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**THE SOLUBILITY OF PURE RADIUM SULFATE.<sup>1</sup>**

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I. Introduction.

In the recovery of radium from its ores by various processes, radium is at some stage always precipitated together with barium as sulfate. The completeness of this precipitation involves relationships not only of great practical but of considerable theoretical importance. In beginning a study of the principles involved, no more logical starting point seemed to present itself than the direct determination of the solubility, hitherto undetermined, of pure radium sulfate. This determination was carried out in water and in different concentrations of sulfuric acid.

If a solution containing a mixture of radium and barium salts be partially precipitated by the addition of some sulfate, it will be found that the Ra/Ba ratio in the precipitate is the same as in the original solution, and consequently no change of relative concentration results. This precludes the possibility of employing fractional precipitation in separating the two elements, and at once suggests a similarity to the behavior of the isotopic elements, generally recognized as wholly inseparable. We know, of course, that radium and barium are not isotopes, have quite different atomic numbers and are easily separated by other methods such as fractional crystallization of their halide salts. It is, however, important to investi-

<sup>1</sup> Published with permission of the Director of the Bureau of Mines.

gate how far reaching is this similarity in behavior to isotopic elements, whether it extends, for example, to identical solubility of corresponding salts of radium and barium.

By the conductivity method, Hulett<sup>1</sup> has found the solubility of barium sulfate in water to be  $2.3 \times 10^{-6}$  g. per cc. at 25°. If the inseparability of radium and barium, when precipitated as sulfates, is due to identical solubility, as in the case of isotopes, this value would also hold for radium sulfate. On the other hand the solubility (g. per cc.) of calcium sulfate<sup>2</sup> at 25° is  $2.09 \times 10^{-2}$  and of strontium sulfate<sup>3</sup>  $1.5 \times 10^{-4}$ . If we compare these three known values of solubility with the rising atomic weights of calcium, strontium and barium and make a rough extrapolation to radium (at. wt. 226.0) the solubility of radium sulfate would appear as at least 100 fold less than that of barium sulfate, or of the order of  $10^{-8}$  g. per cc., which would place radium sulfate among the least soluble salts known. Even so low a solubility as this would, however, fail to recover any radium under working conditions. In the work of the U. S. Bureau of Mines<sup>4</sup> in the production of radium from carnotite, 10-15 mg. of radium were precipitated daily together with a one-million fold excess of barium by the addition of excess of sulfuric acid to a solution 4 to 5 thousand liters in volume. Direct determination of Ra showed  $6.7 \times 10^{-12}$  to  $1.36 \times 10^{-11}$  g. per cc. in the filtrate containing about 0.5% sulfuric acid and 2-3% free nitric acid. Attributing the variations observed to some suspended (radium) barium sulfate and taking into account the increase of solubility by the presence of free nitric acid, it is certain that the weight of radium sulfate truly in solution in 1 cc. of filtrate is of the order  $10^{-12}$  g. (It will be later shown that this low value is not due to the repressive effect of excess of sulfuric acid through mass action, but to an entirely different cause.)

It must be admitted then that three values of widely differing orders  $10^{-6}$ ,  $10^{-8}$  and  $10^{-12}$  g. per cc. come into consideration as possible ones for the solubility of pure radium sulfate. It is the object of the present paper to decide between these by direct determination.

It might also be mentioned that for the quantitative determination of radium one is fortunate in having the "emanation" method, one of far greater sensitiveness than any possessed for ordinary elements. One is therefore enabled to extend solubility measurements into a region which could not hitherto be reached by the use of direct methods. It will therefore be of some additional interest to note whether the effect of mass action manifests itself at great dilutions.

<sup>1</sup> Hulett, *Z. physik. Chem.*, **37**, 398 (1901).

<sup>2</sup> Hulett and Allen, *THIS JOURNAL*, **24**, 667 (1902).

<sup>3</sup> Wolfmann, *Oesterr-Ungar. Z. Zuckind.*, **25**, 988 (1896).

<sup>4</sup> Parsons, Moore, Lind and Schaefer, U. S. Bureau of Mines, *Bull.* **104** (1916).

## 2. General Procedure.

In order to avoid all possibility of illusive results, it was thought best to approach the equilibrium from both sides to insure a true state of solution. Consequently measurements have been made of solutions prepared both by dissolving radium sulfate, and also by precipitating it from solution.

A possible difficulty was foreseen in the mass-action effect of unavoidable small quantities of sulfate in the water used as solvent, which might produce a marked and uncontrollable depression of a solubility already so low. Happily, it has been found that the solubility in water and in concentrations of sulfuric acid from 0.01 *N* to 50%, are approximately identical and therefore no especial precautions in this direction are necessary.

It is a well-known fact, frequently employed analytically for the purification of barium sulfate, that it is quite soluble in conc. sulfuric acid. This is also true of radium barium sulfate mixtures<sup>1</sup> and has here been found to be true of pure radium sulfate also. Occasion was therefore taken to extend the investigation to the higher concentrations of sulfuric acid in order to ascertain at what point this enhancement of solubility occurs.

## 3. Preparation of Pure Radium Sulfate.

As initial substance for the preparation of pure radium sulfate one employs most conveniently 100% radium bromide, which can be readily obtained in this degree of purity by recrystallizing a relatively large quantity of radium (Ba) bromide. Starting with 236.3 mg. of radium (element) in the form of the double bromide containing about 1.25% radium bromide, recrystallization from hydrobromic acid solution<sup>2</sup> was repeated until 150 mg. of radium element were found to have reached 70% purity. This quantity of bromide was then further recrystallized in rapid steps until it was practically certain that the head fraction, now reduced to 35 mg. of element, had reached 100% purity. This salt was then carefully dehydrated at 120° and one portion of 50 mg. (total weight of salt) was quickly weighed on an assay balance, and at once sealed in a glass tube in the usual way for a gamma ray determination of the radium content.<sup>3</sup> 50 mg. radium bromide contain 29.3 mg. radium element, which was exactly the quantity reported by the U. S. Bureau of Standards as contained in the tube on the basis of a gamma ray measurement. After this verification of the purity of the salt, the remaining portion of the same purity (about 5 mg. of element) was divided into two approximately equal portions, one of which was converted into radium sulfate by fuming to dryness several times with pure sulfuric acid.

<sup>1</sup> Schlundt, *J. Phys. Chem.*, 20, 485-94 (1916).

<sup>2</sup> U. S. Bureau of Mines, *Bull.* 104, 80-85 (1916).

<sup>3</sup> Rutherford, "Radioactive Substances and their Radiations," 1913, 657-8.

#### 4. Preparation of the Solutions.

Very small portions of pure radium sulfate were introduced into the following solutions to be saturated with radium sulfate:

*Ia*,  $N - H_2SO_4$ ; *Ib*,  $0.1 N - H_2SO_4$ ; *Ic*,  $0.01 N - H_2SO_4$ ; *Id*, specially distilled water.

The quantities of salt introduced, although small, were later found to be several hundred times the quantity required to saturate 10–15 cc. of the solution, which quantity was sealed in long-neck glass flasks.

For attainment of saturation from the precipitation side, the remainder of the pure radium bromide (about 3 mg. of element) was dissolved in 250 cc. of freshly distilled water. Portions of 10 cc. of each were at once diluted with equal volumes so as to furnish 20 cc. of each of the following solutions:

*Iia*,  $1 N - H_2SO_4$ ; *Iib*,  $0.1 N H_2SO_4$ ; *Iic*,  $0.01 N - H_2SO_4$ ; *Iid*,  $0.1 N - Na_2SO_4$ .

The quantity of radium contained initially in each of these Class II solutions is 4 to 5 hundred times the amount necessary for saturation. A number of more concentrated solutions, from 10% to 90% sulfuric acid, were also saturated by using portions of the same radium bromide solution.

#### 5. Experimental Procedure.

The small flasks containing the solutions to be saturated with radium sulfate were agitated in a thermostat, electrically heated and regulated, until equilibrium at a fixed temperature was attained. No experiments were made to determine the rate of solution nor of precipitation, but no differences in concentration were to be noted after a few days between the values obtained from the two opposite directions, and the values of Class I solutions were found to have remained constant after eleven months.

**Filtration.**—One cc. of solution was found to be a suitable quantity for the "emanation" method. Accordingly pipets were carefully calibrated to deliver 1 cc. Preliminary experiments on Class I solutions showed that while it was sometimes possible to remove the supernatant liquid directly, frequently an invisible particle of radium sulfate would be drawn off which would vitiate the result by 75 to 100 fold. To avoid this a filtering tip was ground for each pipet, by means of which the solution was drawn through a layer of cotton (or asbestos fiber for solutions containing more than 45% sulfuric acid) closely packed below a 1 mm. constriction in the tube constituting the tip. A 1-inch layer of cotton was found to be sufficient in general, though an occasional very high result suggested that a particle of solid might sometimes pass through it if not tightly packed.

**Adsorption by the filter** did not seem greatly to be feared in the short time necessary to draw the solution through, especially as values approximately equal have been occasionally obtained with and without a filter. Nevertheless the following direct test was made: A properly diluted

solution of radium bromide was prepared without any precipitant being added, and was acidulated with some hydrobromic acid to prevent the precipitation of radium carbonate.

Three 1 cc. portions of this solution were withdrawn in a pipet as follows:

Original, without any cotton; (I), with a fresh layer of cotton; (II), using same layer of cotton immediately after (I).

Two sets of determinations (not comparable with each other) gave the following results for radium (element) left in solution under the three conditions, expressed in g.  $\times 10^{-8}$ :

Solution.	Original.	I.	II.
First determination.....	1.156	1.010	1.124
Second determination.....	1.333	1.248	1.395

In each case it will be noted that the first portion (I) drawn through cotton is slightly lower than the original, but that the second portion recovers approximately the initial concentration of Ra. The procedure adopted therefore was to discard the first portion drawn through the filter, and at once draw one or two other portions through the same cotton (or asbestos).

**Radium Measurements.**—The quantity of radium sulfate in solution was determined directly by employing the "emanation" method for the radium itself.<sup>1</sup> The procedure consisted in drawing the solution into the pipet as just described and immediately allowing it to run into a small Pyrex flask (125 cc.) half full of 1-1 nitric acid, which was immediately boiled to expel emanation, sealed a few days for the fresh accumulation of emanation which was boiled off and introduced into the emanation chamber of an "interchangeable" electroscope.<sup>2</sup>

In the cases of the sulfuric acid solutions of higher concentration (above 30%), concentrated sulfuric acid (> 95%) was employed as storing solution instead of 1-1 nitric acid to avoid the possibility of any reprecipitation of radium.

## 6. Experimental Results.

In the following table are given the results for the solubility of radium sulfate, Class I by solution, Classes II and III by precipitation. It will be observed that the values in Classes I and II are practically identical (and also in Class III up to about 50% sulfuric acid indicating that a true state of solution is being dealt with. The absence of repressive effect of excess of sulfuric acid on the solubility of radium sulfate is a very fortunate circumstance, as regards the determination in water (see Introduction) and will also be given further consideration.

<sup>1</sup> Lind, *J. Ind. Eng. Chem.*, 7, 406-10, 1024-29 (1915); U. S. Bureau of Mines, *Bull.* 104, Chap. V.

<sup>2</sup> For details of the "emanation" method see Lind, *Loc. cit.*

TABLE SHOWING SOLUBILITY OF  $\text{RaSO}_4$  IN  $\text{H}_2\text{O}$  AND IN SOLUTIONS OF  $\text{H}_2\text{SO}_4$  AT  $25^\circ$ .

Class I. By Solution of $\text{RaSO}_4$ .		Class II. By Precipitation of $\text{RaSO}_4$ .	
Solvent.	Solubility $\text{RaSO}_4$ in g. $\times 10^{-8}$ per cc.	Solvent.	Solubility $\text{RaSO}_4$ in g. $\times 10^{-8}$ per cc.
$N \text{ H}_2\text{SO}_4$ .....	2.1	$N \text{ H}_2\text{SO}_4$ .....	2.3
$0.1 N \text{ H}_2\text{SO}_4$ .....	2.3	$0.1 N \text{ H}_2\text{SO}_4$ .....	2.1
$0.01 N \text{ H}_2\text{SO}_4$ .....	2.0	$0.01 N \text{ H}_2\text{SO}_4$ .....	2.1
$\text{H}_2\text{O}$ .....	2.1	$0.1 N \text{ Na}_2\text{SO}_4$ .....	(12.0) <sup>1</sup>

Class III. By Precipitation of  $\text{RaSO}_4$ .Solvent  $\text{H}_2\text{SO}_4$ .

10%	2.4
15%	2.4
25%	2.3
30%	2.3

Filtered through Asbestos.

45%	1.9
50%	2.1
55%	3.4
60%	6.3
65%	6.4
70%	(78.8) <sup>2</sup>
80%	(79.2) <sup>2</sup>
90%	(77.6) <sup>2</sup>

To get some idea of the effect of change of temperature on the solubility a few measurements were made at  $35^\circ$  and  $45^\circ$ . In  $0.01 N$  sulfuric acid the solubility at  $35^\circ$  is  $3.0 \times 10^{-8}$  g. per cc., an increase of 50% over the value  $2.0 \times 10^{-8}$  at  $25^\circ$ . In 25% sulfuric acid at  $35^\circ$  the value is  $3.3 \times 10^{-8}$ , an increase of 43.5% over the value  $2.3 \times 10^{-8}$  at  $25^\circ$ , while at  $45^\circ$  in 25% sulfuric acid the value is  $5.0 \times 10^{-8}$  more than double the value at  $25^\circ$  and about 50% higher than at  $35^\circ$ .

## 7. Discussion of Results.

It is quite evident that the observed solubility of radium sulfate in water,  $2.1 \times 10^{-8}$  g. per cc., agrees with that predicted by the physical-chemical method of extrapolating from the solubilities of calcium, strontium and barium sulfates, and is about 100 times less than that of barium sulfate.

The absence of any effect of sulfuric acid up to 50% on the solubility is notable. The result is not the one to be expected from mass action, but as far as the authors are aware no experimental proof of the applicability of this principle has been made by direct methods for difficultly soluble salts of the bi-bivalent type. Z. Karaoglanow<sup>3</sup> has recently observed that the solubility of barium sulfate also appears to be the same in water as in sulfuric acid up to  $0.3 N$ .

<sup>1</sup> Average of several results showing rather wide deviation.

<sup>2</sup> These three values do not represent saturation, and merely indicate that the solubility exceeded the quantity of Ra available, which was the same in all three cases.

<sup>3</sup> Karaoglanow, *Z. anal. Chem.*, **56**, 225-54; *J. Chem. Soc.*, **112**, II, 387-8 (1917).

Since it has been shown that at the higher concentrations of sulfuric acid (above 65%) the solubility of radium sulfate undergoes a marked increase, it might be supposed that at lower concentrations, the solvent effect of the acid is just counterbalancing the repressive effect of sulfate. One experiment with 0.1 *N* sodium sulfate was made to test this hypothesis, which as will be seen, does not lend it any support. The apparently high solubility of radium sulfate in sodium sulfate solution, suggests either formation of a soluble double salt, or difficult coagulation of radium sulfate in absence of H ion. The former suggestion is supported by the results of Karaoglanow, who found that sodium sulfate as well as potassium sulfate and other salts increased the solubility of barium sulfate. While the latter view, that of difficulty of coagulation, is given support by the variability of the measurements in sodium sulfate, as well as by the recent work of H. B. Weiser,<sup>1</sup> who found Na-ion unfavorable to the coagulation of barium sulfate. The practical result would be the same, that the precipitation and filtration of radium sulfate would be incomplete in the presence of sodium or potassium salts. Since, however, barium is usually present in practice, the authors postpone the further investigation of the effect of electrolytes to a later paper dealing with mixtures of radium and barium.

The *effective* concentration of radium sulfate of the order of  $10^{-12}$  g. per cc., which can be attained as already stated, when a radium barium mixture (1 to 1,000,000) is precipitated by an excess of sulfuric of 0.5% concentration, is not to be explained by the mass action effect of excess of precipitant, but by a new and yet imperfectly understood principle of inseparability of certain elements like radium and barium by precipitation. The difference of 100-fold solubility between radium sulfate and barium sulfate shows that the precipitation is in direct controversion of mass action. A fuller discussion will be found in a later paper under the title of "Pseudo-isotopy," which term one of the authors proposed at the Kansas City meeting, (April 7, 1917) of the Amer. Chem. Soc.<sup>2</sup> At present suffice it to say that in a solution with not too great excess of sulfuric acid, the solubility of barium sulfate is  $2.3 \times 10^{-6}$  and the effective solubility of radium sulfate would be this value multiplied by the Ra/Ba ratio obtaining in the solution before precipitation. In case this ratio were 1/1,000,000 its effective solubility would then be of the order  $10^{-12}$  g. per cc., which has actually been found by repeated experiments under these conditions, as stated in the Introduction.

#### Summary.

1. The solubility of pure radium sulfate in 1 cc. of water at 25° is  $2.1 \times 10^{-8}$  g., about 100-fold less than that of barium sulfate.
2. The solubility at 25° of pure radium sulfate in sulfuric acid solutions

<sup>1</sup> H. B. Weiser, *J. phys. Chem.*, 21, 314-35 (1917).

<sup>2</sup> *Science*, 46, 170 (1917).

is identical with that in water from 0.01 *N* up to 50% acid. The same values were obtained either by dissolving or precipitating the radium sulfate indicating a true state of solution.

3. The value found is that predicted from comparison with the decreasing solubilities of calcium, strontium and barium sulfates.

4. Excess of sulfuric acid does not have a repressive effect on the solubility of radium sulfate.

5. On increasing the concentration of sulfuric acid above 65%, a marked rise in solubility of radium sulfate takes place, and it is more than 12 times as soluble in 70% as in 65% acid.

6. An explanation is given of the "effective solubility" of radium sulfate (when precipitated together with large excess of barium) which is found to be far below the actual solubility of radium sulfate.

7. The solubility of radium sulfate in sulfuric acid solutions up to 25% acid is about 50% higher at 35° than at 25° and again increases about 50% in the temperature interval 35° to 45°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## EQUILIBRIA INVOLVING CYANOGEN IODIDE; THE FREE ENERGY OF FORMATION OF CYANOGEN.

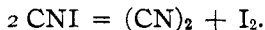
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While there is doubtless an equilibrium between carbon, nitrogen and cyanogen at the temperature of the electric arc, it has not hitherto been found practicable to determine the free energy of formation of cyanogen through a study of this simple equilibrium. It is, however, possible, when the free energy of formation of hydrocyanic acid is known, to obtain that of cyanogen by the aid of two reversible reactions. The study of the equilibrium in these reactions will form the subject of this paper.

### The Dissociation of Cyanogen Iodide.

The two reactions to which we have referred both involve the interesting substance cyanogen iodide (or as it might perhaps better be called, iodine cyanide). This is a white substance which, on moderate heating, decomposes readily according to the reaction



When the substance is heated in a closed tube the dissociation evidently occurs until a definite equilibrium is established, and solid cyanogen iodide remains in the presence of its own vapor, gaseous iodine, and cyanogen. Since the vapor of cyanogen iodide dissociates without change of volume, and since the reaction is evidently too rapid to permit a determination of