

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## THE FRACTIONAL PRECIPITATION OF BARIUM AND RADIUM CHROMATES<sup>1</sup>

BY L. M. HENDERSON AND FRANK C. KRACEK<sup>2</sup>

RECEIVED DECEMBER 24, 1926

PUBLISHED MARCH 9, 1927

A survey of the solubilities of the alkaline-earth chromates shows a decided decrease in solubilities with increasing atomic weight of the alkaline earths. At about 15° the solubility of the metastable, anhydrous calcium chromate is of the order of 25 g. per liter; that of anhydrous strontium chromate, 1.2 g. per liter and of anhydrous barium chromate, 0.0033 g. per liter. It is seen that barium chromate is about 350 times as insoluble as strontium chromate. Generalizing from these figures, it appears probable that radium chromate is the least soluble of the alkaline-earth chromates.<sup>3</sup> That the general trend of solubilities of radium compounds can be predicted with some certainty is evident from a study of the solubilities of chlorides, bromides, sulfates and hydroxides. Radium chloride and radium bromide concentrate in the crystalline phase when solutions of barium-radium chloride and barium-radium bromide are subjected to fractional crystallization. Both the chlorides and bromides of the alkaline earths show a decreasing solubility from calcium to barium. The same is true of the sulfates. The solubility of radium sulfate was determined by Lind, Underwood and Whittemore<sup>4</sup> and was found to be about one one-hundredth that of barium sulfate.

Furthermore, the solubility of alkaline-earth hydroxides increases from calcium to barium. In fractional crystallization of barium-radium hydroxide, the radium remains largely in the liquid phase<sup>5</sup> in agreement with the above generalization. However, such predictions of the solubilities of radium compounds can be made with only approximate accuracy. Radium sulfate is about 100 times as insoluble as barium sulfate, yet fractionation of barium-radium sulfate shows only an insignificant enrichment of radium in the precipitate.

The problem of separation of radium from barium by the fractional precipitation of the chromates of these elements is of interest not only from the standpoint of possible confirmation of the generalization respecting the prediction of the trend of the solubilities of analogous compounds within a given group of the periodic table, but for practical reasons as

<sup>1</sup> From a thesis submitted by Frank C. Kracek in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Minnesota.

<sup>2</sup> Du Pont Fellow.

<sup>3</sup> The figures quoted above are from Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, 1919, 2nd ed.

<sup>4</sup> Lind, Underwood and Whittemore, *THIS JOURNAL*, **40**, 465 (1918).

<sup>5</sup> (a) Strong, *ibid.*, **43**, 440 (1921). (b) McCoy, U. S. pat. 1,103,600, 1914.

well. At the present time, one of the best and most widely used methods for the isolation of radium is the fractional crystallization of the bromides of barium and radium. It was hoped that the chromates would show a greater efficiency than the bromides. Results of the work indicate that the efficiency of the chromate fractionation is approximately equal to the best value reported for the bromides,<sup>6</sup> and exceeds some values.<sup>8</sup>

### Experimental Part

**Preparation of Materials.**—The supply of radium used was obtained from carnotite ore<sup>7</sup> by the Bureau of Mines nitric acid process.<sup>8</sup> The resulting crude barium-radium sulfate was reduced with wood charcoal in an electric-muffle furnace using pure graphite crucibles. The reduced mass was decomposed by hydrochloric acid, filtered and purified. About 250 kg. of carnotite ore worked up in this manner yielded solutions of barium-radium chloride containing in all about 2 mg. of radium associated with a considerable amount of barium. These solutions were carefully standardized with respect to both the barium and radium content.

**Analytical Method.**—Barium was usually determined by weighing barium chromate. For the sake of uniformity, the results have been expressed in terms of the barium, inasmuch as radium is measured always in terms of the element.

Radium measurements were made by the emanation method. Calibration of the electroscopes was based mainly on a radium standard solution measured by the Bureau of Standards in 1917, at which time it contained  $12.3 \times 10^{-9}$  g. of radium per cc. The strength of this solution has not changed appreciably with age, as shown by the fact that a solution prepared from a tube of radium bromide made available in 1923, and containing 2.133 mg. of radium by a Bureau of Standards measurement, checked the electroscope constant determined by using the previous solution to within 2%. The calibration was checked at frequent intervals.

### Experimental Procedure and Results

The fractionation experiments were performed with two different general purposes in view. (1) To ascertain the efficiency of fractionation when different percentages of the total barium content were precipitated from identical solutions under definite conditions. Solutions containing approximately 1 g. of barium having a radium-barium ratio of the order of  $10^{-6}$  g. of radium per g. of barium were chosen for this purpose. The exact values and experimental conditions are given in connection with each series. (2) To ascertain the efficiency of fractionation when solutions of different radium-barium ratio were subjected to fractional precipitation. The range covered in these experiments lies between  $10^{-9}$  and  $10^{-2}$  g.

<sup>6</sup> (a) Nierman, *J. Phys. Chem.*, **24**, 192 (1920). (b) Scholl, *THIS JOURNAL*, **42**, 889 (1920).

<sup>7</sup> Kindly furnished by Dr. H. N. McCoy.

<sup>8</sup> Parsons, Moore, Lind and Schaefer, *Bur. Mines Bull.*, 104 (1915).

of radium per g. of barium. In other words, the richest samples were  $10^7$  times richer in radium than the poorest ones. This range extends from the lowest economical limit in the recovery of radium and was limited at the upper end only by the relatively small amount of radium available.

**Methods of Fractionation.**—The definite procedure followed in making fractional precipitations was suited to each series of experiments, depending upon the conditions imposed. In general, it consisted in treating portions of barium-radium chloride solutions with a definite quantity of hydrochloric acid, followed by slow addition (with stirring) of a definite amount of potassium chromate solution. Some of the experiments were performed in neutral solutions. In such cases the procedure was modified by eliminating the addition of the acid. The solutions were warmed to  $70-90^\circ$  before precipitation. After precipitation the solutions were set aside in a closet at room temperature for a period of one to two days, filtered and analyzed for both radium and barium. The radium and barium content of the original solutions being known, the filtrates only needed to be analyzed. In most cases, however, analyses were made of the precipitates also.

In experiments of Type 2, the fractionation procedure was modified for practical reasons. Here one was dealing with large amounts of solution containing, as a rule, equivalent quantities of barium and chromate in addition to the radium. The barium chromate, kept in solution by sufficient quantities of hydrochloric acid or nitric acid, was partially precipitated by slow addition of a solution of sodium hydroxide or potassium hydroxide in required amounts. In other respects, such as heating, etc., the procedure was parallel to that employed in experiments of Type 1.

Distilled water used throughout the work was tested for impurities capable of precipitating radium.

**Method of Expressing Results.**—In fractional crystallization or precipitation of solutions of two salts capable of separation by this method, an enrichment of one of the constituents in the crystalline phase involves necessarily a corresponding impoverishment of the same constituent in the solution phase. It is obvious that if an enrichment factor  $E_p$  is calculated for the precipitate as the ratio of the two constituents in the precipitate to their amounts in the original solution, there will be a corresponding impoverishment factor  $E_f$  for the solution. These factors individually are without meaning unless the fraction of one of the constituents precipitated or remaining in solution is given. For example, in one of the experiments it was found that 18.4% of barium carried down 77.4% of radium;  $E_p = 4.21$ . In another, 33.2% of barium carried down 89.4% of radium,  $E_p = 2.69$ . Had the radium been carried down quantitatively, the respective values of  $E_p$  would have been 5.43 and 4.01. The impoverishment factor for the solution phase in these two experi-

ments was  $E_f = 0.278$  and  $0.160$ , respectively. It will be seen in subsequent discussion that the quotient of these two factors<sup>9</sup> can be used as a measure of fractionation efficiency irrespective of the fraction of barium precipitated. Thus, in the two experiments quoted,  $D$  (the partition factor) =  $15.1$  and  $15.8$ , respectively. If no separation takes place,  $D = 1.0$ . However, if all of one constituent should either pass into the precipitate or remain in the solution,  $D = \infty$  or  $0$ . The significance of this value will be discussed below.

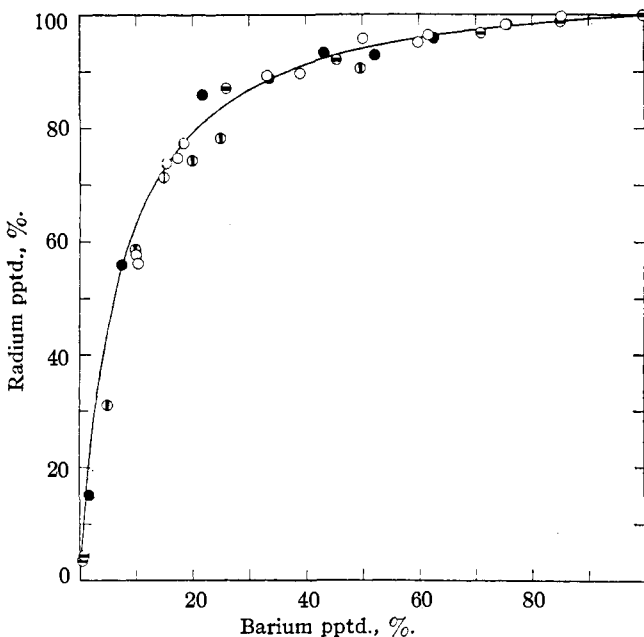


Fig. 1.—The fractional precipitation of barium and radium chromates. ○, Series I, acid; ●, Series II, acid; ⊙, Series III, acid; ⊖, Series IV, neutral. The curve represents values at  $D = 15.5$ .

The following symbols are used in presenting the experimental results:  $Ra_p$ ,  $Ra_f$  = g. of radium;  $Ba_p$ ,  $Ba_f$  = g. of barium;  $R_p$ ,  $R_f$  = radium-barium ratio in precipitate or filtrate, respectively;  $E_p$ ,  $E_f$  = enrichment factor in precipitate and impoverishment factor in filtrate;  $D = (R_p/R_f) = (E_p/E_f)$  = partition factor.

**Effect of the Fraction of Barium Precipitated on the Fraction of Radium Precipitated.**—The experiments comprise four complete series of experiments of Type 1.

Series I and II are parallel in all respects except that in I the acidity

<sup>9</sup> For a discussion of crystallization factors, see Barker and Schlundt, *Univ. Missouri Bull.*, 24, No. 26, 45 (1923).

varies from 0.05 *N* to 0.3 *N*, approximately, while in Series II the volumes of the solutions were adjusted to maintain the acidity quite constant at 0.265 *N*. Each member of these series contained 1.082 g. of barium and  $3.60 \times 10^{-6}$  g. of radium. The warm, acidified radium-barium chloride solutions were treated with quantities of potassium chromate solution stoichiometrically equivalent to the barium present, the amount of barium chromate precipitated being controlled by varying the amounts of acid added to the various members. (See Fig. 1.)

Series III differs from the two preceding ones in that the amount of potassium chromate solution used is equivalent stoichiometrically to five

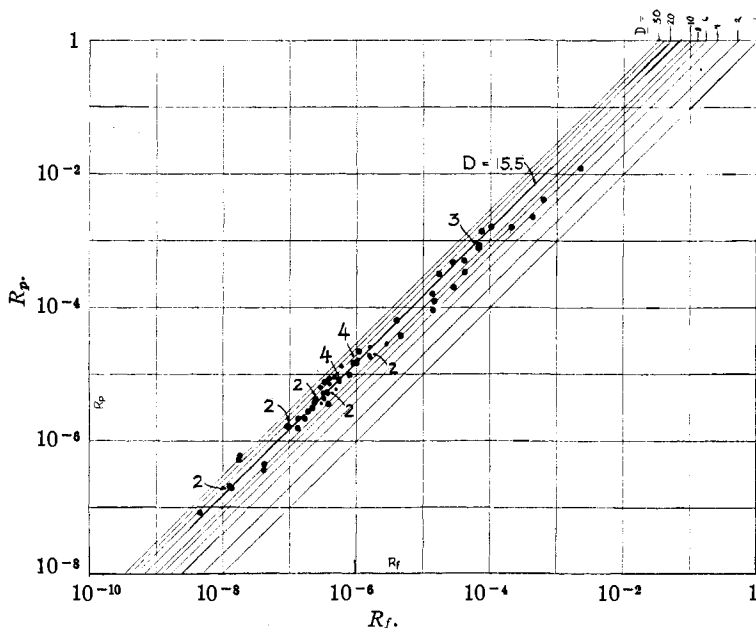


Fig. 2.—Effect of varying the radium-barium ratio on the value of the factor *D*.

times the quantity of barium in each member. Each member of the series contained 0.5073 g. of barium and  $1.36 \times 10^{-6}$  g. of radium. The method of fractionation was similar to that in I and II, correspondingly larger amounts of acid being necessary to keep any desired fraction of barium in solution. Acidity was never allowed to exceed 0.3 *N*.

In Series IV partial precipitation was performed in neutral solutions, just enough potassium chromate solution being added to precipitate a desired fraction of the barium. Each member contained 1.0766 g. of barium and  $4.98 \times 10^{-6}$  g. of radium.

**Effect of Varying the Radium-Barium Ratio.**—To make a sufficiently thorough study of this method of fractional separation of radium from

barium, it is necessary to know the variation of the partition factor over a considerable range of the radium-barium ratio.

The original purified solutions of radium-barium chloride obtained from the carnotite ore were accordingly subjected to fractional precipitation, the leanest mixtures containing about  $10^{-9}$  g. of radium per g. of barium, the richest about  $10^{-2}$  g. As will be seen from the results presented below (Fig. 2), the separation factor averages nearly 15.5 over the entire range except in the region of mixtures very rich in radium. Owing to the extremely small amounts of precipitates worked with in this region, experimental error may account for some of the deviation.

The technique employed in the larger scale fractionations did not differ essentially from that employed in the series of experiments reported above. The results reported in Table I (not included in Fig. 2) were obtained in

TABLE I  
NEUTRAL SOLUTIONS<sup>a</sup>

No.	Original solutions		$R_p \times 10^6$	$R_f \times 10^6$	$D$
	G. of Ra $\times 10^6$	G. of Ba			
1	185.7	65.16	8.33	1.48	5.60
2	192.4	67.63	8.82	1.42	6.20
3	179.8	186.90	3.18	0.733	4.34
4	124.4	169.40	1.67	.625	2.67
5	95.30	151.90	1.46	.534	2.73
6	72.9	136.70	1.59	.415	3.83

<sup>a</sup>  $R_0$  = g. of Ra/g. of Ba in original solution;  $E_p = R_p/R_0$ ,  $E_f = R_f/R_0$ .

TABLE II  
FRACTIONATION OF RADIUM AND BARIUM CHROMATES IN HYDROCHLORIC ACID SOLUTIONS  
Acidity never greater than 0.3  $N$

No.	Original solutions		$R_p \times 10^6$	$R_f \times 10^6$	$D$
	G. of Ra $\times 10^6$	G. of Ba			
1	8.55	36.60	2.14	0.173	12.3
2	1.13	8.40	0.598	.0182	32.8
3	5.17	38.30	0.516	.0175	29.4
4	33.1	19.99	3.70	.239	15.5
5	35.8	57.50	1.54	.1315	11.7
6	131.5	25.11	9.69	.778	12.5
7	131.1	24.63	8.96	.546	16.4
8	131.5	25.11	8.18	.392	20.8
9	131.5	25.11	7.59	.342	22.2
10	58.5	61.00	3.59	.380	9.48
11	58.2	60.40	2.72	.189	14.4
12	58.1	60.00	2.13	.135	15.8
13	58.0	59.60	1.82	.0935	19.4

neutral solutions, while all the others were fractionated in the presence of either hydrochloric or nitric acid. Nitric acid is preferable as its use eliminates the possibility of reduction of the chromate which occasionally takes place when hydrochloric acid is used. In the fractionations in neu-

tral solution, known amounts of potassium chromate solution were added to the warm solution of radium-barium chloride. The precipitate, digested for approximately two hours and then allowed to cool and settle for one to two days, was separated from the solution and analyzed. The solutions fractionated in the presence of acid were first treated with an equivalent quantity of chromate, enough acid being added to the warm solution to dissolve all of the precipitate. It was found that the last traces of precipitate were always very difficult to dissolve. The excess of acid was neutralized with sodium or potassium hydroxide until a slight turbidity appeared. Sufficient base was then added slowly to produce the desired amount of precipitate. The whole was then digested for several hours at about 70°, stirred occasionally then allowed to cool and settle for one or two days. The precipitate was separated from the solution and samples were taken out for analysis. As the radium-barium ratio increased in the

TABLE III

RECOVERY OF RADIUM FROM LEAN MIXTURES BY PRECIPITATING SUCCESSIVE PORTIONS OF THE BARIUM AS CHROMATE FROM A HYDROCHLORIC ACID SOLUTION

A							
No. of ppt.	G. of Ra <sub>p</sub> × 10 <sup>6</sup>	G. of Ba <sub>p</sub>	R <sub>p</sub> × 10 <sup>6</sup>	G. of Ra <sub>f</sub> × 10 <sup>6</sup>	G. of Ba <sub>f</sub>	R <sub>f</sub> × 10 <sup>6</sup>	D
0	...	...	...	2.72	29.14	0.0933	...
1	1.760	4.841	0.364	1.00	24.10	.0415	8.76
2	0.715	3.659	.195	0.285	20.44	.0139	14.00
3	.202	2.453	.0822	.083	17.99	.0046	17.80
By summation.				2.76	28.94		
B							
0	...	...	...	51.10	123.11	0.415	...
1	25.40	8.304	3.06	25.60	114.81	.223	13.7
2	15.40	9.493	1.63	10.20	105.32	.0968	16.8
3	6.32	14.21	0.445	3.90	91.09	.0428	10.4
4	2.94	14.02	.2095	0.985	77.36	.0127	16.5
By summation.				51.05	123.39		

TABLE IV

SYSTEMATIC FRACTIONATION OF MODERATELY RICH MIXTURES IN HYDROCHLORIC ACID SOLUTIONS

No.	G. of Ra <sub>p</sub> <sup>a</sup> × 10 <sup>6</sup>	G. of Ba <sub>p</sub> <sup>a</sup>	R <sub>p</sub> × 10 <sup>6</sup>	G. of Ra <sub>f</sub> × 10 <sup>6</sup>	G. of Ba <sub>f</sub>	R <sub>f</sub> × 10 <sup>6</sup>	D
0	...	...	...	304.0	10.011	30.32	...
1	200.8	2.192	91.6	106.5	8.128	13.1	7.0
2	186.6	1.170	159.5	14.2	1.025	13.85	11.5
3	156.8	0.4683	325	29.8	0.702	42.4	7.67
4	149.4	.2988	500	7.40	.1695	41.2	12.15
5	140.0	.1647	848	9.40	.1341	70.3	12.1
6	132.0	.0830	1590	8.40	.0817	103.0	15.4
By summation.				307.3	10.32		

<sup>a</sup> Precipitates were dissolved and partially reprecipitated.

TABLE V  
SYSTEMATIC FRACTIONATION OF RICH MIXTURES IN NITRIC ACID SOLUTION

No.	G. of $Ra_p^a$ $\times 10^6$	G. of $Ba_p^a$	G. of $Ra_f \times 10^6$	G. of $Ba_f$	$R_p \times 10^6$	$R_f \times 10^6$	$D$
0	...	...	1074	127.9	...	8.397	...
1	986	66.99	50.6	55.57	14.7	0.910	16.15
2	961	44.54	24.6	22.45	21.6	1.095	19.7
3	863	23.24	98.5	21.30	37.1	4.62	8.03
4	821	12.92	41.6	10.32	63.6	4.03	15.8
5	715	5.759	106.3	7.160	124	14.85	7.15
Summation			1037	122.6			
0	..	...	672	5.413	...	124.14	...
6	570	2.820	77.0	2.662	202	28.9	7.0
7	551	1.722	19.1	1.098	320	17.4	18.4
8	534	1.140	16.5	0.582	468	28.35	16.5
9	500	0.6404	34.1	.5001	780	68.2	11.4
10	477	.3474	21.45	.2910	1373	73.7	18.6
11	466	.2961	10.75	.0513	1575	209	7.55
12	419	.1863	47.1	.1098	2250	429	5.25
13	357.1	.0881	61.5	.0982	4050	626	6.45
14	192.5	.0159	164.6	.0722	12100	2280	5.30
Summation.			647	5.482			

<sup>a</sup> Precipitates were dissolved and partially reprecipitated.

precipitate, that precipitate served as the next higher member of the fractionation series. Similarly, the fractionation of the filtrates proceeded toward the lean end of the series. At the conclusion of each series the various members were summarized to serve as a check on the analytical work. (See Tables III-V.)

Fig. 2 contains only results of experiments performed under comparable conditions and in acid solutions, the strength of which never exceeded 0.3 *N*.

### Discussion

From the experimental results presented in Fig. 1, it is noted that the value of the partition factor  $D$  shows no distinct trend one way or the other, as the fraction of the barium precipitated is varied over the whole range. It is true that the individual values of  $D$  differ considerably from member to member in each series. Nevertheless, the absence of a distinct and consistent variation in this factor would seem to indicate that it possesses the characteristics of an equilibrium constant. The average values of  $D$  for the individual series are: Series I, 15.4; II, 15.5; III, 14.6; IV, 11.2. It is significant that the values for Series I and II are identical, certainly within the limit of experimental error. The experimental conditions imposed upon these two series are comparable in all respects except acidity, and this appears to be a minor consideration when not of an excessive de-



gree. The low values of  $D$  for Series III and IV are probably due to non-attainment of equilibrium.

The constancy of  $D$  over the whole range, when the fraction of barium precipitated is varied, suggests that it has the significance of a partition factor or distribution constant. The radium appears to be distributed between the precipitate and solution in a manner analogous to the partition of a solute between two immiscible solvents, the only difference being that one of the solvents (the precipitate) is solid in the present instance. This implies that radium chromate and barium chromate form solid solutions. This is reasonable in view of the close chemical relationship of the two elements and the fact that isomorphism frequently occurs among the compounds of neighboring elements in the same group of the periodic table. The supposition that the precipitate of radium-barium chromate is a solid solution of these two compounds is strengthened by the results of the experiments with varying radium-barium ratio. Fig. 2 shows that the region within which the experimental points lie is parallel to the straight line representing  $D = 15.5$ , except in the region of high radium-barium ratio. The active mass of barium chromate, while approximately constant in precipitates lean in radium, may become variable in precipitates rich in radium.

The deviations of the individual points from the true equilibrium value of  $D$  cannot be ascribed to analytical error except in a small measure. They are undoubtedly due to the slow equalization of concentration within the solid particles of the precipitate. A certain amount of exchange between the precipitate and solution takes place by the dissolution of small crystals and subsequent growth of larger crystals. The presence of acid favors this exchange and assists in the attainment of equilibrium conditions. In Series III the presence of a large excess of chromate in the solution partly nullifies the favorable action of the acid, and a lower average value for  $D$  results. The markedly low results in Series IV and V indicate that the exchange between solution and precipitate takes place very slowly in neutral solutions. The precipitate separates from these solutions very rapidly and each crystal, while forming, draws its supply of radium from its immediate vicinity only and, consequently, cannot be in equilibrium with the solution as a whole. The resulting precipitate contains less radium than it would under conditions of equilibrium. The reciprocal exchange between solution and precipitate must be small in view of the depression of solubility of the already insoluble precipitate by the excess of barium present.

The enrichment of radium in the precipitate might possibly be accounted for by the preferential adsorption of radium by the surface of the barium chromate precipitate. The term "surface adsorption," as generally used, implies the deposition of the adsorptive in a thin layer over the surface of the adsorbent without appreciable penetration into the interior. The ad-

sorption velocity is usually very high.<sup>10</sup> The slowness of attainment of equilibrium in these experiments is perhaps the most valid argument against the view that adsorption plays a significant part in the process. The results of a few experiments designed to dissolve the surface of radium-barium chromate by immersing active barium chromate precipitate in dilute acid solution, as well as those in which lean precipitates were allowed to stand in contact with solutions of higher radium-barium ratio, were negative and provided further argument against adsorption.

**Effect of High Acid Concentration.**—The experimental results thus far presented indicate that variations in acid concentrations from 0.05 to 0.3 *N* have little effect on the distribution of radium between the precipitate and the solution. The effect of high acid concentration, however, is unfavorable. Table VI presents results of a few experiments obtained with solutions of known hydrochloric acid concentration. The value of *D* is low whenever the acid concentration exceeds 0.5 *N*. This is of distinct interest, and unfortunate for practical reasons since it is desirable to maintain volumes of the solutions as small as possible.

TABLE VI  
EFFECT OF ACID CONCENTRATION

No.	HCl, <i>N</i>	<i>D</i>	No.	HCl, <i>N</i>	<i>D</i>
1	0.05	15.0	5	0.19	14.8
2	.085	16.4	6	.20	20.8
3a	.105	9.5	7	.53	4.0
3b	.105	14.5	8	.57	8.05
3c	.105	15.8	9	.77	4.15
4	.17	12.1	10	.90	6.5

**Comparison with Other Methods.**—The bromide method, in common use at the present time, has been studied in recent years by Nierman,<sup>6a</sup> Scholl,<sup>6b</sup> and Strong.<sup>5a</sup> Scholl also gives data on the chloride method. The hydroxide method of McCoy<sup>5b</sup> has been employed by Strong in his study of the isotopy of radium and mesothorium. The fractional precipitation of radium-barium sulfate has been studied by Ebler and van Rhyn,<sup>11</sup> and by Doerner and Hoskins,<sup>12</sup> while Germann<sup>13</sup> has studied the adsorption of radium-barium sulfate. Using the data of these authors, with the exception of those of Germann, the average values of *D* for the various methods have been calculated and their results, together with those of the authors for acid fractionations, have been plotted in Fig. 3. It is noticeable that the points for the chromate method cover the region of the highest separation efficiency reported thus far. The average for the bromides

<sup>10</sup> Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft, Leipzig, 1923, 3rd ed., p. 229.

<sup>11</sup> Ebler and van Rhyn, *Ber.*, 54, 2896 (1921).

<sup>12</sup> Doerner and Hoskins, *THIS JOURNAL*, 47, 662 (1925).

<sup>13</sup> Germann, *ibid.*, 43, 1615 (1921).

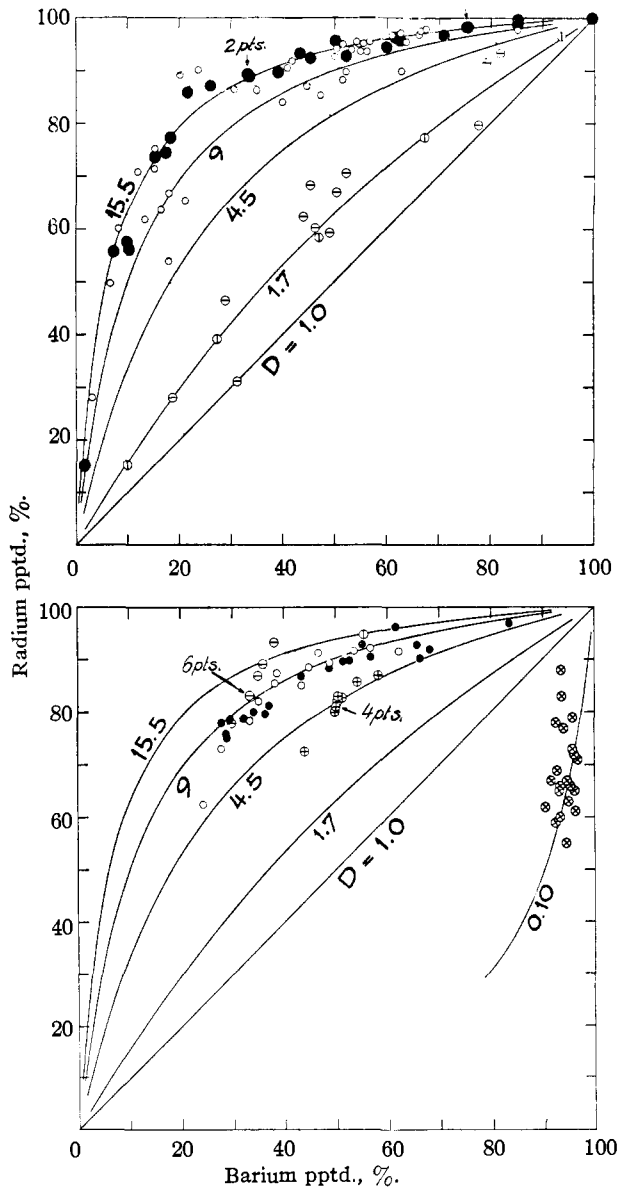


Fig. 3A.—●, Chromates (a), the authors' acid fractionations, Series I, II, III. ○, Chromates (b), the authors' larger acid fractionations. ⊕, Ebler and van Rhyn (Ref. 11). ⊖, Doerner and Hoskins (Ref. 12).

Fig. 3B.—○, Nierman (Ref. 6a), neutral bromides. ●, Nierman, acid bromides. ⊖, Scholl (Ref. 6b). ⊕, Strong, bromides. ⊗, Strong, hydroxides. ⊕, Scholl, chlorides.

appears at about  $D = 9$ . There is reason to believe, however, that in practice the bromide method gives a value for  $D$  of 15 to 16. Strong's average for five crystallization steps is approximately  $D = 15$ , while the highest point reported by Scholl in solution of 1 *N* hydrobromic acid yields a value of 22.2 for  $D$ .

The chromate method does not lend itself readily to the construction of a crystallization system, but it has the advantage of rapid enrichment and the use of comparatively inexpensive chemicals. The bromide method is economically impracticable for the fractionation of mixtures lean in radium. It is in this region that the chromate method should find advantageous application (see Table III). The original solution (B) contained  $51.1 \times 10^{-6}$  g. of radium, and 123 g. of barium as barium chromate, in an acid solution with a radium-barium ratio of  $4.15 \times 10^{-7}$ . After four successive precipitations involving the addition of only the requisite quantity of sodium hydroxide to bring about partial precipitation of the chromate and then decanting the solution, 98.08% of the radium was obtained associated with 37.1% of the barium, having a radium-barium ratio of  $1.09 \times 10^{-6}$ . The final solution contained only 1.92% of the radium and 62.9% of the barium. The ratio of radium to barium in this solution was  $1.27 \times 10^{-8}$ . In this instance a solution containing a mixture of radium and barium too lean to be worked economically by present methods<sup>14</sup> may be easily concentrated to a point where it would be practical to use the present chloride method. In other words, the chromate method could be used to recover radium from mixtures too lean to be worked by other methods. The chromate method may also find application in the concentration of relatively small weights of rich mixtures of radium and barium. It is more convenient to handle small quantities by precipitation methods than by partial evaporation of small volumes of solutions of soluble salts. With small quantities of such soluble salts as barium bromide, the volumes of the solutions become very small and entail considerable difficulties in manipulation.

### Summary

The fractional precipitation of barium-radium chromate affords a means of separating the two elements which is comparable in effectiveness to the best results obtained with the bromide method. The partition factor  $D$  is found to be 15.5 for acid solutions. The chromate method may be used to advantage with relatively small quantities of barium-radium mixtures. It may also be used for recovering radium in radium-barium solutions which are too lean to be economically concentrated with the chloride method.

3144 PASSYUNK AVENUE  
PHILADELPHIA, PENNSYLVANIA

<sup>14</sup> Ref. 8, p. 76.