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1.0

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1.6

1.8

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2.2

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3.6

4.0

4.5

5.0

5.6

6.3

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Tony Mattioli

COPRECIPITATION OF BARIUM SULPHATE
WITH K^+ AND Fe^{3+}

by

Tony Andrea Mattioli

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

Carleton University
Department of Chemistry
Ottawa, Ontario

© June, 1984

ABSTRACT

The effects of coprecipitated K^+ and Fe^{3+} ions on the nature of freshly precipitated barium sulphate were studied. The presence of K^+ in the precipitate is seen to have a pronounced effect on crystal morphology and increases the specific surface area of the crystals. Raman measurements show a progressive shift in the $SO_4^{2-} \nu_1$ band along with a corresponding broadening of this line suggesting mixed crystal formation. Isotopic exchange studies of the $Ba^{2+}(aq) / BaSO_{4(s)}$ systems show that impurity K^+ increases the rate of $^{133}Ba^{2+}(aq)$ incorporation into the solid more than can be accounted for by the increase in measured surface area. The above changes are recognized as factors contributing to the coprecipitation of thorium with barium sulphate. The presence of Fe^{3+} in the precipitate is seen to negligibly affect the above properties of $BaSO_4$. However, the presence of Fe^{3+} in solution decreases the rate of isotopic exchange in the $Ba^{3+}(aq) / BaSO_{4(s)}$ system and slightly suppresses the coprecipitation of K^+ . The interpretation of $Fe^{3+}(aq)$ ions near the solid-solution interface inhibiting the approach of other cations is extended to explain the adverse effects of Fe^{3+} on thorium coprecipitation.

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ABSTRACT

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1. INTRODUCTION

1. Introduction to the Problem

The mining and processing of uranium ores creates large amounts of low-level radioactive wastes known as tailings. Of the various radionuclides present in the mine tailings the ones considered most toxic are the isotopes of radium because of their ability to become incorporated into bone minerals if ingested. Once the radioactivity is retained within the host organism, possible radiation damage of the bone and surrounding tissue may occur. The radioisotope of prime concern is ^{226}Ra because of its extremely long half-life of 1602 years¹. Also of environmental importance are the isotopes of thorium, not so much because of a direct health hazard but, rather, because of an indirect one as thorium is an immediate precursor to radium in the three natural radioactive decay series.

As a consequence of the potential danger of releasing radioisotopes such as ^{230}Th and ^{226}Ra from above-ground tailings ponds, there exists the need for fast, reliable, and sensitive analytical methods to monitor these contaminants in environmental waters and soils. Although they are not numerous, there exist reliable and sensitive methods for

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1. INTRODUCTION

I. Introduction to the Problem

The mining and processing of uranium ores creates large amounts of low-level radioactive wastes known as tailings. Of the various radionuclides present in the mine tailings the ones considered most toxic are the isotopes of radium because of their ability to become incorporated into bone minerals if ingested. Once the radioactivity is retained within the host organism, possible radiation damage of the bone and surrounding tissue may occur. The radioisotope of prime concern is ^{226}Ra because of its extremely long half-life of 1602 years¹. Also of environmental importance are the isotopes of thorium, not so much because of a direct health hazard but, rather, because of an indirect one as thorium is an immediate precursor to radium in the three natural radioactive decay series.

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thorium but often they are laborious and time-consuming. These methods are given in two recent comprehensive reviews^{2,3} on the analytical chemistry of thorium. Since in most environmental samples the radioanalyte is present in the nanogram to picogram range, there is an obvious emphasis on instrumental analysis.

Because of their radioactive nature, radiometric methods are most suitable for most isotopes of thorium but there remains the problem of obtaining radiochemically pure samples which are suited for the appropriate method of counting. Chemical separation methods most effective for thorium have been found to be ion-exchange and solvent extraction. Under special conditions, coprecipitation has also been shown to be a suitable separation method. In most such cases, a carrier is added to simplify the manipulation. This carrier is usually not an isotope of the radioanalyte.

Some methods involve the coprecipitation of thorium with hydrous oxides of Fe^{3+} or Ti^{3+} . However, these precipitates of high specific surface area are notoriously non-specific and yield samples which are not easily filterable and of very poor radiochemical purity if elaborate separations are not performed. Others are colourimetric methods which require the preconcentration of thorium to, at least, microgram quantities, and in no way give information of which isotopes of thorium may be present.

One seemingly practical method for analyzing thorium is coprecipitation with barium sulphate in the presence of a sufficient amount of potassium ions (usually 0.01M)⁴ with the prior removal of radium. The obvious advantages of such a method may be briefly stated as:

1) the coprecipitation with BaSO_4 is done in acid medium so that no hydrolytic precipitation of other cationic impurities may occur, and

2) BaSO_4 is an easily filterable precipitate which gives good samples for alpha spectroscopy. This is especially important when the determination of the thorium isotopes present is required.

Despite the appeal of this method, certain limitations are recognized. The presence of foreign ions seems to influence the extent to which thorium is coprecipitated with barium sulphate. In general, it has been observed that monovalent cations tend to increase thorium recoveries^{4,5,6} while trivalent and quadrivalent cations tend to lower the recoveries.^{4,6} In the absence of any other interfering ions, thorium is quantitatively carried with barium sulphate only if a critical concentration of potassium ions is exceeded in the precipitation solution.^{4,5}

Only recently^{7,8} has the effect of potassium ions on the carrying of thorium with barium sulphate been studied in

depth. Although the phenomenon has been observed since the early 1960's it has never been satisfactorily explained since most of the workers were primarily interested in the analytical chemistry aspects. In recent studies of the nature of the precipitate formed, certain physical properties have been found to be affected^{7,8} depending on the presence of certain ions in the precipitation solution. These studies, with respect to explaining the coprecipitation of thorium with barium sulphate are few but do show promise.

The purpose of this work is to gain a better understanding of why K^+ ions and Fe^{3+} ions affect the carrying of thorium with barium sulphate. In particular, the nature of the precipitates formed in the presence of these cations will be explained in order to identify the changes in chemical and physical properties which contribute to carrying processes in general.

II. Coprecipitation of Foreign Ions with Ionic Crystals

A. General Discussion

Strictly speaking, coprecipitation can be defined as "the contamination of a precipitate by substances that are normally soluble under the conditions of the precipitation."⁹ The fact that two substances are carried down together is not sufficient to classify the phenomenon as coprecipitation. For instance, if the two substances are precipitated under conditions in which both substances are insoluble the phenomenon is usually termed as "simultaneous precipitation" or "gathering". For the case where one substance precipitates at a rate slower than the other so that the slower precipitating substance actually crystallizes on the already formed solid, the phenomenon is known as "postprecipitation". The discussion which follows will deal exclusively with coprecipitation phenomena in the strict definition.

Coprecipitation is a very important chemical process in radiochemical procedures. In such procedures the concentration of the radioanalyte, or tracer, is so low that the addition of a precipitating agent is not enough to exceed the solubility product. To effect precipitation, a carrier is added in sufficient quantities so that the resultant precipitate may carry the tracer. Depending on experimental

conditions or goals, the carrier may or may not be isotopic with the tracer.

On the basis of a number of observations on coprecipitating systems, K. Fajans in 1913⁹ formulated a principle which correlated the amount of the radioelement (as the cation) carried by a precipitate with the low solubility of the compound formed by the radioelement with the anion of the same precipitate. Although attractively simple, the rule was not without many exceptions both in radiochemistry and, on the larger scale, in analytical chemistry. It was clear that factors in addition to that expressed in the Fajans' rule were operating in coprecipitation phenomena.

In 1936, Hahn¹⁰ proposed a tentative classification of carrying processes. The four principle categories he described were:

- 1) isomorphous replacement
- 2) adsorption
- 3) anomalous-mixed-crystal formation
- 4) internal adsorption.

The last two categories are not so well understood and were proposed by Hahn, more or less, to explain coprecipitation phenomena not properly described by the first

two categories. These categories will be discussed only briefly here.

1) Isomorphous Replacement

Two ionic crystals are said to be isomorphous if they crystallize in the same form with nearly identical bond angles. If the ionic sizes of the two sets of crystal ions are nearly the same, then mixed crystals can form by one cation replacing the other at normal cation sites in the lattice. Thus, the tracer ions replace the carrier ions of like charge and similar chemistry. The efficiency of this type of carrying process depends on such factors as, the lattice energies of the two salts, the hydration energies of the two crystal ions, and their ionic radii. This process, which has been regarded as "true" coprecipitation, is not much affected by the precipitation conditions nor can the coprecipitated substance be removed by repeated washing of the precipitate. The very efficient carrying of radium with barium sulphate¹¹ is an example of this class of coprecipitation. The chemical similarity of barium and radium ions is obvious from the data in Table I.

Table I. Pertinent Data¹² Indicating the Chemical
Similarity of Barium and Radium

	Ba	Ra
Ionic Radius/A (crystal)	1.34	1.43
(hydrated) ¹³	4.04	3.98
$\Delta H_f(M^{2+}_{(aq)})/\text{kcal mol}^{-1}$	-129	-126
$\Delta H_f(\text{MSO}_4(s))/\text{kcal mol}^{-1}$	-350	-350
$\log_{10} K_{sp}(\text{MSO}_4)^{14}$	-10.00	-10.37

2) Adsorption

Even if the conditons for isomorphous replacement are not present, freshly formed precipitate crystals with large surface areas may be capable of carrying the tracer by effectively adsorbing the radioelements. It is seen for this process that the Fajans' rule is most significant. The factors which affect this efficiency of this carrying process may be listed as:

- a) The larger the surface area of the precipitate the larger is the fraction of tracer which will be carried.

- b) The more insoluble the compound the tracer ion forms with the oppositely charged lattice ion, the better the tracer is carried.
- c) The charge of the tracer ion is important with respect to the precipitating conditions. For a tracer (cation) to be absorbed, the surface of the precipitate must be oppositely charged. This condition exists when there is an excess of the precipitating anion present in the solution. Also, the higher the charge on the tracer ion the better it is adsorbed. The presence of highly charged ions of the same sign interferes with the carrying of the tracer.
- d) Prolonged standing of the precipitate in contact with the tracer solution, may either increase or decrease the fraction carried. Aging of the precipitate will tend to decrease its surface area which, in turn, tends to decrease the fraction of tracer carried. Recrystallization processes, however, may "bury" already adsorbed tracer leaving a new surface for further adsorption.

It is evident from the above factors that unlike the isomorphous replacement mechanism, the precipitation conditions (such as acidity, order of reagent addition)

strongly influence the carrying of the tracer when adsorption processes are occurring. In many instances an appreciable amount of adsorbed tracer may be removed by washing.

3) Anomalous-Mixed-Crystal Formation

This ambiguous category includes cases where a tracer has been carried by a preceipitate (presumably incorporated into the lattice) despite the absence of conditions required for both isomorphous replacement and adsorption. Lead isotopes are carried by $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals¹⁰ in a manner resembling isomorphous replacement processes, hardly affected by the charge on the precipitate with results which are quite reproducible. The capacity of barium chloride for lead atoms has been found to be limited to about 0.1 mole percent lead in the crystals. It would seem that the similarity of the ionic radii of barium and lead ions (1.34A and 1.20A, respectively) is an important factor in the carrying process.

4) Internal Adsorption

There are some cases of carrying that do not fit into any of the three categories already discussed and are typically characterized by a spotty distribution of the tracer within the crystal as revealed by autoradiography. These results are also associated with very poor carrying of the tracer.

The internal adsorption process was described by Hahn as being due to the adsorption of the tracer on the surface of a growing or recrystallizing crystal and consequently becoming "trapped" by subsequent layers. For this to occur the tracer must be tightly adsorbed on the surface layer by strong attractive forces which result in insoluble compounds and stable complexes (Fajans' Rule).

Like the simple adsorption mechanism, internal adsorption is also characterized by poor reproducibility of results under the same precipitating conditions, and a suppression of tracer carrying in the presence of an excess of the lattice in whose charge is the same as that of the tracer. The one notable difference in the two adsorption processes is the observation of a discontinuous distribution of the tracer within the precipitate.

From the preceding discussion it is clear that Hahn recognizes two broad categories of coprecipitation:

- 1) adsorption of the tracer on surfaces of the precipitate during its formation (this includes on surfaces of primary colloidal particles which become a type of "internal" surface of coagulated colloids) and,
- 2) incorporation of the tracer into the crystal lattice of the precipitate by whatever mechanism it may occur.

In most practical situations a combination of these features is involved and the best the experimentalist can do is speculate as to the mechanism of the carrying process by observing the sensitivity or insensitivity of the carrying to experimental conditions. Clearly, no direct evidence of the chemical state of the tracer may be obtained from such observations and such speculation has led to much controversy in the literature where coprecipitation systems which were thought to belong to one classification could also be described in terms of other mechanisms based on new observations.^{45,56}

B. Coprecipitation of Foreign Ions with Barium Sulphate

The notorious carrying of impurities by barium sulphate has long been recognized as a serious problem in analytical chemistry, particularly in the gravimetric determination of sulphate.¹⁵ This property of barium sulphate, however, has been exploited by many workers^{4,5,6,16,17} to separate microgram and submicrogram quantities of radionuclides from aqueous solution. It was Sill⁴ who first used barium sulphate to collect thorium isotopes and thus preparing a sample suitable for alpha spectroscopy in the process. Later, the method was recommended for the collection of most trans-uranium¹⁸ elements as well, using reduction-oxidation

cycles for greater purity, indicating that size and charge played important roles in their carrying with barium sulphate. In this discussion we will be interested only in thorium isotopes although the results may be applicable to other systems.

During the extensive study of these carrying systems, it was found that the carrying of thorium is greatly improved (as are the uranium and transuranium elements) if a sufficient amount of monovalent ions is present in the solution. In particular, K^+ was found to have the greatest effect. The nature of the coprecipitation of thorium with barium sulphate in the presence of potassium is shown in Figure 1. It is noted that the more pronounced effect is shown by the potassium ions. The effects of ammonium and sodium ions are essentially the same but considerably less than that of potassium. Burk, de Jong and Wiles⁶ have also shown that thorium recovery is suppressed as increasing amounts of ter- and quadrivalent ions are present in the precipitation solution. The effect of ferric ions is seen in Figure 2. It is interesting to note that ferrous ions do not interfere in thorium coprecipitation to the same extent as ferric ions as seen in Table II.

Figure 1. Percent ^{234}Th carried by barium sulphate as a function of alkali cation concentration. (from reference 22)

Figure 2. Percent ^{234}Th carried by barium sulphate as a function of various heterovalent cations. (from reference 22)

Table II. ^{234}Th Recovery in the Presence
of Fe^{2+} and Fe^{3+} Ions

Ion Present (pFe=2.4)	% Recovery ^{234}Th
Fe^{3+}	52.3, 47.8
Fe^{2+}	87, 81

(Data from reference 19.)

The amount of iron coprecipitated with barium sulphate is also different with Fe^{3+} ions showing the greater tendency to be carried.²⁸ It is quite clear that adsorption processes are influential in this case since the higher charged ion is better carried. Fajans' rule is also evident in this case as the complexing ability of Fe^{3+} with SO_4^{2-} ions (and HSO_4^-) is greater than that of Fe^{2+} . Some authors^{4,6} have observed that even increasing the amount of thorium in solution reduces the radiochemical recovery of ^{234}Th . This, in fact, is an indication of a limiting amount of thorium that can be carried by a given amount of barium sulphate.

Ambe and Lieser²⁰ have shown that the presence of potassium is not required to give complete thorium recoveries. They have observed that complete thorium recoveries may be obtained if a sufficiently large amount of barium sulphate is precipitated, which supports the idea of limiting amounts of thorium in barium sulphate. This is not usually desirable, as large quantities of precipitate results in poor samples for alpha spectroscopy. Their results also indicate that the thorium recovery may reach a maximum if a large excess of sulphuric acid is used. The obvious dependence upon experimental conditions suggests that the coprecipitation of thorium with barium sulphate is dependent upon adsorption processes.

The question of why potassium ions have such a pronounced effect on the carrying of thorium with barium sulphate has never been satisfactorily addressed. The following is a brief review of the possible explanations which have been proposed in the literature.

Sill and Willis²¹ postulated the formation of a separate insoluble compound such as "a double potassium barium sulphatothorate, $K_2Ba[Th(SO_4)_4]$ " during the precipitation of barium sulphate. However, if one is dealing with trace amounts of thorium ($<10^{-9}$ grams) it is unlikely that the solubility of $Th(SO_4)_2$ or the postulated compound above could ever be exceeded. Indeed, no direct evidence of this compound has been published.

In the work of Wiles and de Jong,²² where they fit calculated curves based on proposed equilibrium models to experimental data, the formation of a simple compound such as $K_2Th(SO_4)_3$ has been questioned. They dismissed this possibility and state that it is more likely that the potassium and thorium ions occupy cation sites in the normal $BaSO_4$ lattice with the condition that the K:Th ratio be kept at 2:1 to conserve charge.

The results of Ambe and Lieser²⁰ also show that there is a distinct correlation between the concentrations of thorium and of potassium in the precipitated barium sulphate. They have found that the mole ratio of K:Th is 2:1 in the greater part of the crystal which lends strong evidence in favour of anomalous-mixed-crystal formation. It was also found that all the cations in the precipitate were present in the ratio of

$$K^+:Th^{4+}:Ba^{2+} = 2:1:6$$

which meets the requirements of both electrical neutrality and conserving the number of cation substitutions (i.e. 2 K^+ ions and 1 Th^{4+} ion may substitute for 3 Ba^{2+} ions with an excess of barium ions to preserve the original $BaSO_4$ structure). Although attractive and very convincing, the $K^+:Th^{4+}$ ratio of 2:1 was observed only for a certain concentration region where the ratio of $K^+:Th^{4+}$ in solution

ion exchange is the interdiffusion of the exchanging ions regardless of the chemical process which either vacated or filled the site.

For this discussion, we will be concerned with the special case of isotopic exchange reactions (in actual fact we will only be concerned with a special case of isotopic exchange termed heterogeneous isotopic exchange). A simple isotopic exchange is defined³⁶ as an exchange reaction in which chemically equivalent atoms of one species are exchanged with isotopic atoms of another species. If the two species are uniformly distributed in the same phase and all conditions except the distribution of the radioactive atoms between the reactants are constant, then a homogeneous stable system is established. A simple isotopic exchange in a homogeneous, stable system follows a simple exponential law regardless of the mechanism whereby the exchange occurs. A brief mathematical treatment follows.

B. Mathematical Treatment of Homogeneous Isotopic Exchange

McKay³⁷ was the first to derive the exponential law for the simple case of one exchangeable atom per species (see Appendix 1). For the homogeneous exchange reaction

For example, La^{3+} is coprecipitated with CaSO_4 in the presence of an excess of Na^+ ions. We may note the coprecipitation systems as:

His limited number of examples, however, provide no information as to the actual mechanism of the coprecipitations.

It was Melikhov and Chaliyan²⁵ who first recognized that the presence of these excess foreign ions actually modifies the precipitate used to carry the heterovalent tracer ions. In an ambiguous manner, they stated that the presence of foreign ions such as potassium and sodium, created definite "geometrical" and "chemical contours" on the surface of the precipitate itself (BaSO_4) and that thorium ions precipitated on steps in the growing crystal face. They did not clearly identify the role of the potassium ions.

Up until this point little attention has been paid to the actual nature of the barium sulphate precipitates formed in the presence of these foreign ions to discern whether the

effect is one of crystal reactivity or one due to influences within the solution. Burk and Wiles⁸ have addressed this question and were able to identify some of the influences. They were able to show that the number of adsorption sites for Th^{4+} on the solid barium sulphate increases when precipitated in the presence of potassium ions. The invariance of activation energies of the Th^{4+} precipitation on doped and undoped BaSO_4 shows that their nature does not change. The Th precipitation increases faster than can be accounted for by the increase in surface area. Burk²⁶ has postulated the existence of local negative charges arising from the substitution of a potassium ion in the barium sulphate lattice:

where [] represents a unit at the surface of the crystal in contact with the solution. This local negative charge could then influence the coprecipitation of thorium as a result of the attraction of the ion to the negatively charged site. He goes further to explain the effects of other ions. According to his model substitution of, say, a ferric ion for a barium could generate a local positive charge.

thus deterring the adsorption of thorium. This model seems to explain why Fe^{2+} ions in the crystal do not show as great

an influence as Fe^{3+} ions.

It is known that K^+ ions and Fe^{3+} (and Fe^{2+}) ions coprecipitate with barium sulphate in appreciable amounts.^{27,28} If this is so, then clearly the nature of the resultant precipitate will be altered and possess physical and possibly chemical properties different from those of the pure precipitate. For instance, it is accepted that the coprecipitation of K^+ with barium sulphate is probably due to mixed crystal formation²⁷ especially in the presence of NO_3^- ions because K^+ and Ba^{2+} ions have very similar ionic radii. Also, $\text{KNO}_3(\text{II})$, K_2SO_4 , and BaSO_4 all belong to the orthorhombic crystal group with similar lattice dimensions.⁴⁷

Table III. Lattice Parameters

Crystal	System	a_0 Å	b_0 Å	c_0 Å	Volume $\text{\AA}^3$
BaSO_4	orthorhombic	7.155	8.882	5.456	346.73
$\text{K}_2\text{SO}_4(\text{II})$	orthorhombic	7.456	10.08	5.776	434.10
$\text{KNO}_3(\text{II})$	orthorhombic	6.431	9.164	5.414	319.07

Ferric ions are not expected to form mixed crystals with barium sulphate because of their small ionic radius ($0.64\text{\AA}$)¹² and the fact that ferric sulphate precipitates to give hydrated monoclinic crystals.⁴⁷ Ferrous ions however have an ionic radius of $0.74\text{\AA}$ ⁴⁷ which is larger and thus more compatible for mixed crystal formation with barium sulphate but which is still too small for isomorphous replacement. Despite the fact that the anhydrous FeSO_4 compound belongs to the orthorhombic system which favours mixed crystal formation with BaSO_4 , Geyer and Winzer²⁸ observed that Fe^{2+} ion coprecipitated approximately five times less than Fe^{3+} ions. Thus one expects the coprecipitation of Fe^{3+} ions to be due to adsorption processes probably due to the strong bonding of these ions with SO_4^{2-} ions on the growing surface. Based on a number of observations, Geyer and Winzer concluded that Fe^{3+} ions did coprecipitate via adsorption processes but did not exclude the possibility that some of the ferric ions could have become incorporated into the lattice.

With the above observations and inferences as to the chemical state of K^+ and Fe^{3+} ions in barium sulphate, the study of the nature of precipitates contaminated by these ions is a worthwhile venture as the changes observed may shed new light upon why these ions influence the carrying of thorium with barium sulphate. Furthermore, insight as to the chemical state of thorium in barium sulphate may also be expanded.

III. Heterogenous Exchange Reactions

A. General Discussion

The phenomenon of surface-solution exchange can shed much light upon the nature of coprecipitation especially when solid surface effects are involved. Since heterogeneous exchange reactions are greatly influenced by the structure of the solid surface²⁹, they may be used to probe changes on the barium sulphate surface which may occur as a result of the precipitate being formed in the presence of ions such as K^+ or Fe^{3+} (i.e. incorporated ions or merely adsorbed ions, possibly internally adsorbed). The changes in exchange rates may be due to either changes in the solid's chemical reactivity or to a simple physical property such as an increase in surface area.

Helffferich³⁵ defines ion exchange as, essentially, a diffusion process having little, if any, relation to chemical reaction kinetics in the usual sense. Simply stated, ion exchange is the replacement of an ion by another similar ion at an exchange site which has been vacated (by whatever physical or chemical process) by the original ion. The occupation of the site may only occur after the migration of the replacing ion. Thus, the rate-determining step of a true

ion exchange is the interdiffusion of the exchanging ions regardless of the chemical process which either vacated or filled the site.

For this discussion, we will be concerned with the special case of isotopic exchange reactions (in actual fact we will only be concerned with a special case of isotopic exchange termed heterogeneous isotopic exchange). A simple isotopic exchange is defined³⁶ as an exchange reaction in which chemically equivalent atoms of one species are exchanged with isotopic atoms of another species. If the two species are uniformly distributed in the same phase and all conditions except the distribution of the radioactive atoms between the reactants are constant, then a homogeneous stable system is established. A simple isotopic exchange in a homogeneous, stable system follows a simple exponential law regardless of the mechanism whereby the exchange occurs. A brief mathematical treatment follows.

B. Mathematical Treatment of Homogeneous Isotopic Exchange

McKay³⁷ was the first to derive the exponential law for the simple case of one exchangeable atom per species (see Appendix 1). For the homogeneous exchange reaction

where AX and BX are the two chemical species with X as the common, exchangeable atom (* denotes the tracer isotope), the following equation was derived

$$\ln(1-F) = -[(1/A) + (1/B)] kt$$

where

A = concentration of X (active+inactive) in the A form

B = concentration of X (active+inactive) in the B form

k = rate constant of the isotopic exchange reaction

t = time

F = the fraction of exchange which is defined as the ratio of the amount exchanged at time t to that exchanged at infinite time (equilibrium).

(A and B are constants since the system is assumed to be in chemical equilibrium).

If one is monitoring the increase in radioactivity in one of the species as a function of time then it is convenient to write F in the following form

$$F = (S_B - S_{B_0}) / (S_{B_\infty} - S_{B_0})$$

where S_B = the specific activity of B at time t

S_{B_0} = the specific activity of B at time zero

S_{B_∞} = the specific activity of B at infinite time

For the case when all the radioactivity is initially in the other species, A, then $S_{B_0}=0$ and the above relation reduces to

$$F = S_B / S_{B_\infty}$$

The problem now becomes one of determining S_{B_∞} . In most cases, the experimentalist will plot the data "assuming" that all of the radioactivity will be found in the initially non-reactive species at infinite time. In other words, the data will be plotted with S_{B_∞} being assigned the value of S_{A_0} . For such a case it is convenient to plot $\ln(S_A/S_{A_0})$ versus time (see Appendix 2). This curve can now be corrected for the equilibrium value (or true value) of F by the back-extrapolation of the straight-line segment of the curve which represents the equilibrium state of the exchange (see Figure 3). The subtraction of the extrapolated line from the curve of $\ln(S_A/S_{A_0})$ gives a straight line which also describes the exchange reaction but is translated away from the origin.

Figure 3. Exchange curve not corrected for equilibrium F value. $\ln(i/i_0)$ versus time.

- (a) the ratio i/i_0
- (b) i_∞/i_0 (extrapolated)
- (c) $(i - i_\infty)/i_0$
- (d) $1 - F$

Another method (which is used in this work) may be employed to analyze the exchange data and it is described later in the experimental discussion. In monitoring the decrease in the radioactivity in the aqueous solution, the notation of Lieser et al will be used. The data will be plotted as $\ln(i/i_0)$ versus time where i denotes the total activity of the solution. The exchange system studied will be

C. Ionic Crystals

Heterogeneous isotopic exchange reactions involving ionic crystals have been studied by many authors²⁹⁻³³. For barium sulphate and other crystals, it has been observed that two processes occur. The two processes are apparent by the resolution of the $\ln(1-F)$ versus time curve into two straight lines, indicating two first-order processes. In the case of barium ions in barium sulphate exchanging with barium ions in solution, Lieser^{29,30} states the initial, fast process is the actual exchange step, while the slower step is the incorporation of the exchanged ion into the lattice via recrystallization processes.

The following is a brief and simple discussion on the

nature of the solid-solution interface between ionic crystals and aqueous solutions which will shed light upon the actual exchange mechanism.

The surface of an ionic crystal may be electrically neutral or carry a net charge when it is immersed into an aqueous solution. If the barium sulphate is in contact with a solution containing barium ions, the crystal will tend to acquire a net positive charge as the barium ions will adsorb on preferred sites on the surface. For the same reasons, barium sulphate crystals will acquire a net negative charge when in contact with a solution containing sulphate ions. The charge on the crystals is balanced by an equal and opposite charge due to ions in solution in the vicinity of the surface. These latter ions form the outer, more diffuse layer of the electrical double layer³⁸. Figure 4 schematically shows the constitution of the electrical double layer associated with a BaSO_4 crystal in contact with an aqueous solution of Na_2SO_4 . The layer of potential-determining ions (SO_4^{2-}) is surrounded by the diffuse layer of counter-ions (Na^+), a few of which are held by the electrostatic attraction of the negative inner layer. The diffuse nature of the outer layer is due to the thermal energy of the Na^+ ions compared with the relatively small influence of the crystal.

Figure 4. Schematic diagram of the electrical double layer of solid barium sulphate in an aqueous sodium sulphate solution.

1. Solid
2. Rigid inner layer (potential-determining ions)
3. Diffuse outer layer (counter-ions)

Other foreign ions may participate in the double layer³⁹. Any ion of the right charge may become part of the outer, diffuse layer but more importantly, if these counter-ions are capable of entering the lattice and forming solid solutions, they may enter the inner layer and act as potential-determining ions. X-ray data suggest⁴⁰ that potassium is incorporated into the barium sulphate lattice with thermal treatments of the crystals in the mother-liquor for a period of time. This, according to the above argument allows the possibility of potassium ions to act as potential-determining ions.

The amount of an ion which is present in the outer layer depends on its ability to compete with other ions present in solution for positions in the layer. The factors which influence this competition are electrostatic in nature. Ions with high charge that can polarize or be polarized by the potential-determining ions are good competitors for positions in the outer layer because of strong electrostatic and dipole interactions. Other factors include hydrated ionic radii and hydration energies of the ions, which determine a close approach to the surface. The concentration of the ion is also important, of course.

With this view of the interface between ionic solids and aqueous solutions a plausible mechanism explaining the two processes observed during exchange in the $\text{Ba}^{2+}_{(\text{aq})}/\text{BaSO}_{4(\text{s})}$

system may be described. The initial first step can be envisioned as barium ions diffusing towards the surface of the crystal and occupying a site in the electrical double layer, a site which is near the inner layer. The slower step which would follow is the incorporation of the barium ion into the rigid inner layer or even the crystal itself. While the first process would require little or no activation energy at all, it is clear that the second process would require an activation energy to totally or partially strip the hydration shell. Burk and Wiles^{8,26} have determined the activation energy of the second process to be 11.4 kcal mol⁻¹ which corresponds well to the value of 12.0 kcal mol⁻¹ obtained by Lieser et al.⁴¹ This energy was attributed to the fact that barium ions must be stripped of some of its hydration shell before being incorporated into the barium sulphate lattice.

Bovington and Jones,⁴² in studying the kinetics of dissolution of barium sulphate crystals, have postulated a two-step mechanism

where $\text{Ba}^{2+}\text{SO}_4^{2-}(\text{aq})$ is described as being the intermediate in the hydrated monolayer at the surface of the solid. It is possible that the reverse of the above mechanism may be considered as a plausible mechanism for the isotopic ion-exchange by realizing the barium ion must pass through a

measurable intermediate before assuming the final site position in the crystal. Thus we may write the forward reaction of the exchange as

comprised of two first-order processes.

IV. Other Methods

In order to make definite statements concerning the chemical state of an impurity in a precipitate, sensitive physical methods which probe the crystal structure and chemical environments within the crystal are required. In this work, X-ray diffraction and Raman spectroscopy were used.

A. X-ray Diffraction

A mixture of two or more substances gives a diffraction pattern consisting of the superimposed patterns of the individual components provided that these components exist as separate crystals in the powder sample.

One limitation of the powder diffraction method is that very often it is not possible to detect less than 5% of a constituent. The minimum proportion of a substance which can be detected varies enormously. It is usually specific for each substance and depends on factors such as crystal symmetry and the diffracting (or scattering) power of the atoms composing it.

Mixed crystals or crystalline solid solutions present problems different from those of mechanical mixtures. A

mixed crystal gives a diffraction pattern which is an intermediate between those of the pure components. Identification of crystal species can be effected if this relation between a given pattern and those of known pure constituents is recognized.

B. Raman Spectroscopy

Because the samples which were studied were in powder form, the micro-Raman technique was employed. With the considerably more narrow laser beam, the scattered background light is kept at a minimum.

The vibrations of SO_4^{2-} ions in the barium sulphate precipitate should be quite sensitive to changes in its environment as a result of replacing a barium ion with another. Thus, monitoring any such changes using a sensitive probe such as Raman spectroscopy should reveal changes in the chemical environment of the SO_4^{2-} ions and provide information concerning the state of the coprecipitated impurity.

Vojtech^{48,49} et al have shown that the ν_1 vibrational mode of SO_4^{2-} ions in BaSO_4 - CaSO_4 solid solutions shifts in frequency reflecting the composition of the solid solution. Their results are reproduced in Figure 5. It is noted that as the mole fraction of barium in the solution increases, the

frequency of the ν_1 mode shifts from one which is characteristic of pure CaSO_4 to one which is characteristic of pure BaSO_4 . In the spectrum of the sample with 40% BaSO_4 two peaks were observed. The authors attribute this to a rather "high degree of a chaotic arrangement of the crystal lattice" for that particular sample.

By observing frequency shifts of the ν_1 mode of the sulphate ions of barium sulphate precipitates substituted with potassium or iron, one can make clear statements regarding the chemical state of these impurities. This method may also be used to establish clearly the chemical state of thorium in BaSO_4 precipitates and thereby postulate a more reasonable and concrete mechanism to describe the corprecipitation.

Figure 5. Frequency shift in the $\text{SO}_4^{2-} \nu_1$ band as a function of composition in the BaSO_4 - CaSO_4 system. (from reference 49)

V. The Present Study

The present work takes the barium sulphate problem as was described by Burk and by Ambe and Lieser and attempts to clarify the influences of both K^+ and Fe^{3+} ions. In using the methods provided by exchange studies, X-ray diffraction studies and Raman studies, it attempts to answer the following questions.

1. Are the foreign cations incorporated into the barium sulphate lattice?
2. What physical and chemical properties which would influence the coprecipitation of thorium with barium sulphate are affected and how?
3. Do these changes in the physical and chemical properties occur as a result of the foreign cation being present in the crystals or in solution?

This study recognizes, of course, that the subject of coprecipitation is very complex and that many questions will remain unanswered. For example, we will herein touch upon aspects such as the distribution of the impurities in the barium sulphate, and the actual role of potassium ions in the coprecipitation of thorium with barium sulphate. Further questions will not be addressed, such as, the energy required

to place a specified foreign cation in the barium sulphate lattice, and the specific effects of ionic strength upon the precipitation of barium sulphate and the coprecipitation of other ions. The role of coprecipitated NO_3^- ions will also not be addressed.

2. EXPERIMENTAL

I. Methodology

It was seen that the present problem is quite complex. Because of this, a variety of experimental approaches should be used. This follows the practice of Burk²⁶ and extends the range of methods further.

This work analyzes the nature of barium sulphate precipitates which are formed under the experimental conditions of typical thorium-determining procedures used in this^{6,8} and other laboratories.⁴ For this reason, the general procedure used to precipitate barium sulphate in the presence of foreign cations simulates a standard thorium determination used in this laboratory. In any analytical determination, the precipitation conditions are chosen (so that quantitative carrying of the analyte is achieved. In most of the experiments in this work, the conditions used gave reproducible results but not necessarily quantitative results for the carrying of thorium with barium sulphate. In this way the influences and coprecipitation characteristics of foreign ions could be more easily seen.

Preliminary experiments measuring the exchange rate of

CrO_4^{2-} ions in solution with SO_4^{2-} ions in solid BaSO_4 have shown⁶⁷ that the surface areas of the precipitates are not acceptably reproducible when compared to the precision of most of the experiments performed. It is well known that precipitates formed by direct mixing of reagents are difficult to reproduce since the experimentalist has very little control over nucleation and crystal growth under these experimental conditions. For this reason, when relatively large amounts of barium sulphate had to be prepared for certain experiments (such as exchange studies or surface area determinations) many separate precipitations from dilute barium solutions were prepared. The crystals of these many preparations were then mixed together thoroughly to give a stock supply in which small differences in each preparation were averaged and a more representative sample would result. This technique has resulted in greatly reducing the scattering of data points.

The micro-Raman technique is proving to be a good spectroscopic technique in providing new information to the understanding of coprecipitation processes sheds light on the chemical state of the contaminants. The spectroscopic studies in this work are limited and concentrate only on the ν_1 band of the SO_4^{2-} in the crystals because of its prominence and because it was found to display an obvious dependence on potassium concentration. Quantitative determination of the spectral parameters were done using the HP-9836 mini-computer system.

II. Experimental Methods

A. Reagents

All reagents used were of reagent grade and were used without further purification. All stock solutions were filtered using 0.45 μ m membrane filters (GELMAN DM-450). The potassium stock solutions were 0.1M and 1M KNO_3 (Allied Chemicals) in 0.1M HNO_3 . The iron stock solutions were 0.1M and 1M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (BDH Chemicals) analytical grade in 0.1M HNO_3 . The sulphuric and nitric acids used (Allied Chemical) were of reagent grade. The barium stock solutions used were 1mg $\text{Ba}^{2+}\text{ml}^{-1}$ and 25mg $\text{Ba}^{2+}\text{ml}^{-1}$ in 0.1M HNO_3 .

The stated maximum limits of potassium and iron in the reagents used are given in Table IV.

TABLE IV. Maximum Limits in the Reagents Used

Reagents	K	Fe
$\text{Ba}(\text{NO}_3)_2$	0.050%(alkalies)	0.0002%
KNO_3		0.0001%
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.01%	
HNO_3 (conc.)	1ppm	0.1%
H_2SO_4 (conc.)	1ppm	0.2%
distilled H_2O	<1ppm ⁵⁰	<1ppm ⁵⁰

The ^{133}Ba tracer solution was obtained from Amersham Corp. and had a specific activity of 15.6 mCi/mg Ba. The solution was diluted in 0.1M HNO_3 to give a standard reference solution of approximately 80 counts per second per millilitre of solution.

The ^{234}Th tracer solution was prepared by separating thorium from uranyl nitrate by ether extraction as described in reference 8. The final solution was made up in 1.0M HNO_3 giving a ^{234}Th activity of approximately 1000 counts per second per millilitre of solution at the time of preparation.

The ^{59}Fe tracer was obtained from Atomic Energy of Canada Limited and had a specific activity of 9 mCi/mg Fe. This was diluted in 0.1M HNO_3 to give a solution with an activity of about 6000 counts per second per millilitre, at the time of preparation.

Tracer solutions of ^{42}K were prepared by dissolving neutron-irradiated solid KNO_3 (analytical grade) in 0.1M HNO_3 . The solid (0.1g and 1.0g samples) was irradiated in the SLOWPOKE reactor at AECL Products Division in Ottawa for one hour with a neutron flux of 5×10^{11} neutrons $\text{cm}^{-2} \text{s}^{-1}$. The solid was then dissolved in 100ml of 0.1M HNO_3 yielding a solution with an activity of approximately 1000 counts per second per millilitre at the time of preparation. The radiochemical purity of the $^{42}\text{KNO}_3$ solution was verified by

Figure 7. Schematic diagram of micro-Raman apparatus.

Several of these BaSO_4 preparations were mixed together thoroughly to give a stock batch. In this way, the effects of any slight differences between preparations are minimized and a more representative sample is established.

The above procedure was also used when preparing samples for surface area determinations.

2. ^{42}K and ^{59}Fe Coprecipitation Studies

These experiments were performed in a manner such that a standard ^{234}Th determination using the barium sulphate coprecipitation method was simulated. In this way it was possible to study phenomena occurring in a typical determination.

The procedure is essentially the same as the preceeding one, except that 1mg of barium was used and appropriate tracer solutions were added prior to the addition of the sulphuric acid depending upon which cation was being monitored. The precipitate was filtered 30.0 minutes after the time of the sulphuric acid addition and was washed in the usual manner. The filter along with the precipitate was dried under a heat lamp for 15 minutes and placed on an aluminum planchette in a plastic dish. The gamma spectrum was immediately recorded.

3. Other BaSO_4 Samples

All other barium sulphate samples used for studies such as Raman spectroscopy, X-ray diffraction, and electron microscopy were prepared in the same manner as above except that 10mg of barium per 100ml of solution was used.

C. Exchange Studies

The experimental conditions under which the $\text{Ba}^{2+}_{(\text{aq})}/\text{BaSO}_{4(\text{s})}$ system was studied were similar to those of the precipitation procedures. Unless otherwise stated, 90mg of the barium sulphate precipitate was added to the exchange solution which was held constant at $(25.0 \pm 0.1)^{\circ}\text{C}$ and was stirred at the rate of 900 rpm with a Teflon impeller (this rate of stirring ensured that the solid was well suspended within the solution and that no crystals remained settled at the bottom the beaker). The exchange solution consisted of 100ml of 0.1M HNO_3 , the required amounts of K^{+} and Fe^{3+} ions to give the desired cation concentrations, and a known amount of the $^{133}\text{Ba}^{2+}$ tracer solution. After a predetermined contact time, the suspension was filtered through a $0.45\mu\text{m}$ membrane filter and the crystals were washed first with 50ml of 0.1M HNO_3 and then with 50ml of distilled water. The filter containing the crystals was placed in an aluminum planchette and dried under a heat lamp. The gamma spectrum was immediately recorded.

D. Radioactivity Measurements

The gamma spectra were recorded using a 3in. x 3in. Na(Tl)I crystal scintillation spectrometer system. The crystal was mounted on the window of a photomultiplier tube. Pulses from the PMT were passed through a preamplifier and then to a multichannel pulse height analyzer (Northern Scientific NS-900). The Na(Tl)I crystal, PMT, and preamplifier were housed in a "castle" of 3 inch-thick lead bricks lined with cadmium (to absorb lead X-rays) and with copper (to absorb cadmium X-rays).

Radiochemical recoveries were calculated by comparing the radioactivity in the BaSO₄ crystals with the radioactivity of a dried aliquot of the appropriate reference tracer solution. The gamma spectrum of the sample was obtained by accumulating pulses (counts) from the PMT for a convenient period of time (usually 10.0 minutes). The peak of the resulting spectrum was then integrated to give the activity of the sample. A typical spectrum for ¹³³Ba is shown in Figure 6. The radiochemical recovery for barium may be calculated as

$$\text{Radiochemical recovery} = \frac{\text{area of } ^{133}\text{Ba peak of sample}}{\text{area of } ^{133}\text{Ba peak of standard}}$$

A typical calculation is estimated to have an uncertainty of no more than +4%.

Figure 6. The gamma spectrum of ^{133}Ba .

The following table lists the energies of the gamma peaks used to calculate the radiochemical recoveries of the different radionuclides used.

Table V. Gamma Energies of Radionuclides Used to Calculate Recoveries

Radionuclide	Gamma Peaks/MeV
^{133}Ba	0.274, 0.355
^{42}K	1.52
^{59}Fe	1.10 , 1.29
^{234}Th	0.063, 0.093

E. Surface Area Measurements

The surface areas of the prepared barium sulphate samples were measured using the Micrometrics Model 2200 High Speed Surface Analyser by determining the quantity of nitrogen gas necessary to form a monolayer of gas molecules on the surface of the sample. For this purpose dry nitrogen gas of high purity was used.

Approximately one gram of sample was used in the surface area determination. Before the actual testing of the surface area, the sample was outgassed at 175°C for 40 minutes while continuously purging with nitrogen gas to sweep gases released by the heating. Doubling the outgassing time showed no change in the surface area values obtained.

The instrument was calibrated with a standard carbon black sample (STERLING MT prepared at 3100°C) which had a specific surface area of $(7.27 \pm 0.05) \text{ m}^2 \text{ g}^{-1}$. The determined surface area of this sample was found to be $(5.8 \pm 0.1) \text{ m}^2 \text{ g}^{-1}$. Since the instrument's specifications state that greatest accuracy is obtained with samples having areas greater than 10 m^2 , the surface areas determined were correct by a factor of 1.25. The standard deviation of the surface area determinations was found to be no more than $0.2 \text{ m}^2 \text{ g}^{-1}$.

F. Raman Spectroscopy

The Raman spectroscopic studies were done on small barium sulphate samples mounted on a microscope slide under the 4880.0Å beam of an argon ion laser. The apparatus, schematically represented in Figure 7, has been fully described elsewhere.^{51,52}

Figure 7. Schematic diagram of micro-Raman apparatus.

The laser beam (with an unfocused diameter of 4mm) was focused using an adapted Zeiss-Winkel microscope. Using the following equations, the diameter D and the length L of the focal cylinder may be calculated and thus the area of irradiation can be estimated:

$$D = 4 \lambda f / \pi d$$

$$L = 16 \lambda f / \pi d^2$$

where λ is the wavelength of the laser radiation, d is the diameter of the unfocused laser beam, and f is the focal length of the focusing lens. For a microscope objective with a focal length of 1.6mm and an unfocused beam of diameter 4mm and wavelength 4878.5Å, the region of irradiation was estimated to have a diameter of approximately one micrometer.

Quantitative determination of the spectral parameters was done using the Hewlett-Packard 9111A graphics digit tablet connected to the Hewlett-Packard 9836 mini-computer. Hard copies were plotted using the Hewlett-Packard 7470A plotter.

G. Mathematical and Computational Methods

1. Exchange Studies

As was previously mentioned, the determination of i_{∞} is necessary for the accurate analysis of the exchange data since the true exchange reaction is described by the plot of $\ln [(i-i_{\infty})/(i_0-i_{\infty})]$ versus time. The exchange curve, however, may be obtained in a different manner as described by Adamson.⁵⁸ For the case when i_{∞} cannot be properly determined owing to an inconveniently long period of time required to observe the completion of the reaction, or other side reactions which may begin to perturb the results (such as aging or recrystallization of the crystals) at long times, the first-order reversible reaction may be determined by observing the change in i/i_0 for successive equal time intervals. That is

i/i_0 is measured at $t = 0$

$t = \Delta t$

$t = 2\Delta t$

$t = 3\Delta t$ and so on.

If $i/i_0 = e^{-Kt}$ where $K = k(a+b)/(ab)$

then we have

$$i_0/i_0 = 1 = e^{-0} = 1$$

at $t = 0$

$$i_1/i_0 = e^{-K\Delta t}$$

at $t = \Delta t$

$$i_2/i_0 = e^{-2K\Delta t}$$

at $t = 2\Delta t$

$$i_3/i_0 = e^{-3K\Delta t}$$

at $t = 3\Delta t$ and so

Figure 8. Example of computer "peak-folding"
technique. The Raman spectrum of
barium sulphate precipitated at $pK=0.5$.

- (a) spectral peak (asymmetric)
- (b) synthesized peak (symmetric)
- (c) residual

splined to give new digitized spectra with 512 equally spaced data points and retaining the same spectral characteristics as the original digitized spectra.

The asymmetries found in the spectral band shapes were quantified in the following manner. The high frequency side of the digitized, splined spectral band was reflected through an imaginary vertical mirror positioned at the peak of the band. This "peak-folding" technique produced a synthesized, symmetric band which was then subtracted from the asymmetric spectral peak. The resulting residual (Figure 8) was integrated to give the area which was used as a measure of the degree of asymmetry. This technique was found to be quite sensitive to noise present at the peak of the spectral band.

The peak frequencies were determined both manually and via computer. The error on the manual peak determination was estimated at $\pm 0.2\text{cm}^{-1}$ while that for the computer determination was estimated at $\pm 0.19\text{cm}^{-1}$. Table VI lists the peak frequencies for some typical spectra. The results indicate that there is good agreement between the two methods.

Table VI. Peak Frequencies for Some Typical Spectra

Sample	ν_1 Manual Determination *	ν_1 Computer Determination	Difference
1	988.18 $\pm$ 0.10	988.01	0.17
2	987.65 $\pm$ 0.10	987.86	-0.21
3	986.53 $\pm$ 0.10	986.52	0.01
4	987.97 $\pm$ 0.15	987.86	0.11

* These values represent the average of 4 determinations - 2 separate determinations of 2 separate spectra. The errors listed with these values are the standard deviations.

The bandwidth at half-maximum was determined manually from the computer plots of the normalized spectra. The error on these values were estimated to be no more than $\pm 0.3\text{cm}^{-1}$.

To check the reproducibility of the digitization process, a test curve (Figure 9) was digitized (and splined to 512 equally spaced points) 12 times. The average of the determined peak position was 50.03 (arbitrary units) which agreed quite well with the expected value of 50.0. The

standard deviation was found to be 0.1% of the range of the digitized points.

Figure 8. Example of computer "peak-folding"
technique. The Raman spectrum of
barium sulphate precipitated at $\text{pK}=0.5$.

- (a) spectral peak (asymmetric)
- (b) synthesized peak (symmetric)
- (c) residual

Figure 9. Test curve for the computer digitization process. The peak is at 50.0 (arbitrary units).

3. RESULTS AND DISCUSSION

I. Coprecipitation of Potassium and Iron (Fe^{3+})

The coprecipitation of potassium ions with barium sulphate as a function of potassium ion concentration in the precipitation solution is shown in Figure 10. For convenience, the amount carried has been normalized to the amount of BaSO_4 formed (assuming complete precipitation). Although these results cover a wider concentration range, they are analogous to those of Winzer and Geyer²⁷, and indicate that under the experimental conditions used, a mole ratio of K:Ba up to at least 0.28 can be obtained in the precipitate. A logarithmic plot of the amount of potassium carried versus the amount in solution shows essentially a straight line which suggests that there is no observable limit to the amount of potassium carried for the concentration range studies (Figure 11).

Tracer studies using ^{42}K have shown that the presence of ferric ions in solution suppresses the carrying of potassium (Figure 12). At this point it is unclear why ferric ions have this effect. One possibility is that the ferric ions and the potassium ions are competing for sites in the electrical double layer. With ferric ions in the double

layer, the approach of a potassium ion is deterred due to repulsive electrostatic forces so that the effect is one of competing for initial adsorption sites. On the other hand, one may argue that the presence of the foreign ions will change the rate and extent of BaSO_4 precipitation and in this way affect the observed carrying of ions. Figure 13 illustrates this point as the amount of barium sulphate (measured as the % recovery of $^{133}\text{Ba}^{2+}$) precipitated is plotted versus the solution concentrations of K^+ and Fe^{3+} ions. To enhance the observable effect, the precipitates were filtered 5 minutes after the addition of the sulphuric acid (instead of the usual 30 minutes). According to Burk's data,⁴³ barium sulphate precipitates essentially to completion up to a pM ($\text{M}=\text{K}^+, \text{Fe}^{3+}$) value of 1.5 after 30 minutes which indicates the effect shown in Figure 13 is one of rate. The slow growth of barium sulphate in the presence of Fe^{3+} ions could account for the low carrying of K^+ ions.

Preliminary results using $^{59}\text{Fe}^{3+}$ tracer have shown that there was an indication of saturation with respect to the amount of iron carried by the precipitate within the same cation concentration range as was used for the potassium study. This is shown in Figure 14 where the essentially straight line at lower Fe^{3+} solution concentrations in the logarithmic plot reaches a plateau. These results are typical within the potassium concentration range between pK = 4.0 to 1.5. The limit is more clearly seen in Figure 15 where the experimental conditions are slightly different

(i.e. 10mg of Ba^{2+} is used instead of 1mg). The limiting value in Figure 15 gives an estimated Fe:Ba ratio of 0.11. It is clear that Fe^{3+} coprecipitates with barium sulphate in a manner different from that of potassium and that more potassium may be carried than iron (approximately 3 times more).

It is interesting to note that the presence of potassium does not affect the coprecipitation of iron. This was shown by the invariance of the amount of iron carried in Figure 14 when plotted for several potassium concentrations and by Figure 16 which plots the amount of Fe^{3+} carried versus the potassium concentration for several Fe^{3+} concentrations. The horizontal lines generated by such a plot shows no observable effect of the K^+ ions.

From the data presented thus far, it can be seen that over a considerable concentration range, the following relationship holds

$$(\text{mol } \text{K}^+ \text{ in solid}) = C (\text{mol } \text{K}^+ \text{ in solution})$$

where C is a proportionality constant when $[\text{Ba}^{2+}]$ in solution is 100mg per litre. This resembles a homogeneous distribution law¹⁰

$$\frac{\text{mol } \text{K}^+}{\text{mol } \text{Ba}^{2+}} \text{ solid} = D \frac{\text{mol } \text{K}^+}{\text{mol } \text{Ba}^{2+}} \text{ solution}$$

considering the amounts of Ba^{2+} in the solid and solution are constants since complete precipitation and negligible

solubility effects are assumed. This suggests a quasi-equilibrium even though the precipitation is only an approach to equilibrium rather than the equilibrium itself. It also suggests that the potassium is being incorporated into the barium sulphate lattice since the distribution law above is consistent only with the isomorphous replacement and/or anomalous-mixed-crystal formation categories.¹⁰

The iron coprecipitation, on the other hand, seems to be following a Freundlich or some other analogous isotherm in which an approach to a limit is seen. This suggests that adsorption processes are present, or, the iron has low, limited solubility within the precipitate. Further evidence presented in this work will indicate that the iron is not incorporated into the barium sulphate lattice to a large extent but, rather, is present in some other state.

The effects of a highly charged cation such as Fe^{3+} has been shown to suppress the carrying of K^+ ions but not the reverse. Burk and Wiles⁸ have clearly shown that there is an increase in the surface area of barium sulphate when precipitated in the presence of potassium ions. Thus, we may conclude that the coprecipitation of iron with barium sulphate cannot be described in terms of Hahn's adsorption category since an increase in the amount of iron carried reflecting the increase in surface area was not observed. This, however, does not eliminate the internal adsorption category.

Figures 10-16. K^+ and Fe^{3+} coprecipitation with
barium sulphate.

Figure 10. Amount of K^+ carried by BaSO_4 (10mg Ba^{2+} per 100ml of solution) as a function of K^+ concentration. Samples were analysed using atomic absorption spectroscopy.

Figure 13. The radiochemical recovery of ^{133}Ba as BaSO_4 as a function K^+ and Fe^{3+} concentration for a precipitation time of 5min. .

Figure 13. The radiochemical recovery of ^{133}Ba as BaSO_4 as a function K^+ and Fe^{3+} concentration for a precipitation time of 5min. .

Figure 14. Logarithmic plot of the amount of Fe^{3+} carried by BaSO_4 (1mg Ba^{2+} per 100ml of solution) versus the amount of Fe^{3+} in solution. ^{59}Fe was used as the tracer.

Figure 15. Amount of Fe^{3+} carried by $BaSO_4$ as a function of Fe^{3+} concentration. The samples were analyzed using atomic absorption spectroscopy. The amount of Ba^{2+} used was 10mg per 100ml of solution.

recrystallization processes whereby the labelled ions are buried into subsequent layers of the crystal is not the mechanism by which the second process occurs. This process would take place in a matter of days rather than minutes.

It is interesting to note that the half-time of the first process is essentially unchanged. Since the barium ions are diffusing towards sites in the electrical layer near the crystal surface, the presence of H^+ ions in solution do not seem to affect this process. However, it is known that ionic crystals tend to adsorb H^+ ions⁵⁴ which would then hinder the initial adsorption of a labelled barium ion and thus decrease the rate of the second process which is seen in the preceeding table.

The effect of potassium ions upon the exchange rates of barium sulphate studied by Burk and Wiles⁸ have shown that the presence of potassium ions in the precipitate affects the rate markedly while the effects of potassium ions in solution show relatively minor changes. The exchange curves in Figure 19(a) are those for barium sulphate freshly precipitated from solutions which do and do not contain added potassium ions. The half-times for the exchange processes were found to be:

II. Exchange Studies

In order to investigate changes in the reactivity of barium sulphate precipitates containing potassium and iron, isotopic exchange reactions using ^{133}Ba have been studied. This work represents an extension of the work done by Burk and Wiles⁸ who studied the reaction

Figure 17 shows typical $\ln(i/i_0)$ versus time curves for two different amounts of barium sulphate used. Analysis of these curves by the method previously described and using $\Delta t = 5$ minutes, a curve as shown in Figure 18 is obtained. The resolution of this latter curve into two straight lines indicates the occurrence of two first-order processes whose half-times are readily determined. The half-times of the resolved lines were found to be:

	$t_{1/2} / \text{min}$	
	Fast Process	Slow Process
0.090g BaSO_4^*	5 ± 1	51 ± 4
0.30g BaSO_4^*	4 ± 1	14 ± 2

(* Baker and Adamson Reagent BaSO_4 digested for 4 days at

•25°C)

It is observed that the fast process does not change when the amount of barium sulphate used in the exchange study is increased. The slow process, however, does show the expected increase in rate, which is due to the increase in surface area:

$$\frac{0.30\text{g}}{0.09\text{g}} = 3.3 \quad \frac{51\text{min}}{14\text{min}} = 3.6$$

Since the second process is sensitive to the changes in the amount of precipitate which is in contact with the solution, it will serve as a probe in the proceeding studies. Since it was this second, slower process which was studied by Burk and Wiles who determined the activation energy of this step to be consistent with the stripping of part of the hydration, it is most likely to be the step in which the $^{133}\text{Ba}^{2+}$ ions chemically bind with SO_4^{2-} ions on the surface. This is the process we are interested in since it yields greater information about crystal reactivity. The initial fast process is probably one in which the $^{133}\text{Ba}^{2+}$ ion exchanges with another Ba^{2+} ion in the electrical layer near the actual crystal surface so that it is in an initial adsorbed state after which the ion may become incorporated into the lattice. Its invariance to the amount of barium sulphate added may be due to insensitivity resulting from the experimental conditions chosen (in particular, due to the small amounts of solid used).

In order to verify that the curvature in the plots of $\ln[(i_j - i_{j+1})/i_o]$ versus time was not a manifestation of improper control of experimental conditions or observable aging of the precipitate, several experiments were performed.

To ensure that the curvature was not due to the aging of the barium sulphate while in contact with 0.1M HNO_3 , reagent grade BaSO_4 crystals were digested in distilled water at 25°C for one day and four day periods before performing an exchange experiment. Also, to ensure the curvature was not due to any net dissolution process occurring during the immersion of the barium sulphate into the exchange solution, 0.1mg of BaSO_4 was added to the solution prior to the addition of the bulk of the solid so that a saturated solution would result. Neither of these precautions removed the curvature. After the barium sulphate was digested in water for four days, it was also digested in 0.1M HNO_3 for 30 and 120 minute periods. The exchange curves for these last two samples were very similar.

All of the above experiments failed to remove the curvature in the plot of $\ln[(i_j - i_{j+1})/i_o]$ versus time and it was concluded that two first order processes are present in the isotopic exchange in the $\text{Ba}^{2+}_{(\text{aq})}/\text{BaSO}_{4(\text{s})}$ system, confirming previous reports.^{29,30} Factors which affect the exchange may be seen comparing exchanges done in 0.1M HNO_3 and in distilled water.

It is known that the solubility of an ionic compound increases when it is placed in an electrolytic solution such as nitric acid and with this increase, an acceleration of the recrystallization is associated.⁴⁴ Thus, if the slower process in isotopic exchanges is due to recrystallization processes, as according to Lieser^{29,30}, one would expect an increase in the half-time of this process when barium sulphate is placed in 0.1M HNO₃ rather than distilled water. Figure 19 shows that greater exchange has occurred with barium sulphate in contact with water rather than 0.1M HNO₃. When the data are analyzed, the following half-times are obtained

	$t_{1/2}$ / min	
	<u>Fast Process</u>	<u>Slow Process</u>
BaSO ₄ exchange in 0.1M HNO ₃	5 ± 1	51 ± 4
BaSO ₄ exchange in H ₂ O	6 ± 1	19 ± 2

(0.090g of Baker and Adamson reagent grade

BaSO₄ digested for 4 days in H₂O at 25°C).

It is seen that although there is no marked change in the fast process, the second process occurs at a greater rate when the solid is in contact with water. This shows that

recrystallization processes whereby the labelled ions are buried into subsequent layers of the crystal is not the mechanism by which the second process occurs. This process would take place in a matter of days rather than minutes.

It is interesting to note that the half-time of the first process is essentially unchanged. Since the barium ions are diffusing towards sites in the electrical layer near the crystal surface, the presence of H^+ ions in solution do not seem to affect this process. However, it is known that ionic crystals tend to adsorb H^+ ions⁵⁴ which would then hinder the initial adsorption of a labelled barium ion and thus decrease the rate of the second process which is seen in the preceeding table.

The effect of potassium ions upon the exchange rates of barium sulphate studied by Burk and Wiles⁸ have shown that the presence of potassium ions in the precipitate affects the rate markedly while the effects of potassium ions in solution show relatively minor changes. The exchange curves in Figure 19(a) are those for barium sulphate freshly precipitated from solutions which do and do not contain added potassium ions. The half-times for the exchange processes were found to be:

<u>pK of Precipitation Solution</u>	<u>t_{1/2} / min</u>	
	<u>Fast Process</u>	<u>Slow Process</u>
4.8 (no added K ⁺ ions)	3 ± 1	98 ± 6
1.6	4.5 ± 1	23 ± 3

(0.090g of freshly precipitated BaSO₄)

Again it is observed that the fast process changes only slightly compared to the slower process which shows a four-fold increase in rate. Since it was found⁸ that the activation of the slow process did not change on the addition of K⁺, this suggests that there is a four-fold increase in the number of available exchange sites and not necessarily a change in their nature.

The effect of ferric ions in the barium sulphate crystals upon the exchange is quite different from that of the potassium ions. Figure 19(b) shows that barium sulphate precipitated from a solution 10⁻²M in Fe³⁺ exhibits the same exchange characteristics as those of barium sulphate precipitated in the absence of any added cation (excluding H⁺). Even when the precipitate was formed in the presence of both K⁺ and Fe³⁺ ions, the change in rate is predominantly due to the potassium (Figure 19(b)). The half-times of the processes were

<u>pM of Precipitation Solution</u>	<u>t_{1/2} / min</u>	
	<u>Fast Process</u>	<u>Slow Process</u>
pK=pFe=4.8 (no added ions)	4 ± 1	35 ± 3
pFe=2.0	7 ± 2	41 ± 4
pK=1.6	4 ± 1	21 ± 2
pK=1.6, pFe=2.0	7 ± 2	21 ± 3

(0.090g of freshly precipitated BaSO₄)

It is evident that unlike the case for potassium ions, the presence of ferric ions in the precipitate does not affect the rate of the second process.

Ferric ions in solution, however, show greater effects on the exchange rate as is seen in Figure 19(c). The results show that as the concentration of Fe³⁺ ions in the exchange solution increases, the rate of exchange decreases. Comparing the exchange rates of exchange of a barium sulphate precipitate in contact with a solution containing ferric ions (pFe = 2.0) and one in contact with a solution not containing ferric ions, it is seen that both processes of the exchange are affected in such a way that the half-times are lengthened:

<u>pFe of Exchange Solution</u>	<u>t_{1/2} / min</u>	
	<u>Fast Process</u>	<u>Slow Process</u>
✓ 4.8 (no added K ⁺ ions)	3 ± 1	98 ± 6
2.0	14 ± 2	148 ± 10

The ferric ions in solution not only decrease the rate of the incorporation of barium sulphate into the lattice but they also decrease the rate of the first process which is the initial adsorption of the barium ions.

It is evident that the presence of ferric ions in solution interferes with the isotopic exchange of barium ions with barium sulphate probably in such a manner that they occupy critical sites in the double layer and on the surface so as to suppress the initial adsorption of barium ions. This would explain why Fe³⁺ ions suppress the carrying of K⁺ ions and even Th⁴⁺ ions. With the Fe³⁺ ions present in the crystal, these adverse effects are not present.

As was previously mentioned, the effect of K⁺ ions in solution did not greatly affect the exchange rates as compared to the case where these ions were present in the precipitate. The results in Figure 19(d) show that K⁺ ions in solution increase the exchange rate but to a lesser degree. The half-times are given below:

Figures 17-19(e). Exchange studies.

<u>Sample</u>	<u>t_{1/2} / min</u>	
	<u>Fast Process</u>	<u>Slow Process</u>
Exchange in 0.1M HNO ₃		
BaSO ₄	3 ± 1	98 ± 6
BaSO ₄ (pK=1.6)	4 ± 1	22 ± 2
Exchange in 0.1M HNO ₃ pK=2.0		
BaSO ₄	3 ± 1	70 ± 5
BaSO ₄ (pK=1.6)	4 ± 1	19 ± 2

It has been suggested²⁶ that the increase in exchange rate is due to the fact that K⁺ ions are continuously being incorporated into the precipitate and only then do they influence the exchange. If this is correct then we should be able to observe a curvature in the plot of $\ln(i/i_0)$ showing a gradual increase in slope as the concentration of lattice-bound K⁺ builds up.

Figure 19(e) shows the curvature predicted for the exchange of barium ions with barium sulphate which has been digested for 2.0 hours in 0.1M HNO₃ at 25°C before the K⁺ ions and ¹³³Ba²⁺ tracer were added.

At this point it is clear that the presence of K⁺ ions in the precipitate increases the exchange rate while the presence of ferric ions in the precipitate do not. The effect of the ferric ions is clearly seen when they are present in the exchange solution where their interference

with the exchange process is interpreted as being one of occupying potential exchange sites either on the crystal or in the electrical double layer which also explains the suppression in the carrying of potassium.

The fact that ferric ions in the precipitate do not affect exchange rates as do potassium ions may be an indication that these impurities are carried down by different processes which is also indicated by their different coprecipitation characteristics (i.e. Figures 11 and 15).

Figures 17-19(e). Exchange studies.

Figure 17. The plot of $\ln(I/I_0)$ versus time for different amounts of BaSO_4 used.

Figure 18. The plot of $\ln[(1_j - 1_{j+1})/1_0]$ versus time.
(0.30g of reagent grade BaSO_4 used)

Figure 19. The plot of $\ln(I/I_0)$ versus time for the case of distilled water as the exchange solution.

- exchange solution is 0.1M HNO_3 .
- exchange solution is distilled water

Figure 19(a). The plot of $\ln(i/i_0)$ versus time for the following precipitates:

- BaSO_4 precipitated in the absence of K^+ and Fe^{3+}
- BaSO_4 precipitated from a solution at $\text{pK}=1.6$.

Figure 19(b). The plot of $\ln(I/I_0)$ versus time for:

- BaSO_4 precipitated in the absence of K^+ and Fe^{3+}
- BaSO_4 precipitated from a solution at $\text{pFe}=2.0$
- △ BaSO_4 precipitated from a solution at $\text{pK}=1.6$
- ⊙ BaSO_4 precipitated from a solution at $\text{pK}=1.6$
 $\text{pFe}=2.0$

Figure 19(c). The plot of $\ln(i/i_0)$ versus time for BaSO_4 precipitated from a solution at $\text{pFe}=2.0$.

- exchange solution at $\text{pFe}=2.0$
- exchange solution at $\text{pFe}=3.0$
- △ no added Fe^{3+} in exchange solution

Figure 19(d). The plot of $\ln(i/i_0)$ versus time for:

- BaSO_4 (no added K^+ or Fe^{3+}), 0.1M HNO_3 exchange solution
- △ BaSO_4 (no added K^+ or Fe^{3+}), exchange solution at $\text{pK}=2.0$
- BaSO_4 (prepared at $\text{pK}=1.6$), 0.1M HNO_3 exchange solution
- ▽ BaSO_4 (prepared at $\text{pK}=1.6$), exchange solution at $\text{pK}=2.0$

Figure 19(e). The plot of $\ln(I/I_0)$ for BaSO_4 prepared in the absence of K^+ and Fe^{3+} . The exchange solution is at $\text{pK}=1.6$.

III. Precipitate Morphology

It is well known that the conditions of precipitation of an ionic solid greatly affects the appearance of the crystals formed and that the presence of foreign ions also influences crystal morphology.⁵⁵ In general, the morphology of a precipitate is determined by nucleation, growth rates, recrystallization and aging processes, and habit modifications brought about by solvent effects or by ions present in solution. It has been pointed out by Walton⁵⁶ that foreign ions which are known to form mixed crystals with the precipitate being formed cause definite changes in habit modification and that, in general, ions which are only adsorbed onto to crystal surface do not cause major changes in crystalline morphology.

Scanning electron micrographs show quite clearly that potassium ions have a pronounced effect upon the morphology of barium sulphate crystals.⁸ Figure 20(a) shows a representative electron micrograph of barium sulphate crystals precipitated from 0.1M HNO_3 solutions. The morphologies are completely analogous with those reported by Fischer and Rhinehammer⁵⁵ for the precipitation conditions employed. The effect of potassium ions (Figure 20(b)) is seen to increase lateral growth from the main axis of the crystal. It also appears that dendritic growth is increased as well as particle size and specific area. The drastic

change in morphology may indicate that potassium ions are actually incorporated in the BaSO_4 lattice as is expected and has been suggested by other authors.⁴⁰

The effect of ferric ions is not as pronounced as those of potassium (Figure 21). The electron micrograph in Figure 21 shows that the morphology of BaSO_4 crystals precipitated from a solution of $\text{pFe}=3.0$ is essentially the same as that of the precipitate in Figure 20(a). It is interesting to note that at the same concentration of potassium ions (i.e. $\text{pK}=3.0$) Burk and Wiles were still able to observe morphological changes in the crystals.

The results indicate that Fe^{3+} ions are not incorporated, to a great extent, into the BaSO_4 lattice and suggests that they are carried by adsorption processes. If this is so then one would expect to see the effects of potassium ions reduced. This is seen in Figure 22 where the electron micrograph of a precipitate formed in the presence of K^+ and Fe^{3+} ions ($\text{pK}=2.3$, $\text{pFe}=3.0$) is shown. Comparing this micrograph with that in Figure 20(a), it is seen that the change in morphology due to potassium ions is not as pronounced when ferric ions are also present in solution.

By observing the electron micrographs it is easy to see why the exchange rates increase for precipitates formed in the presence of potassium ions and remain essentially the same for those formed in the presence of ferric ions. It

appears that there is an increase in the specific surface area of the potassium-doped precipitates which would increase the rate of exchange. A surface area measurement would confirm this point but one must consider that with such a dramatic change in morphology, there exists the possibility that certain faces which may be richer in barium exchange sites are exposed to a greater or lesser degree. This would also affect the exchange rate.

Figures 21(a)-22. Scanning electron micrographs
of various BaSO_4 precipitates.

ELECTRON MICROGRAPHS

Figure 20(a). BaSO_4 precipitated in the absence of K^+ and Fe^{3+} .

Figure 20(b) BaSO_4 precipitated from a solution at $\text{pK}=2.3$.

Figure 21. BaSO_4 precipitated from a solution at $\text{pFe}=3.0$.

Figure 22. BaSO_4 precipitated from a solution at $\text{pK}=2.3$ and $\text{pFe}=3.0$.

10mg Ba^{2+} per 100ml of 0.1M HNO_3 was used in the preparation of the above samples. Magnification is 3000X.

Fig. 20(a)

Fig. 20(b)

Fig. 21

Fig. 22

IV. Surface Area Measurement

As was previously mentioned, surface area measurements of the differently prepared precipitates would confirm the apparent increase in surface area. The results are given in Table VII below.

Table VII. Surface Area of BaSO₄ Precipitates

Sample	Surface Area/m ² g ⁻¹
BaSO ₄ (no added cations)	1.9 ± 0.2
BaSO ₄ (pK=1.6)	3.6 ± 0.1
BaSO ₄ (pFe=2.0)	1.8 ± 0.2

(The values in the parentheses indicate the concentration of the cation in the precipitation solution)

The above table clearly shows that the presence of potassium ions in solution results in a precipitate with a greater specific surface area as was suggested by the electron micrographs. Also as expected, the precipitate formed in the presence of ferric ions showed a surface area similar to that of the precipitate formed in the absence of

both K^+ and Fe^{3+} ions.

One should note that the surface area of the potassium-doped precipitate is twice that of barium sulphate precipitated in the absence of K^+ and Fe^{3+} . The exchange data, however, suggested that there is a four-fold increase in the number of exchange sites for the potassium-doped precipitate. It is clear that the morphological changes in the crystal not only produced crystals with a greater physical surface area but also exposed more barium exchange sites. This will have obvious effects upon the carrying of other impurities especially those which are adsorbed. Since ferric ions show symptoms of being carried by barium sulphate via adsorption processes but are not influenced by the presence of potassium ions which obviously increase the surface area of the precipitate, it is possible that iron is being carried in a manner as described by the "internal adsorption" category.

V. X-Ray Diffraction Study

The X-ray diffraction patterns obtained for various barium sulphate precipitates containing potassium and ferric ions showed no lines other than those of barium sulphate. The only observable changes in the patterns were shifts and changes in relative intensities of the lines. This suggests that some degree of solid solution may be occurring for both cations present in the precipitate.

Since K^+ has the same ionic radius as barium ions, one would expect the lattice parameters of the impure barium sulphate to remain essentially the same. For ferric ions, however, their radii are considerably smaller than those of barium so one would expect changes in the lattice parameters if ferric ions were becoming incorporated into the $BaSO_4$ lattice. Table VIII below lists the lattice parameters and unit cell volumes of some barium sulphate precipitates studied.

2

Figures 23(a) and (b). X-ray diffraction studies
of BaSO_4 precipitates.

H_2SO_4 was then fumed off and the sample was annealed overnight at 690°C

It is clear from the above table that no definite conclusions can be drawn except to say that the lattice parameters for the contaminated precipitates do not change markedly and that any change is within the stated uncertainties. The trend shown by samples numbered 6 through 8 indicates that the cell volume decreases as the concentration of ferric ions in the precipitation solution increases. One would expect the cell volume of barium sulphate to decrease as a smaller cation such as Fe^{3+} is incorporated into the lattice but it is known from Figure 15 that the precipitate formed in the presence of ferric ions at a concentration of 1M contains less of the impurity than the precipitate formed at $\text{pFe} = 1.5$. Thus, any observed trends in Table VIII may be misleading. Clearly a more sensitive technique (such as the micro-Raman technique) is needed.

Although new lines were not observed, there were visible changes in their relative intensities particularly for those precipitates containing K^+ ions. Precipitates formed in solutions containing ferric ions did not show great changes in the relative intensities of the diffraction lines (Figure 23). To prove that the changes in relative intensities were not due to sample preparation, two separate samples were prepared for each precipitate and each sample was rotated

90° within the diffractometer. The resulting patterns for each precipitate showed that the relative intensities of the lines had remained unchanged after the new preparation and rotation, verifying that the observed effect was real.

Since the potassium-doped precipitates showed the most changes, it was assumed that the effect was due to K^+ ions replacing Ba^{2+} ions in the lattice. If this were the case then the lines showing the greatest change in intensity would be those representing lattice planes which showed greatest sensitivity towards the replacement. A calculation of the structure factor, F , (Appendix 3) of such planes would show that the value of F would be greatly dependent upon the barium ions present and thus decrease in value as the barium ions are replaced by ions such as K^+ and Fe^{3+} which are less effective scatterers than Ba^{2+} ions.

Calculations of F for various planes (diffraction lines) showed that all were highly dependent upon the Ba^{2+} ions (70% to 85% dependent on Ba) and no correlation could be made between decrease in intensity and ion replacement. Since Ba atoms are exceedingly better scatterers than S and O atoms, a great fraction of the intensity of the lines observed are mainly due to the presence of Ba atoms and no one line was calculated to be more sensitive than another with respect to barium atom replacement.

Another likely explanation for changes in the line

intensities, which has supporting evidence, is the change in crystal morphology. Since BaSO_4 precipitates which contain potassium have greater morphological changes in the crystals, they show the greatest fluctuations in relative line intensities. The increase (or decrease) in these line intensities is directly due to the greater (or lesser) exposure of certain planes of the crystal. This is supported by the electron micrographs in the previous section.

2

Figures 23(a) and (b). X-ray diffraction studies
of BaSO_4 precipitates.

Figure 23. X-ray diffraction patterns of BaSO_4
precipitates containing

- (a) K^+
- (b) Fe^{3+} .

The cation concentration of the precipitation solution
is given above the respective pattern.

REL. INTENSITY

VI. Micro-Raman Spectroscopy Study

The Raman studies described here mark a significant improvement in probing the state of the impurity in barium sulphate precipitates and has shown the existence of solid-solution formation.

Raman data for BaSO_4 precipitated in the presence of potassium show there is a definite shift in frequency of the ν_1 vibrational mode of the SO_4^{2-} ions. It is seen in Figure 24 that the ν_1 band is shifting in the direction approaching the ν_1 vibrational mode of sulphate ions in K_2SO_4 , a crystal whose symmetry is similar to that of BaSO_4 .^{57,58} The shift appears to be linear with respect to the amount of potassium present in the crystals, which is consistent with solid-solution formation. The presence of an apparent anomaly at the K:Ba ratio of about 0.12 has been observed in previous studies⁶⁰ for different preparation at pH values between 2.3 and 1.5 in the precipitation solutions. Although these particular preparations were not analysed for potassium content, it is likely that the K:Ba ratio in the crystal was about 0.1.

The width of the ν_1 band is also affected by the presence of potassium in the crystals. This is seen in Figure 25 where the bandwidth at half-maximum is plotted versus the weight % of K in the precipitate. Again, there is an anomaly in the curve at K:Ba = 0.08 which also is in

agreement with preliminary experiments.⁶⁰ The cause of the anomaly is not yet known and is still under investigation but the implication is that there is a marked change in the environment of the SO_4^{2-} ion in precipitates with K:Ba ratios in the vicinity of 0.10 .

The results for barium sulphate samples prepared in the presence of ferric ions are quite different from those of potassium-doped precipitates which seems to be the general trend of all the studies presented in this work. Figure 26 clearly shows that the ν_1 band frequency is essentially unaffected by the presence of iron in the precipitate suggesting that these ions are present in such a way as not to affect the environment of the SO_4^{2-} ions. There is an anomaly in this curve also which appears in the sample with Fe:Ba = 0.12 . Excluding the anomaly, the invariance of the ν_1 frequency with the amount of iron in the precipitate suggests that solid-solution formation is probably not occurring which is consistent with previous observations.

The variance of the bandwidth of ν_1 with coprecipitated ferric ions (Figure 27) is similar to the results of the potassium-doped precipitates except that there is much more scatter in the data.

The results thus far indicate there is solid-solution formation occurring with coprecipitated K^+ ions whereas this is not obvious with the coprecipitation of ferric ions. To

illustrate this point, hypothetical curves showing the change in the ν_1 frequency for the SO_4^{2-} ions as its environment changes from one of pure BaSO_4 to that of pure K_2SO_4 , FeSO_4 , or $\text{Fe}_2(\text{SO}_4)_3$ (Figure 28) assuming a linear shift in ν_1 as the moles of foreign cations in the solid-solution increases. It is clear that the shift in ν_1 for the potassium-doped precipitates follows the hypothetical curve approaching a K_2SO_4 environment quite closely while the same is not observed for the iron-doped precipitates, at least to the extent Fe^{3+} coprecipitation has taken place. This observation further shows that the iron in the precipitate is present in such a manner as not to change the SO_4^{2-} environment in the region of the crystal probed by the laser beam indicating that solid-solution formation has not occurred to a significant extent. If the laser beam is probing only the surface of the crystals, then the environment of the SO_4^{2-} ions on the surface is one of BaSO_4 only and that any iron present must be found in deeper layers of the crystal. This is consistent with occlusion or "internal adsorption" processes and would explain why coprecipitated iron does not markedly change isotopic exchange rates.

Along with changes in the frequency and width of the ν_1 there was an asymmetry present in the low frequency side. In Figure 29 a symmetric, synthesized band (synthesized by reflecting the high frequency half of the spectral band onto the low frequency side) is subtracted from the actual

asymmetric band. The result is a positive residual located at the low frequency side of the spectral peak. This asymmetry was present in all spectra of the freshly precipitated barium sulphate samples regardless of the cation impurity (Figures 29, 30 and 31).

It is this asymmetry in the ν_1 band of freshly precipitated barium sulphate which distinguishes the precipitates from naturally occurring barite. Figure 32 shows the resulting residual of the described subtraction process for the spectrum of the natural barite sample. The negative residual indicates there is an asymmetry at the high frequency side of the ν_1 band. This asymmetry, however, occurs to a smaller degree than the asymmetry for the freshly precipitated BaSO_4 crystals. Table IX shows the difference in area between the spectral band and the synthesized band for natural barite and barium sulphate freshly precipitated in the absence of K^+ and Fe^{3+} ions.

Table IX. Difference in Area of the Spectral Band
and the Synthesized Symmetry Band

Sample	Difference in Area (arbitrary units)	Bandwidth at Half-Maximum
natural barite	-0.14	10.4cm^{-1}
freshly precipitated BaSO_4	0.34	11.0cm^{-1}

It is noted from the above table that the bandwidth of the barite spectrum is narrower than that of the freshly precipitated barium sulphate which is interpreted as being due to greater crystal perfection and structural order⁶¹ of the barite sample.

In order to determine the cause of the asymmetry a number of experiments were performed exploring various possibilities. At first it was thought that the asymmetry could be due to the fact that the BaSO_4 was being precipitated in an acid medium which could result in the precipitation of HSO_4^- anions or the adsorption of H^+ ions on the surface which could affect the spectrum. The Raman spectrum of a BaSO_4 sample precipitated from a neutral solution of $\text{Ba}(\text{NO}_3)_2$ and Na_2SO_4 showed that the asymmetry still existed. Based on the data of reference 62, no observable peaks which could be attributed to the presence of HSO_4^- ions in the BaSO_4 precipitate.

It was also thought that coprecipitated NO_3^- ions in the lattice could have caused the asymmetry. Barium sulphate is known to carry NO_3^- ions^{63,64} and their presence has been spectroscopically observed in the present work. The preparation of BaSO_4 in the absence of nitrate ions by mixing neutral solutions of BaCl_2 and Na_2SO_4 (Cl^- ions are known to coprecipitate with BaSO_4 ⁶³ to a lesser degree than NO_3^- ions) failed to remove the asymmetry.

To investigate the possibility that coprecipitated water⁶⁵ might be the cause of the asymmetry, the barium sulphate was prepared in the presence of D_2O . The Raman spectrum of such a sample showed that the asymmetry remained but that the entire band was shifted down in frequency. This seems to suggest that H_2O , H^+ , or OH^- is "part" of the $BaSO_4$ lattice somehow influencing the SO_4^{2-} vibration.

It was found that the asymmetry in the ν_1 band was minimumized when the freshly precipitated $BaSO_4$ crystals were digested in distilled water at $90^\circ C$ for 4 hours. The resulting Raman spectrum is given in Figure 33. The bandwidth of the precipitate has gone from $11.0cm^{-1}$ to $10.5cm^{-1}$ after digestion and the tail of the asymmetry has been reduced. It is clear that the digestion process has improved crystal perfection and structural order resulting in a narrower band with less asymmetry.

The increase in asymmetry with potassium content is an indication that the asymmetry may be due to solid-solution formation with the K^+ ions which, obviously disturbs the structural order of $BaSO_4$. Although the data in Figure 34 show much scatter, it is clear that the general trend is one of increasing asymmetry as the amount of potassium in the precipitate increases. The data for iron contaminated precipitates also show scatter but no clear trend can be observed. Also, the amount of asymmetry in the iron

contaminated precipitates, as measured by the area of the residual, shows that it is comparable to the asymmetry present in precipitates prepared in the absence of K^+ and Fe^{3+} ions indicating that the presence of iron in the precipitate does not significantly affect the asymmetry.

Preliminary experiments with barium sulphate precipitates formed in the presence of thorium indicate that there is a frequency shift in the ν_1 mode when thorium is coprecipitated. Table X below lists the ν_1 frequencies of some barium sulphate containing thorium:

Table X. ν_1 Frequencies of Some $BaSO_4$ Precipitates
Containing Thorium

Sample	ν_1 $\pm 0.2 \text{ cm}^{-1}$	Bandwidth at Half Maximum $\pm 0.2 \text{ cm}^{-1}$
1	988.01	11.10
2	986.21	11.8
3	987.48	11.9
4	987.88	13.0

Description:

1. $BaSO_4$ precipitated in the absence of foreign cations
2. $BaSO_4$ precipitated in the presence of Th^{4+} (0.01g)

3. BaSO_4 precipitated in the presence of K^+ ($\text{pK} = 2.3$ in solution)
4. BaSO_4 precipitated in the presence of K^+ ($\text{pK} = 2.3$ in solution) and Th^{4+} (0.01g)

It is seen that there is a significant decrease in the frequency of ν_1 when thorium is present in the precipitate indicating the SO_4^{2-} environment has been altered by its presence (samples 1 and 2). When both Th^{4+} and K^+ ions are, the effects on the ν_1 frequency are those mainly due to the potassium in the crystal as is indicated by the slight change in the ν_1 frequency. The table above also shows that thorium's presence in the crystal increases the bandwidth which is an indication of increased structural disorder. As seen in Figure 35, this increase is probably due to an asymmetry present at the high frequency side of the band (as indicated by the negative residual). The presence of this asymmetry is also seen indirectly in Figure 36 where the asymmetry at the low frequency side of the band due to the presence of potassium (Figure 29) is no longer prominent when the band is reflected and subtracted in the usual manner. The tail, however, is still present and marks the presence of the potassium in the precipitate.

It is seen that unlike iron coprecipitation, thorium affects the ν_1 band of the SO_4^{2-} vibration in barium sulphate in such a way as to promote structural disorder. The effects of thorium, however, seem not to be as great as those of the

potassium probably due to the fact that potassium ions may become incorporated into the BaSO_4 lattice much more easily and thus more readily form solid-solutions to a greater extent.

Figures 24-36. Micro-Raman studies.

Figure 24. ν_1 versus weight percent K^+ in precipitates formed in the presence of K^+ .

Figure 25. ν_1 bandwidth at half-maximum versus weight percent of K^+ in precipitates formed in the presence of K^+ .

Figure 26. ν_1 versus weight percent of Fe^{3+} in precipitates formed in the presence of Fe^{3+} .

Figure 27. ν_1 bandwidth at half-maximum versus weight percent Fe^{3+} in precipitates formed in the presence of Fe^{3+} .

Figure 28. ν_1 versus precipitate composition.

The hypothetical lines show a progressive shift in ν_1 from pure BaSO_4 to pure $M_x(\text{SO}_4)_y$, where $M = \text{K}^+, \text{Fe}^{2+}, \text{Fe}^{3+}$.

Figure 29. Raman spectrum of BaSO_4 precipitated
from a solution at $\text{pK}=2.3$.

Figure 30. Raman spectrum of BaSO_4 precipitated
from a solution at $\text{pFe}=2.3$.

Figure 31. Raman spectrum of BaSO_4 precipitated
in the absence of K^+ and Fe^{3+} .

Figure 32. Raman spectrum of natural barite.

Figure 33. Raman spectrum of digested BaSO_4 .

Figure 34. Area of residual versus the K:Ba ratio in precipitates containing K^+ .

Figure 35. Raman spectrum of BaSO_4 precipitated from a solution containing 0.01g of thorium.

Figure 36. Raman spectrum of BaSO_4 precipitated from a solution containing 0.01g of thorium at $\text{pK}=2.3$.

VII. SUMMARY

It has been shown that K^+ ions coprecipitate with barium sulphate to a greater extent than do Fe^{3+} ions for equal cation concentrations in the precipitation solution. Furthermore, a limit as to the amount of iron coprecipitated was observed whereas no such limit was present in the potassium coprecipitation curves even at potassium concentration as high as 1M. This is interpreted as being due to different coprecipitation mechanisms for each cation rather than ionic strength effects. There also seems to be a competition between K^+ and Fe^{3+} ions as the presence of Fe^{3+} in solution is seen to slightly suppress K^+ coprecipitation. The presence of K^+ in solution is seen neither to suppress nor enhance the iron coprecipitation.

Precipitates of barium sulphate containing potassium show changes in properties such as morphology, and specific surface area whereas those containing iron do not, at least to the same extent, under the conditions used.

Exchange studies with freshly precipitated barium sulphate have shown the presence of two processes which are interpreted as being the actual ion-exchange occurring at the solid-solution interface followed by the incorporation of the exchanged ion into the solid. The presence of potassium in

the crystals increases the rate of incorporation of $^{133}\text{Ba}^{2+}$ (aq) into the solid whereas the presence of iron in the crystals has negligible effects upon the rate. The presence of iron in the exchange solution, however, decreases the rate of both processes.

Raman data show structural changes in potassium-doped barium sulphate crystals which X-ray diffraction data could not. The progressive shift in the ν_1 frequency for the SO_4^{2-} ion suggests that mixed crystal formation is occurring. The invariance of the ν_1 frequency in iron-doped precipitates indicates that the iron is present in a manner which does not affect the SO_4^{2-} environment and that solid-solution formation is not observed for this case. Thorium is also observed to cause structural changes in barium sulphate precipitates suggesting mixed crystal formation is occurring to some extent.

4. CONCLUSIONS

The present work represents a new approach to an old problem. The study of precipitates formed in the presence of foreign ions has shed much light upon coprecipitation phenomena and why some ions influence the carrying of other ions. Although the scope of this work is restricted to the case of the barium sulphate - potassium - iron(III) coprecipitation system, it seems likely that the results may be extended to other systems.

It appears that K^+ and Fe^{3+} ions coprecipitate with barium sulphate via different mechanisms. From the evidence presented in this work, the potassium seems to be carried down by mixed crystal formation whereas the iron by adsorption processes, most likely described by Hahn's internal adsorption category.

The first indications that the two cations coprecipitated via different processes were shown in their respective coprecipitation curves (Figures 6 and 9) which indicated a curved line with a limiting value for iron and, essentially, a linear relationship for potassium. These results indicated a quasi-equilibrium distribution between K^+ ions in the solid barium sulphate and the solution but an adsorption type isotherm for the Fe^{3+} ions. Further work to obtain a homogeneous, D, or logarithmic, λ , distribution coefficient

by fractional precipitation of barium sulphate would prove rewarding. Also, measuring the adsorption of Fe^{3+} and K^+ ions on preformed barium sulphate should show different characteristics if one is adsorbed (such as Fe^{3+} and thus yield a Freundlich-type adsorption isotherm) and one is incorporated into the lattice (such as K^+ which should "penetrate" to a greater extent and continue to do so over a period of time).

With these different coprecipitation mechanisms, the effects of each cation upon certain properties of barium is not expected to be similar or occur to the same extent. For instance, a cation which is actually incorporated into the crystal lattice is expected to greatly change chemical and physical properties of the precipitate since its incorporation will, without doubt, cause structural changes in the crystal. On the other hand, an impurity which is merely adsorbed or occluded within "pockets" of the imperfect precipitate should not have the same pronounced effects.

Indeed, throughout this work the general trend has been the observation of changes in certain properties of barium sulphate for precipitates doped with potassium and not, at least to the same extent, for those containing iron impurities. This is clearly seen by the pronounced changes in crystal morphology (as indicated by relative intensity changes in X-ray diffraction lines and by direct visual evidence from the electron micrographs), the increase in

specific surface area and the increase in the incorporation of $^{133}\text{Ba}^{2+}_{(\text{aq})}$ into the solid, for the potassium-doped precipitates. Influences due to the presence of iron were only clearly observed when the iron was present in solution. For instance, iron in the precipitate did not affect the rate of incorporation of $^{133}\text{Ba}^{2+}_{(\text{aq})}$ into the solid by any appreciable amount. However, the presence of iron in the exchange solution decreased this rate and was interpreted as being due to the electrostatic repulsion of Ba^{2+} ions by Fe^{3+} ions in the electrical double layer which would hinder the approach of Ba^{2+} ions towards the crystal surface.

From the above paragraph we can relate the effects of the K^{+} and Fe^{3+} and their possible influence on the carrying of thorium with barium sulphate. It is seen that all the changes in the properties of barium sulphate which result from the incorporation of potassium would have favourable influences upon the carrying of thorium. The suppression of thorium coprecipitation in the presence of Fe^{3+} may be explained in the same manner as the decrease in the rate of $^{133}\text{Ba}^{2+}$ incorporation was interpreted, namely, the presence of Fe^{3+} in the electrical double layer would repel approaching Th^{4+} ions. This seems to be a likely explanation since the presence of Fe^{3+} in the crystals does not apparently have any influence on any other properties. To confirm this, the monitoring of Th^{4+} incorporation into preformed barium sulphate, precipitated in the presence of iron, would be a likely experiment to perform.

The Raman data leave little doubt that potassium forms mixed crystals with barium sulphate. The state of the iron impurities is less certain except that it is present in such a manner as not to alter the SO_4^{2-} environment in the lattice. Further understanding of contaminated precipitates could be gained by continuing these experiments with other ions such as Na^+ and NH_4^+ (which are known to increase thorium coprecipitation), and NO_3^- (which is known to increase potassium coprecipitation). Also, the asymmetry present in the ν_1 band of the SO_4^{2-} ion in freshly precipitated barium sulphate may be more clearly identified by studying the Raman spectra of damaged BaSO_4 crystals.

Evidence presented in this and other studies indicates that thorium is coprecipitated with barium sulphate by forming mixed crystals. Contrary to this, it has been suggested²⁶ that thorium may be carried by adsorption processes in which the increase in surface area of the crystals due to the presence of potassium can only partly account for the effect. Clearly, because of the dependence upon precipitation conditions, the initial adsorption of Th^{4+} ions on the BaSO_4 crystals must play an important role in the carrying of that ion before the ultimate formation of a mixed crystal. The formation of mixed crystals with Th^{4+} is facilitated if another heterovalent cation which is known to readily form mixed crystals with BaSO_4 is present. Potassium ions are well suited for this purpose because of

its +1 valence state and its ability to form mixed crystals with BaSO_4 . The pronounced effect of potassium upon the carrying of thorium as compared to other monovalent ions such as Na^+ and NH_4^+ is then obvious, since K^+ and Ba^{2+} ions have identical crystal radii. The experiment which would confirm this mechanism would be to measure the rate of precipitation of Th^{4+} ions onto preformed BaSO_4 crystals (not doped with potassium) in the presence of potassium in solution. If there is a cooperative effect between Th^{4+} and K^+ one should observe an increase in Th^{4+} precipitation as well as an increase in the K^+ precipitation.

In order to further this work, the following studies are suggested.

In order to improve the sensitivity in measuring the initial fast process found in the exchange studies, the amount of solid barium sulphate used could be increased to one gram quantities. With this increase, the filtering and counting of the solid will be impractical, thus filtered aliquots of the exchange solution must be counted. Monitoring the reaction in the reverse direction (i.e. with the radioactivity initially in the solid) as well as studying the SO_4^{2-} exchange would prove rewarding in better understanding the actual exchange mechanism and the influences of foreign ions.

Further crystallographic work in identifying which faces

are affected by the presence of foreign ions would prove interesting especially if one could correlate the enhancement of specific faces with the ion present in the precipitation solution.

5. APPENDICESAPPENDIX 1. Derivation of the McKay Equation

The reaction type we will consider is

where AX and BX are the two chemical species having atom X in common which is exchanging between the two species. The normal exchange procedure consists of establishing an equilibrium between the two chemical species and following the rate of appearance of labelled BX (denoted by asterisk) if the labelling was originally present in AX.

Since the system described by equation (1) is at chemical equilibrium - that is, the amounts of AX and BX are not changing with time - it follows that the rate of the forward reaction, R_f (the rate at which the chemical species AX forms BX) is just equal to the rate of the backward reaction R_b . Let a and b denote the total amounts of AX and BX, respectively, and let x and y denote the total amounts of AX^* and BX^* , respectively.

Let x_0 denote the initial amount of AX^* (and $y_0 = 0$).

portion may be subtracted from the curve of $\ln (S_A / S_{A_0})$ to give a straight line which gives the half-time of the reaction but is translated from the origin:

$$(S_A / S_{A_0}) - (S_{A_\infty} / S_{A_0}) = (S_A - S_{A_\infty}) / S_{A_0}$$

Figure 3 illustrates this curve as well as the other curves.

Some authors²⁹ plot $\ln (S_A - S_{A_\infty}) / (S_{A_0} - S_{A_\infty})$ versus time.

We can show that this is just equal to the $\ln (1 - F)$ versus time curve already defined.

$$1 - (S_B / S_{B_\infty}) = (S_{B_\infty} - S_B) / S_{B_\infty}$$

$$\text{since } S_{A_0} = S_{B_\infty} + S_{A_\infty} = S_A + S_B \Leftrightarrow S_{B_\infty} - S_B = S_A - S_{A_\infty}$$

$$\begin{aligned} 1 - S_B / S_{B_\infty} &= (S_{B_\infty} - S_B) / (S_{A_0} - S_{A_\infty}) \\ &= (S_A - S_{A_\infty}) / (S_{A_0} - S_{A_\infty}) \end{aligned}$$

$$\text{therefore } 1 - F = (S_A - S_{A_\infty}) / (S_{A_0} - S_{A_\infty})$$

thus

$$(Rx_0 / a) = Ry_\infty (a + b) / ab = cy_\infty$$

The final form of the exchange rate equation is

$$1 - y/y_\infty = e^{-ct} \quad (6)$$

or

$$\ln(1-F) = -R[(1/a) + (1/b)]t \quad (7)$$

$$\ln(1-F) = -R[(a + b) / (ab)]t$$

(R is sometimes denoted as the exchange rate constant k)

We note that the kinetics of an exchange reaction will always be of the first-order, reversible type regardless of the mechanism whereby the exchange occurs.

The half-time, $t_{1/2}$, of the exchange reaction is written as

$$t_{1/2} = (\ln 2 / R) \cdot (ab / a+b)$$

APPENDIX 2.

From equation (7) we may write

$$1 - F = 1 - (S_B / S_{B_\infty})$$

If we assign the value of S_{A_0} to S_{B_∞} , implying that all of the initial radioactivity will be present in species B at infinite time, then we have

$$1 - F = 1 - (S_B / S_{A_0}) = (S_{A_0} - S_B) / S_{A_0}$$

Since $S_{A_0} = S_B + S_A$ at any time, then

$$1 - F = S_A / S_{A_0}$$

Thus the plot of $\ln (S_A / S_{A_0})$ versus time will represent the exchange curve not corrected for the equilibrium state of the exchange reaction. The back-extrapolation of the straight-line, horizontal portion of this curve to $t = 0$ will give the intercept S_{A_∞} / S_{A_0} . Since

$$S_{A_0} = S_{A_\infty} + S_{B_\infty}$$

the value of S_{B_∞} may be determined and the corrected value of F may be calculated.

The subtraction of the back-extrapolated straight-line

portion may be subtracted from the curve of $\ln (S_A / S_{A0})$ to give a straight line which gives the half-time of the reaction but is translated from the origin:

$$(S_A / S_{A0}) - (S_{A\infty} / S_{A0}) = (S_A - S_{A\infty}) / S_{A0}$$

Figure 3 illustrates this curve as well as the other curves.

Some authors²⁹ plot $\ln (S_A - S_{A\infty}) / (S_{A0} - S_{A\infty})$ versus time.

We can show that this is just equal to the $\ln (1 - F)$ versus time curve already defined.

$$1 - (S_B / S_{B\infty}) = (S_{B\infty} - S_B) / S_{B\infty}$$

$$\text{since } S_{A0} = S_{B\infty} + S_{A\infty} = S_A + S_B \Leftrightarrow S_{B\infty} - S_B = S_A - S_{A\infty}$$

$$\begin{aligned} 1 - S_B / S_{B\infty} &= (S_{B\infty} - S_B) / (S_{A0} - S_{A\infty}) \\ &= (S_A - S_{A\infty}) / (S_{A0} - S_{A\infty}) \end{aligned}$$

$$\text{therefore } 1 - F = (S_A - S_{A\infty}) / (S_{A0} - S_{A\infty})$$

APPENDIX 3.

The wave scattered by a crystal can be characterized by the complex quantity $F(h\ k\ l)$ commonly known as the structure factor. It may be written in the following form⁵⁹:

$$F(h\ k\ l) = \sum f_j \cos 2\pi (hx_j + ky_j + lz_j) + i \sum f_j \sin 2\pi (hx_j + ky_j + lz_j)$$

where f_j is the atomic scattering factor for the j^{th} atom

h, k, l are the Miller indices

and x_j, y_j, z_j are the fractional coordinates of the j^{th} atom in the unit cell.

The intensity of the above scattered wave is given as the square of the magnitude of the structure factor:

$$\text{Intensity} = |F(h\ k\ l)|^2 = A^2 + B^2$$

$$\text{where } A = \sum f_j \cos 2\pi (hx_j + ky_j + lz_j)$$

$$\text{and } B = \sum f_j \sin 2\pi (hx_j + ky_j + lz_j)$$

It is seen by the above equations that the intensity of a diffraction line arising from a plane in the crystal is dependent of f and thus on the nature of the atoms in the crystal. The greater the number of electrons associated with the atom the greater will be the scattering power of that atom. Since barium ions have a greater number of electrons than potassium or iron ions one would expect to observe a decrease in line intensity as barium ions are replaced by the lighter ions. This will be observed for lines whose

intensities are highly dependent on the barium atoms.

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