

## OFFICIAL ASH.

|                               | Lime. | Magnesia. |
|-------------------------------|-------|-----------|
| Washing precipitate .....     | 11.62 | 5.74      |
| Not washing precipitate ..... | 11.95 | 5.78      |

In the case of ashes which contain a larger per cent. of phosphoric acid than that included in the limits of this paper, a small correction may be necessary for the volume occupied by the precipitate. On account of lack of time I will reserve the investigation of this subject for a future paper.

## THE EFFECT OF DI-IONIC ELECTROLYTES ON THE SOLUBILITY OF TRI-IONIC ELECTROLYTES WITH DIFFERENT IONS.<sup>1</sup>

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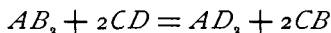
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### I. THE OBJECT OF THE INVESTIGATION.

THE theory of the effect of one di-ionic electrolyte upon the solubility of another with different ions has already been developed by Noyes<sup>2</sup>, and confirmed by our researches<sup>3</sup> and those of Noyes and Schwartz.<sup>4</sup> The solubility of tri-ionic electrolytes in the presence of other electrolytes with an ion in common has also been investigated.<sup>5</sup> The solubility of tri-ionic electrolytes in the presence of other electrolytes with different ions has, however, heretofore not been considered, except from a purely theoretical standpoint. The object of this article is to discuss theoretically a special case of this phase of solubility effect, and to communicate experiments, which confirm the theory. The special case chosen is the solubility of calcium hydroxide in the presence of ammonium chloride, in which case a weakly dissociated substance, ammonium hydroxide, is formed by metathesis.

### 2. THEORY OF THE SOLUBILITY EFFECT.

Consider a solution of any di-ionic electrolyte,  $CD$ , which is saturated with a tri-ionic electrolyte,  $AB_2$ . In accordance with the reaction



<sup>1</sup> Read at the Boston Meeting of the American Chemical Society, August 25, 1898.

<sup>2</sup> *Zischr. phys. Chem.*, 27, 267.

<sup>3</sup> This JOURNAL, 20, 751.

<sup>4</sup> *Ibid.*, 20, 742.

<sup>5</sup> *Zischr. phys. Chem.*, 9, 623; 26, 152.

certain quantities of the undissociated substances  $AD_2$  and  $CB$  will be formed, so that the solubility of  $AB_2$  will be greater than that in pure water; for it exists in the solution not only in the form  $AB_2$  and its ions (as in pure water), but also in the form  $AD_2$  and  $CB$ . Suppose that the substances  $CD$  and  $AD_2$  are strongly dissociated, in which case their undissociated amounts may be determined with sufficient exactness from their electrical conductivities;<sup>1</sup> and suppose that the substance  $CB$  on the contrary is only slightly dissociated, and that it conforms to the laws of mass action. Designate the molecular concentrations of the ions  $A$ ,  $B$ ,  $C$ , and  $D$  by the same capital letters; the molecular concentrations of the undissociated portions of the four substances  $AB_2$ ,  $CD$ ,  $AD_2$ , and  $CB$  by  $a$ ,  $b$ ,  $c$ , and  $d$  respectively; the solubility of  $AB_2$  in pure water by  $m_0$ ; the corresponding degree of its dissociation by  $a_0$ ; the solubility of  $AB_2$  in a solution of  $CD$  of concentration  $n$  by  $m$ ; the product  $4 m_0^3 a_0^3$  by  $k_a$ ; and the dissociation constant of  $CB$  by  $k_d$ . The two following equilibrium equations then hold true, the first expressing the constancy of the product of the concentrations of the ions of any tri-ionic salt with which a solution is saturated, and the second the relation between the concentration of the undissociated portion and those of the ions of any di-ionic salt.

$$A \times B^2 = k_a \quad (1)$$

$$C \times B = k_d d \quad (2)$$

From the conditions of the case the three following equations may be derived:

$$A + a + c = m \quad (3)$$

$$B + 2a + d = 2m \quad (4)$$

$$C + b + d = n \quad (5)$$

These five equations contain only five unknown quantities  $A$ ,  $B$ ,  $C$ ,  $d$ , and  $m$ , and can therefore be solved for  $m$ . For brevity we substitute

$$x = m - a, e = n - b \text{ and } r = \frac{4 k_a^2}{k_d}$$

After elimination the following equation is obtained:

$$rx^4 - (2rc + 4)x^3 + (rc^2 + 4e + 4c)x^2 - [(k_d + e)^2 + 4ec]x + [c(k_d + e)^2 + k_d] = 0, \quad (6)$$

<sup>1</sup> *Ztschr. phys. Chem.*, 27, 270.

an equation, which after the substitution of the numerical values, may be solved in the usual manner. The method of calculating the values of  $b$  and  $c$  (here considered to be known) will be explained later by an example.

When the solutions of  $AB_2$  or of  $CD$  are very dilute, or when in the case of moderately concentrated solutions approximate values only are desired, the values of  $b$  and of  $c$  may be neglected, and the equation becomes

$$rx^4 - 4x^3 + 4nx^2 - (k_d + n)^2x + k_a = 0. \quad (7)$$

When, on the contrary, as in the case to be considered, the substance  $AB_2$  is moderately soluble, the concentration of  $CD$  is considerable, and the substance  $CB$  is slightly dissociated—the values  $r$ ,  $k_d$ , and  $b$  are negligible, while  $c$  is appreciable. The equation then becomes

$$4x^3 - 4(n + c)x^2 + (n^2 + 4nc)x - (cn^2 + k_a) = 0. \quad (8)$$

### 3. DESCRIPTION OF THE EXPERIMENTS.

In order to test these principles, we have determined the solubility of calcium hydroxide in water and in three ammonium chloride solutions of different concentrations. The calcium hydroxide was prepared from a supposedly pure sample of the same by dissolving in hydrochloric acid, treating with ammonium hydroxide to remove other metals, precipitating with ammonium carbonate, and igniting this precipitate just before using in small portions in a platinum crucible. The ammonium chloride was prepared by precipitating with strong hydrochloric acid, a concentrated solution of the commercial article, and three times recrystallizing the product from hot water. Two solutions of ammonium chloride, each about 0.087 normal, were prepared independently. From these were prepared by dilution solutions of one-half and one-fourth the original concentration. The concentrations of the strong solutions were determined gravimetrically by precipitation with silver nitrate.

The solutions were saturated in the usual manner.<sup>1</sup> As they would not settle, they were filtered.

On account of the tendency of the calcium hydroxide to absorb carbon dioxide from the air, this was done in air free from this gas within a vacuum desiccator containing potassium hydroxide.

<sup>1</sup> *Ztschr. phys. Chem.*, 9, 603.

The apparatus was so arranged that the saturated solutions were sucked from the bottles in which saturation took place directly into the desiccator through a hole in the top onto filters which stood in graduated flasks. The flasks were filled a little over the mark. The desiccator was then opened, the liquid in the flasks was brought exactly to the mark with filter-paper and was then emptied into Erlenmeyer flasks containing not quite enough standard hydrochloric acid to neutralize the dissolved calcium hydroxide. The titration was then quickly completed with more hydrochloric acid, using methyl orange as an indicator.

#### 4. THE EXPERIMENTAL RESULTS.

The following table contains the values of the solubility of the calcium hydroxide at 25° expressed in millimols (thousandths of a molecular weight) per liter.

| Exp. No. | Conc of NH <sub>4</sub> Cl o.o. | Conc. of NH <sub>4</sub> Cl 21.76 millimols. | Conc. of NH <sub>4</sub> Cl 43.52 millimols. | Conc. of NH <sub>4</sub> Cl 87.03 millimols. |
|----------|---------------------------------|--|--|--|
| 1        | 20.24                           | 28.99  | 39.12  | 59.45  |
| 2        | 20.21                           | 29.09  | 39.31  | 59.96  |
| 3        | 20.23                           | 29.06  | 39.31  | 59.60  |
| 4        | 20.26                           | 29.13  | 39.22  | 59.67  |
| 5        | 20.14                           | 29.13  | 39.30  | 59.74  |
| Mean     | 20.22                           | 29.08  | 39.23  | 59.68  |

In order to test the theory, it is necessary to know in addition to these solubility values, the degree of dissociation of the substances involved. In the case of ammonium chloride, calcium chloride, and ammonium hydroxide, reliable measurements of their electrical conductivities had been previously made; but in the case of calcium hydroxide in pure water, there were no data available, and therefore we have measured it ourselves. The solutions were saturated in the rotating apparatus, and their conductivities were then measured by the usual method of Kohlrausch. The value of the molecular conductivity of a 0.02022 molecular solution of calcium hydroxide was found to be 400.7<sup>1</sup> at 25°. This corresponds to a degree of dissociation of 0.808, if according to Kohlrausch<sup>2</sup> ( $\mu_{\infty}(\text{OH}) = 186$ ) and to Bredig<sup>3</sup> ( $\mu_{\infty}(\text{Ca}) = 124$ ), 496 is assumed as the limiting value of the molecular conductivity of calcium hydroxide.

<sup>1</sup> Two independent solutions gave 400.5 and 400.9.

<sup>2</sup> Wied. Ann., 50, 408. Kohlrausch gives 165 as the value for  $\mu_{\infty}(\text{OH})$  at 18° from which, and from the temperature coefficient, follows the value 186 at 25°.

<sup>3</sup> Ztschr. phys. Chem., 13, 235.

## 5. CALCULATION OF THE THEORETICAL VALUES AND COMPARISON OF THEM WITH THE EXPERIMENTAL ONES.

We have calculated the theoretical values by equation (8); for the value of  $r$  (0.000085) and that of  $k_d$  (0.000019), are extremely small, and that of  $b$ , even in the most concentrated solution (about one-tenth normal) is but  $0.001 \times n$ . The small value of  $b$ , the quantity of undissociated ammonium chloride, is explained by the fact that the concentration of the ammonium ions, on account of the weakness of the ammonium hydroxide, is extremely small. The constant  $k_a (= 4m_0^2 a_0^2)$  which appears in the equation is equal to 0.00001748; for according to our experiments  $m_0 = 0.02022$ , and  $a_0 = 0.808$ . The value of  $c$ , the undissociated quantity of calcium chloride, varies with the value of  $n$ . In order to determine the value of  $c$  in the different cases, we have made use of the conductivity measurements of MacGregory.<sup>1</sup> From his data at the concentrations 0.01, 0.05, and 0.1 normal we calculated first the degree of dissociation by dividing by the limiting value ( $\mu_\infty (\frac{1}{2} \text{CaCl}_2) = 110$ ), and then the empirical dissociation constant  $k'_c$  by van't Hoff's<sup>2</sup> formula,

$$k'_c = \frac{c_i^3}{c_s^2},$$

where  $c_i$  represents the concentration of the ions and  $c_s$  that of the undissociated substance. From this constant the values of  $c$  may then be calculated conversely with sufficient exactness by the equation:

$$k'_c = \frac{A \times D^2}{c^2},$$

in which  $A$  may be put equal to  $x$  (an estimated value of  $x$  being used) and  $D$  equal to  $n$ . The values of  $c$  thus calculated are: 0.0032 for  $n = 0.0217$ ; 0.0074 for  $n = 0.0435$ ; and 0.0180 for  $n = 0.087$ . They are, therefore, appreciable quantities.

The following table contains the calculated solubilities together with those found by experiment, both expressed in millimols per liter.

<sup>1</sup> *Phys. Review*, 2, 370.

<sup>2</sup> *Ztschr. phys. Chem.*, 18, 300.

| Concentration of ammonium chloride. | Solubility of calcium hydroxide. |             |
|-------------------------------------|----------------------------------|-------------|
|                                     | Found.                           | Calculated. |
| 0                                   | 20.22                            | ....        |
| 21.76                               | 29.08                            | 28.09       |
| 43.52                               | 39.23                            | 38.6        |
| 87.03                               | 59.69                            | 58.3        |

The agreement is satisfactory. The theory developed regarding the effect of di-ionic electrolytes on the solubility of tri-ionic electrolytes with different ions is therefore confirmed.

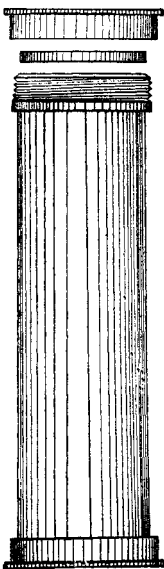
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, March, 1899.

### MEASUREMENTS OF "TURBIDITY" IN WATER.

BY W. P. MASON.

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THE method of expressing turbidity in words is so unsatisfactory that the writer has for some time past employed the following means of securing numerical results: The change



has proved of decided advantage, particularly for an examination of filtrates and storage waters.

Use is made of a brass tube two and one-half inches in diameter and two feet long, closed at the ends by disks of quarter-inch plate glass held in place by screw-caps.<sup>1</sup> Such tubes are easily cleaned and give excellent satisfaction.

For the purpose of measuring the amount of turbidity, a standard is prepared, consisting of one gram of exceedingly fine kaolin (obtained by elutriation) suspended in one liter of distilled water. Each cubic centimeter of this preparation will contain one milligram of suspended clay.

Having nearly filled the duplicate observation-tube with distilled water, enough of the "clay standard" is added to make the turbidity equal to that of the water under examination in the other tube. Knowing the volume of water operated upon and the amount of "clay standard" used, the turbidity expressed in parts per million can readily be calculated. It should be noted that although the tube containing the "clay standard" is, of necessity, not completely full, yet by inclining

<sup>1</sup> Such tubes may be obtained from Richards & Co., 30 East 18th St., New York City.