THE THEORY OF THE SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM FROM THE MIXED SULPHATES.

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A mixture of a soluble sulphate and carbonate transforms strontium and calcium sulphates into carbonates, leaving barium sulphate unchanged. Ammonium carbonate has also this same effect, so that the use of the soluble sulphate seems superfluous. The object of this paper is to show the action with both solvents, to calculate the effect of the sulphate added or formed, and also to show how the theories of physical chemistry may be applied to analytical chemistry. By Nernst's Laws,[1] for saturated solutions the undissociated portion of an insoluble salt remains constant even after addition of a salt with an ion in common. In the equation of equilibrium for a binary salt,

$$Kc = c_1 c_2, \qquad (1)$$

where c is the concentration of undissociated salt (in gram-molecules per liter) and c_1 and c_2 are those of the two ions, K being the ionization constant ; K and c are both constant for a saturated solution, hence

$$c_1 c_2 = \text{constant} = \text{solubility product}. \qquad (2)$$

The meaning of this product may be expressed as follows : for any one constant temperature the two ions may exist free to such a concentration that the product just reaches this value. If we add to such a solution a salt with an ion in common, an undissociated portion is formed from equivalent amounts of the two ions, until the product of those remaining just reaches the value of the solubility product. The undissociated portion being increased by the addition, it is necessary that a certain amount of it separates out in the solid form, since the solution was saturated. In exactly the same way a substance is always less soluble in a solution containing an ion in common than it is in pure water. In such a case, one ion being present to a large extent, the substance can dissolve only so long as the product of the concentration of the one ion into the sum of those of the two portions of the other is less than or

[1] See Morgan and Gotthelf : This Journal, 21, 494.

equal to the solubility product.   These relations are best shown by an alteration of equation 2; we have then,

$$c_1'(c_2' + x) = \text{solubility product,} \qquad (3)$$

when $c_1' = c_2'$ is the present solubility of the salt, in terms normal, and x is the concentration of the ions added, expressed in the same terms.   When x and the solubility product are both known it is simple to find $c_1' = c_2'$; or when $c_1' = c_2'$ is known as well as the solubility product we can find x.   In all cases where $c_1' = c_2'$ is very small and x is large, c_2' may be neglected as compared with x and we have

$$c_1'x = \text{solubility product.} \qquad (4)$$

In all cases of insoluble salts such as those used in an analysis, we may neglect the undissociated portion, and consider the major portion of the substance as present in the ionic state, for in such dilute solutions the undissociated portion, while still existing, must be exceedingly small.

By use of these equations, and especially (2) and (3), it is possible to calculate from the solubility of a substance in water its solubility product and also its solubility in presence of like ions of any definite concentration.   The solubilities which form the basis of this paper are taken from Holleman.[1]

For the sulphates and carbonates of barium, strontium and calcium by (2) at 20° C., we have,

$$\overset{++}{Ba} \times \overset{--}{SO_4} = 0.0000000001 \qquad (5)$$

$$\overset{++}{Ba} \times \overset{--}{CO_3} = 0.0000000105 \qquad (6)$$

$$\overset{++}{Sr} \times \overset{--}{SO_4} = 0.00000029 \qquad (7)$$

$$\overset{++}{Sr} \times \overset{--}{CO_3} = 0.000000005 \qquad (8)$$

$$\overset{++}{Ca} \times \overset{--}{SO_4} = 0.0029 \qquad (9)$$

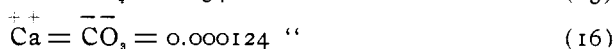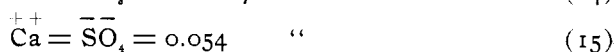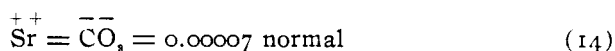$$\overset{++}{Ca} \times \overset{--}{CO_3} = 0.0000000154 \qquad (10)$$

In saturated water solutions of these salts we have then ionic concentrations as follows :

$$\overset{++}{Ba} = \overset{--}{SO_4} = 0.00001 \text{ normal} \qquad (11)$$

$$\overset{++}{Ba} = \overset{--}{CO_3} = 0.0001 \qquad `` \qquad (12)$$

$$\overset{++}{Sr} = \overset{--}{SO_4} = 0.00054 \qquad `` \qquad (13)$$

$$\overset{++}{Sr} = \overset{--}{CO_3} = 0.00007 \text{ normal} \tag{14}$$

$$\overset{++}{Ca} = \overset{--}{SO_4} = 0.054 \qquad `` \tag{15}$$

$$\overset{++}{Ca} = \overset{--}{CO_3} = 0.000124 `` \tag{16}$$

We see from these results that the carbonates of strontium and calcium are less soluble than the sulphates, while for barium the relation is reversed. From the results already given it is quite simple to find the concentration of $\overset{--}{CO_3}$ ions necessary to form the carbonate from the sulphate. Thus for barium, by (6) and (11) we find that,

$$x = \frac{0.0000000105}{0.00001} = 0.00115 \, ;$$

i. e., it is necessary to have a minimum of 0.00105 gram-molecules of CO_3 ions to the liter to cause the solubility product of barium carbonate to be reached in a saturated solution of barium sulphate.

In a like manner we find values of $\overset{--}{CO_3}$ for strontium and calcium to be :

$$CO_{3(Sr)} = x = \frac{0.000000005}{0.00054} = 0.0000092 \text{ normal (by (8) and}$$
(13)).

$$CO_{3(Ca)} = x = \frac{0.0000000154}{0.054} = 0.000000385 \text{ normal (by (10)}$$
and (15)).

These values would not cause the complete transformation of the sulphate into carbonate, but anything over them would cause some of the carbonate to be formed. It must always be borne in mind that an alkali sulphate is formed by the transformation, and that the $\overset{--}{SO_4}$ ions of this decrease the solubility of the insoluble sulphate so that equilibrium would be reached unless a sufficient excess of $\overset{--}{CO_3}$ ions are present. The relation between the effect of the $\overset{--}{SO_4}$ ions, and those of $\overset{--}{CO_3}$ may be readily calculated. Thus for barium sulphate, the solubility is depressed from 0.00001 normal to 0.000000001 normal by a tenth-normal solution of $\overset{--}{SO_4}$ ions ; *i. e.*,

$$y + 0.1 = 0.0000000001.$$

$$y = 0.000000001 = \text{concentration of } \overset{++}{Ba} \text{ ions.}$$

The amount of $\overline{\overline{CO}}_3$ ions necessary to cause the solubility product of the barium carbonate to be reached is then,

$$0.000000001 \times x = 0.0000000105$$
$$x = 10.5 \text{ normal.}$$

In other words a tenth-normal solution of $\overline{\overline{SO}}_4$ makes it necessary to add an equal amount of a 10.5 normal solution of $\overline{\overline{CO}}_3$ to cause the solubility product of barium carbonate to be reached, and until that concentration is exceeded no barium carbonate can be formed. The tenth-normal solution of $\overline{\overline{SO}}_4$ has not such a marked effect upon the formation of the carbonates of strontium and calcium. Thus:

$$\overset{++}{Sr} \times 0.1\overline{\overline{SO}}_4 = 0.00000029$$
$$\overset{++}{Sr} = 0.0000029 \text{ solubility of } SrSO_4 \text{ in presence of}$$
tenth-normal $\overset{++}{SO}_4$.

$$0.0000029 \times \overline{\overline{CO}}_3 = 0.000000005$$
$$\overline{\overline{CO}}_3 = 0.0017 \text{ normal.}$$

By this it is possible to explain the non-solution of barium sulphate in ammonium carbonate and in a solution of a sulphate and carbonate. In the case of ammonium carbonate acting upon the three sulphates, those of strontium and calcium form rapidly, even though the concentration of the $\overline{\overline{CO}}_3$ ions is small. The barium sulphate may also dissolve slightly, but the soluble sulphate formed during the reaction will soon prevent any further formation, and that formed from the strontium and calcium salts will cause the reverse transformation to take place, so that the barium sulphate transformed, will be formed again and its solubility decreased in proportion to the amount of $\overline{\overline{SO}}_4$ ions. Since our object is to make the precipitates as insoluble as possible it is always well to have an excess of the precipitant. According to Fresenius it is advisable to use a solution containing by weight one-third as much sulphate as carbonate. The carbonate and sulphate of potassium will then be related in terms normal as 1 : 0.4 ; and if we use a normal solution of potassium carbonate mixed with a 0.4 normal solution of potassium sulphate, the rela-

tion of the ions of $\overline{\overline{CO_3}}$ and $\overline{\overline{SO_4}}$ will be as 0.48 is to 0.21 normal.
Absolutely no barium carbonate will then be produced and the
solubility of the barium sulphate will be depressed to

$$\overset{++}{Ba} \times 0.21 = 0.0000000001$$
$$\overset{++}{Ba} = 0.0000000005 \text{ normal.}$$

The solubility of the strontium as well as of the calcium sul-
phate will be depressed but slightly.

$$\overset{++}{Sr} \times 0.21 = 0.00000029$$
$$\overset{++}{Sr} = 0.0000013$$
$$0.0000013 \times \overline{\overline{CO_3}} = 0.000000005$$
$$\overline{\overline{CO_3}} = 0.004 = \text{amount necessary to form solubility}$$

product.

$$\overset{++}{Ca} \times 0.21 = 0.0029$$
$$\overset{++}{Ca} = 0.014$$
$$0.014 \times \overline{\overline{CO_3}} = 0.000000154$$
$$\overline{\overline{CO_3}} = 0.0000011 = \text{amount necessary to form solu-}$$

bility product.

And even with the soluble sulphate formed during the reac-
tion the carbonates will be produced very rapidly. The speed of
the transformation will in all cases be proportional to the differ-
ence between the concentration of the metallic ions from the
carbonate and sulphate. The separation in presence of ammo-
nium carbonate, then, is caused by the soluble sulphate formed
during the reaction acting upon the barium sulphate, thus
making it more insoluble, while it has practically no retarding
effect upon the transformation of the other two sulphates. When
one molecule of $\overline{\overline{SO_4}}$ is present with barium sulphate, it counter-
acts the influence of 105 molecules of $\overline{\overline{CO_3}}$. In the case of the
mixture of carbonate and sulphate the amount of sulphate has
but a slight depressing effect upon the strontium and calcium
sulphates, while it depresses, to a very great extent, the solu-
bility of the barium sulphate. The excess of $\overline{\overline{CO_3}}$ ions has
the same effect upon the two carbonates so that the three salts
are made as insoluble as possible and are separated by hydro-

chloric acid, the calcium and strontium being then separated by other reagents.

All the above, as far as concerns the carbonates, is modified slightly by the hydrolytic dissociation which takes place in the solutions. The relations, however, between the carbonates and sulphates will remain unchanged since the hydrolytic dissociation will take place to nearly the same extent in the solutions of all three.

REVIEW.

A BRIEF HISTORY OF THE MOVEMENT FOR INCREASING THE ACCURACY AND FOR IMPROVING THE CONSTRUCTION OF CHEMICAL MEASURING INSTRUMENTS.

The greater part of the matter contained in this paper was compiled for the use of the " Committee on Standards for Chemical Measuring Instruments" of this society and formed a part of that committee's report, which was read at the New York meeting in December last, and which is now before the committee for the reconsideration of some minor details, in accordance with a promise made to a minority of the committee. I may state, however, that the committee has unanimously agreed to the proposition that the society extend a formal invitation to the U. S. Office of Standard Weights and Measures to adopt regulations governing the construction, calibration, and testing of volumetric apparatus, similar to the regulations of the Kaiserliche Normal-Aichungs-Commission of Germany. This was the most important recommendation contained in the report of the committee as presented at New York, and it will soon be before the council of the society for action.

It is at the suggestion of my fellow members of the committee that I now present the following data in this form.

THE WORK OF EUROPEAN CHEMISTS.

As early as 1891, the " Deutsche Gesellschaft für angewandte Chemie" and the " Verein deutschen Eisenhüttenleute" had taken up the question of standards for chemical measuring instruments, and it was with the assistance and coöperation of these associations that the excellent regulations of the German Normal-Aichungs-Commission for testing volumetric apparatus were perfected and finally adopted. These regulations, as published in 1893, were as follows:

NOTICE IN REGARD TO THE TESTING OF CHEMICAL MEASURING FLASKS, ETC.

[From Zeitschrift für angewandte Chemie. 1893, pp. 557-559].

The Kaiserliche Normal-Aichungs-Commission published the