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(Radium Volume)

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SUMMARY

The purpose of the research work reported in this volume is the development of a process for the separation and subsequent purification of radium from the K-65 (pitchblende) residue. Except for the accumulation of additional experimental data the process is essentially complete.

After a preliminary extraction of about 85 per cent of the lead and 40 per cent of the silica with a 40 per cent sodium hydroxide solution, the residue is treated with a solution containing both sodium hydroxide and sodium carbonate to obtain additional lead removal and partial conversion of the radium and barium sulfates to carbonates. After leaching out the soluble carbonates, the residue containing unconverted sulfates is treated with a sodium carbonate solution at 170° under pressure. A study of the amount and concentration of sodium carbonate required to obtain a satisfactory conversion of the sulfates (p. 6) has shown that the total sodium carbonate may be reduced by 40 per cent and that smaller volumes of solution may be employed without serious decrease in the efficiency of the conversion.

In order to make calculations on the number of steps and tank sizes for the radium-barium separation by fractional precipitation, equations have been developed to calculate this information from the theoretical separation factors determined experimentally (p. 10).

Three methods for carrying out the radium-barium separation by fractional precipitation of chromates have been studied and the separation factors determined (p. 14). The methods differ in the reagent and temperature employed for the neutralization of the nitric acid solution of the chromates. The separation factor improves with decrease in temperature, and a marked improvement has been found by replacing urea which requires boiling temperatures for hydrolysis with potassium cyanate which hydrolyzes at much lower temperatures.

The comparative efficiencies are as follows:

REAGENT	TEMPERATURE	ENRICHMENT PER STEP
UREA	100°	3.00
POTASSIUM CYANATE	25°	3.55
POTASSIUM CYANATE	0°	4.26

Radium of over 40 per cent purity has been obtained by the chromate fractionation methods (p. 24).

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Solubility studies of barium chromate in nitric acid have been made to determine the upper limit on the barium concentration which can be used in the chromate fractionation procedure (p 29)

Additional runs have been made on the ion exchange separation of radium and barium to determine the effect of pH and temperature on the efficiency of the separation (p 33) Since the solubility of the barium citrate appeared to be the limiting factor on the capacity of the ion exchange column for handling barium, solubility studies were made (p 41) The results indicate that, from the solubility standpoint, the best operating conditions should be found for citrate concentrations of about 0.24 molar at a pH of about 5.6

Some engineering studies have been made on the filtration characteristics of the process slurries in an effort to obtain more specific data for filter design (p 64)

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Problem Title - Carbonation of Barium Sulfate Under Pressure

Report By E. F. Joy

Work Done By - E. F. Joy

INTRODUCTION

A study of the pressure carbonation of barium sulfate with sodium carbonate solution has been undertaken as a guide to the carbonation of K-65 residue for the recovery of barium and radium. The effect of time and temperature on the reaction has been observed over certain ranges and the results have been reported.¹ This work has been extended to cover the effect of varying molar excess of sodium carbonate and of the concentration of sodium carbonate on the reaction equilibrium.

DETAILED REPORT

The equipment and procedure previously described was used in carrying out the pressure carbonations. One additional experiment on the effect of temperature on the conversion of barium sulfate was made at 190°. A slight drop in conversion to 98.6 per cent was found when compared with the previously obtained conversion of 99.2 per cent at 170°. The remaining experiments were all made at 170° and at a gauge pressure of 93 pounds per square inch.

The effect of the molar ratio of sodium carbonate to barium sulfate was studied in a series of experiments summarized in Table I and Figure 1. Experiments 14 and 18 were duplicates, carried out at a mole ratio of 2:1 and gave conversions of 73.6 and 72.4 per cent. The sharp rise in conversion obtained on increasing the mole ratio from 2:1 to 3:1 should be noted. Only a slight further increase in conversion was obtained at the molar ratio of 5:1 which has been used for the carbonation of K-65 residues in the past. These experiments suggested that a considerable reduction in the use of sodium carbonate could be made with only a slight loss in conversion. K-65 carbonation experiments at a molar ratio of 3:1 now in progress, confirm this conclusion.

Experiments on the effect of sodium carbonate concentration on the reaction equilibrium are summarized in Table II and Figure 2. In the range of fifteen to twenty-five per cent sodium carbonate the conversions change slightly. Sodium carbonate concentration is a minor factor in the conversion of barium sulfate and can be varied within limits to satisfy other conditions such as the filtration rate.

Good recoveries of barium sulfate, varying from 98.4 per cent to 100.0 per cent were obtained in all experiments.

REFERENCE

1. Joy, E. F., Rept. Gen. Res., MLM-498, p. 14 June 26 - September 18, 1950.

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TABLE I
PRESSURE CARBONATION OF BARIUM SULFATE AT 170°
(EFFECT OF MOLE RATIO $\text{Na}_2\text{CO}_3/\text{BaSO}_4$)

EXPERIMENT NUMBER	BaSO_4 (g)	Na_2CO_3 (g)	H_2O (g)	Na_2CO_3 CONC. (per cent by weight)	MOLE RATIO $\text{Na}_2\text{CO}_3/\text{BaSO}_4$	UNCONVERTED BaSO_4 (g)	BaSO_4 CONVERTED TO BaCO_3 (g)	BaSO_4 ACCOUNTED FOR (per cent)	CONVERSION (per cent)	$K = [\text{SO}_4^{2-}]/[\text{CO}_3^{2-}]$
14	400	363	1452	20	2	105.6	288.0	98.4	73.6	0.582
18	600	545	2180	20	2	165.5	429.0	99.1	72.4	0.568
16	400	545	2180	20	3	6.01	390.5	99.1	98.5	0.489
17	300	545	2180	20	4	3.09	295.5	99.5	99.0	0.329
10	200	454	1816	20	5	1.65	195.6	98.6	99.2	0.248

TABLE II
PRESSURE CARBONATION OF BARIUM SULFATE AT 170°
(EFFECT OF Na_2CO_3 CONCENTRATION)

20	400	545	2088	15	3	4.76	394.5	99.8	98.8	0.491
16	400	545	2180	20	3	6.01	390.5	99.1	98.5	0.489
19	400	545	1635	25	3	7.97	392.0	100.0	98.0	0.485

CONVERSION OF BARIUM SULFATE TO BARIUM CARBONATE. EFFECT OF EXCESS SODIUM CARBONATE.

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MLM 511

Problem Title Fractional Precipitation Scheme
Report By E F Joy
Work Done By E F Joy

INTRODUCTION

The general principles underlying the separation of mixtures by fractionation procedures have been discussed by Tipson¹. In setting up a repeated fractional precipitation scheme such as has been proposed for the separation of barium and radium it is a desirable condition that solids and solutions of the same composition be combined in order to avoid loss of efficiency in the separation. In order to operate such a scheme on a continuous basis it is also necessary that fractions of the same composition recur at regular intervals, so that addition of starting material can be made at the proper point. For any specific separation this may require the use of a great many containers depending on the relationship of the enrichment and depletion factors^{2,3}. In practice a sacrifice in efficiency of separation is often made in order to reduce the number of containers.

For the simplest fractionation scheme involving no loss in efficiency it is necessary for the enrichment factor to be the reciprocal of the depletion factor for each component. A hypothetical batch fractionation scheme using this principle has been described by Tipson,¹ page 634. Figures 16 and 17. As applied to fractional precipitation the fraction x of one component is precipitated leaving the fraction $1-x$ in solution. In general a different fraction, y , of the second component will be precipitated and $1-y$ will be left in solution. If conditions can be controlled so that the sum of the fractions of each component precipitated $x+y$ is equal to one, i.e., $y=1-x$, then the reciprocal relationship between the enrichment and depletion factors is established and a simplified scheme can be set up.

Under these conditions the fraction $1-x$ of the second component will be carried by fraction x of the first component. On refractionating the first precipitate a solution will be obtained whose composition is the same as the starting material. In like manner refractionating the first solution will give a precipitate having the same composition as the starting material. Solution and precipitate of the same composition can be combined and fresh starting material added at each refractionation. A countercurrent batch-fractionation scheme based on this principle has been set up and equations have been developed to express the enrichment for any number of precipitation steps and the amounts of the two constituents in each fraction at equilibrium.

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DETAILED REPORT

The proposed fractionation scheme is outlined in Figure 1A for Component A. The flow of A in the solution is indicated by the upper arrows and in the precipitates by the lower arrows. Feed of the starting mixture enters at the central Fraction, 0, and removal of the final precipitate and solution after k fractionation steps is indicated at k and -k respectively. For a material balance

$$A_F = A_k + A_{-k} \quad (1)$$

where A_F is the amount of Component A added in the feed and A_k and A_{-k} are the amounts of A removed in the final precipitate and solution, respectively

At each step the fraction x of Component A is precipitated and 1-x is left in solution. (A complementary relation holds for Component B, i.e., the fraction 1-x is precipitated and x remains in solution.) The enrichment occurring at each step is therefore $E = \frac{1-x}{x}$ and in k steps the enrichment $E_k = \left(\frac{1-x}{x}\right)^k$. The corresponding depletions are $D = \frac{x}{1-x}$ and $D_k = \left(\frac{x}{1-x}\right)^k$. The ratio of A in the final solution to A in the final precipitate is given by

$$\frac{A_{-k}}{A_k} = \left(\frac{1-x}{x}\right)^k \quad (2)$$

The amount of A in the Fraction 0 can be shown to be

$$A_0 = \frac{A_{-k} - A_k}{1-2x} \quad (3)$$

Starting with Fraction 0, the general equation for the amount of Component A in Fraction N can be found as follows:

$$P_1 = A_0 x \text{ and } S_1 = A_0 (1-x)$$

where P_1 and S_1 are the amounts of Component A in the precipitate and solution respectively as designated in Figure 1A. Similar equations hold for the precipitate and filtrate from Fraction 1,

$$P_2 = A_1 x \text{ and } S_2 = A_1 (1-x)$$

From a material balance of the overall cycle,

$$S_2 = P_1 - A_k - A_0 x - A_k$$

By combining the two equations for S_2 , A_1 in terms of A_0 can be obtained.

$$A_1 = \frac{A_0 x - A_k}{1-x} \quad (4)$$

From this basic equation A_2 in terms of A_0 is found to be

$$A_2 = A_0 \left(\frac{x}{1-x}\right)^2 - \frac{A_k}{1-x} \left(\frac{x}{1-x} + 1\right)$$

Letting $z = \frac{x}{1-x}$, and rearranging terms, the general equation for A_n in terms of A_0 is found to be

$$A_n = A_0 z^n - \frac{A_k}{1-x} \left(1 + z + z^2 + \dots + z^{n-1}\right) \quad (5)$$

where $0 < n < k$

For fractions to the right of the feed, a similar relationship holds

$$A_{-n} = A_0 y^n - \frac{A_{-k}}{x} \left(1 + y + y^2 + \dots + y^{n-1}\right) \quad (6)$$

where $y = \frac{1-x}{x}$

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Because of the reciprocal relationships between the enrichment of A and B equation 5 can be used to calculate the amounts of B in the fractions to the right of the feed and equation 6 for the amounts of B to the left of the feed. The preceding equations in general apply only for an equal number of enrichment and depletion steps.

For the fractionation of mixtures where one component is present in relatively small amounts as is the case with barium and radium, the total weight of each fraction can be taken to be that of the component present in excess.

A numerical example for the separation scheme is given in Figure 1B as it might be applied to the separation of barium and radium. It is assumed that 20 per cent of the barium is precipitated at each step and that it carries 80 per cent of the radium, $x = 0.20$ and $1-x = 0.80$, and that four fractionations are carried out on the enrichment and depletion sides. The distribution of barium is shown (Figure 1B) assuming that one part of barium is removed at the radium-rich end, $A_k = 1$.

The enrichment per step is then $\frac{0.80}{0.20} = 4.0$ and for four steps $E_4 = \left(\frac{1-x}{x}\right)^4 = 256$ (also equals A_k). From equation 1, the feed $A_F = 257$ and from equation 3, $A_0 = 425$. Using equations 5 and 6, the values for A_1, A_2, A_3 and for A_{-1}, A_{-2} and A_{-3} were calculated in terms of $A_0 = 425$.

The reciprocal relationship for radium can be shown from the numerical example by assuming a feed containing 257 grams of barium and 257 micrograms of radium. The final precipitate recovered as A_4 would contain 1 gram of barium and 256 micrograms of radium, and the discard solution would contain 256 grams of barium and 1 microgram of radium. Expressed on a percentage basis, 99.61 per cent of the radium would be recovered in 0.39 per cent of the barium. The overall enrichment factor of 256 would bring the barium-radium ratio from 1,000,000:1 down to 3,906:1 for the four steps considered.

REFERENCES

1. Tipson, R. Stuart, Anal. Chem., 22, 628 (1950)
2. Schull, C. E., J. Am. Chem. Soc., 42, 889 (1920)
3. Stites, J. G., Rept. Gen. Res., MLM-498, 27 (June 26 - September 18, 1950)

A FRACTIONAL PRECIPITATION SCHEME GENERAL CASE

B NUMERICAL EXAMPLE. SHOWING DISTRIBUTION OF BARIUM IN A 4 STEP FRACTIONATION WITH 20% OF THE BARIUM CARRYING 80% OF THE RADIUM.

FIGURE 1

Problem Title - The Concentration of Radium from Barium Rich Mixtures

Report By M L Salutsky and J G Stites

Work Done By - M L Salutsky and J G Stites

INTRODUCTION

Radium and barium are difficult to separate principally because all known salts of these two elements are isomorphous; hence fractional methods are required for their separation. These methods depend on the fact that precipitation of a specific fraction of barium salt will carry from solution a somewhat different fraction of the radium salt. Some of the compounds which have been used for the concentration of radium from barium-rich mixtures are the bromides,^{1,2,3} chlorides,² sulfates,⁴ chromates,^{5,6,7} hydroxides,⁸ and carbonates.^{9,8}

The primary objective of this study is the development of a continuous fractionation scheme for the concentration of radium which is both rapid and inexpensive. For a procedure to be continuous,¹⁰ it is necessary that the sum of the per cent of total radium and per cent of total barium precipitated equal 100.

$$\% Ra_p + \% Ba_p = 100$$

The separation is most efficient when the per cent of the total barium precipitated is very small and the per cent of the total radium carried is very large. A working ratio (R) of 80:20 would mean that 80 per cent of the radium is carried from solution by the precipitation of 20 per cent of the barium. The radium enrichment factor per fractionation step would equal 4.00 (80/20 = 4.00). A procedure developed on this ratio would be more efficient and require fewer fractionation steps than one dependent on a working ratio of R = 70:30. In the following study attempts have been made to find the conditions which yield the most favorable working ratio.

For a comparison of the several fractionation methods, two types of distribution constants (partition factors) have been used. One type follows a linear rule, the other a logarithmic rule. The linear relationship of Henderson and Kracek⁵ assumes that the radium-barium ratio of the crystals is proportional to the radium-barium ratio of the dissolved salt.

$$\frac{Ra_p}{Ba_p} = D \frac{Ra_s}{Ba_s}$$

Ra_p represents the concentration of the radium in precipitate (crystals), Ba_p the concentration of barium in the precipitate, Ra_s , radium in solution, Ba_s , barium in solution and D , a distribution constant. The above equation is dependent on the attainment of true equilibrium between crystals and solution. If equilibrium is not obtained, D will vary with the amount of barium salt precipitated.

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When precipitations are made slowly i.e. fractional crystallization or precipitation from homogeneous solution the linear relationship does not apply. The solution and the crystal surfaces, not the entire crystal, are in equilibrium and as successive layers are deposited on the crystals, the composition of the solution changes. Hence the crystals from such precipitations should consist of a series of layers with the barium-radium ratio varying continuously from layer to layer. These systems are described best by the logarithmic rule of Doerner and Hoskins⁴

$$\log \frac{Ra_f}{Ra_0} = \lambda \log \frac{Ba_f}{Ba_0}$$

Ra_f represents the amount of radium in solution after precipitation, Ra_0 , the amount of radium in solution before precipitation, Ba_f , the amount of barium after precipitation, Ba_0 , that of barium before precipitation and λ is the distribution constant.

Walter and Schlundt¹ calculated λ values for the fractional crystallization of the bromides, chlorides, and sulfates and found values of 5.64, 2.74, and 1.80, respectively. It is evident that the fractional crystallization of the bromides is the most efficient of these methods. However, this comparison cannot be made when the fractionation methods follow different precipitation rules. The fractional crystallization of radium-barium bromides cannot be compared with the fractional precipitation of radium-barium chromates as carried out by Henderson and Kracek⁵, and by Murkulova⁶ since the former procedure involves a logarithmic rule and the latter a linear relationship. A direct comparison of λ values with D values has no meaning.

Henderson and Kracek⁵ indicate that greater enrichments per fractionation step can be obtained by the fractional precipitation of barium-radium chromates than by any of the other known fractional methods. Their work was confirmed by Murkulova⁶ who showed that the efficiency per fractionation step is greatly improved if the precipitations are carried out at room temperature instead of from hot solutions. In agreement with Henderson and Kracek he found that greater enrichments were obtained if the precipitations were made from acid solutions (0.1-0.25 M HNO_3) rather than from neutral solutions. Nikitin¹¹ attempted to separate barium and radium chromates in a manner similar to that used for the separation of barium and strontium chromates. Instead of precipitating the chromates from an acetic acid solution, he chose a stronger acid, namely trichloroacetic acid. Nikitin reports that this reaction, although not quantitative, is qualitative and between narrow limits of radium concentration can serve as a means of rapidly concentrating radium.

Although chromate precipitations seem to give better enrichments than any of the other fractional procedures, no systematic fractionation scheme has previously been developed. The control of the amount of barium chromate precipitated has been a major difficulty. The chromates are usually quite gelatinous and difficult to filter. This results from the manner in which the precipitation was made. The chromates were precipitated from acid solutions by the addition of a base. Rapid precipitations of this type generally yield gelatinous precipitates.

If the chromates are precipitated from homogeneous solution by the hydrolysis of urea or potassium cyanate granular precipitates are produced and filtration is rapid. The chromate urea method for the concentration of radium from barium-rich mixtures was discussed in an earlier report.⁷

The mechanism for the hydrolysis of urea was reported by Warner^{1,2} as being

From examination of the above reaction it was concluded that (1) a cyanate might be substituted for urea in the homogeneous phase precipitation for radium enrichment and (2) the decomposition might be carried out at a lower temperature than that required for the decomposition of urea. Murkulova³ reports that enrichment is much better when the chromates of barium and radium are precipitated from solutions at room temperature than when they are precipitated from hot solution.

These hypotheses were verified by experimentation and a procedure was devised in which potassium cyanate was used.

DETAILED REPORT

Several attempts were made in the laboratory to institute a continuous scheme for separation of radium from barium utilizing the timed chromate-urea method.⁷ The amounts of barium chromate precipitated under identical conditions were inconsistent.

The discrepancies in the quantities of barium precipitated could be eliminated however if the amount of chromate present could be limited to that required for the precipitation of the desired fraction of barium. Such a change in procedure would necessitate the removal of excess chromate ions before the reaction was started.

Studies on the solubility of barium chromate in nitric acid have been made in this laboratory¹³ and from examination of the data it was noted that barium chromate is converted to barium nitrate by nitric acid. The solubility of barium nitrate in concentrated nitric acid was reported in the literature to be negligibly small¹⁴ and Willard and Goodspeed¹⁵ have devised a quantitative separation of barium utilizing this knowledge.

The conversion of barium chromate to barium nitrate involves the digestion of the chromate with hot concentrated nitric acid (approximately 5 milliliters of concentrated nitric acid per gram of barium chromate) transferring the hot mixture to a sintered glass funnel and washing several times with hot concentrated nitric acid. About 5 milliliters of concentrated nitric acid per gram of barium chromate is required for wash. Some nitric acid is retained on the crystals. The last traces of chromate and the nitric acid on the crystals of barium nitrate can be removed by washing with dry acetone. There is a virtually complete recovery of the barium and radium by this method. The chromate (as chromic acid) can be recovered from the extract by distillation of the nitric acid.

A more efficient means of conversion would be to place the barium chromate in a column and pass hot concentrated nitric acid through the column

PROCEDURE

Three procedures have been devised for the enrichment of radium in radium-barium mixtures. These procedures may be entitled (1) chromate precipitation by the hydrolysis of urea at 100° (2) chromate precipitation by the hydrolysis of cyanate at 25° and (3) chromate precipitation by the hydrolysis of cyanate at 0°

Procedure 1 Chromate Precipitation by the Hydrolysis of Urea at 100°

This method with some changes has been reported⁸. In general the method consists of adding concentrated nitric acid to about 7.4 grams of radium-barium carbonate (this amount of carbonate is equivalent to five grams of barium) until no further effervescence was noted. The barium nitrate so formed was diluted to 500 milliliters with 0.1 normal nitric acid and then, was heated to 90°. A weighed quantity of potassium chromate (the amount weighed depended on the fraction of barium to be precipitated) was dissolved in 50 milliliters of hot 1.0 normal nitric acid and added slowly with stirring to the hot barium nitrate solution. About 30 grams of urea was added and the solution was boiled and stirred. As the urea hydrolyzed the excess nitric acid was neutralized and radium enriched barium chromate precipitated.

During the neutralization of the acid the color of the mixture changed from orange to lemon yellow. The solution reached a pH of 5 to 6 before all of the chromate had been precipitated. Barium chromate is practically insoluble in this pH range so that the supernatant liquid became colorless. Both the precipitate and the liquid phase were analyzed for barium and radium. Before analysis the barium in the liquid phase was precipitated as the carbonate.

Procedure 2 Chromate Precipitation by the Hydrolysis of Cyanate at 25°

About 7.4 grams of radium-barium carbonate was dissolved in seven milliliters of concentrated nitric acid diluted to 500 milliliters with water. A weighed amount of potassium chromate was dissolved in 3.3 milliliters of concentrated nitric acid diluted to 50 milliliters with water. The amount of potassium chromate weighed depended on the fraction of barium to be precipitated. The chromate solution was added with stirring to the barium nitrate solution. After these solutions had been thoroughly mixed, five grams of potassium cyanate dissolved in ten milliliters of water was added to the reaction mixture. The reaction was carried out at room temperature (~25°). Precipitation started approximately three minutes after the addition of the cyanate and was complete as evidenced by the colorless supernatant liquid, in about 20 minutes. Both the precipitate and the supernatant liquid were analyzed for barium and radium.

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The amount of chromate precipitate found in each experiment was consistently high. Analyses showed that some barium carbonate was coprecipitated with the barium chromate. To remedy this five milliliters of glacial acetic acid was added to the reaction mixture in addition to the seven milliliters of concentrated nitric acid. The acetic acid acted as a buffer for the reaction since the quantity of potassium cyanate added was less than that amount necessary for the complete neutralization of all the acid present. At the end of the reaction to which the acetic acid had been added the solution was pH 3 to 4. There was no evidence of barium carbonate in the precipitate. These reactions were stirred by aeration in an attempt also to decrease the carbon dioxide concentration.

In spite of the precautions precipitates were obtained which weighed more than that expected from theoretical calculations. Qualitative tests applied to a hot wash water from the precipitates showed both barium ions and nitrate ions to be present. The coprecipitation of barium nitrate with barium chromate was not observed in the precipitations from hot solutions because of the increased solubility of the barium nitrate.

Barium sulfate when precipitated from solutions containing an excess of barium ions carries with it both barium and alkali metal salts as contaminants.¹⁰ Since barium sulfate and barium chromate are isomorphous coprecipitation of the contaminating salts is to be expected.

When the chromate precipitates were washed thoroughly with hot water the coprecipitated contaminants could be washed out. However proportionate quantities of radium were also removed from the crystals so that the enrichment was not improved by washing the precipitate.

Procedure 3 Chromate Precipitation by the Hydrolysis of Cyanate at 0°

This method parallels the procedure outlined for the chromate-cyanate precipitation at room temperature (25°)

About 7.4 grams of barium carbonate (equivalent to approximately five grams of barium) was dissolved in seven milliliters of concentrated nitric acid and five milliliters of glacial acetic acid diluted to about 500 milliliters with water. To the barium acetate-nitrate solution was added an aliquot of a standard potassium dichromate solution. (The volume of the dichromate solution added depended on the amount of barium to be precipitated.) To the reaction solution which had been cooled to 0° was added four grams of potassium cyanate. Precipitation started approximately one minute after the addition of the last cyanate. The reaction mixture was stirred by aeration. The reaction was stopped approximately two hours after the precipitation started. Both the precipitate and the filtrate were analyzed for barium and radium. In each experiment the supernatant liquid was colored slightly yellow which indicates an incomplete precipitation or a slight solubility of the barium chromate in the acid solution. There was a negligible discrepancy in the amount of precipitate obtained in respect to the theoretical amount. It is of interest to note that if the mixture were allowed to warm to room temperature the precipitation was completed.

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Several experiments on each of the separation procedures were carried out to determine the amount of radium chromate carried from solution by the precipitation of specific amounts of barium chromate. The fraction of barium precipitated in each case was fixed by the amount of alkali chromate or dichromate added to the original solution. The amount of chromate added was varied so that different percentages of the barium could be precipitated. The data for the concentration of radium by the chromate-urea method have been tabulated in Table I, while similar data for the chromate-cyanate method at 25° and 0° are found in Tables II and III respectively. It is to be noted that the λ values remain reasonably constant for any given set of data thereby indicating that precipitation from homogeneous solution proceeds according to the logarithmic rule of Doerner and Hoskins⁴. The average λ values for Procedures 1, 2 and 3 are 4.41, 5.62 and 7.95 respectively. The last is larger than any λ value as yet reported for the fractionation of barium and radium. The highest distribution constant found in the literature is 5.64, reported for the fractional crystallization of radium-barium bromides¹. A comparison of distribution constants shows the chromate-cyanate method at 25° to be equivalent in efficiency per fractionation step to the fractional crystallization of radium barium bromides.

The data tabulated in Tables I, II, and III are plotted in Figure 1. The curves represent the percentages of radium carried by the precipitation of various percentages of barium by the three procedures. The straight line extending from points (0, 0) to (100, 100) is the line of no separation. The straight line extending from points (0, 100) to (50, 50) represents a series of working ratios since the sum of the coordinate values of any point along this line equals 100. Therefore, any of the ratios represented by this line could be employed in a method of continuous separation.¹⁰ The best method is that which most closely precipitates 100 per cent of the radium and 0 per cent of the barium. The points of intersection of the curves with this straight line represent the working ratio for each of the three procedures. Thus for the chromate-urea method at 100° the working ratio is 75:25, for the chromate-cyanate method at 25° it is 78:22, and for the chromate-cyanate method at 0° 81:19. The enrichment per fractionation step is 3.00, 3.55 and 4.26 respectively. The significance of these enrichment factors is shown in Table IV.

The chromate-cyanate method at 0° gives the best enrichment factor. However, in spite of a lower enrichment factor the chromate-cyanate method at 25° has the advantage that no heating or cooling of the reaction is necessary. The chromate-urea method gives the poorest enrichment per step but has the advantage of inexpensiveness of reagents.

The cost of potassium cyanate is roughly ten times that of urea. However, on a weight basis six to eight times as much urea is required as is potassium cyanate. Also the cyanate methods require no heating, and fewer steps are necessary for the same enrichment (Table IV). In four steps the chromate-cyanate method at 0° would yield four times the enrichment obtained by the chromate-urea method and likewise, in four steps the chromate-cyanate method at 25° would yield twice the enrichment obtained by the chromate-urea method.

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Before any definite statement can be made in defense of one method over another a careful cost estimate would have to be made in view of the many variables which must be considered.

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TABLE I

CONCENTRATION OF RADIUM BY THE CHROMATE-UREA METHOD AT 100°

BARIUM PRECIPITATED (per cent)	RADIUM CARRIED (per cent)	DISTRIBUTION CONSTANT (λ)
20.6	65.3	4.59
20.9	67.9	4.85
25.2	69.8	4.12
25.2	75.3	4.82
35.8	88.6	4.90
37.3	86.9	4.35
48.5	91.9	3.79
50.6	95.2	4.39
52.4	94.3	3.86
<i>Average</i>		4.41

WORKING RATIO (R = 75.25)

ENRICHMENT PER FRACTIONATION STEP 3.00

TABLE II

CONCENTRATION OF RADIUM BY THE CHROMATE CYANATE METHOD AT 25°

BARIUM PRECIPITATED (per cent)	RADIUM CARRIED (per cent)	DISTRIBUTION CONSTANT (λ)
6.0	29.7	5.69
11.3	50.3	5.83
11.7	50.6	5.78
21.9	79.6	6.43
22.1	75.7	5.66
22.2	77.0	5.86
27.9	86.4	6.10
33.4	89.8	5.62
34.1	89.9	5.50
43.7	95.1	5.25
43.8	93.2	4.66
54.5	98.7	5.51
64.5	99.5	5.12
<i>Average</i>		5.62

WORKING RATIO (R = 78.22)

ENRICHMENT PER FRACTIONATION STEP 3.55

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TABLE III

CONCENTRATION OF RADIUM BY THE CHROMATE-CYANATE METHOD AT 0

BARIUM PRECIPITATED (per cent)	RADIUM CARRIED (per cent)	DISTRIBUTION CONSTANT (λ)
5.5	39.4	8.84
9.8	56.2	8.00
20.1	83.2	7.95
23.4	86.6	7.54
29.8	92.7	7.40
Average		7.95

WORKING RATIO (R = 81.19)

ENRICHMENT PER FRACTIONATION STEP 4.26

TABLE IV

COMPARISON OF ENRICHMENTS BY THE CHROMATE PROCEDURES

NUMBER OF FRACTIONATION STEPS	BA RA RATIOS		
	CHROMATE UREA (100°)	CHROMATE-CYANATE (25°)	CHROMATE CYANATE (0°)
ORIGINAL	100,000.1	100,000.1	100,000.1
1	33,300.1	28,200.1	23,500.1
2	11,100.1	7,940.1	5,520.1
3	3,700.1	2,240.1	1,300.1
4	1,270.1	630.1	300.1
ENRICHMENT PER STEP	3.00	3.55	4.26

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FRACTIONATION OF RADIUM AND BARIUM BY
 PARTIAL PRECIPITATION AS CHROMATES.

Problem Title The Concentration of Radium from Radium-Rich Mixtures

Report By A W. Martin

Work Done By A W Martin

INTRODUCTION

A discussion of methods which may be used for the concentration of radium from barium-radium mixtures was presented in previous reports.^{1,2} A series of fractional chromate precipitations by the chromate-urea procedure was presented in the previous quarterly report.² Application of the chromate-urea procedure to the enrichment of radium from a barium-radium mixture has been continued on samples having a barium to radium ratio of approximately 2,000 to one. In order to adapt the fractional chromate-urea precipitation method to the enrichment of radium from barium-radium mixtures which were richer in radium it was necessary to modify the previously described procedure² as well as the technique used in carrying out these precipitations. A sample of barium-radium chromates containing 1.7 milligrams of barium and 1.2 milligrams of radium has been obtained from K-65 residues.

DETAILED REPORT

A sample of barium-radium chromate having a barium to radium ratio of 2.064 to one was fractionally precipitated by a time-controlled chromate-urea method.² The procedure used, based upon five grams of barium-radium chromate was as follows:

- 1 The barium-radium chromate was dissolved in 75 milliliters of hot, one-molar, nitric acid.
- 2 One hundred milliliters of water was added, and the nitric acid solution of chromates was then cooled in an ice bath.
- 3 Part of the excess acid needed to obtain solution of the chromates was neutralized with 25 milliliters of one molar aqueous ammonia.
- 4 The solution was heated to 95° in a boiling point apparatus (Figure 1).
- 5 To this hot solution was added 7.25 grams of urea dissolved in 50 milliliters of water.
- 6 The reaction was carried out at the temperature of boiling water for 77 minutes.
- 7 This hydrolysis reaction was stopped by immersion of the reaction tube in an ice bath.
- 8 The chromate precipitate was filtered out, washed with water, dried, weighed, and the radium content determined by the alpha-slide, aeration method of Tompkins and co-workers.
- 9 To the filtrate was added an excess of chromate ion (potassium chromate), the solution was heated, and the remaining barium was precipitated as barium chromate.
- 10 This barium chromate precipitated from the filtrate was filtered, washed, dried, weighed, and the radium content determined.

Six fractionations were carried out by the procedure described above with a resulting enrichment of a barium radium ratio of 67 to one. Results of these fractionation steps are tabulated in Table I.

The per cent precipitated as chromate in the residue (Table I) should have been 50 per cent in each step provided the time of the chromate-urea precipitation could have been controlled as planned. Experience showed that control of 50 per cent precipitation was not practicable and that a change in the procedure was to be considered.

A second sample of barium-radium chromate having barium to radium ratio of 1,529 to one was fractionally precipitated. The data for these fractionation steps are presented in Table II. In steps A and B (Table II) the following procedure was used. Quantities in this procedure are based on 10 grams of barium chromate.

- 1 Chromates were dissolved in 150 milliliters of hot, one-molar nitric acid.
- 2 To the nitric acid chromate solution was added 10 grams of urea and the solution was diluted with water to make a total volume of 291 milliliters
- 3 Reacting time was 220 minutes.
- 4 This hydrolysis reaction was carried out in the apparatus previously described (Figure 1)
- 5 At the end of the required heating time, the reaction tube was immersed in an ice bath.
- 6 The chromate precipitate was filtered out, washed, dried, weighed, and analyzed for radium content.
- 7 The filtrate was treated with an excess of chromate (potassium chromate) which precipitated the remaining barium-radium as chromates. This chromate was filtered out, washed, dried, weighed, and analyzed for radium.

A change in procedure from a time-controlled reaction to a reaction in which sufficient chromate was present to precipitate 50 per cent of the barium and radium as chromates was used in steps C, D, E, and F (Table II). This procedure based on 10 grams of barium chromate is as follows

- 1 The chromate residue was treated with hot concentrated nitric, and insoluble barium-radium nitrate remained after filtering.
- 2 The barium radium nitrate was dissolved in hot water
- 3 This solution was made 0.2 molar with nitric acid.
- 4 Sufficient potassium chromate, calculated amount, was added to precipitate 50 per cent of the barium-radium as chromate.
- 5 To the nitric acid, chromate solution was added 10 grams of urea, and the reaction mixture was heated for one hour at the temperature of boiling water in the apparatus described in Figure 1.
- 6 The chromate which precipitated was filtered out, washed, dried, weighed, and analyzed for radium content.
- 7 The barium and radium in the filtrate was precipitated as carbonate with sodium carbonate.
- 8 This carbonate precipitate was filtered out, washed, dried, weighed, and analyzed for radium content.

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TABLE I

	BARIUM		RADIUM		BARIUM PER GRAM OF RADIUM		CHROMATES PRECIPITATED IN RESIDUE (per cent)
	IN RESIDUE (g)	IN FILTRATE (g)	IN RESIDUE (μ g)	IN FILTRATE (μ g)	IN RESIDUE (g)	IN FILTRATE (g)	
sample	3.467		1,680		2,064		
STEP A	1.478	1.973	1,502	178	984	11,059	43.1
STEP B	0.924	0.570	1,388	114	666	5,036	61.9
STEP C	0.252	0.642	1,097	291	230	2,213	44.0
STEP D	0.1395	0.1129	928	169	150	668	59.1
STEP E	0.0863	0.0679	882	45.8	98	1,480	57.8
STEP F	0.0501	0.0281	749	32.5	67	865	51.7

TABLE II

	BARIUM		RADIUM		BARIUM PER GRAM OF RADIUM		CHROMATES PRECIPITATED IN RESIDUE (per cent)
	IN RESIDUE (g)	IN FILTRATE (g)	IN RESIDUE (μ g)	IN FILTRATE (μ g)	IN RESIDUE (g)	IN FILTRATE (g)	
sample	2.58		1,687		1,529		
STEP A	1.014	1.568	1,295	392	783	4,000	38.4
STEP B	0.6884	0.3856	1,498	25.4	460	15,200	58.8
STEP C	0.3442	0.3492	1,395	103	247	3,390	48.8
STEP D	0.1710	0.1732	1,382	13.1	124	13,190	49.7
STEP E	0.0837	0.0873	1,286	95.5	65	913	48.9
STEP F	0.0295	0.1020	1,735	300.5	17	339	48.3
STEP G	0.0141	0.0296	1,669	65.8	8.4	450	RA 96.2 BA 47.8
STEP H	0.0066	0.0150	1,522	146.7	4.3	102	RA 91.2 BA 46.8
STEP I	0.0017	0.0049	1,209	313	1.4	15.7	RA 79.4 BA 25.7

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In steps E and F (Table II) difficulty was encountered by a hold up of nitric acid in the barium nitrate precipitate. This difficulty is noticeable with small precipitates. In order to neutralize a portion of the excess acid, aqueous ammonia was used. In steps G and H the excess of nitric acid was washed out with dry acetone.

In the final step (Step I, Table II) the procedure used was the chromate cyanate 50 per cent precipitation method⁴. This procedure was shown to yield a better enrichment in radium from barium-radium mixture. The reaction was carried out at room temperature with centrifuge tubes and microtechniques.

CONCLUSIONS

Samples (Table I and Table II) were obtained from K-65 residues by enrichment of radium from barium-radium extraction mixtures. The barium radium extracted from the K 65 residues is in a ratio of approximately 80 000 milligrams of barium to one milligram of radium. An enrichment to 1.4 milligrams of barium per milligram of radium has been obtained (Step I, Table II). The logarithmic distribution according to Doerner and Hoskins⁵

$$\ln \frac{\text{amount of radium in solution after precipitation}}{\text{amount of radium in solution before precipitation}}$$

$$\lambda \ln \frac{\text{amount of barium in solution after precipitation}}{\text{amount of barium in solution before precipitation}}$$

was calculated as 5.6 for Step I (Table II). This λ value of 5.6 is identical with that reported elsewhere⁴ for the distribution between barium and radium in those mixtures which are poorer in radium. The distribution between barium and radium in the rich samples indicates that in the sample obtained radium is not showing its property as an insoluble chromate that is independent of the precipitated barium chromate.

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APPARATUS FOR FRACTIONAL PRECIPITATION.

Problem Title - **Determination of the Solubility of Barium Chromate in Various Concentrations of Nitric Acid**

Report By **M Economides**

Work Done By - **M Economides**

INTRODUCTION

The solubility of barium chromate has been determined in concentrations of nitric acid ranging from 0.1 normal through 5.0 normal. The barium in solution was determined by precipitation and weighing as sulfate.

DETAILED REPORT

Various concentrations of nitric acid were standardized by titrating potentiometrically weighed samples of sodium carbonate.

The barium chromate was prepared by precipitation from acid solution by the chromate-urea method¹. Approximately 0.5 gram of barium chromate was placed in a series of test tubes, the midsections of which had been constricted so that they might later be sealed off. This amount of barium chromate was sufficient to form a saturated solution with approximately three milliliters of nitric acid. The tubes were sealed and agitated by tumbling in a constant temperature bath at 23.5° for at least 18 hours.

After this interval, the ampules were opened, and two aliquots of one-milliliter each were pipetted into 30-milliliter beakers. In this first series of experiments, barium chromate was precipitated with ammonium hydroxide and filtered through preweighed, sintered-glass crucibles, then dried at 110° and weighed again. Weights from this run were not consistent.

In the second series, after the one-milliliter aliquots of barium chromate in solution were pipetted into the small beakers, sulfuric acid was added to form barium sulfate. The material was filtered, and the filtrate was collected for further chromate analysis. The precipitate in the filter paper was placed in prepared porcelain crucibles, ignited with a gas flame, and placed in a muffle furnace for two hours at 700°. After removal from the muffle furnace, the crucibles were allowed to cool in a desiccator and weighed. The barium sulfate was then covered with a few drops of sulfuric acid to reconvert any reduced material formed by igniting the filter paper, to barium sulfate. The crucibles were again ignited and returned to the muffle furnace for two hours at 700°. On cooling they were reweighed and from these weights the solubility of barium chromate was determined. The solubility values at each acid concentration were treated statistically, and certain ones eliminated according to Chauvenet's Criterion.

The results which are presented in Table I and Figure 1 show that barium chromate is most soluble in 1.0 to 1.2 normal nitric acid. The barium nitrate curve, constructed from the data literature,² shows that the solubility of the nitrate also decreases as the acid concentration increases and that the two curves are coincidental at the higher acid concentrations. The coincidence of these curves indicates that in higher nitric acid concentrations barium chromate is converted to barium nitrate and measurements made are not representative of the solubility of barium chromate.

Filtrates and rinsings from barium precipitation were analyzed with sodium thiosulfate, but the data are incomplete and unsatisfactory. Further experimentation is now in progress so that more consistent data may be obtained.

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TABLE I

SOLUBILITY OF BARIUM CHROMATE IN NITRIC ACID

ACID CONCENTRATION (normality)	BARIUM (grams/liter)	BARIUM CHROMATE (grams/liter)	BARIUM CHROMATE AVERAGE VALUE (grams/liter)
0.1	2.80	5.15	5.28
	2.94	5.43	
	2.85	4.85	
0.25	6.56	12.09	12.29
	6.71	12.37	
	6.75	12.44	
	6.66	12.27	
0.5	14.18	26.15	26.01
	14.31	26.39	
	14.00	25.82	
	14.12	26.02	
0.75	22.76	41.98	41.61
	22.58	41.63	
	22.49	41.47	
	22.44	41.38	
1.0	27.71	51.09	51.33
	28.00	51.64	
	28.10	51.81	
	27.92	51.48	
1.2	27.54	50.79	50.97
	27.62	50.92	
	27.58	50.84	
	27.73	51.14	
1.5	28.07	51.32	51.32
	28.13	51.86	
	28.12	51.84	
	27.81	51.26	
2.0	14.00	25.81	26.79
	13.94	25.70	
	16.48	30.38	
	13.72	25.30	
3.0	5.97	11.00	10.31
	6.10	11.24	
	5.27	9.72	
	5.03	9.28	
4.0	3.21	5.91	5.89
	3.32	6.13	
	3.19	5.88	
	3.07	5.66	
5.0	2.54	4.68	4.26
	2.50	4.61	
	2.01	3.70	
	2.14	3.94

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Problem Title - The Separation of Radium and Barium by Ion Exchange

Report By - W C McCluggage

Work Done By - W C. McCluggage, M P Hauenstein, and G D Nelson

INTRODUCTION

The first separation of radium and barium by use of Dowex-50 ion exchange resin was made on a microscale by E R Tompkins at Oak Ridge.¹ The primary effort at this laboratory has been to determine the best conditions for the separation of radium and barium by ion exchange and to develop the Tompkins process to serve either as a single method of separation and purification or as the purification step after the concentration of the radium by some other process.

Nearly total separation of 30,000 parts of barium to one of radium has been accomplished, but material cost and time consumption were prohibitive for large-scale operation.² A good separation of 2,000 parts of barium from one of radium has been made by the elution of radium and barium on a 25-centimeter bed of Dowex-50 with 0.5 molar ammonium citrate at pH 4.9.³ The process was limited chiefly by the fact that precipitates of barium citrate occurred if more than a few per cent of the total column capacity was occupied by barium at the start of the elution.

Recent work has been directed toward increasing the amount of barium that can be placed on a column by operating at elevated temperatures and by elution with ammonium citrate solution with pH lower than 4.9.

DETAILED REPORT

Radium and Barium Separations

A typical radium-barium separation has been previously described.³ For purposes of comparison the elution curve for that separation is given by Figure 1. Three other column separations have been made with all conditions, except elution temperature and pH, the same as for the above mentioned work. (See Table I for column design and operation data.) The process summary and the results of a radium-barium separation carried out at $75^{\circ} \pm 1^{\circ}$ at pH 4.9 are given in Figure 2 and Tables II and III. The effect of higher temperature has been to shorten the separation time and to reduce the required volume of elutriant; however, the separation itself is not as complete as at room temperature. It is possible that temperature increase adversely affects the instability constants and distribution coefficients of barium and radium, since the change in the location of the elution curve peaks is greater for radium than for barium.

Limitations Caused By the Limited Solubility of Barium Citrate

The slight solubility of barium citrate creates one of the principle limitations on the use of the citrate system for elution. The maximum permissible barium band depth

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that could be placed at the top of a column and then eluted with citrate solution without precipitation of barium citrate was studied by adding specific amounts of barium to columns and eluting at 25° under conditions tabulated by Table I. When 0.178 gram of barium (0.78 centimeter depth or 3.1 per cent of the column capacity) was eluted, no precipitation was noticed while 0.200 gram of barium (0.88-centimeter depth or 3.5 per cent of the column capacity) caused precipitation. These experiments were repeated at 90° in the hope that solubilities would be greater at the higher temperature but no appreciably greater quantity of barium could be eluted from a column at 90° without precipitation.

The effect of varying the acidity of citrate elutriants upon the precipitation of barium citrate on the resin column was studied by placing a series of five-gram samples of barium-saturated Dowex-50 in contact with 25 milliliters of 0.44 molar ammonium citrate solution of various pH values and allowing them to stand overnight (Table IV). Precipitates formed only in those solutions that had pH's above 3.5. Accordingly, a separation of barium and radium was made with 0.5 molar ammonium citrate at pH 3.5 as the elutriant. (See Tables I, V, and VI for the column characteristics and the process summary.) The barium elution curve is low and covers a large volume range (Figure 3). After the passage of 61 column volumes (920 milliliters) of elutriant, 98.7 per cent of the barium was removed. The column was then stripped with 250 milliliters of six molar ammonium acetate which resulted in the recovery of 98.7 per cent of the radium. The separation in this run was good but obviously too costly in time and material. The first maximum in the barium elution curve at 33 to 38 column volumes (Figure 3) is believed to be caused by channeling of the barium feed solution resulting in a false barium maximum during the elution.

An elution with ammonium citrate at pH 3.5 but at 75° instead of at room temperature showed essentially the same results, a low barium elution curve requiring a large volume of elutriant.

The reason for the slow rate of separation at pH 3.5 probably can be explained by the meager complexing action of citrate ion for barium at that acidity.

Other eluting systems

Since no data concerning the use of hydrochloric acid or acetic acid ammonium acetate mixtures for elution of barium and radium is available, these materials are being studied with the object of increasing the maximum allowable barium content that can be handled without precipitation.

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TABLE I
COLUMN DESIGN AND OPERATION

ITEM	DATA
RESIN	DOWEX-50 70-100 MESH AMMONIA FORM RESIN
BED DEPTH	25 CENTIMETERS
BED DIAMETER	1.3 CENTIMETERS
WEIGHT OF RESIN (oven-dried)	16.3 GRAMS
LIQUID ABOVE RESIN	10 CENTIMETERS
BED VOLUME	33.2 MILLILITERS
COLUMN VOLUME	16.6 MILLILITERS
FEED SOLUTION DROP RATE	1 ± 0.1 MILLILITER/CENTIMETER ² /MINUTE
ELUTRIANT DROP RATE	0.3 ± 0.03 MILLILITER/CENTIMETER ² /MINUTE
CAPACITY OF OVEN-DRIED DOWEX-50 RESIN	5.1 MILLIEQUIVALENTS OF BARIUM PER GRAM ¹

TABLE II
PROCESS SUMMARY
ELUTION AT 75°, PH 4.9

PROCESS STEPS	REAGENTS USED	VOLUME REQUIRED (milliliters)	CATION RETURN	
			BARIUM (per cent)	RADIUM (per cent)
FEED SOLUTION	0.1375 GRAM BA AS THE CHROMATE 36.75 MILLIGRAM RA 0.2N HNO ₃	500		
BARIUM ELUTION	0.5M AMMONIUM CITRATE AT PH 4.9	200	97.2	
RADIUM ELUTION	0.5M AMMONIUM CITRATE AT PH 4.9	235		90.0

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TABLE III

RADIUM AND BARIUM ELUTION WITH 0.5 MOLAR AMMONIUM CITRATE PH 4.9
AT 75°

COL	VOL	BA CONTENT (g)	TOTAL BA (per cent)	RA CONTENT (μ g)	TOTAL RA (per cent)
1					
2					
3		0.0012	0.88		
4		0.0660	48.00		
5		0.0274	19.90		
6		0.0211	15.30	0.275	0.75
7		0.0083	6.00	6.66	18.12
8		0.0039	2.90	14.43	39.40
9		0.0026	1.91	7.42	20.20
10-11		0.0020	1.43	3.64	9.91
12				0.36	0.99
13				0.18	0.50

TABLE IV

STUDY OF ACIDITY UPON THE PRECIPITATION OF BARIUM CITRATE IN THE
PRESENCE OF FIVE GRAMS OF BARIUM FORM DOWEX-50

NO	CITRIC ACID 0.44 M (ml.)	(NH ₄) ₂ CIT 0.44 M PH 8 (ml.)	PPT	PH	ORIGINAL STOCK SOLUTION pH
1	25.0	0	No		
2	22.5	2.5	No	-	
3	21.25	3.75	No	-	
4	20.0	5.00	No	-	
5	18.75	6.25	No	3.40	3.44
6	17.50	7.50	YES	3.56	3.68
7	16.25	8.75	YES	3.67	3.89

PRECIPITATION WAS OBSERVED THROUGHOUT THE RANGE PH 3.56 - 9.0.

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TABLE V
PROCESS SUMMARY
ELUTION AT 25° PH 3.5

PROCESS STEPS	REAGENTS USED	VOLUME REQUIRED (milliliters)	CATION RETURN	
			BARIUM (per cent)	RADIUM (per cent)
FEED SOLUTION	0.2355 GRAM BA AS THE ACETATE 25 MILLILITERS RA STOCK SOLUTION CONTAINING 36.7 MILLIGRAMS RA PH 2.0	500		
BARIUM ELUTION	0.5M CITRIC ACID, 1M NH ₄ OH PH ADJUSTED BY ADDITION OF 46 MILLILITERS CONCENTRATED HCL PER LITER	920	98.7	
RADIUM ELUTION	6M NH ₄ C ₂ H ₃ O ₂	250		95.0

TABLE VI
BARIUM ELUTION WITH 0.5 MOLAR AMMONIUM CITRATE PH 3.5 AT 25°

COLUMN VOLUME	BA CONTENT (g)	TOTAL BARIUM (per cent)
3-8*	0.0179	7.32
9-14	0.0103	4.34
15-20	0.0096	4.07
21-26	0.0086	3.66
27-32	0.0298	12.65
33-34	0.0286	12.15
35	0.0148	6.30
36	0.0131	5.56
37-38	0.0148	6.30
39	0.0047	2.00
40-43	0.0193	8.20
44-45	0.0114	4.84
46-47	0.0131	5.56
48-49	0.0114	4.85
50-55	0.0160	6.80
56-61	0.0096	4.07

* INCLUSIVE

NOTE THE RADIUM IN THIS SEPARATION WAS ELUTED WITH 250 MILLILITERS OF 6M AMMONIUM ACETATE AND 95.0 PER CENT WAS RECOVERED

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FIGURE 1

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FIGURE 2

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ELUTION CURVE FOR THE SEPARATION OF
RADIUM AND BARIUM AT 75°

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FIGURE 3

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SPECIFICATIONS

RESIN: DOWEX 50; NH_4R
70-100 MESH

FEED: Ba-Ra ACETATE
pH 2.0

ELUTRIANT: 0.5 MOLAR CITRIC ACID
pH 3.5

COLUMN VOLUME: 16.6 ML.

— BARIUM

THE BARIUM ELUTION CURVE IN A RADIUM
BARIUM SEPARATION AT 25°

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Problem Title - The Solubility of Barium in Citrate Solution

Report By - G D Nelson

Work Done By G D Nelson and M. F. Hauenstein

INTRODUCTION

The final step in the proposed process for recovering radium from the K-65 residue involves the separation of barium from radium on Dowex-50, a cationic exchange resin. The radium-barium mixture is absorbed on the top of the resin column from a chromate solution⁴ and subsequently is eluted with diammonium citrate solution which removes the barium more rapidly than the radium.¹ If large amounts of barium are on the column, the elution with citrate solution causes a precipitate to form.^{2,3,4} In an equilibrium study it was found that the barium form of the resin in contact with citrate solution would give this precipitate at any point in the pH range 3.5 to 9.0.¹² Since any precipitation may plug the column, the amount of barium that can be held on the column is greatly limited. Also if a precipitate forms on the resin the principle reaction taking place in the column is not the desired ion exchange between the resin and the surrounding solution.

Because the ion exchange process for separating barium from radium was found to be limited by the solubility of the barium, a knowledge of the solubility of barium in citrate solution was necessary to determine whether suitable conditions could be found which would remove this limitation.

The following information on barium citrate heptahydrate has been reported in the literature. The solubility of barium citrate at 25° is reported as 0.0572 gram in one hundred milliliters of water. Information on the complex ions of barium in citrate solution and their dissociation constants gives K (dissociation) ~ 0.1 ⁸ for the reaction $\text{BaHCit} \rightleftharpoons \text{Ba}^{++} + \text{HCit}^-$ and K (dissociation) = 5 and 17×10^{-3} ⁷ for the reaction $\text{BaCit}^- \rightleftharpoons \text{Ba}^{++} + \text{Cit}^{--}$ in 0.16 and 1.05 molar ammonium chloride, respectively. The percentages of each of the ions of citric acid in ammonium hydroxide-citric acid solutions at various pH values have been calculated⁵ for an ionic strength of 0.1 by Schubert⁹ from equations of Bjerrum and Unmack.⁸

Values which have been assigned to the dissociation constants of barium complexes in order to explain the solubility measurements reported here have lead to a clearer concept of the constituents present in aqueous phase during the ion exchange separation of barium from radium.

DETAILED REPORT

Preparation of Barium Citrate Heptahydrate - Since a method for preparing barium citrate was not in the literature, the general conditions for preparing an insoluble salt were employed. Barium citrate was prepared by the reaction

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One-tenth mole of citric acid solution was heated to boiling and 0.15 mole of barium hydroxide solution was added slowly. After the solution was cooled to room temperature, a white solid was filtered from it, washed with water, and dried at 110° for 16 hours. This material was analyzed for barium and citrate, and an X-ray diffraction pattern obtained. The expected barium to citrate ratio of 3:2 was obtained; the X-ray diffraction pattern agreed with that in the Hanawalt tables,⁹ but the degree of hydration was lower than that expected for barium citrate heptahydrate. The relationship between the temperature of drying to constant weight and the degree of hydration for barium citrate heptahydrate is shown in Figure 1. The X-ray diffraction pattern of the material containing the calculated amount of water of hydration does not agree with the pattern for the heptahydrate in the Hanawalt tables. However, the ratio of barium to citrate is in good agreement with the calculated ratio for the normal salt as shown in Table 1.

Solubility Determinations at 25° - Excess solid barium citrate was stirred with a magnetic stirrer in contact with zero, one, two, five, and ten per cent diammonium citrate and five and ten per cent citric acid until equilibrium was attained. The pH of the solutions was adjusted by the addition of ammonia gas. At equilibrium, (24 or more hours stirring at 25° and 8 or more hours at 75°) the solid material was filtered off, the filtrate was analyzed for total barium and total citrate, and the pH was determined. The amount of solution necessary for analyses depended on the pH and the citrate concentration and ranged from 12 to 75 milliliters. The amount removed for analysis was replaced by a stock solution with the same concentration of citrate with ammonia gas added to increase the pH for a new equilibrium point. In this way the solutions progressed to a more alkaline state at a rate which depended on the buffer capacity of the solution. As a result more points were obtained for the ten per cent citrate solutions.

In the experiments carried out at 75° the solutions were allowed to settle over night. On the succeeding morning the requisite amount of supernatant was removed for the analyses. The solution was then supercooled to 25° and the pH determined immediately before any precipitation occurred.

Analysis of Equilibrium Solutions - The pH of the equilibrium solutions was determined on a Leeds and Northrup research model pH meter to within ±0.05 pH units. The pH's of the 75° equilibrium solutions were slightly lower when measured at temperatures above 25°.

The total barium in each equilibrium solution was determined by an indirect iodimetric method. In order to destroy the citric acid the sample was heated with perchloric acid until white fumes appeared. If the citrate is not decomposed, low results are obtained because of incomplete barium chromate precipitation. The barium, after precipitation as the chromate, was filtered, washed free of excess chromate, and dissolved in ten per cent hydrochloric acid. This solution was treated with potassium iodide and starch indicator and

titrated with standard sodium thiosulfate. The thiosulfate solution was standardized against a weighed amount of pure barium chromate which was prepared by the urea method¹³ and carried through the above procedure. The analysis was found reproducible to ± 0.0001 mole per liter of barium for a given sample.

The total citrate in each equilibrium solution was determined by a modification of the method of G. F. Smith and F. R. Duke^{10,11}. The sample of citric acid or citrate is heated for ten minutes at 50° with a known excess of perchlorato ceric acid. The citric acid is oxidized according to the equation:

After the solution is cooled, the excess perchlorato cerate is back titrated with standard sodium oxalate solution. Portions of the perchlorato cerate were run as blanks each day, along with the samples, since the reaction is dependent on time and temperature, and the solution decomposes on standing. The average deviation for a sample, which was run six times, was one per cent of the total citrate present with a maximum deviation of two per cent.

Experimental Results - The results of the solubility determinations (Figures 2, 3, and 4) were interpolated at even pH values to give the results shown in Tables II and III. Inconsistent values for the solubility were obtained around pH 5. The solubilities obtained in diammonium citrate were higher than those in citric acid solutions of the same composition brought step wise up to a pH of 5.0. The difference in solubility can be explained only by assuming that a different solid phase was in equilibrium with each of these solutions. It seems reasonable to assume that the normal salt is the solid phase at pH 7 to 9, since the solubility is essentially independent of pH and the citric acid is completely ionized to Cit^{3-} over this range. Consequently, if a different solid phase is present in more acid solutions, one would expect to find an acid salt.

In order to check this possibility, the following method was used to determine the barium to citrate ratio in the solid phase in citric acid. A weighed amount of the normal salt was stirred, until equilibrium was reached at a pH of approximately 2.7 in a solution containing a known quantity of citric acid. The solution which existed at equilibrium was analyzed for total barium and total citrate by the above methods. The composition of the solid phase calculated by difference showed that the ratio of barium to citrate at this pH was 1:1. Since the salt must be uncharged, the simplest compound of barium and citrate of this ratio which could exist is BaHCit . It may be concluded from the high citrate that the normal salt is present in a metastable state below a pH of 5.55 and that the conversion from the normal salt to the acid salt is not completed in the 24 hours stirring time. The only other possibility would be BaNH_4Cit , but this is unlikely since the ammonium ion concentration decreases with decreasing pH.

Discussion of Results - The results of the solubility measurements can be explained by assuming the presence in solution of only those complexes that have been reported in the literature. Thus in addition to the uncomplexed barium ion and the ions produced by the stepwise dissociation of citric acid (Figure 5), the BaHCit and BaCit complexes must be considered. This information on the solution phase, together with the information which has been obtained on the solid phases, provide a semiquantitative picture of the system being treated by ion exchange.

The experimental results indicate that saturated solutions containing 0.5 molar citrate have a hydrated, normal barium citrate as the solid phase at a pH greater than 5.55. Barium citrate which precipitated from solution at a pH of about 6 gave on analysis the 3:2 barium to citrate ratio expected for this salt. Furthermore, saturated solutions of barium citrate in water and dilute ammonium hydroxide show the 3:2 ratio in solution over a pH range of 6.5 to 10, which would not be true if the normal salt was not stable over this range.

Below a pH of 5.55 in 0.5 molar citrate solutions the barium monohydrogen citrate is the solid phase. The change is evident from the discontinuity of the solubility curve at this pH and from the inconsistent and high solubility obtained when the metastable normal salt is added to solutions below a pH of 5.55. Indirect analysis of the solid phase at a pH of 2.7 established the composition as the barium monohydrogen citrate of unknown hydration. While the solid phase has not been analyzed over the pH range 2.7 to 5.55 there is no reason to suspect the presence of other solid phases.

On the assumption that no new complexes were taking part in the reaction the various solubility products and dissociation constants required to express the solubility were selected by trial and error method. The final value assigned these constants gave concentrations of the barium ion and barium complexes which, when added together gave a total barium concentration in agreement with the total barium concentration determined by analysis (Figure 6). The equilibrium constants selected and the corresponding equations are as follows:

EQUILIBRIUM CONSTANT

EQUATION	CALCULATED	LITERATURE	REFERENCE
(3)	7.4×10^{-4}		
(4)	3.16×10^{-10}		
(5)	0.057	ABOUT 0.1	(6)
(6)	8.0×10^{-3}	5×10^{-3} A 17×10^{-3} B	(7)

A - IN 0.165 Molar NH_4Cl

B - IN 1.05 Molar NH_4Cl

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(Italics have been used to denote solid phase)

In solutions of high pH (above 7) the citrate is essentially all in the form of Cit^{--} and the barium in the form of BaCit . The solubility may be represented by combining equations 4 and 6

As would be expected from the preceding equation the solubility is essentially independent of pH

From Equations 3 and 5 it is found that

As long as the acid salt is present as the solid phase, the concentration of the corresponding complex is constant

In general the agreement between the calculated and literature values of the dissociation constants are remarkably close considering the fact that changes in activity coefficients have been neglected. However, it becomes evident that the results are only approximate when an attempt is made to calculate the effect on the solubility of changing the total citrate concentration. For example, one would expect that in solution of high pH the total barium in solution to be proportional to the cube root of the total citrate concentration (Equation 7). Actually it appears to be very close to a linear relationship (Figure 4). Since no reasonable mechanism seemed capable of explaining this relationship, it was concluded that the results must be greatly influenced by the change in activity coefficients with total salt concentration.

Conclusions - In order to apply the foregoing results to the problem of precipitation of insoluble barium citrate in an ion exchange column it is necessary to consider the equilibrium between the barium and ammonium form of the ion-exchange resin and the ions in solution

From the standpoint of solubility alone precipitation may be prevented by carrying out the elution at a pH of 3.5 with a total citrate concentration of 0.5 molar.¹² By reference to Figure 2 it may be seen that the solubility at pH 3.5 is about the same as at pH 5 where most of the data on column operation have been obtained.¹ Consequently, precipitation is

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prevented not by increasing the solubility but by suppressing the amount of barium leaving the resin (Equation 9), that is, increasing the free barium ion concentration in solution and decreasing the ammonium ion concentration. At pH 3.5, less than half of the barium is complexed (Figure 6) and the ammonium concentration is 48 per cent of that present at pH 5 (Table VI). If it is assumed that nine column volumes are required to reach the barium elution peak at pH 5, then it is estimated that 297 column volumes would be required at pH 3.5 (Calculation I). If the ammonium concentration is kept the same as that at pH 5 by addition of ammonium chloride and the pH maintained at 3.5 then the barium peak should appear at about 63 column volumes which is in fair agreement with the observed results.¹² However, the elution rate is still too slow and precipitation would again be expected for high barium concentrations under the latter conditions. Furthermore, with the degree of complexing greatly decreased one would expect the efficiency of the radium-barium separation to be noticeably less.

From a qualitative viewpoint the solubility curve shows that the best conditions for carrying out the ion exchange process exist at pH 5.6 since without increasing the ammonium ion concentration appreciably, a marked increase in solubility is achieved.

It was observed experimentally that 0.5 molar citrate solutions precipitate barium as a citrate from the barium form of Dowex 50 above pH 3.5 and not below. Taking into consideration all the various equilibria concerned it can be shown that at pH 5 and 5.6, if precipitation did not occur, the solution would be super saturated by a factor of 33 and 43 respectively (Calculation I). However, the elution rate studies give a barium peak at nine column volumes at pH 5 and a calculated value of three column volumes at pH 5.6. Under the latter conditions the elution rate is too rapid, and the solubility problem can be partially solved by operation at lower ammonium citrate concentrations. It has been estimated that at 0.07 molar citrate no precipitation should occur but 918 column volumes would be required to reach the barium peak (Calculation II).

Although the operation of the column at 75° would probably increase the elution rate by a factor of two it is still necessary to make a compromise between a reasonable elution rate and possible precipitation. At an intermediate citrate concentration of 0.24 the barium peak should occur at 28 column volumes at 25° and roughly 14 column volumes at 75°. Under these conditions the theoretical super-saturation would be 11.6 at 25°.

To summarize, it is concluded that operation at 0.24 molar citrate at 75°, pH 5.6, compared with 0.5 molar citrate at 25°, pH 5.0, would require about 50 per cent more citrate solution at approximately 50 per cent less concentration and should permit the handling of about three times the quantity of barium. This should reduce the overall consumption of ammonium citrate to about 25 per cent of that formerly employed. These conditions appear to be the optimum conditions for the barium with citrate elution.

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CALCULATION I

If barium resin is in contact with ammonium citrate solution, the ratio of barium ion in equilibrium with the barium resin in two solutions of different ammonium ion content is proportional to the square of the ammonium ion concentration. (See Equation 9.)

If $[Ba_t]_x$ is the total barium concentration of a solution at pH X, then by Equations 3, 5, and 6,

$$[Ba_t]_x = ([Ba^{++}] + [BaHCit] + [BaCit^-])_x$$

The ratio of total barium in solution in contact with barium resin for two solutions of pH X and pH Y, therefore is

$$\text{Ratio} = \frac{[NH_4^+]_x^2 (1 + \frac{[HCit^-]}{.057} + \frac{[Cit^{--}]}{8 \times 10^{-3}})_x}{[NH_4^+]_y^2 (1 + \frac{[HCit^-]}{.057} + \frac{[Cit^{--}]}{8 \times 10^{-3}})_y}$$

If the specific pH's are 5 and 3.5,

$$\text{Ratio} = \frac{.061^2}{.4462} \times \frac{12.62}{1.781} = 33$$

Therefore if nine column volumes is required for a barium elution peak at pH 5, 9 times 33 or 297 column volumes is required at pH 3.5

CALCULATION II

When a series of 0.5 molar citrate solutions of differing pH were placed in contact with barium resin, solutions with a pH of 3.5 or lower did not cause precipitation of barium citrate. The barium solubility for the above solution at 25° is 0.027 molar (Figure 6). By the use of equation 9 it can be shown that 3.11 times as much barium is present in a solution of pH 3.5 and 0.5 molar in citrate after it comes to equilibrium with barium resin than is present in a solution of pH 5.6 and 0.07 molar in citrate. The solubility of barium in the last solution is 0.009 molar (Figure 8). The degree of saturation is therefore

$$\frac{0.027}{3.11} \times \frac{1}{0.009} \sim 1$$

According to equation 10, 102 times as much barium is in a solution, 0.5 molar in citrate and pH 5, in contact with barium resin as in a solution 0.07 molar in citrate and at pH 5.6. The number of column volumes required for elution of the more dilute solution would therefore be 102 times 9 or 918 column volumes.

TABLE I

THE DRYING OF BARIUM CITRATE HEPTAHYDRATE AT VARIOUS TEMPERATURES

TEMPERATURE * (°)	AFTER DRYING		MOLES BARIUM MOLES CITRATE	WATER * BY DIFFERENCE (per cent)
	BARIUM (per cent)	CITRATE (per cent)		
105	51.36	45.93	1 54	2 71
88	47.82	45 02	1 46	7 16
79	46 25	41 40	1 54	12 35
69	45 27	42 07	1 48	12 66
59	44 65	41 52	1 48	13 83
49	45 06	41 15	1 51	13 79
$Ba_3(Cit)_2 \cdot 7H_2O$	44.98	41.27	1 50	13 75

* PLOTTED IN FIGURE 1.

TABLE II

THE SOLUBILITY OF BARIUM IN CITRATE SOLUTION AT 25

NOMINAL CITRATE (per cent)	PH	TOTAL BARIUM moles liter	TOTAL CITRATE moles liter	NOMINAL CITRATE (per cent)	PH	TOTAL BARIUM moles liter	TOTAL CITRATE moles liter
5	3 0	0 0735	0 265	10	6 0	0 0635	0 516
10	3 0	0 0863	0 505	0	6 5	0 0034	0 0025
5	3 5	0 0225	0 227	1	6 5	0 0106	0 0560
10	3 5	0 0315	0 469	2	6 5	0 0156	0 104
5	4 0	0 0130	0 206	5	6 5	0 0314	0 252
10	4 0	0 0195	0 452	10	6 5	0 0644	0 519
5	4 5	0 0122	0 200	0	7 0	0 0035	0 0025
10	4 5	0 0183	0 256	1	7 0	0 0107	0 0561
1	5 0	0 0090	0 0560	2	7 0	0 0157	0 105
2	5 0	0 0123	0 100	5	7 0	0 0315	0 250
5	5 0	0 0148	0 214	10	7 0	0 0647	0 519
10	5 0	0 0243	0 479	0	8 0	0 0035	0 0026
0	5 5	0 0050	0 0040	1	8 0	0 0108	0 0561
1	5 5	0 0088	0 0552	2	8 0	0 0159	0 105
2	5 5	0 0128	0 100	5	8 0	0 0316	0 250
5	5 5	0 0247	0 242	10	8 0	0 0650	0 518
10	5 5	0 0502	0 502	0	9 0	0 0035	0 0027
0	6 0	0 0037	0 0031	1	9 0	0 0110	0 0561
1	6 0	0 0097	0 0557	2	9 0	0 0160	0 105
2	6 0	0 0148	0 102	5	9 0	0 0317	0 249
5	6 0	0 0315	0 252	10	9 0	0 0653	0 518

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TABLE III

THE SOLUBILITY OF BARIUM IN CITRATE SOLUTION AT 75°

NOMINAL CITRATE (per cent)	PH	TOTAL BARIUM (moles/liter)	TOTAL CITRATE
5	3.1	0.100	0.277
10	3.0	0.126	0.520
5	3.5	0.0375	0.236
10	3.5	0.0466	0.448
5	4.0	0.0230	0.222
10	4.0	0.0267	0.432
5	4.5	0.0180	0.219
10	4.5	0.0296	0.451
5	5.0	0.0245	0.230
10	5.0	0.0537	0.489
5	5.5	0.0385	0.245
10	5.5	0.0737	0.501
5	6.0	0.0458	0.251
10	6.0	0.0833	0.502
5	6.5	0.0462	0.256
10	6.5	0.0852	0.502
5	7.0	0.0462	0.258
10	7.0	0.0865	0.502
5	8.0	0.0462	0.260
10	8.0	0.0872	0.502
5	9.0	0.0463	0.260
10	9.0	0.0870	0.502

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TABLE IV
ANALYSES FOR SOLID PHASE BAHCIT

	BARIUM (mole)	CITRATE
SOLID ADDED	0.0252	0.0168
SOLUTION ADDED	0.0000	0.0224
TOTAL IN MIXTURE	0.0252	0.0392
ANALYSIS OF FINAL SOLUTION	0.0037	0.0173
AMOUNT LEFT IN SOLID	0.0215	0.0219

DIFFERENCE: CITRATE - BARIUM = 0.0004 MOLE
RATIO BA CITRATE = 1:1 WITHIN LIMITS OF ANALYSIS

TABLE V
IONIC SPECIES OF BARIUM PRESENT IN CITRATE SOLUTION
(Calculated from Equations 3, 4, 5, and 6)

PH	BA ⁺⁺ (per cent)	BAHCIT (per cent)	(BACIT) (per cent)	TOTAL BARIUM (mole/liter)
3.0	84.4	15.6	0.0	0.0800
3.5	50.9	47.2	1.9	0.0280
4.0	30.8	61.5	7.7	0.0195
4.5	14.9	58.6	26.5	0.0214
5.0	7.3	45.4	47.3	0.0275
5.6	4.2	24.4	71.4	0.0595
6.0	2.3	8.4	89.3	0.0634
7.0	1.6	0.9	97.5	0.0679

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TABLE VI

THE RELATION OF $\text{NH}_4^+/\text{CIT}_T$ AS RELATED TO PH

(Calculated from Values Derived from Equations of Bjerrum and Unmack³ by Jack Schubert⁸)

<u>PH</u>	<u>$\text{NH}_4^+/\text{CIT}_T$</u>
3.0	0.565
3.5	0.893
4.0	1.215
4.5	1.570
5.0	1.923
5.5	2.195
6.0	2.580
6.5	2.837
7.0	3.000

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MLM-518

Problem Title - Chemical Engineering Development of the Radium Process

Report By - H. L. Rawlings

Work Done By - H. L. Rawlings

INTRODUCTION

Since the radium process research program had progressed to the point where work with larger batches of K 65 residue had become feasible, an incorporation of the bench scale development work into the larger scale chemical research program became expedient. Engineering development is at present being confined to furnishing an engineering viewpoint to the chemistry group performing the research work and application of their data to an engineering flowsheet. A method for the determination of filtration data has been tested and found to be applicable to our work.

DETAILED REPORT

Contact with equipment manufacturers has emphasized that a determination of the filtering characteristics of each slurry involved in the process is desirable in selecting the proper types and sizes of filtration equipment. Accordingly, an investigation was made of various methods of determining the filtration rate employing a simulated K-65 residue.

A very close correlation between observed and calculated rates was obtained with the method developed by Sperry.¹ The application of this method to vacuum filtration is based on the assumption that this type of filtration will proceed as a constant-pressure filtration after a precoat has been built up and is kept to a constant thickness by scrapers. Therefore, the time, T , and the filtrate quantity, Q , which are used in calculating the filtration equation, were taken as starting at the point where the pressure became constant. The resulting filtration equation is thus invalid for the precoating period but gives a close correlation to the observed quantities for the actual filtration time.

The method demonstrated by these results appears to be practical and will be employed to determine the filtering characteristics of various slurries as the need arises.

REFERENCE

- 1 Sperry, D. R., Analysis of Filtration Data, Ind. Eng. Chem., 36 323, (1944).

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TABLE I
DETERMINATION OF THE FILTRATION CHARACTERISTICS OF A SIMULATED K-65 RESIDUE

T (min.)	Q OB. (ml. sq.in.)	VACUUM (in. Hg.)	T ₁ = T-3	Q ₁ = Q-67	T ₁ /Q ₁	$C = \frac{Q_1 - Q_0}{T_1/Q_1 - T_0/Q_0}$	N = C/2 x T ₁ /Q ₁	Q ₁ 2	Q CALC. (ml./sq.in.)
0	0	0	..	..	..	..	..		0
2	54	17.0	..	..	..	..	..		..
3	67	20.5	0	0	..	..	..		67.0
5	91.5	20.5	2	24.5	0.082	..	..		91.5
7	107	21.0	4	40	0.100	850	22.5		107.3
9	120	21.0	6	53	0.113	915	25.2		120.2
11	131	21.0	8	64	0.125	915	25.2		130.7
13	141	21.0	10	74	0.135	930	25.8		140.6
15	149	21.0	12	82	0.146	900	25.0		149.4
17	157	21.5	14	90	0.156	885	24.1		157.5
19	164	21.5	16	97	0.165	875	24.0		164.8

$C_{AV} = 895$

$N_{AV} = 24.5$

THE FILTRATION EQUATION USED IS $Q_1 = \sqrt{C_{AV}} \sqrt{T_1 + \frac{N_{AV}^2}{C_{AV}}} - N_{AV}$

WHERE $Q_1 = Q-67$ AND $T_1 = T-3$

BY SUBSTITUTION Q CALC = $30 \sqrt{T - 2.33} + 42.5$

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MLM 518

Problem Title **The Solubility of Barium Sulfate in Solutions of Sodium Hydroxide**

Report By **R. W. Moshier**

Work Done By **S. A. Barth and R. W. Moshier**

INTRODUCTION

In an endeavor to devise an electrolytic deposition method for lead, a predigestion of a sample of K 65 residue, used in the Radium Process, showed nearly complete solution of the sample in 50 per cent sodium hydroxide. Some precipitate reformed upon aqueous dilution preparatory to electrolysis. Likewise the same phenomenon occurred with samples of coprecipitated lead sulfate barium sulfate, whereas lead sulfate alone will remain in solution upon aqueous dilution. Since no such observation had been described in the literature, a study was started to determine the factors governing the solubility of barium sulfate in aqueous sodium hydroxide.

DETAILED REPORT

Solutions of sodium hydroxide 50 per cent or more by weight were prepared and filtered to free them from sodium carbonate. The solutions were assayed volumetrically and dilution of these solutions to the desired concentrations were prepared for use in this study. As containers, paraffin lined test tubes were used. A refrigerator was used for the 2° study, and a thermostated water bath was used for the other temperatures i.e. 25°, 33°, and 42°.

Qualitatively it has been observed that barium sulfate is appreciably more soluble in sodium hydroxide at elevated temperatures. In preparing a solution, therefore, an excess of barium sulfate was triturated in a small beaker with a glass rod while the solution was brought to near boiling temperature. The solution was allowed to cool below the melting point of paraffin (approximately 52°) and then emptied into one of the paraffin-lined test tubes stoppered, and placed in the bath. All samples were allowed at least 16 hours to come to equilibrium. Samples from the 2° and 25° study were centrifuged before sampling. The samples at higher temperatures being at a lower viscosity were believed to be settled and were sampled without centrifuging since precipitation would likely occur during cooling while centrifuging. Weighed samples were titrated to determine their sodium hydroxide content. The barium sulfate content was determined gravimetrically.

Figure 1 presents incomplete data showing the effect of temperature and of sodium hydroxide concentration on the solubility of barium sulfate.

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CONCLUSION

Barium sulfate exhibits an abnormally increased solubility behavior in aqueous sodium hydroxide. The abnormality begins at approximately 45 per cent sodium hydroxide. The temperature coefficient of solubility appears to be normal.

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SOLUBILITY OF BARIUM SULFATE
IN AQUEOUS SODIUM HYDROXIDE.

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