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Robert Burk

THE COPRECIPITATION OF THORIUM
WITH BARIUM SULFATE

by

Robert Charles Burk

A report submitted to the Department
of Chemistry in partial fulfilment of
the requirements for the degree of
Master of Science

Carleton University
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April, 1982

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Abstract

The effect of potassium on the coprecipitation of thorium by barium sulfate was studied. Increased potassium concentration was found to increase the efficiency of the carrying of thorium.

The activation energy for the precipitation of thorium by preformed barium sulfate was 24.1 ± 1 kcal/mole, regardless of potassium concentration.

The exchange of barium between barium sulfate and solution was found to be faster in the presence of potassium, especially when the potassium was in the barium sulfate itself. The activation energy of this process was found to be 11.4 ± 1 kcal/mole, regardless of the potassium concentration.

The surface area of barium sulfate precipitated in the presence of added potassium was found to be larger than that of barium sulfate precipitated in the absence of added potassium.

The increase in the rate of precipitation of thorium can be only partly accounted for by the larger surface area of the precipitate. A series of simple reactions has been postulated to describe the precipitation of thorium by preformed barium sulfate.

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The assistance of Ina de Jong was appreciated, especially with experimental details.

TO MY MOTHER

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ABSTRACT

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I INTRODUCTION

Background Information

Canada is the world's second largest producer of uranium (5400 metric tons in 1980 ⁽¹⁾). As the grade of uranium ore is often only 1% or less U_3O_8 , there is a substantial amount of waste produced from the milling operations. Although this volume of waste is small in comparison to the waste produced by other types of mining operations, uranium mill wastes are unique in that they are radioactive.

Whether by accident or negligence, effluents from uranium mill waste storage areas have, in some instances, been discharged into the environment. A number of the radioactive isotopes present in the waste may have negative impacts on the environment. Figure 1 shows the three radioactive decay series associated with uranium ores. (The third series is present only in those ores which contain natural thorium.) The half-lives of the longer lived isotopes are indicated on the diagram. The long half-lives of three thorium isotopes indicate that thorium is definitely an element of concern in uranium mill wastes. ⁽²⁾ There has also been an interest in the use of thorium as a component of nuclear fuels, and thus the need for analytical procedures for thorium is evident.

Various methods have been used to analyze for thorium, depending on the information sought. If the concentration of ^{232}Th (essentially total thorium) is sought, two of the most sensitive methods are chemical procedures, namely a fluorometric

Figure 1. The three decay series. The half-lives of some of the longer lived isotopes are indicated.

method,⁽³⁾ and a colorimetric method.⁽⁴⁾ The low specific radioactivity of ^{232}Th makes the use of radiochemical procedures for its determination difficult at best.

When the concentrations of individual thorium isotopes are sought, it is necessary to separate the thorium in a form suitable for alpha particle spectroscopy. This may be accomplished either by electrodeposition,⁽⁵⁾ or by carrying of the thorium on an insoluble precipitate, such as barium sulfate.⁽⁶⁾

The barium sulfate method is simple and rapid, and quantitative carrying of thorium can be achieved under suitable precipitating conditions. The presence of foreign ions during the precipitation, however, can have a strong influence on the extent to which thorium is carried by barium sulfate. In general, the presence of univalent cations increases the efficiency with which thorium is carried,⁽⁶⁻¹⁰⁾ while the presence of ter- and quadrivalent cations decreases it.^(6,8) Samples for thorium determination, especially environmental samples, will contain varying amounts of these ions, and so it will be necessary to adjust the precipitating conditions to obtain the maximum efficiency of carrying of thorium. It is the purpose of this work to gain a better understanding of why these ions have an influence on the carrying of thorium by barium sulfate. In particular, the effects of potassium ion on the system are examined, with a view towards generalizing the observations to other ions as well.

The Precipitation of Barium Sulfate

In order to examine the carrying of thorium by barium sulfate, it is first necessary to be familiar with some phenomena associated with the precipitation of barium sulfate itself. It is convenient to distinguish the steps in a precipitation as nucleation, growth, ripening, and recrystallization (or aging).⁽¹¹⁾ These steps are difficult to distinguish in practice, as they will always overlap one another in time.

Nucleation can be either homogeneous, in which case dissolved ions combine to form larger and larger particles, or heterogeneous, where ions are deposited on a preformed surface, thus forming a nucleus for further growth. Nucleation will only occur when a critical supersaturation has been reached. The supersaturation, S , is defined by

$$S = c/c_s$$

where c is the actual concentration of dissolved ions (those forming the precipitate) and c_s is the saturation concentration (i.e. the solubility.)

The method used to precipitate barium sulfate (or any other crystalline precipitate) will determine the ultimate crystal size and degree of perfection. If the supersaturation is initially very high, nucleation will be very rapid, and many crystals will be formed. The crystals are usually very small and imperfect. Lower initial supersaturations lead to fewer, but larger and less imperfect crystals.

Once a suitably large nucleus has formed, growth can occur. The basic model proposed for growth is illustrated in Figure 2. A site such as the one marked "A" is a preferred location for the deposition of a new crystal unit, and a new, identical site is formed adjacent to the old one.

The crystals resulting from nucleation and growth will usually contain many imperfections. Processes leading to more perfect crystals are collectively known as ripening. According to the Ostwald mechanism for ripening, the smaller crystals dissolve, while the larger, more thermodynamically stable crystals continue to grow.

Recrystallization processes are thought to occur continuously throughout the development of the crystals, but since they are relatively slow processes, they are noticeable only after crystal growth has stopped. The surface of an ionic precipitate is in dynamic equilibrium with the solution throughout all stages of its development. This is manifested in a continuous exchange of matter between the solid and the solution. This may be contrasted with crystal growth, which is essentially a one-way process.

During recrystallization, the numbers and sizes of crystals do not change significantly, but the process tends to yield thermodynamically more stable crystals with fewer imperfections, and often with smaller surface areas.

Figure 2. The site marked "A" is the preferred location for the deposition of a new crystal unit.

Coprecipitation of Other Ions by Barium Sulfate

If barium sulfate is precipitated from solution in the presence of other ions, many of these ions will be carried, or coprecipitated, by the barium sulfate. The manner in which these ions are coprecipitated may be one of the following:

- (a) Isomorphous replacement
- (b) Adsorption
- (c) Formation of anomalous mixed crystals
- (d) Internal adsorption

We shall review each of these in turn.

(a) Isomorphous replacement

Coprecipitation via isomorphous replacement will occur if the carrier ions (barium in this case) and the tracer ions have similar ionic radii, hydration energies, and lattice energies in the carrier compound. For instance, radium is carried very efficiently by barium sulfate.⁽¹²⁾ The chemical similarity of barium and radium ions is evident from the following data:

	Ba	Ra
Ionic Radius ⁽¹⁾	1.34	1.43
$\Delta H_f^\circ(2) (M^{+2}_{(aq)})$	-129	-126
$\Delta H_f^\circ(2) (MSO_{4(s)})$	-350	-350

notes: (1) Angstroms ($10^{-10}m$)

(2) kcal/mole

(data from reference 30)

If equilibrium between the ions in solution and the ions in the interior of the precipitate is somehow established, the distribution of the tracer will follow the homogeneous distribution law:

$$\frac{[\text{Tracer}]}{[\text{Carrier}]}_{\text{solid}} = D \frac{[\text{Tracer}]}{[\text{Carrier}]}_{\text{solution}}$$

where D is the homogeneous distribution coefficient. The equilibrium between solid and solution is generally thought to be attained through recrystallization and solid diffusion.

It is possible that equilibrium is attained between ions on the surface of the precipitate and ions in solution as each new crystal layer is formed, but that recrystallization and solid diffusion are negligible. In such a case, the inhomogeneous, or logarithmic distribution law is followed:⁽¹⁴⁾

$$\log \frac{[\text{Tracer}_{\text{total}}]}{[\text{Tracer}_{\text{solution}}]} = \lambda \log \frac{[\text{Carrier}_{\text{total}}]}{[\text{Carrier}_{\text{solution}}]}$$

where λ is the logarithmic distribution coefficient.

The method by which a precipitate is formed will determine which distribution law is followed. If the precipitate is formed rapidly by agitation of a highly supersaturated solution and immediately filtered, the logarithmic distribution law is followed. Prolonged digestion of such a precipitate will result in a homogeneous distribution of the tracer, equilibrium being attained through recrystallization.⁽¹⁵⁾ Precipitation from dilute solutions will result in a homogeneous distribution also.

There is a qualitative correlation between the observed

values of the distribution coefficients and the ratios of the solubility products of the carrier and tracer compounds in many instances. (22) However, this correlation is not good enough to allow prediction of distribution coefficients with much accuracy.

If the distribution coefficient is greater than unity, then the coprecipitation is termed an "enrichment" process. In other words, the precipitate is enriched in tracer compared to the solution. Distribution coefficients less than unity represent "derichment" processes, where the precipitate is deficient in tracer relative to the solution.

(b) Adsorption

In cases where the tracer ions are not sufficiently similar to the carrier ions to fit into the carrier compound crystal lattice, coprecipitation by adsorption may occur. The following factors affect the efficiency of carrying by adsorption:

(1) The larger the surface area of the precipitate, the larger is the fraction of tracer carried. Thus a rapidly formed precipitate carries a tracer by adsorption more efficiently than a slowly formed one.

(2) The more insoluble is the compound that the tracer forms with the oppositely charged lattice ion, the more efficiently the tracer is carried.

(3) A tracer ion is adsorbed only if the sign of the charge on the precipitate is opposite to that of the tracer ion.

(4) Standing of the precipitate in contact with the tracer

solution may increase or decrease the fraction of the tracer carried. Recrystallization decreases the fraction of the tracer carried due to the decreased surface area of the precipitate, unless the tracer is trapped (occluded) at the surface.

(c) Anomalous Mixed Crystal Formation

It may happen that a tracer is carried by a precipitate even though macro amounts of the tracer ion do not form isomorphous mixed crystals with the carrier, and conditions for adsorption are absent. This may be due to anomalous mixed crystal formation or internal adsorption, two processes which are difficult to distinguish from one another.

An example of an anomalous mixed crystal formation is the coprecipitation of lead with barium chloride. Despite the crystallographic differences between BaCl_2 and PbCl_2 , macro amounts of the former and trace amounts of the latter do form a mixed crystal - in other words an anomalous mixed crystal.⁽¹⁶⁾ This form of coprecipitation is not usually affected by external conditions, such as the charge on the precipitate, or the presence of foreign ions during the precipitation.

(d) Internal Adsorption

Coprecipitation by internal adsorption is the adsorption of the tracer on the surfaces of a growing crystal, such that it is trapped by the newly forming crystal layers. Often, the distribution coefficients obtained under the same conditions are not reproducible when internal adsorption is involved. The presence of an excess of the lattice ion whose charge is the same as that of the tracer will suppress coprecipitation by internal adsorption.

Coprecipitation of Thorium by Barium Sulfate

The effects of foreign ions on the coprecipitation of thorium by barium sulfate are well documented.⁽⁶⁻¹⁰⁾ (By foreign, we mean any ion added before precipitation, or which is unavoidably present, other than the thorium and the barium sulfate itself.) The causes of these effects must occur either in the solution, or on the surface of the barium sulfate. Most of the evidence in this work indicates that the latter is of more importance.

De Jong and Wiles⁽⁸⁾ found that the fraction of thorium carried by barium sulfate varied with the potassium concentration in the manner illustrated in Figure 3. Ambe and Lieser's results⁽⁹⁾ were similar. The effect of ferric ions⁽⁸⁾ is shown in Figure 4.

What follows is a review of possible explanations for the effect of potassium.

Sill and Willis⁽¹⁷⁾ have postulated that the addition of potassium during the barium sulfate precipitation causes the formation of an insoluble barium potassium salt of a thorium sulfato complex (i.e. $K_2Ba[Th(SO_4)_4]$). In the presence of sulfate ion, thorium likely exists as $Th(SO_4)^{+2}$ ⁽¹⁸⁾ Also, the double salts of potassium thorium sulfate are known to be less soluble than thorium sulfate itself.⁽¹⁹⁾ Thus, argues Sill, a barium potassium thorium salt is likely to be even less soluble. However, during the precipitation of a trace amount (about 10^{-12} gram) of thorium, the presence of potassium still has a profound effect.⁽⁸⁾ At such low concentrations of thorium, it is inconceivable that the solubility of thorium sulfate, or

Figure 3. Percent of thorium carried versus pK^+ .
(from reference 8.)

Figure 4. Percent of thorium carried versus pFe^{+3}
(from reference 8.)

of barium potassium thorium sulfate, could be exceeded. Therefore, formation of $K_2Ba[Th(SO_4)_4]$ seems unlikely. Indeed, no direct evidence for the formation of this compound has been published.

De Jong and Wiles⁽⁸⁾ proposed the equilibrium

- where M^+ is a cation such as potassium and M_2Th^{+6} describes a loosely coordinated unit at the surface of the barium sulfate crystal lattice. This unit could then compete with ter- and quadrivalent ions at the surface. For instance,

Although this predicts correctly the effects of added cations, no evidence has been found for the existence of a unit such as M_2Th^{+6} .

The Bronsted equation predicts that the logarithm of the rate constant for an ionic reaction is directly related to the square root of the ionic strength. If this were the case for the carrying of thorium by barium sulfate, then adding a univalent cation would have the same effect as adding a ter- or quadrivalent cation. Such is not the case, and at any rate, the amount of added electrolyte required to produce a large change in the rate of precipitation of thorium by barium sulfate is smaller than that predicted by the Bronsted equation.

The influences of foreign ions on the morphology of barium sulfate crystals have been studied.⁽²⁰⁻²³⁾ Thus it is known that barium sulfate crystals precipitated in the presence of

K^+ , Na^+ , or NH_4^+ tend to be larger than those precipitated in the absence of foreign ions. A possible explanation for this is the decrease in supersaturation of barium sulfate which occurs upon addition of an electrolyte. The solubility product, K_{sp} , is defined by

$$K_{sp} = \frac{K_a}{\gamma_{\pm}}$$

where K_a is the activity product of barium and sulfate ions, and $\gamma_{\pm}$ is the mean activity coefficient for the two ions. The Debye-Huckel limiting law relates the mean activity coefficient to the ionic strength as follows

$$\log_{10} \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

where z_+ and z_- are the charges on the barium and sulfate ions respectively, and I is the ionic strength;

$$I = \frac{1}{2} \sum_i m_i z_i^2$$

where the summation is taken over all ionic species in solution with respective molalities and charges m_i and z_i .

The effect of added electrolyte then, is to increase the ionic strength, which has the effect of increasing K_{sp} , the solubility product. Since the supersaturation, S , can be written as

$$S = \frac{[Ba^{+2}][SO_4^{-2}]}{K_{sp}}$$

adding electrolyte tends to decrease S , and, as stated earlier, larger particles will result. It is likely that the surface area of a precipitate will also be affected, since not only are particle sizes different, but the number of imperfections of barium sulfate crystals has also been observed to change with electrolyte concentration. For instance, Fischer and Rhinehammer⁽²⁰⁾ found that more potassium ion in solution increases crystal perfection of barium sulfate, while Liu, Nancollas and Gasiecki⁽²⁴⁾ found that increased sodium ion concentration actually decreases it.

If the ionic strength were the only factor involved, then adding a univalent cation should have the same effect as adding a tervalent cation, but such is not the case. Thus, the ionic strength may in some ways affect the precipitation of thorium by barium sulfate, but it is not the only reason for the observed changes incurred by foreign cations.

Ambé and Lieser⁽⁹⁾ found, under certain conditions, that anomalous mixed crystals of barium sulfate containing potassium and thorium in a ratio of 2:1 were formed. They postulated that two K^+ ions and one Th^{+4} ion should be able to substitute for three Ba^{+2} ions in a barium sulfate lattice. Whereas the ionic radii for barium and potassium are similar (1.34 and 1.33 Å respectively), that of thorium is only 1.02 Å. Thus the difference in radii between barium and thorium is greater than that generally found in mixed crystals. Furthermore, x-ray powder diffractions of a $Th-BaSO_4$ coprecipitate showed no lines other than those of barium sulfate itself, indicating that no new

compounds ($K_2Ba[Th(SO_4)_4]$, for instance) were formed.

Syromyatnikov and Trofimova⁽²⁵⁾ did find some new x-ray lines in a $Th-BaSO_4$ coprecipitate, and attributed them to a double salt of the form $nBaSO_4 \cdot mTh(SO_4)_2$. It is not clear whether or not potassium was present during the precipitation.

The idea of a simple substitution of three barium ions by two potassium and one thorium ion is convincing, in that it conserves charge, the number of atoms, and perhaps even the lattice energy.⁽⁷⁾ This idea does not, however, explain why multiply charged cations tend to reduce the coprecipitation of thorium, nor does it explain why such a large excess of potassium is necessary for quantitative coprecipitation of thorium.

Barium sulfate precipitates will attain a net negative charge if precipitated with an excess of sulfate ion, as is often done. It is possible, therefore, that the coprecipitation of thorium occurs simply as a result of the attraction between the positively charged thorium ion and the negatively charged surface of the barium sulfate. A local negative charge could also arise from the substitution of a potassium ion for a barium ion in the barium sulfate lattice ;

where the square brackets represent a unit at the surface of the crystal in contact with the solution. Sizeable amounts of potassium are known to be precipitated by barium sulfate. In one reported case,⁽⁹⁾ the mole ratio of potassium to barium in

the precipitate was 0.15:1.

Substitution of, say, ferric ion for barium ion could generate a local positive charge;

and effectively prevent a positively charged species, such as thorium, from adsorbing at that site on the crystal surface. (Ferric ions are also known to be coprecipitated by barium sulfate. (26))

If processes such as these are responsible for changing the extent to which thorium is coprecipitated by barium sulfate, then the thermodynamics of the precipitation are likely affected by foreign ions as well. Although no information on exactly this has been published, the thermodynamics of the dissolution of barium sulfate, and of the exchange of barium ion at the surface of barium sulfate, have been reported. Lieser, Gütlich, and Rosenbaum (27) measured the rate of exchange of radioactive barium between a barium sulfate precipitate and aqueous solution as a function of temperature. Their calculated enthalpy of activation for this process was 12.0 kcal/mole. This was explained by the authors by the fact that at least some of the waters of hydration of the barium ion must be stripped off before insertion of the ion into the barium sulfate lattice. A positive change in the enthalpy is in agreement with the idea that the activation step is the partial dehydration of the barium ion.

The kinetics of the dissolution of barium sulfate were

investigated by Bovington and Jones,⁽²⁸⁾ who found an activation energy of 5.9 kcal/mole. The postulated the following mechanism;

where $\text{Ba}^{+2}\text{SO}_4^{-2}(\text{aq})$ is described by the authors as being the activated intermediate in the hydrated monolayer at the surface of the solid. E_s is the activation energy for dissolution, and E_c , the activation energy for crystal growth, was calculated by the authors to be about 2 kcal/mole. Interestingly, neither of these values corresponds to the activation energy found by Lieser et al for the exchange of barium ion.

2 Methods

In an analytical determination of thorium by barium sulfate precipitation, the precipitating conditions are chosen to give as high a distribution coefficient as possible. This may be accomplished by precipitating the barium sulfate from dilute solutions of barium and sulfate ions, often with heating, to obtain easily filtered crystals. In this work, precipitating conditions which gave reproducible, but not quantitative carrying of thorium were used so that the influences of foreign ions were more easily seen. In most experiments, therefore, a small volume of concentrated sulphuric acid was quickly added to a dilute solution of $\text{Ba}(\text{NO}_3)_2$ containing the thorium tracer and any added foreign ions. The crystals so formed were filtered off, and the fraction of thorium carried was determined by comparison of the radioactivity of these crystals with that of a standard of the thorium tracer solution used.

When it was desired to distinguish between solution phase and surface effects of, say, foreign ions, it was necessary to precipitate the barium sulfate, wash it free from adsorbed impurities, and transfer it to a new solution. In this way, it was possible to study the system with the foreign ions only in solution, or only in the barium sulfate.

The method of Kolthoff⁽²⁹⁾ was used as an indicator of surface area of barium sulfate. This method involves measuring the amount of chromate ion adsorbed onto the surface of the precipitate as a result of the exchange of sulfate ion with

chromate ion. The decrease in chromate ion concentration was followed iodometrically.

3 Experimental

A. Reagents

The potassium stock solution was 5% reagent grade KNO_3 (Allied Chemical, N.Y., N.Y.) in distilled water.

The ^{133}Ba tracer solution, obtained from Amersham Corp., Oakville, Ontario, was diluted to give a γ -activity of approximately $550 \text{ counts s}^{-1} \text{ ml}^{-1}$, with a specific activity of 15.6 mCi/mg Ba . Thus, if 1.00 ml of this solution were used in an experiment in a total volume of 100 ml , the concentration of barium would be approximately $6.9 \times 10^{-11} \text{ M}$ (if no other barium were present.)

Nitric and sulfuric acids were reagent grade. (Allied Chemical, Quebec.)

The thorium used was ^{234}Th , obtained by solvent extraction from an ether solution of $\text{UO}_2(\text{NO}_3)_2$ into 0.1 M HNO_3 , followed by cleanup on an ion exchange column of DOWEX-1 (100/200 mesh). The final solution was made up in 1.0 M HNO_3 . At the time of preparation, the ^{234}Th activity was approximately $1000 \text{ counts s}^{-1} \text{ ml}^{-1}$. An effort was made to use this solution quickly because the half life of ^{234}Th is only 24.1 days, so a considerable amount will have decayed in a few weeks.

The stated maximum limits of potassium in the reagents were:

$\text{Ba}(\text{NO}_3)_2$	0.05% alkalis
$\text{HNO}_3(\text{conc.})$	1 ppm
$\text{H}_2\text{SO}_4(\text{conc.})$	1 ppm

Thus, the potassium concentration due to these reagents in a

solution of 100 ml 0.1 M HNO_3 , 1.00 mg Ba, and 2 ml 9M H_2SO_4 was at most 0.03 ppm. The potassium ion concentration in the distilled water used was estimated at <1 ppm.⁽³³⁾ Based on this information, the value of pK^+ for precipitating solutions with no added KNO_3 was estimated at 4.8.

B. Precipitation Procedures

Precipitation experiments were carried out in 100 ml 0.1 M HNO_3 in a 250 ml beaker. 1.00 ml of a $\text{Ba}(\text{NO}_3)_2$ solution containing 1.00 mg Ba per ml was added, followed by 1.00 ml of a ^{133}Ba solution when required. The thorium and potassium ions were added, followed by 2.00 ml 9 M H_2SO_4 with stirring. The beaker was suspended in a thermostatted water bath and stirred by a Teflon impeller attached to a stirring motor suspended over head. Unless otherwise stated, the solution temperature was maintained at 22.0 ± 0.1 °C.

After the desired time had elapsed, (time was measured starting with addition of the H_2SO_4) the solution was immediately filtered through filter paper with a nominal pore size of 0.45 μm . (Gelman DM-450) The precipitate was washed with 40 ml 0.1 M HNO_3 , then with 40 ml water. The filter paper (with the precipitate) was dried under a heat lamp for 15 minutes, and placed on an aluminum planchette in a covered plastic dish. A gamma spectrum was immediately recorded.

When it was necessary to precipitate the barium sulfate under certain conditions, and use it in a different solution, the precipitate was washed as described above before

being introduced into the second solution.

C. Surface Area Measurements

Specific surface areas were determined by measuring the change in concentration of chromate ion of a solution in contact with the precipitate. Approximately 40 mg of the precipitate was suspended by vigorous stirring in 50 ml 0.05 M Na_2CrO_4 . After a measured time, the precipitate was filtered off, washed, dried, and weighed. The chromate ion concentration in the filtrate was determined iodometrically. The necessary calculations are outlined in the discussion. (cf page 38.)

D. Activation Energy Measurements

Activation energies for the precipitation of barium and of thorium on preformed barium sulfate were found by measuring the rates of precipitation over a temperature range of approximately 22 °C to 55 °C. Each of the measurements was performed at two different potassium concentrations. ($\text{pK}^+ = 4.8$ and $\text{pK}^+ = 2.3$) The potassium concentration during the formation of the barium sulfate was the same as that during the measurement of the rate of precipitation of thorium or barium onto the preformed barium sulfate. The procedure was as follows. After precipitation of 47 mg of barium sulfate from 100 ml 0.1 M HNO_3 , a small amount of it (less than 10 mg) was transferred to a stirred, thermostatted beaker containing a known amount of ^{133}Ba or ^{234}Th . After a measured time, the precipitate was filtered, washed and dried. The actual mass of precipitate used was determined in one of two ways:

- (1) The precipitate was weighed, or
- (2) The precipitate was labelled with ^{133}Ba , giving a known specific activity, and the activity of ^{133}Ba in the final sample was measured, from which the mass could be calculated.

The extent of precipitation of thorium or of barium was measured 5.0, 10.0, 15.0, and 20.0 minutes after initial contact between the barium sulfate and the tracer. Reaction rates were determined from plots of $(\ln(1-F))/[\text{BaSO}_4]$ versus time, where F is the fraction of thorium or barium precipitated onto the preformed surface.

E. Radioactivity Measurements

Gamma spectra were recorded using a 3 in. x 3 in. NaI (Tl) scintillation crystal mounted on the window of a photomultiplier tube. Pulses from the photomultiplier tube were fed to a preamplifier, then to a Northern Scientific model NS-900 pulse height analyzer using 256 channels. The scintillation crystal, photomultiplier tube and preamplifier were housed in an enclosure of 3 in. thick lead, lined with cadmium (to absorb lead x-rays) and with copper (to absorb cadmium x-rays.)

Pulses were accumulated for 10.0 minutes. Then the sample was removed, and the instrument set to subtract counts from the appropriate channels for a further 10.0 minutes. In this manner, background radiation was subtracted, yielding a spectrum of the sample only.

For ^{234}Th , the peaks at energies of 63 keV and 93 keV were used, and for ^{133}Ba , those at 355 keV and 274 keV. The net

count rate was determined by a manual integration of these peaks. The chemical recoveries of thorium (or barium) were found by comparing the net count rate to that of a standard sample prepared from the same stock solution.

In cases where both ^{234}Th and ^{133}Ba were added to the same sample, it was necessary to "strip" the spectrum - in other words to separate the contributions to the total activity from each of thorium and barium. This was necessary because some lower energy peaks of ^{133}Ba overlap the 63 keV and 93 keV peaks of ^{234}Th , due to the limited resolution of the NaI scintillation crystal. To obtain the net ^{234}Th count rate, it was necessary to subtract a portion ($66.5 \pm 0.2\%$) of the 355 - 274 keV ^{133}Ba peaks from the portion of the spectrum containing the 63 keV and 93 keV ^{234}Th peaks.

For example, a typical spectrum containing both ^{133}Ba and ^{234}Th is shown in Figure 5. The area marked "B" contains the 274 and 355 keV peaks of ^{133}Ba . The area marked "A" contains the 63 and 93 keV peaks of ^{234}Th , as well as ^{133}Ba x-rays:

$$\text{area B} = 11068 \pm 105 \text{ counts (in 1000 s.)}$$

$$\text{area A} = 14901 \pm 122 \text{ counts (in 1000 s.)}$$

$$\begin{aligned} \text{therefore, counts } ^{234}\text{Th} &= 14901 \pm 122 - ((.665 \pm .002) \times (11068 \pm 105)) \\ &= 7541 \pm 142 \\ &= 7.54 \pm .14 \text{ counts s}^{-1} \end{aligned}$$

The fraction $0.665 \pm .002$ was the average of three measurements of the ratio of area "A" to area "B" in a sample containing ^{133}Ba , but no ^{234}Th .

In order to verify that this method was justified, the count

Figure 5. A gamma spectrum of a sample containing both ^{133}Ba and ^{234}Th . The area marked "B" contains peaks of ^{133}Ba only, while that marked "A" contains peaks of both ^{133}Ba and ^{234}Th .

rate of the ^{234}Th in a combined $^{234}\text{Th} - ^{133}\text{Ba}$ standard was measured in this manner regularly for 36 days. The data are presented in Figure 6, a plot of $\ln(^{234}\text{Th count rate})$ versus time. The plot is linear, and the calculated half life for the ^{234}Th is 24.6 ± 0.4 days, in good agreement with the accepted value of 24.1 days. This indicates that the activity measured by this method is that of ^{234}Th only.

Figure 6. $\ln(^{234}\text{Th activity})$ versus time. The calculated half life is 24.6 ± 0.4 days.

4 Results and Discussion

A. Effect of Potassium

Previous reports on the effects of potassium on the coprecipitation of thorium with barium sulfate were confirmed and extended. For instance, Figure 7 shows the fraction of thorium carried as a function of pK^+ under typical conditions. (1.7 mg $BaSO_4$ at 22.0° C.) Note that, for this experiment, the precipitation was done with heating and prolonged digestion (one hour) to give as complete a recovery of thorium as possible.

The effects of sodium and ammonium ions were found to be similar to, but not as pronounced as those of potassium ions.

Thus, complete recovery of thorium required the presence of much greater amounts of sodium or ammonium ions than of potassium ions. This also was confirmation of earlier reports. (8)

With small concentrations of potassium ion, complete recovery of thorium is not observed, even with prolonged digestion of the precipitate with heating. However, above a potassium concentration of approximately 0.001 M, the thorium recovery rises sharply.

The total thorium concentration in solution in these experiments was approximately 2.5×10^{-13} M, therefore precipitation of thorium sulfate proper could not occur, since the solubility of $Th(SO_4)_2$ (30) is quite large. (1.5 g/100 ml) At any rate, the solubility of $Th(SO_4)_2$ actually increases in a solution of K_2SO_4 , which does not explain the observed effect of potassium ion. (19)

The same experiment was done without heating or prolonged digestion. Figure 8 shows the recovery of thorium relative to that

Figure 7. Percent thorium carried versus pK^+ .

Figure 8. Percent thorium precipitated relative to that of barium versus pK^+ .

of barium, plotted as a function of pK^+ . Figure 8 shows clearly that the fraction of thorium carried per unit mass of barium sulfate increases with increasing potassium concentration. Since this method of precipitation gave essentially the same results as are shown in Figure 7, it was employed throughout the rest of this work.

The concentration of potassium apparently has an effect on the precipitation of barium sulfate itself. With no added potassium ion ($pK^+=4.8$) the recovery of barium as barium sulfate was lower than when potassium was added. A possible explanation for this is that the decrease in supersaturation due to the presence of the added potassium has caused the formation of larger particles, as described earlier. These larger particles would be more efficiently filtered, and thus the precipitation of barium sulfate would appear to be greater. It was necessary, therefore, to correct for the amount of barium sulfate actually filtered, as was done in Figure 8.

Scanning electron micrographs revealed that the potassium does indeed have an effect on the particle size of barium sulfate. Figures 9 and 10 are electron micrographs (3000x) of barium sulfate precipitated at $pK^+=4.8$ and $pK^+=2.0$ respectively. At low potassium concentrations (Figure 9) the particles have many shapes, with dendrites extending in many directions. Addition of potassium during the precipitation causes the formation of particles which all appear very similar. Referring to Figure 10, growth has occurred along one axis to a much greater extent than the others. This is interesting in that it may imply that potassium has its effect to differing degrees on the different crystallographic faces of barium sulfate crystals. The relevance of this, however, is not well understood.

Figure 9. Scanning electron micrograph of
barium sulfate particles
precipitated at $\text{pH} = 4.8$
(3000 x)

Figure 10. Scanning electron micrograph of
barium sulfate particles
precipitated at $\text{pH} = 2.0$
(3000 x)

Figures 7 and 8 showed the total amount of thorium precipitated under certain conditions in a given time. Thus, the question arises as to whether the potassium affects the rate at which thorium is being incorporated into barium sulfate, or merely the extent, as Figures 7 and 8 would have us believe. Experiments were done in which the amounts of barium and thorium precipitated were determined as functions of time. Figure 11 shows the fraction of thorium precipitated versus time from three solutions of different potassium concentrations. The concentration of potassium in these experiments was great enough that the apparent rate of precipitation of barium (as barium sulfate) was very fast. Complete precipitation of barium was achieved within 4 minutes after the addition of sulfuric acid, so it was not necessary to account for the amount of barium sulfate precipitated.

The rate of precipitation of thorium is greatly increased in the presence of potassium. Furthermore, and perhaps more importantly, the precipitation of thorium continues even after 100% of the barium has precipitated. In other words, coprecipitation of thorium does not require the crystal surface to still be growing. Thus, we may conclude that the coprecipitation of thorium does not occur as a result of internal adsorption, since this mode of coprecipitation occurs when the tracer is occluded by newly forming crystal layers. The potassium is thus accelerating the incorporation of thorium into the barium sulfate at a preformed surface.

With very little potassium in solution ($pK^+ = 3.3$, Figure 11), not only is the rate of precipitation of thorium smaller, but the

Figure 11. Thorium carried versus time from three solutions of different potassium concentrations. The values of pK^+ are indicated on the curves.

extent of precipitation does not approach 100%, even when the experiment was extended to 70 minutes.

Measurement of distribution coefficients did not clearly show whether the homogeneous or logarithmic distribution law was being followed. The scatter in the data was such that no definite conclusions concerning distribution coefficients could be drawn.

B. Surface Area of Barium Sulfate Precipitates

The surface area of the barium sulfate precipitates is a consideration when measuring the rate of removal of thorium from solution. Inspection of Figures 9 and 10 shows that the concentration of potassium likely has an effect on the surface area of the crystals. Higher potassium concentrations tend to yield particles whose surfaces appear rougher.

The surface areas of two barium sulfate precipitates that were formed in the presence of different potassium concentrations were measured by the chromate adsorption method. Figure 12 shows plots of percent of chromate ion adsorbed versus time for the two precipitates. There is initially a very fast uptake of chromate ion from solution by the precipitates, attributed to the reaction;

(where (surf) denotes a unit at the surface in contact with the solution.) This is followed by the slower process of recrystallization, which tends to bury the adsorbed ions deeper into the crystal.

Extrapolation of the curves to zero time yields the amount of chromate ion adsorbed, which may be used to calculate a surface area.

The following equilibrium constant was reported: ⁽²⁹⁾

$$\frac{[\text{SO}_4^{-2}(\text{aq})][\text{CrO}_4^{-2}(\text{surf})]}{[\text{SO}_4^{-2}(\text{surf})][\text{CrO}_4^{-2}(\text{aq})]} = 1.1$$

When the adsorption of chromate is complete, the amount of sulfate

Figure 12. Percent of chromate ion adsorbed onto two barium sulfate precipitates versus time. The value of pK^+ during the barium sulfate precipitation is indicated for each precipitate.

per gram of barium sulfate is;

$$[SO_4^{-2}(\text{surf})] = \frac{[CrO_4^{-2}(\text{surf})][SO_4^{-2}(\text{aq})]}{1.1m[CrO_4^{-2}(\text{aq})]}$$

where m is the mass of barium sulfate. The amount of sulfate on the surface of the original precipitate is this value plus the amount of chromate ion adsorbed. Using an area of $25 \times 10^{-20} \text{ m}^2$ per $BaSO_4$ unit at the surface, ⁽²⁹⁾ the specific surface areas shown below were calculated.

pK^+	Specific Surface Area, $\text{m}^2 \text{ g}^{-1}$
4.8	1.6 ± 1
2.3	5.1 ± 2

In the presence of more potassium ion, barium sulfate precipitates having larger specific surface areas are produced. When the value of pK^+ is decreased from 4.8 to 2.3, the specific surface area increases approximately three times.

Figure 12 also demonstrates that the presence of potassium in barium sulfate influences the rate at which chromate ions at the surface are buried deeper into the crystal lattice. With a large amount of potassium present ($pK^+ = 2.3$) chromate ion continues to be exchanged even after adsorption at the surface is complete. It seems likely that potassium is accelerating the recrystallization processes at the surface, and that the same effect would take place for any species adsorbed at the surface. In other words, the potassium may have the same effect on thorium as

Since, for these experiments, the mass of BaSO_4 used was constant, we may also incorporate it into the rate constant. Using the fact that $[^{133}\text{Ba}^{+2}(\text{aq})] = [^{133}\text{Ba}(\text{total})] - C_{^{133}\text{BaSO}_4}$, integration of the rate equation yields;

$$\frac{C_{^{133}\text{BaSO}_4}}{[^{133}\text{Ba}(\text{total})]} = -k''t$$

where k'' is the rate constant incorporating m , as well as A and n .

A plot of the left hand side of this equation versus time should have a slope of $-k''$. Figure 13 is such a plot for barium sulfate precipitated from a solution with no added potassium, and exchanged with $^{133}\text{Ba}^{+2}(\text{aq})$ in the presence of various concentrations of potassium. Note that the barium sulfate was first washed free of sulfate ion, so the $^{133}\text{Ba}^{+2}(\text{aq})$ was not simply precipitating as barium sulfate.

It is apparent that the amount of potassium in solution has an effect on the rate of exchange of barium with barium sulfate. The effect is much greater, however, if the barium sulfate is precipitated in the presence of the potassium, as illustrated in Figure 14. For the experiments shown in Figure 14, the potassium concentration was the same during the precipitation as during the exchange.

The data for Figures 13 and 14 are summarized in the table on page 48 as half-times for the exchange (the time necessary for the concentration of $^{133}\text{Ba}^{+2}(\text{aq})$ to decrease to one half of its initial value).

In general, the exchange is much faster with barium sulfate precipitated in the presence of potassium. This indicates that it is the potassium in the solid barium sulfate, not that in solution, which influences the rate at which barium is exchanged.

C. Exchange of Barium

It is known⁽²⁶⁾ that potassium is precipitated by barium sulfate. This is to be expected, on the basis of the similar ionic radii of barium ($1.34 \text{ \AA}$) and potassium ($1.33 \text{ \AA}$). The charges of the two ions are different, however, and the substitution of a potassium for a barium would create a local negative charge, as was indicated earlier. This local negative charge would attract any positively charged species from solution, including thorium and barium ions.

For the production of these sites on the surface of barium sulfate crystals, we have

and increasing the potassium concentration in solution will tend to increase the concentration of $\text{KSO}_4^-(\text{surf})$ and of $\text{Ba}^{+2}(\text{aq})$. At equilibrium, the dissolution and re-precipitation of barium sulfate will occur simultaneously;

and increasing $[\text{Ba}^{+2}(\text{aq})]$ will increase the rate of the re-precipitation reaction, tending to decrease $[\text{Ba}^{+2}(\text{aq})]$ again. Thus, one might expect that the effect of potassium would be to increase the rate of exchange of barium ion between barium sulfate and solution.

In order to study this possibility, the rate of exchange of barium ion was measured as a function of potassium concentration.

For reasons to be explained later, it was first necessary to demonstrate that the reaction

occurs as an exchange. In other words, that the rates of the forward and reverse reactions shown above are equal, else there would be a net dissolution or precipitation of BaSO_4 .

A large amount (89 mg) of freshly precipitated BaSO_4 was stirred with an equivalent molar amount of barium ion (as nitrate) in a small volume (8.0 ml) for 19.5 hours. The ${}^{133}\text{Ba}$ tracer was initially either all in solution, or all in the solid BaSO_4 . Since the amounts of barium as $\text{Ba}^{+2}(\text{aq})$ and as BaSO_4 were initially equivalent, then at equilibrium the tracer should be equally distributed between solid and solution. The degree to which this position is approached in a given time is a measure of the exchange rate. The extent of exchange was determined by measuring the ${}^{133}\text{Ba}$ activity in both the solid and solution, as shown below.

Initial Location of ${}^{133}\text{Ba}$	Fraction of ${}^{133}\text{Ba}$ in BaSO_4 after exchange	Fraction of ${}^{133}\text{Ba}$ in solution after exchange	% Exchange
Solution	$.15 \pm .01$	$.85 \pm .01$	30 ± 2
Solid	$.83 \pm .01$	$.17 \pm .01$	34 ± 2

It is seen from these data that 15% of the ${}^{133}\text{Ba}$ originally in solution had been exchanged into the barium sulfate after 19.5 hours. Complete exchange would require 50% of the ${}^{133}\text{Ba}$ to be in the barium sulfate. Thus,

$$\% \text{ exchange} = \frac{0.15 \pm 0.01}{0.50} \times 100 = 30 \pm 2\%$$

Similarly, the percent exchange found with the ^{133}Ba initially in the barium sulfate was $34 \pm 2\%$. Since these values are equal within experimental error, we may conclude that the reaction is an exchange, and not a net reaction.

The effect of potassium ions on the rate of exchange of barium ion was studied by measuring the rate of incorporation of ^{133}Ba ions into preformed barium sulfate. The reaction studied was thus;

Since the previous experiments showed that there is a true exchange of barium ion, then the rate of this one-way reaction should be the same as the rate of exchange. This is a one-way reaction, because the experiments were performed with only a trace amount of barium in solution, so only the forward reaction could be observed.

The ${}^{133}\text{Ba}^{+2}(\text{aq})$ concentration will decrease according to

$$\frac{-d[{}^{133}\text{Ba}^{+2}(\text{aq})]}{dt} = k[{}^{133}\text{Ba}^{+2}(\text{aq})] \times C_{\text{BaSO}_4}$$

where C_{BaSO_4} is the number of moles of $\text{BaSO}_4(\text{s})$ per liter of solution. To be correct, in place of C_{BaSO_4} , we should use the number of moles of BaSO_4 units in contact with the solution per liter, N ;

$$N = mAn/V$$

where m is the mass of BaSO_4 , A is its specific surface area, and n is the number of moles of BaSO_4 units at the surface per unit surface area in a volume V of solution. However, we will assume for now that A and n are constant, incorporate them into the rate constant, and call the new rate constant k' .

Since, for these experiments, the mass of BaSO_4 used was constant, we may also incorporate it into the rate constant. Using the fact that $[^{133}\text{Ba}^{+2}(\text{aq})] = [^{133}\text{Ba}(\text{total})] - C_{^{133}\text{BaSO}_4}$, integration of the rate equation yields;

$$\frac{C_{^{133}\text{BaSO}_4}}{[^{133}\text{Ba}(\text{total})]} = -k''t$$

where k'' is the rate constant incorporating m , as well as A and n .

A plot of the left hand side of this equation versus time should have a slope of $-k''$. Figure 13 is such a plot for barium sulfate precipitated from a solution with no added potassium, and exchanged with $^{133}\text{Ba}^{+2}(\text{aq})$ in the presence of various concentrations of potassium. Note that the barium sulfate was first washed free of sulfate ion, so the $^{133}\text{Ba}^{+2}(\text{aq})$ was not simply precipitating as barium sulfate.

It is apparent that the amount of potassium in solution has an effect on the rate of exchange of barium with barium sulfate. The effect is much greater, however, if the barium sulfate is precipitated in the presence of the potassium, as illustrated in Figure 14. For the experiments shown in Figure 14, the potassium concentration was the same during the precipitation as during the exchange.

The data for Figures 13 and 14 are summarized in the table on page 48 as half-times for the exchange (the time necessary for the concentration of $^{133}\text{Ba}^{+2}(\text{aq})$ to decrease to one half of its initial value).

In general, the exchange is much faster with barium sulfate precipitated in the presence of potassium. This indicates that it is the potassium in the solid barium sulfate, not that in solution, which influences the rate at which barium is exchanged.

Figure 13. $\ln(1-F)$ versus time, where F is the fraction of ^{137}Ba in the precipitate. The values of pK^+ during the exchange are indicated for each plot.

Figure 14. $\ln(1-F)$ versus time, where F is the fraction of ^{134}Ba in the precipitate. The values of pK^+ during the precipitation and the exchange are indicated for each plot.

pK^+	half-time min. (a)	half-time min. (b)
4.8	109	109
3.3	95.6	64.5
2.3	76.6	32.5
1.8	nd	17.6
1.6	66.6	9.9

notes: (a) K^+ in exchange solution only

(b) K^+ in precipitating and exchange solutions

nd - not determined

Geyer and Winzer⁽²⁶⁾ found that the amount of potassium carried by barium sulfate from a solution of KNO_3 varied linearly with the KNO_3 concentration. Figure 15 is a plot of $1/\text{half-time}$ versus the concentration of potassium ion for the experiments in which barium sulfate was precipitated in the presence of added potassium. The plot is linear, indicating that the rate of exchange of barium is directly proportional to the potassium concentration during precipitation of the barium sulfate. Thus, the rate is directly proportional to the amount of potassium in the barium sulfate.

It is interesting then, that the potassium in solution (see Figure 13) has any effect at all. A likely explanation for this is that the potassium in solution is continuously being incorporated into the barium sulfate, and only then does it influence the exchange of barium.

Figure 15. $1/\text{half-time}$ versus the potassium concentration during the precipitation of the barium sulfate.

D. Kinetics of Precipitation of Thorium on Barium Sulfate

If thorium is adsorbed at the surface of a growing barium sulfate crystal, the presence of potassium should have the same effect on thorium as on barium. An inspection of Figure 11 shows that the thorium is being precipitated after most of the barium has precipitated, as noted earlier. Therefore, experiments were done to determine the influence of potassium on the precipitation of thorium by preformed barium sulfate.

As a simple approximation, we may write

where $\text{Th}(\text{s})$ represents a thorium atom in the solid BaSO_4 . (Strictly speaking, we should use a concentration of sites on the surface of the barium sulfate, rather than the concentration of barium sulfate itself, but we shall assume that the number of sites per unit mass of barium sulfate is constant for this approximation.)

Thus, we have

$$\frac{d[\text{Th}^{+4}(\text{aq})]}{dt} = -k[\text{Th}^{+4}(\text{aq})] C_{\text{BaSO}_4}$$

and integration yields;

$$\frac{\ln 1 - \frac{[\text{Th}(\text{s})]}{[\text{Th}(\text{total})]}}{C_{\text{BaSO}_4}} = -kt$$

where $[\text{Th}(\text{total})] = [\text{Th}(\text{s})] + [\text{Th}^{+4}(\text{aq})]$

A plot of the left hand side of this equation versus time will have a slope of $-k$. The factor C_{BaSO_4} was retained since, for these experiments, it was not a constant.

Figure 16 presents these plots for the carrying of thorium on barium sulfate precipitated from solutions of various potassium concentrations. The linearity of the plots confirms the first order kinetics of the process. It is apparent that the amount of potassium in the barium sulfate influences the rate at which thorium is precipitated.

By analogy with the precipitation of barium ion, it is possible that the thorium is being adsorbed at sites created by the substitution of a barium by a potassium:

where $[\text{Th}^{+4} \cdot \text{KSO}_4^-]_{(\text{surf})}$ represents a hydrated thorium ion which has been adsorbed at the surface of the barium sulfate. If this is the case, the rate at which thorium is precipitated should be directly related to the amount of potassium in the barium sulfate, hence to the potassium concentration in solution during the precipitation of the barium sulfate. For the rates, we can use the slopes of the lines shown in Figure 16. Figure 17 is a plot of these rates as a function of potassium concentration. The plot is linear, showing again the first order dependence on potassium.

If the influence of potassium on the rate of precipitation of thorium were due only to changes in the specific surface area of the precipitate, we would expect a threefold increase

Figure 16.: $\ln(1-F)/1000 C_{BaSO_4}$ versus time, where F is the fraction of ^{234}Th in the precipitate. The factor 1000 is merely to scale the values. The values of pK^+ during the precipitation are indicated for each plot.

Figure 17. Rate of precipitation of thorium with preformed barium sulfate versus the potassium concentration during the barium sulfate precipitation.

in this rate when pK^+ is decreased from 4.8 to 2.3. (cf section on surface area measurements.) However, the data in Figure 17 reveal that the rate increases almost eight times. Thus, while surface area does affect the rate of precipitation of thorium, the presence of potassium has a much greater effect.

E. Activation Energy Measurements

Rate constants for the precipitation of thorium and of barium onto freshly precipitated barium sulfate were measured as functions of temperature to determine activation energies for the processes.

The rate constant k , in terms of the Arrhenius equation, is

$$k = Ae^{-E_a/RT}$$

where A is a constant often called the frequency factor, and E_a is the activation energy. We have neglected any temperature dependence of the pre-exponential factor, which is justified if $E_a \gg RT$, as is usually the case.

Thus, a plot of $\ln k$ versus $1/T$ will have a slope of $-E_a/R$, from which the activation energy may be calculated.

The plots for barium and thorium are presented in Figures 18 and 19 respectively for each of two different potassium concentrations. The potassium concentration for each experiment was the same during precipitation of the barium sulfate as during the measurement of the rate constant. The activation energies are summarized in the table on page 58.

The plots of Figures 18 and 19 are linear, indicating that the activation energies are independent of temperature over the small temperature range used (approximately 20°C to 55°C).

It is unlikely that the adsorption of the hydrated barium or thorium ion is the rate determining step of the process. The activation energy for such a process would be very small or zero, ⁽³¹⁾ since it involves only the attraction of two oppositely charged species. However, the measured activation energies are greater than zero.

Figure 8: $\ln k$ versus $1/T$ for the precipitation of barium by freshly precipitated barium sulfate. The value of pK^+ during the precipitation is indicated for each plot.

Figure 19. $\ln k$ versus $1/T$ for the precipitation of thorium by freshly precipitated barium sulfate. The value of pK^+ during the precipitation is indicated for each plot.

	Barium	Thorium
$pK^+ = 4.8$	11.4 ± 1	24.4 ± 1
$pK^+ = 2.3$	11.4 ± 1	24.4 ± 1

Measured activation energies, kcal/mole

Furthermore, if the adsorption did have a measurable activation energy, one would expect that for thorium to be lower than that for barium, on the basis of their respective charges. However, the value of E_a found for thorium is actually much higher than that found for barium.

It is worthwhile to mention here, that, as stated in the introduction, thorium likely exists in solution as $\text{Th}(\text{SO}_4)^{+2}$. The free energy change for the reaction

has been measured⁽³²⁾ as -3.03 ± 0.03 kcal/mole. Therefore, we may assume that the reverse of this reaction, which would have a free energy change of $+3.03$ kcal/mole, is probably not the activation step in the precipitation of thorium onto preformed barium sulfate.

Lieser et al⁽²⁷⁾ found an activation energy of 12.0 ± 4.0 kcal/mole for the exchange of barium between barium sulfate and solution. This was attributed to the need for barium to shed at least some of its waters of hydration before insertion into the barium sulfate lattice is possible. By analogy, it is possible that the second step in the precipitation of thorium by barium sulfate is

and that this partial dehydration of the adsorbed thorium ion gives rise to the activation energy of 24.4 kcal/mole. Since the charge on the barium ion is only one half that of the thorium ion, the smaller activation energy for the precipitation of barium is reasonable.

- The enthalpy of dehydration of barium is 128.7 kcal/mole, while that for thorium is 183.0 kcal/mole. (30)

The activation energies are not affected by the potassium concentration. There is no reason to believe that potassium should have an effect on the dehydration of a barium or thorium ion. The increase in the rate of precipitation of thorium, for instance, must be due simply to the increase in concentration of the species $[\text{Th}^{+4}_{(\text{aq})} \cdot \text{KSO}_4^{-}]_{(\text{surf})}$, which in turn is due to the increase in the concentration of the species $[\text{KSO}_4^{-}]_{(\text{surf})}$.

F. Summary.

It has been found that the effect of potassium is to increase the rate at which thorium is precipitated by barium sulfate. An increase in surface area can only partly account for this increase in rate.

Potassium was shown to increase the rate of the exchange of barium between barium sulfate and solution. This effect was much more pronounced if the potassium was in the barium sulfate itself, as opposed to in solution.

Based on the fact that potassium is precipitated by barium sulfate, the production of sites of local negative charge was postulated:

Positively charged species such as thorium should be preferentially adsorbed at these sites:

The activation enthalpy measured for the precipitation of thorium supports the idea that the activation process is the partial dehydration of the adsorbed thorium ion:

5 Conclusions

The results of this work represent an improvement in the understanding of the effect of foreign ions on coprecipitation phenomena. Although the scope of this work was limited to the effect of potassium on the coprecipitation of thorium with barium sulfate, it seems likely that other systems are analogous. The effects of other ions, although only briefly studied, and not presented in any detail here, support this idea.

The effects of potassium appear to be many: The adsorption of Ba^{+2} (aq) or of Th^{+4} (aq) is faster on barium sulfate containing potassium ions. The surface area of barium sulfate precipitated in the presence of potassium is greater. The recrystallization of barium sulfate precipitates containing potassium appears to be greater (which may be a manifestation of the larger surface area.)

The species KSO_4^- (surf) was proposed because it satisfactorily explains the observations that potassium is precipitated by barium sulfate, and that thorium is efficiently carried by a BaSO_4 precipitate containing potassium. Further study is required to determine the exact nature of the interaction between the barium sulfate lattice and potassium ions. This may then allow study of the interaction between, say, a thorium ion in solution, and the surface of a barium sulfate precipitate containing potassium.

The results leave little doubt that it is the potassium in the barium sulfate, not that in solution, which has the greatest influence on the coprecipitation of thorium.

The activation energy measurements have indicated that the

62.

thorium is being adsorbed at a site such as KSO_4^- (surf), when potassium is present in the precipitate, or at an equally favorable site (energetically speaking) when no potassium is present. It is the concentration of these sites which influences the rate at which thorium is coprecipitated by the solid.

Electron micrographs provided direct visual evidence of the effect of potassium on the morphology of barium sulfate precipitates. Further study of this could prove very rewarding. The electron micrographs appeared to show that the potassium affects the growth at different crystallographic faces to different degrees. It would be interesting to correlate the activities of specific crystallographic faces to the composition of the lattice, and/or the composition of the solution in contact with the lattice.

In order to further this work, it is recommended that a study be undertaken to determine the amount of potassium precipitated by barium sulfate as a function of the potassium concentration in solution.

Furthermore, the effects of several ions of different valencies than potassium on the coprecipitation of thorium should be studied. The results of this work are probably applicable to many other coprecipitation systems.

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