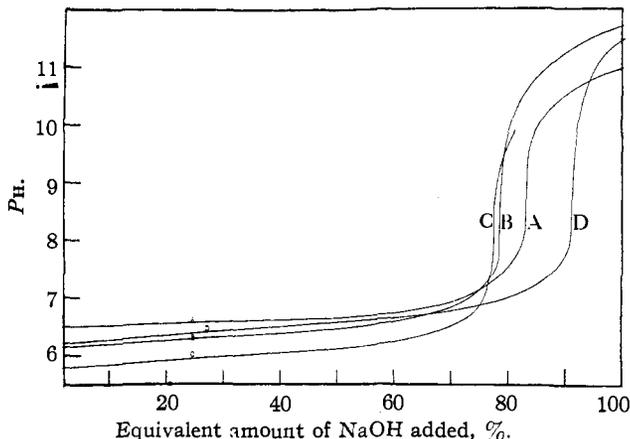


Fig. 2.—Potentiometric titration curves of zinc sulfate with sodium hydroxide. A, 25 ml. of 0.01 *M*  $ZnSO_4$  titrated with 0.1983 *N*  $NaOH$ ; B, 25 ml. of 0.05 *M*  $ZnSO_4$  titrated with 1.0046 *N*  $NaOH$ ; C, 25 ml. of 0.25 *M*  $ZnSO_4$  titrated with 1.0046 *M*  $NaOH$ ; D, 25 ml. of 0.05 *M*  $ZnCl_2$  titrated with 0.1988 *M*  $NaOH$ .

hydrous oxide containing adsorbed sulfuric acid is formed. The location of the jump is almost independent of the concentration of the zinc solutions titrated. Figures are given in Table VI.

TABLE VI

END-POINTS IN ZINC SULFATE TITRATION DERIVED FROM POTENTIOMETRIC TITRATION AT 25°

| Solution, molar | Jump in potential after addition of $NaOH$ equivalents to |
|-----------------|---|
| $ZnSO_4$ 0.01   | 83%   |
| $ZnSO_4$ .05    | 79%   |
| $ZnSO_4$ .25    | 78%   |
| $ZnCl_2$ .05    | 92%   |

The precipitate formed in the titration of zinc chloride is much less basic than that from zinc sulfate. H. T. S. Britton<sup>13</sup> found the precipitation of 0.025 molar zinc sulfate complete after addition of 77.5% of the equivalent

amount of sodium hydroxide, which is in good agreement with the data reported.

It seemed interesting to investigate how the composition of the hydrous oxide formed changes during the precipitation. In the titration of aluminum sulfate with sodium hydroxide Miller<sup>17</sup> has found that the hydrous oxide precipitated contains more acid, the less base has been added. As will be shown below, the precipitate formed on the addition of sodium hydroxide to zinc sulfate has a fairly constant composition until quite near the end-point.

In addition it was of interest to see how the  $P_H$  of the solution and the composition of the precipitate change on aging. In one set of experiments mixtures of zinc sulfate and sodium hydroxide were shaken for ten days at 25° and thereafter analyzed. In another set mixtures were kept for three hundred days at room temperature and then analyzed. Finally the temperature effect has been studied by heating mixtures of zinc sulfate and sodium hydroxide for ten days at 80°; they were analyzed after cooling.

The experiments were made in the following way. Known amounts of zinc sulfate dissolved in water were mixed with a definite volume of standardized sodium hydroxide. The mixture was immediately diluted with water in a volumetric flask so that the initial concentration of zinc sulfate in all cases corresponded to 0.05 molar. Immediately or after the indicated time of standing the  $P_H$  was determined with the hydrogen electrode adapted for measurements of unbuffered solutions. The filtrate was used for the further analysis. In part of the filtrate the  $P_H$  was determined colorimetrically with adjusted brom thymol blue as an indicator. The data obtained were not exactly the same as those found potentiometrically. As the salt error of the indicator under the conditions of these experiments is not exactly known, the data found colorimetrically have been omitted in the tables. In another part of the filtrate the zinc concentration was determined by precipitation with *o*-hydroxyquinoline. The precipitate was weighed or, if the zinc concentration was very small, titrated bromometrically. Both procedures give very accurate results. From the original zinc sulfate content, the amount of base added and the zinc concentration found in the precipitate, the composition of the hydrous oxide could be calculated. However, in order to check the analyses in all cases, the sulfate content in the filtrate was determined by a conductimetric titration with barium chloride in a thermostat at 25°. Details of this investigation will be described elsewhere. It may be stated here that the results calculated from the zinc analysis checked to within 1% with those obtained from the sulfate titrations.

Table VII gives the change of  $P_H$  of zinc sulfate solutions to which small amounts of sodium hydroxide had been added. The electrometric measure-

<sup>17</sup> Miller, *U. S. Publ. Health Repts.*, **38**, 1995 (1923).

ments were made at 25° immediately after addition of base, after fifteen days' shaking at room temperature and after sixteen days' heating at 80°.

TABLE VII  
EFFECT OF AGING UPON PH OF ZINC SULFATE WITH SMALL AMOUNTS OF SODIUM HYDROXIDE

| Concn. of zinc sulfate, molar | Added sodium hydroxide in equivalents | PH immediately after mixing | PH after 16 days at 25° | PH after 16 days at 80° |
|-------------------------------|---------------------------------------|-----------------------------|-------------------------|-------------------------|
| 0.01                          | 5%                                    | 6.49                        | 6.42                    | 6.29                    |
| .05                           | 5%                                    | 6.17                        | 6.09                    | 5.94                    |
| .25                           | 5%                                    | 5.80                        | 5.80                    | 5.72                    |

In Table VIII a summary of all the analytical results has been given. In all cases the original concentration of zinc sulfate was equal to 0.05 molar. The first column gives the equivalent amount of sodium hydroxide added expressed in percentage, the second column the composition of the precipitate by the ratio  $ZnO:ZnSO_4$  as derived from the analysis after immediate filtration. The third gives the same ratio after ten days' shaking at room temperature and the fourth the same after standing for ten days at 80°.

TABLE VIII  
COMPOSITION OF HYDROUS ZINC OXIDE BY PRECIPITATION FROM 0.05 MOLAR ZINC SULFATE

| Equivalent amount of sodium hydroxide added | Ratio $ZnO:ZnSO_4$              |                      |                      |
|---|---------------------------------|----------------------|----------------------|
|   | Immediately after precipitation | After 10 days at 25° | After 10 days at 80° |
| 25%   | 3.2:1                           | 3.3:1                | 5.9:1                |
| 50%   | 3.1:1                           | 3.5:1                | 5.0:1                |
| 75%   | 3.2:1                           | 3.7:1                | 4.6:1                |

Finally, Table IX shows the effect of aging for three hundred days at room temperature upon the composition of the precipitate.

TABLE IX  
COMPOSITION OF HYDROUS ZINC OXIDE AFTER 300 DAYS AT ROOM TEMPERATURE

| Equivalent amount of sodium hydroxide added to 0.05 molar zinc sulfate | 10%   | 20%   | 50%   | 80%   | 90%   |
|--|-------|-------|-------|-------|-------|
| Ratio $ZnO:ZnSO_4$ in precipitate                                      | 3.5:1 | 3.6:1 | 3.4:1 | 4.2:1 | 8.8:1 |

From the last three tables it may be inferred that the composition of hydrous zinc oxide precipitated from zinc sulfate solution by sodium hydroxide is fairly constant from the beginning to the end of the precipitation, corresponding to the separation of a basic salt  $3ZnO \cdot ZnSO_4 \cdot xH_2O$ . The jumps in potential in the potentiometric titration discussed before also indicate approximately a similar composition. Pickering<sup>18</sup> concluded that after complete precipitation of all the zinc the precipitate had the composition  $4ZnO \cdot ZnSO_4$ . However, it seems that just at the equivalence point, where no excess of zinc sulfate is present, the precipitate is no longer

<sup>18</sup> Pickering, *J. Chem. Soc.*, 91, 1981 (1907).

stable, as may be seen from the last two figures in the last table. According to Zubkowskaja<sup>19</sup> only the basic salt  $3\text{ZnO}\cdot\text{ZnSO}_4\cdot x\text{H}_2\text{O}$  is a definite compound. The latter is slowly decomposed by water, as shown by experiments of W. Feitknecht.<sup>20</sup>

From experiments of the latter, one would conclude that the basic salt is only stable in 0.00075 molar zinc sulfate or more concentrated solutions. Therefore, the composition derived from experiments where the precipitation is just complete, has no exact significance. The basic compound is fairly stable at room temperature; even after standing for three hundred days with the supernatant liquid the basicity of the precipitate increases only slightly ( $3.5\text{ZnO}:\text{ZnSO}_4$ ) whereas the  $P_{\text{H}}$  of the solution practically does not change. However, at higher temperatures the precipitate loses acid and becomes definitely more basic. Accordingly the  $P_{\text{H}}$  of the supernatant liquid decreases, as may be seen from the tables, in which the influence of heating for ten days at  $80^\circ$  has been shown. Though the composition of the precipitate formed at room temperature corresponds to  $3\text{ZnO}\cdot\text{ZnSO}_4\cdot x\text{H}_2\text{O}$ , it is not possible to conclude with certainty from the above experiments whether the latter is a definite compound. The fact that the ratio of  $\text{ZnO}:\text{ZnSO}_4$  is constant during the entire precipitation is an indication in this direction.

### Summary

1. An exact study has been made of the hydrolysis of solutions of pure zinc sulfate at  $25^\circ$ . It could be concluded that zinc hydroxide as a monoacid base is very strong; its second ionization constant at  $25^\circ$  is equal to  $4.4 (=0.4) \times 10^{-5}$ .

2. The solubility of hydrous zinc oxide precipitated from zinc sulfate is at  $25^\circ$  about  $1 \times 10^{-6}$  molar. This figure is smaller than most data reported in the literature.

3. The  $P_{\text{H}}$  of a zinc sulfate solution saturated with zinc hydroxide is practically independent of the kind of zinc hydroxide or zinc oxide present as solid.

4. The hydrous oxide formed on the addition of sodium hydroxide to zinc sulfate solutions at  $25^\circ$  has a fairly constant composition during the entire precipitation, corresponding to the formation of a basic salt  $3\text{ZnO}\cdot\text{ZnSO}_4$ . The effect of aging at room temperature is small. Heating the precipitate with the supernatant liquid for ten days at  $80^\circ$  changes the composition of the hydrous oxide. It becomes more basic, and the  $P_{\text{H}}$  of the supernatant solution decreases.

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<sup>19</sup> Zubkowskaja, *Chem. Zentr.*, I, 797 (1908).

<sup>20</sup> W. Feitknecht, *Helv. Chim. Acta*, 13, 22 (1930).