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CO-PRECIPITATION OF RADIUM AND BARIUM SULFATES[1]

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Introduction

It has been generally recognized that when a solution of radium and barium chlorides is treated with an excess of sulfuric acid, both the barium and radium are precipitated quantitatively, even though the concentration of radium is so small that its true solubility as sulfate is far from being reached. In every case the amount of radium left in solution is many times less than would be expected from the solubility of pure radium sulfate.[2] In *partial precipitation,* the radium-barium ratios of the precipitate and filtrate are usually about equal, and this similarity to the behavior of isotopic elements has never been satisfactorily explained.

F. E. E. Germann[3] has studied the effect of digesting solid barium sulfate in a radium-barium chloride solution for 18 hours under the restricted conditions of constant time, temperature, volume, acidity and concentrations of radium and barium ions. His results indicate that the amounts of radium removed from the solution by varying the amounts of barium sulfate are in agreement with the adsorption laws of Freundlich[4] and Kroeker.[5] He concluded that the practically complete precipitation of radium, when sulfuric acid is used in excess on a radium-barium chloride solution, is due to the adsorption of *radium chloride* on the very large surface of barium sulfate exposed during precipitation.

Both these reactions were studied in the present work and extensive variations introduced in the conditions which Germann kept constant. The result of addition of sulfuric acid to a radium-barium chloride solution will be termed "*Co-precipitation*" and the action of a radium-barium chloride solution on barium sulfate will be called "*Replacement.*" The justification for this latter term will be considered later.

Assumptions and Mathematical Development

Preliminary experiments following Germann's procedure confirmed his results; but the adsorption equations used by him entirely fail to account for results obtained by varying the concentration of the barium ion, nor could they explain the quantitative results obtained by co-pre-

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[1] Published with the permission of the Director of the Bureau of Mines.

[2] Lind, Underwood and Whittemore, THIS JOURNAL, **40,** 465 (1918).

[3] Germann, *ibid.,* **43,** 1615 (1921).

[4] Freundlich, *Z. physik Chem..* **57,** 385 (1907).

[5] Kroeker, *Thesis,* Berlin, **1892.**

cipitation. A different interpretation, therefore, seemed to be necessary. A large body of data was applied to the adsorption equation and, by *empirical* modification, two equations were obtained which satisfied data from the replacement and co-precipitation experiments, respectively. From a number of considerations, a theory of the mechanism of the reaction was deduced and a plausible postulate was formulated. Finally, *equations identical with those determined empirically were mathematically derived from that postulate as follows.*

Consider a surface consisting of a radium and barium sulfate in equilibrium with a solution containing radium and barium ions. At the small concentrations used (approximately 25×10^{-8} g. of radium per liter and 0.2 g. of barium per liter) it may be assumed that the tendencies of radium ion and barium ion to precipitate, for example, as sulfates, are proportional to their respective concentrations in the solution; and since radium sulfate and barium sulfate are isomorphous it may also be assumed that the tendencies of radium ion and barium ion to escape from the surface of the solid and pass into the solution are proportional to their relative amounts (or to their "concentrations"), on the surface. Hence, at equilibrium the following condition will be true:

$$\frac{\text{(Radium atoms) on surface}}{\text{(Barium atoms) on surface}} = K\,\frac{\text{(Radium ions) in solution}}{\text{(Barium ions) in solution}} \qquad (1)$$

where K is a combination of the individual factors of proportionality.

The postulate may be stated as follows: *the radium-barium ratio of the crystal surface is proportional to the radium-barium ratio of the solution.* This is an extension of the ordinary partition law to the case of two solutes which crystallize from the solution to form mixed crystals. If pure solid barium sulfate is introduced into a solution containing radium and barium ions, a reaction will occur by which radium ions go from the solution and deposit as radium sulfate on the surface until the above condition is fulfilled. The most reasonable mechanism is the reaction

$$BaSO_4 \text{ (at surface)} + RaCl_2 \text{ (in soln.)} = BaCl_2 \text{ (in soln.)} + RaSO_4 \text{ (on surface)} \qquad (A)$$

and accordingly the process is called "Replacement." This reaction will actually take place between barium ions and sulfate ions coming from the barium sulfate surface and radium ions already present in the solution, and hence its rate will be affected by all conditions which affect the solubility of barium sulfate. By Equation 1 it is evident that *some radium will precipitate no matter how small its concentration.*

Replacement.—

$$\underset{(m_s)}{BaSO_4} + \underset{(y)}{RaCl_2} = \underset{(x)}{RaSO_4} + \underset{(n)}{BaCl_2} \qquad (B)$$

Suppose that successive small portions of barium sulfate, each having a surface containing Δm_s atoms of barium, be added to a solution of radium-barium chloride, and the above reaction be allowed to proceed to equilibrium. If the increments (or decrements) of the four substances that occur as a result of this reaction be represented by differentials, the initial and final states may be represented as follows:

	Initial values	Final values	Equivalent of final values
$BaSO_4$ (m_s)	0	$\Delta m_s - dm_s$	$= \Delta m_s - dy$
$RaSO_4$ (x)	0	dx	$= -dy$
$BaCl_2$ (n)	b	$n - dn$	$= C - y + dy$
$RaCl_2$ (y)	a	$y - dy$	$= y - dy$

It is evident from the reaction Equation B that, in terms of *molecular quantities*, all increments must have the same value, that is, $dm_s = dy = -dx = -dn$, and the total amount of the two chlorides is constant, hence: $n + y = C$, or $n = C - y$.

By substituting the equivalents of the final (or equilibrium) values into Equation 1 and neglecting dy in comparison with y,

$$\frac{-dy}{\Delta m_s - dy} = \frac{(Ky - dy)}{C - y + dy} = \frac{Ky}{C - y}.$$

Rearranging, $K\Delta m_s = [K + 1 - (C/y)]dy$. Integrating between initial and final values: $Km_s = (K + 1)(y - a) - C\,ln(y/a)$.
Substituting $n + y = C$ and rearranging,

$$ln(y/a) = -\frac{Km_s}{n + y} + \frac{(K + 1)\,(y - a)}{n + y} \qquad (2)$$

But for the radium-barium ratio used (1 part per million), $n + y$ is not measurably greater than n and the last term is negligible, so the equation[6] becomes,

$$ln(y/a) = -Km_s/n, \text{ or } ln\frac{\text{Ra}^{++}\text{ final}}{\text{Ra}^{++}\text{ initial}} = -K\frac{\text{total Ba atoms on BaSO}_4\text{ surface}}{\text{Ba}^{++}\text{ total}} \qquad (3)$$

If the increments of barium sulfate are of uniform average crystal size, the mass added is proportional to the surface, and Equation 3 may be written:

$$\log\frac{y}{a} = \lambda\frac{m}{n}, \text{ or } \log\frac{\text{Ra}^{++}\text{ final}}{\text{Ra}^{++}\text{ initial}} = \lambda\frac{\text{Wt. BaSO}_4}{\text{Ba}^{++}\text{ total}} \qquad (4)$$

The equation of Kroeker which was used by Germann has the form,

$$\log\frac{y}{a} = \lambda'\frac{m}{v} \qquad (5)$$

It is evident that the two equations are equivalent when, as in Germann's tests, the volume and concentration of barium ion are constant.

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[6] Equation 1 may be expressed either in terms of concentrations or total amounts present. In deriving Equation 2, it was necessary to express increments in terms of *molecular quantities* and not concentrations. By substituting dy for dx and dm_s (the latter cannot be measured as concentrations) we get in Equation 3 the term, m_s/n. Since m_s cannot be a concentration, n must be expressed in terms of quantity, that is, concentration times volume. Hence, the rational form for the equation is, $ln\frac{y}{a} = -K\frac{m_s}{nv}$, where v represents volume. Since the ratios of the total quantities present are the significant factors, all data have been expressed as quantities and not concentrations, thus enabling measured and not calculated values to be used.

Co-precipitation.—In the case in which sulfuric acid is added to a radium-barium chloride solution, the total effect may be considered as the result of two reactions:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl \qquad (C)$$
$$BaSO_4 + RaCl_2 = BaCl_2 + RaSO_4 \qquad (D)$$

Let sulfuric acid be added in differential amounts to a solution of radium-barium chloride. The effects of the two reactions may be combined and the following conditions set up as in the previous section.

	Initial values	Final values	Equivalent of final values
$BaSO_4$ (m)	0	dm	= dn
$RaSO_4$ (x)	0	dx	= dy
$BaCl_2$ (n)	b	n − dn	= n − dn
$RaCl_2$ (y)	a	y − dy	= y − dy

The last column follows from the obvious fact that the total barium sulfate formed equals the total barium chloride lost and the total radium sulfate formed equals the total radium chloride lost. Substituting in Equation 1: $\frac{dy}{dn} = K\frac{y-dy}{n-dn}$. Neglecting d$y$ in comparison with y and dn in comparison with n, and rearranging, this becomes $\frac{dy}{y} = K\frac{dn}{n}$. This equation may be integrated between the initial and final concentrations of radium chloride and barium chloride, giving

$$ln\,\frac{y}{a} = K\,ln\,\frac{n}{b}, \quad \text{or} \log\frac{(Ra^{++})\ \text{final}}{(Ra^{++})\ \text{initial}} = K\log\frac{(Ba^{++})\ \text{final}}{(Ba^{++})\ \text{initial}} \qquad (6)$$

It is worth noting that if the solubility product of radium sulfate were exceeded, that substance would be precipitated as a mixed crystal with barium sulfate by a reaction analogous to (A) above, but the derivation and equation would still be true. Since Equations 2, 3 and 6 are derived from Equation 1 it follows that K is the same in each case.

Preparation of Material

About 50 g. of crude radium-barium sulfate was fused with sodium-potassium carbonate and the melt digested in hot water and washed with dil. ammonium hydroxide. The insoluble barium and radium carbonates were dissolved in hydrochloric acid, the solutions diluted and boiled until free from carbon dioxide. Ammonium hydroxide and hydrogen sulfide were added to precipitate iron, lead, etc., and the solution was again filtered. After precipitation with excess of sulfuric acid, these operations were repeated on the sulfates. By repeated fractional crystallization of the chlorides four pure products of varying radium-barium ratio were obtained and made up into standard solutions.

Analytical Methods

The radium determinations were made according to the procedure of Lind[7] and are believed to be accurate within 2%. The instruments were standardized with the stand-

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[7] Lind, *J. Ind. Eng. Chem.*, **7**, 1024 (1915).

ard solutions prepared from pure radium chloride by Lind and Roberts.[8] All reagents were tested and found to be free from radium.

Adsorbed barium chloride was determined by the following modification of a method developed by Duschak and Hulett.[9] After filtering and drying at a low temperature, the barium sulfate was placed in a small glass retort with 30 cc. of concd. sulfuric acid and heated on a water-bath. Purified air, aspirated through the retort, carried the liberated hydrogen chloride gas to a Liebig bulb containing dil. potassium hydroxide solution. After two hours' aspiration the alkali solution was washed out of the Liebig bulb, acidified with dil. nitric acid and then made just alkaline with potassium carbonate solution, using methyl orange as an indicator. Then with 0.5 cc. of a 1% solution of potassium chromate as an indicator, the solution was titrated to a faint pink with standard silver nitrate solution. All reagents were measured and a blank was run with the same amounts. This method gave a sharp end-point and duplicate experiments checked very closely. The barium sulfate used in the replacement experiments was precipitated from a C. P. barium chloride solution with sulfuric acid.

Replacement

Experimental Method.—The usual procedure was as follows. A weighed portion of barium sulfate mixed with 10 cc. of a standardized radium-barium chloride solution in a flask was made up to 80 cc. with distilled water. The flask was connected to a reflux condenser and the liquid was boiled for a definite time. The barium sulfate was then filtered from the hot solution and usually ignited and weighed or analyzed for ad-

TABLE I

REPLACEMENT

$$\log (y/a) = \lambda (m/n)$$
$$Ba^{++} (n) = 0.0150 \text{ g.}$$

Test	$Ra^{++} \times 10^8$ g. [Initial (a) 2.01] Final y	—Log (y/a)	$BaSO_4$ m G.	Ba^{++} (n) G.	m/n	Eq. 4 $-\lambda$	Eq. 5 $-\lambda'$
A 1	1.486	0.1303	0.10	...	6.67	0.0195	0.104
2	1.080	.2685	.20	...	13.33	.0201	.107
3	0.814	.3914	.30	...	20.00	.0196	.104
4	.618	.5110	.40	...	26.67	.0192	.102
5	.458	.6415	.50	...	33.33	.0193	.103
$BaSO_4$ (m) = 0.30 g.							
B 1	0.378	0.7247	..	0.015	20.00	0.0362	0.1935
2	.768	.4168	..	.030	10.00	.0417	.1111
3	1.235	.2104	..	.060	5.00	.0421	.0561
4	1.456	.1391	..	.090	3.33	.0417	.0371
5	1.563	.1079	..	.120	2.50	.0432	.0287

A. Effect of variation in amount of $BaSO_4$. Time, 20 hours. Volume, 80 cc. HCl acidity, 0.0053 *N*. Preparation of $BaSO_4$; precipitate hot, digest for 2 hours, filter, ignite.

B. Effect of variation in concentration of $BaCl_2$. Time, 20 hours. Volume, 80 cc. HCl acidity, 0.185 *N*. Preparation of $BaSO_4$; precipitate cold, filter, ignite.

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[8] Lind and Roberts, THIS JOURNAL, **42,** 1170 (1920).

[9] Duschak and Hulett, *Z. anorg. Chem.*, **40,** 196 (1904).

sorbed barium chloride. The radium content of the filtrate was determined by the emanation method. All variations in the procedure are fully indicated in the tables.

Repetition of Germann's Work.—The results of repeating Germann's work, in which only the barium sulfate, m_s, is varied, are shown in Table I, A. The constancy of the numbers in the column headed $-\lambda$ shows that Equation 4 holds very closely. The column headed $-\lambda'$, calculated by use of Equation 5, shows that under these conditions Kroeker's equation also holds. In Fig. 1, Curve A is a plot of the results of this series.

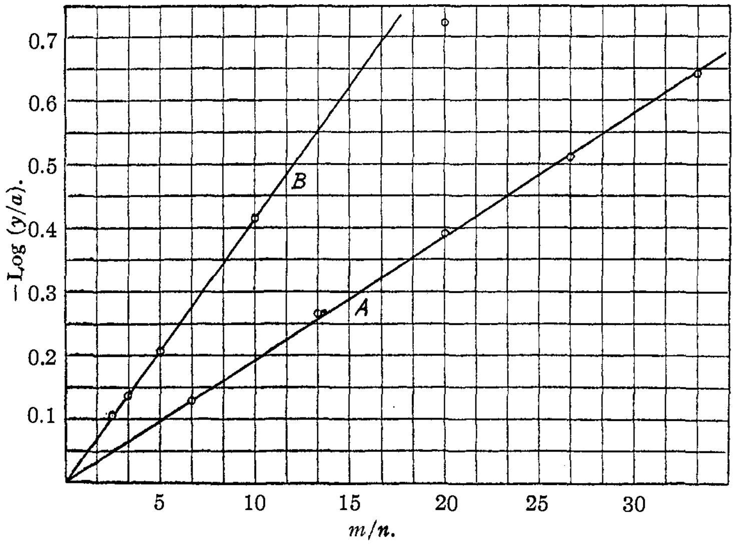

Fig. 1.—Replacement. Eq. 4.

Variations in the Radium-Barium Ratio.—The effect of varying the initial radium-barium ratio of the solution while adding a constant amount of barium sulfate is shown in Table I, B, and the results are plotted as Curve B in Fig. 1. Evidently, Equation 4 holds very well, but the wide variation in λ' shows the inadequacy of Kroeker's equation.

Variation of Volume.—When the concentration of free hydrochloric acid is kept constant, dilution has no appreciable effect upon the equilibrium or the value of $-\lambda$.

Variation in Time of Digestion.—It has been noted by numerous workers that in true adsorption, equilibrium is reached rapidly. A study of the progress of the equilibrium with time seemed likely to throw light on the mechanism of the process. Accordingly, several series of tests were made in which identical conditions were maintained for various periods. The data listed in Table II and plotted in Fig. 2, show that the reaction does not reach equilibrium in five days and, in solutions of low acidity, very little change in the rate of the reaction takes place during that time.

TABLE II

REPLACEMENT

$$\text{Log}\ (y/a) = \lambda(m/n)$$

EFFECTS OF TIME, ACIDITY AND CRYSTAL SIZE

Test	$Ra^{++} \times 10^8$ g. [Initial (*a*) 5.075] Final *y*	—Log(*y*/*a*)	$BaSO_4$ (*m*) G.	Time hours	Eq. 4 —λ
A 1	4.57	0.0453	0.4725	24	0.0006
2	4.23	.0792	.4616	48	.0011
3	3.56	.1538	.4500	96	.0022
4	3.21	.1987	.4448	120	.0029
B 1	1.820	.4456	.4575	24	.0062
2	1.300	.5911	.4494	48	.0084
3	0.449	1.0531	.4676	96	.0144
4	.411	1.0916	.4593	120	.0152
[Initial (*a*) 201]					
C 1	1.685	0.0755	1.00	1	.0011
2	1.524	.1189	1.00	2	.0078
3	1.200	.2253	1.00	4	.0034
4	0.225	.8500	1.00	16	.0128
5	.217	.9657	1.00	24	.0145
D 1	.588	.5340	0.2090	24	.0383
2	.368	.7372	.2090	48	.0529
3	.336	.7767	.2090	72	.0558
4	.233	.9360	.2090	120	.0672

A and B. Preparation of $BaSO_4$: Precipitate and digest for three days in 0.2 *N* HCl. $Ba^{++}(n)$, 0.0064 g. HCl, 0.006 *N*.

C and D. Preparation of $BaSO_4$: Precipitate, digest for two hours, filter, ignite; volume, 80 cc. $Ba^{++}(n)$, 0.0150 g. HCl, (C), 0.06 *N*, (D) 0.12 *N*.

Equilibrium with a fixed surface area would be expected in a much shorter period of time by either adsorption or replacement. The results seemed to be explicable only by assuming crystal growth during a process of replacement.

Effect of Crystal Growth.—Barium sulfate prepared, as this was, by precipitation always shows considerable variation in the size of the particles. Since the smaller particles have greater solubility,[10] during digestion the larger particles will grow at the expense of the smaller. Microscopic observations indicate that there is also marked rearrangement of crystal forms. The process causes a considerable reduction in the total surface exposed. Since the term "adsorption" can be considered as excluding any manner of inclusion *beneath* a crystal surface, the amount of adsorption will depend upon the surface area of the barium sulfate *at equilibrium*, and any crystal growth during digestion will decrease

[10] Hulett, *Z. physik. Chem.*, **37**, 385 (1901).

the surface area and therefore the amount of radium adsorbed. Deposition by replacement, on the contrary, depends upon the total surface exposed during the total time of contact and will be greatly increased by crystal growth. As long as crystal growth continues, radium sulfate will

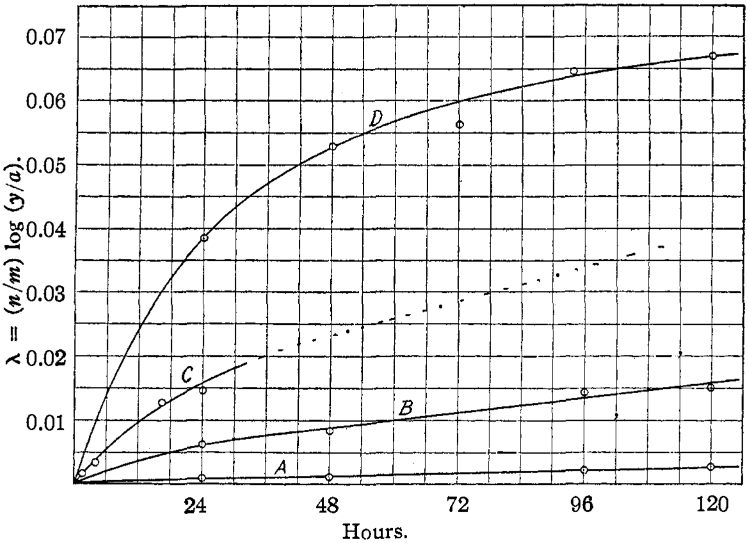

Fig. 2.—Replacement. Eq. 4.

Table III

Replacement vs. Adsorption

Test	$Ra^{++} \times 10^8$ g. [Initial (*a*), 2.01] Final *y*	—Log(*y*/*a*)	$BaSO_4$ (*m*) G.	HCl *N*	$BaCl_2$ adsorbed Mg.	—λ
A 1	1.890	0.0253	0.222	0.000	2.4	0.0017
2	1.500	.1258	.216	.0375	0.8	.0087
3	1.345	.1732	.211	.0560	.6	.0123
4	1.206	.2201	.236	.1686	.4	.0140
5	0.644	.4935	.223	.9350	.0	.0331

Test	$Ra^{++} \times 10^{12}$ ions [Initial (*a*), 53.8] Final *y*	—*ln*(*y*/*a*)	Ba atoms (*n*)10^{18}	HCl *N*	Sq. cm.[a] G.	*K*
B 1	50.7	0.0110	0.1676	0.00	1795	4.32
2	40.2	.0544	.1238	.0375	1364	29.00
3	36.1	.0753	.9940	.0560	1116	50.00
4	32.4	.0957	.1180	.1686	1188	53.50
5	17.3	.2147	.1133	.9350	1206	125.10

$BaSO_4$ digested for seven days before adding radium-barium chloride solution. Reaction time, three days; volume, 80 cc.

A. Calculated by Eq. 4, $\log (y/a) = \lambda(m/n)$. Ba^{++} (n), 0.0150 g.

B. Calculated by Eq. 3, $ln\ (y/a) = -K(m_s/n)$. Ba^{++} $(n \times 10^{18}$ ions), 6.6.

[a] Approximate crystal surface, sq. cm. per g.

be buried in the larger crystals, and fresh surfaces of barium sulfate will be exposed for continued deposition. The chief factors affecting the rate of crystal growth, namely, acidity, crystal size and temperature, will be considered.

Effect of Hydrochloric Acid.—It is well known that the presence of hydrochloric acid increases the solubility of barium sulfate which, in turn, favors crystal growth. The previous discussion indicates that increasing acidity should be accompanied by an increasing rate of replacement as measured by the increase of $-\lambda$ with time. Fig. 2 shows this to be the case. In Table III, A, and Fig. 3 are shown the effects of various acidities on the value of $-\lambda$ and the amount of barium chloride adsorbed during a fixed time of 20 hours. Since radium and barium are so similar, it would be reasonable to assume that the decrease in the adsorption of barium chloride with increasing acidity would be accompanied by a decrease in the amount of radium chloride adsorbed. But the total amount of radium removed from solution increased rapidly as the acidity increased, a fact which cannot be accounted for by adsorption, but could be predicted by the replacement theory.

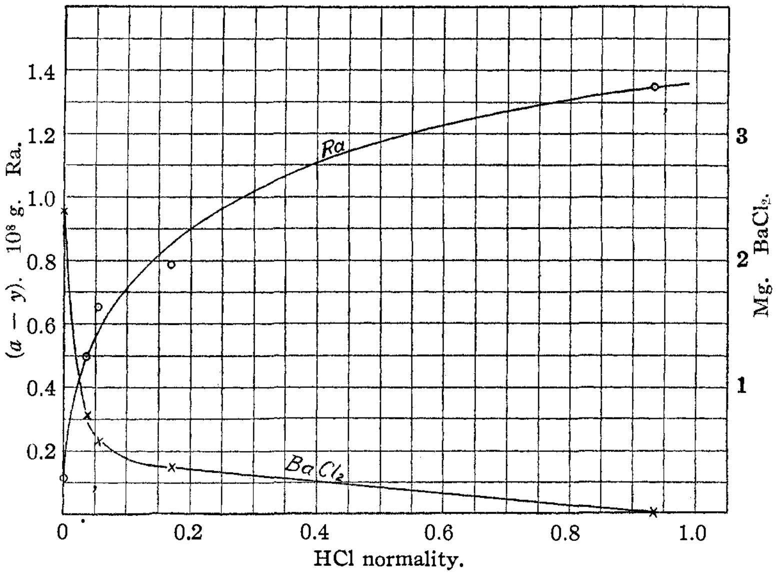

Fig. 3.—Replacement *vs.* adsorption.

Effect of Crystal Size.—The rate of crystal growth and therefore the rate of replacement, must decrease as the average crystal size increases. A comparison of the rates of reaction with differently prepared samples of barium sulfate shows that replacement is more rapid on the precipitates of finer grain. For example, in Test 2, A and B, crystal growth during reaction was reduced to a minimum by three days of *previous* digestion of the barium sulfate in 0.2 *N* hydrochloric acid; while in Test 2, C and D, the sulfate had been filtered and ignited after only two hours' digestion. In Test 1, A and B, the difference in the values of λ is due to preparation of the barium sulfate by precipitation from a hot acid solution and a cold neutral solution, respectively.

Effect of Temperature.—The *amount* of *adsorption* at equilibrium should be highest from a cold, neutral solution. Under these conditions the concentration of sulfate ion is extremely low, and therefore very little crystal growth and minimum replacement would be expected. Four days' contact of barium sulfate with a cold, neutral solution of radium-barium chloride gave *no measurable deposition of radium,* but a duplicate test on a hot plate without agitation deposited about 50% of the radium on the barium sulfate. *It is evident that adsorption must be a negligible factor.*

Reversibility.—A number of tests were made to determine to what extent the replacement reaction was reversible. The barium sulfate was precipitated hot and digested for two hours before the radium-barium chloride solution was added. The final acidity was 0.06 *N*, so considerable crystal growth, with resultant irreversibility, was to be expected. After twenty hours' digestion the crystals were filtered off, washed and transferred to 125 cc. of a 0.06 *N* hydrochloric acid solution containing 0.375 g. of barium, as chloride. After digestion for 20 hours, 5.2% of the radium originally on the barium sulfate had dissolved. This indicated that most of the radium was in the interior of the crystals, for in such a concentrated barium solution nearly all of the radium on the surface would pass into solution in accordance with the equilibrium expressed in Equation 1. In a duplicate test, the barium chloride was omitted from the second solution and in this case only 1.7% of the radium passed into solution.

Calculation of the Distribution Constant.—Since the derivation of Equation 3 is based upon the assumption of no crystal growth, *K* can be evaluated only by eliminating this factor. With that end in view, several portions of barium sulfate were digested in various concentrations of hydrochloric acid for seven days. Microscopic examination revealed rapid crystal growth and rearrangement at first, especially in those tests showing a marked acidity. During the last three days the change in *average* crystal size was not measurable, although crystal growth undoubtedly took place. The solutions were then removed by decantation and replaced by radium-barium chloride solutions having the same acidities, respectively, as the solutions replaced. The digestion was continued for three more days; then filtration and radium measurements were made as usual. The results are listed in Table III, A.

Measurements of average crystal size permitted a calculation of the total number of barium sulfate molecules on the surface of the crystals, and the number replaced by radium was determined by the amount of radium removed from solution. These data were substituted in Equation 3 and are tabulated in Table III, B. The values found for K range from 125.1 in the solution of highest acidity to 4.32 for that of lowest acidity.

Referring to Fig. 2, A, which is based upon a test, comparable to Test 3, B, 1, it is evident that there is no definite point at which replacement due to crystal growth becomes a major factor. It is fairly reasonable to assume, however, that equilibrium with the *initial* surface would be practically complete in 24 hours. The value of λ and therefore of K after 24 hours is about 40% of the value obtained after three days. Assuming that equilibrium with the initial surface is practically complete and the effect of crystal growth negligible, after 24 hours, the *most probable* value for K is 40% of 4.32 or about 1.7.

Distinction between Adsorption and Replacement.—If the effects of crystal growth were eliminated it would be difficult to distinguish between adsorption and replacement. *The process of adsorption of two solutes should reach an equilibrium expressible in the form of the "Replacement" equation.* It is not the agreement of data with Equation 4 that disproves adsorption as a major factor, but the *effects of crystal growth* as discussed under "Time of Digestion," "Acidity," "Crystal Size," "Temperature" and "Reversibility."

Co-precipitation

Experimental Method.—These experiments were performed in three different ways.

(1) Sulfuric acid was added to radium-barium chloride solutions without special regard to temperature or agitation. The precipitate was removed by filtration, dried and weighed and the radium remaining in the solution found by the usual emanation method. From these measurements the final concentrations of both radium ion and barium ion could be calculated for substitution in Equation 6.

(2) Dil. sulfuric acid was added in very small portions to the hot, agitated radium-barium chloride solution and the crystals were digested between each addition of acid. The subsequent procedure was the same as described above.

(3) Dil. sulfuric acid was added to the radium-barium chlorides dissolved in such a large volume of solution that no precipitation of sulfates occurred. By subsequent evaporation and cooling the sulfates were obtained.

Rapid Precipitation.—By Equation 3 it is evident that complete precipitation of barium involves complete precipitation of radium. The equation is based upon the assumption that equilibrium is established after each increment of precipitation and experimental procedure must effect this in order to obtain the correct value for K. But if, during a partial precipitation, the sulfuric acid precipitates practically *all* the barium ions in its vicinity, then by Equation 3 all the radium ions in the vicinity will also be precipitated. Hence, no enrichment will take place and the *apparent* value of K will be unity. Decreasing the initial concentration of the radium-barium chloride solution, or increasing the concentration of hydrochloric acid, will result in a somewhat smaller fraction being precipitated in this way and the distribution equilibrium will result in *some* enrichment of one constituent. This is illustrated by the increasing values of K in Table IV, A. For the reasons discussed under "Crystal Growth," these facts may be interpreted by the theory of replacement, but do not appear to be consistent with a theory based upon adsorption.

TABLE IV

CO-PRECIPITATION

Equation 6; $\log (y/a) = K \log (n/b)$

Test	$Ra^{++} \times 10^8$ g. a Initial	y Final	—Log(y/a)	Ba^{++} (b) Initial	g (n) Final	—Log(n/b)	HCl N	K (×)
A 1	5.075	3.49	0.1630	0.381	0.262	0.1626	0.04	1.003
2	5.075	1.03	.6928	.381	.085	.6522	.04	0.061
3	33.56	16.70	.3032	.250	.134	.2710	.11	1.119
4	107.0	47.15	.3560	.131	.065	.3060	.20	1.163
5	266.0	108.0	.3909	.058	.0295	.2976	.40	1.314
								(△)
B 1	10.02	0.840	1.0755	.075	.0155	.6861	0.80	1.568
2	10.02	.673	1.1725	.075	.0139	.7328	1.10	1.595
3	8.02	5.760	0.1436	.060	.0488	.0899	0.80	1.598
4	5.01	1.885	.4245	.0375	.0210	.2518	.40	1.686
								(⊙)
C 1	5.37	1.583	.5302	.0378	.0185	.3096	.67	1.713
2	2.15	1.150	.2718	.0750	.0533	.1482	.67	1.833
3	5.01	1.595	.4969	.0375	.0205	.2625	.80	1.893

A. Rapid precipitation; increasing values of K attributed to increase of acidity or small precipitate, that is, $b - n$.

B. Slow addition of acid with rapid agitation.

C. Precipitation during concentration and cooling. Initial volume, 200 cc. Final volume, 50 cc.

Slow Precipitation.—The results of slow addition of sulfuric acid to the hot, agitated solutions of radium-barium chlorides gave an average value for K of 1.6, as shown in Table IV, B. Since special precautions were taken to prevent complete local precipitation this value is probably quite close to the true value of the distribution constant. Apparently the initial concentration and fraction precipitated have no appreciable effects on the value of K.

Precipitation by slow evaporation is the ideal method for obtaining the true distribution constant, for equilibrium may be very closely approached throughout the process. Table IV, C, gives some representative data. The average value of K is approximately 1.8 for all the experiments of this type.

In Fig. 4 are plotted typical data by each method of precipitation, in which the results of the three methods are distinguished by different symbols. If rapid precipitations are eliminated, the values for K are fairly constant over a wide range of concentrations and fraction precipitated and there is *no trend* from a straight line. The variations should be attributed to a failure to reach equilibrium at every stage of precipitation rather than to analytical error.[11] Therefore the value, $K = 1.6$, is probably low and the actual value is close to 1.8, with a probable accuracy of ± 0.1.

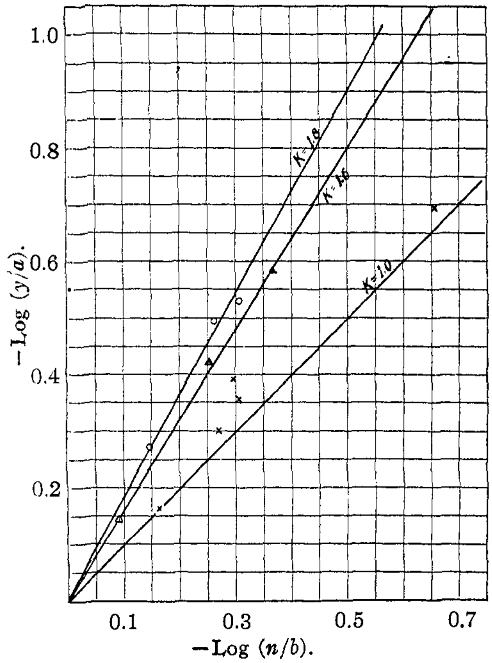

Fig. 4.—Co-precipitation. Eq. 6.

Discussion

The time required to reach equilibrium and the value obtained for "K" by co-precipitation confirm the assumptions made in estimating the *probable value* of 1.7 by the data on replacement. From more than three hundred tests no datum was obtained which was not consistent with the replacement theory. The essential difference between co-precipitation and replacement lies in the condition that

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[11] Co-precipitation and fractional crystallization are analogous and, under certain conditions, identical phenomena. It is suggested that the equation, $\log (y/a) = K \log (n/b)$, may express a more exact relation than the empirical formula, $Q = e^{kp}$, previously used for fractional crystallization [Schlundt, Herman, "Mesothorium," *Bur. Mines Tech. Paper*, No. 265, 35 (1922)], in which Q is the fraction of one constituent remaining in the mother liquor and p is the percentage of salt separated in the crystals.

It has been recognized that the equation, $Q = e^{kp}$, is not exact, because when p becomes unity, Q does not become zero as it should. Equation 2 has no such limitation and the theoretical considerations by which the equation is derived apply with exactness to the conditions of fractional crystallization. The *partition factor, K, should not be confused with the enrichment factor* (that is, the "Ra-Ba" ratio of the crystals divided by that of the original solution). It may be noted that the enrichment factor for a 40% precipitation of radium and barium sulfates, 1.39, is of the same order of magnitude as that for the chlorides, 1.6, and the bromides, 2.2.

for the latter only the *surface* of the *added* barium sulfate comes to equilibrium with the radium-barium chloride solution, while in the former, each crystal layer as it forms is in distribution equilibrium with the particular concentration of solution existing *at that time.*

Since the solution has a decreasing radium-barium ratio as the precipitation proceeds, the crystals will not be uniform in composition throughout their mass, unless distribution equilibrium in a solid solution is established comparatively rapidly, which is not probable. The assumption has been made in both instances that distribution equilibrium within a *solid* solution comes about so slowly that it does not interfere with the establishment of distribution equilibrium between the *surface* and the *solution.*

It seems probable that these equations are laws that will hold for any isomorphic salts formed by two similar elements with a common ion. But just as the laws of solution are accurate only for dilute solutions, similar theoretical reasons indicate that these relations may be modified when the ratios of the two elements are closer to unity. It is only with radio-active salts that accurate measurements can be made at the very low concentrations required to give ratios of the high order of magnitude in which a constant value for K may be expected.

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Summary

In the presence of a large excess of barium over radium, sulfate ions will precipitate radium even though the solubility product of radium sulfate is not exceeded. This unexplained phenomenon was investigated by a quantitative study of the reactions of a radium-barium chloride solution with (a) sulfuric acid, and (b) barium sulfate.

At equilibrium, the reversible reaction, $BaSO_4 + RaCl_2 \rightleftarrows BaCl_2 + RaSO_4$, gives a distribution of radium and barium represented by the equation

$$\frac{Ra^{++}\text{ (final)}}{Ra^{++}\text{ (initial)}} = K\frac{Ba^{++}\text{ (final)}}{Ba^{++}\text{ (initial)}}$$

From this fundamental equation, special equations, adapted to the quantities measured by each experimental method, were derived. These equations were identical with empirical equations deduced from quantitative data. K was evaluated by each method as approximately 1.8. Crystal growth was found to have a very great influence on the equilibrium.

The possible application of the equations to adsorption, fractional crystallization and co-precipitation is discussed.

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