[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

THE PARTITION COEFFICIENT IN THE FRACTIONAL CRYSTALLIZATION OF RADIUM-BARIUM BROMIDE SOLUTIONS[1]

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The latter stages in the preparation of a pure radium salt have usually been carried out by the fractional crystallization of a radium–barium chloride or bromide solution. From a consideration of the alkaline earth group of the periodic table, the general trend of the solubilities of radium salts may be safely predicted. True to expectation, the solubilities of radium bromide,[2] chloride, sulfate[3] and chromate[4] have been found to be less than the corresponding barium compounds and this factor has been generally quoted to account for the enrichment of radium in the crystalline phase. Furthermore, since the solubility of the alkaline earth hydroxides increases with increasing atomic weight, the radium in this instance should remain in the mother liquor. McCoy[5] has satisfactorily demonstrated this prediction.

At least two other theories have been advanced to explain the mechanism of the enrichment of radium in the crystalline phase. One of these theories,[6] advanced by Germann, would explain the phenomenon on the basis of adsorption. The other theory stated by Doerner and Hoskins would explain the mechanism of the enrichment of the crystalline phase as one in which radium atoms replace barium atoms in isomorphous crystals of the barium salt.

Further, irrespective of any theory, at least three different equations have been proposed to explain the regularities observed in the enrichment of radium by the process of fractional crystallization or precipitation.

The experimental part of this paper will present some evidence to test the validity of the respective equations and will include a new procedure by means of which the crystals separated are more completely freed from the mother liquor.

Experimental

(A) **Source of Material.**—The source material which was used in these experiments consisted of a sample of purified barium chloride, 250 g.,

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[1] Abstract of a thesis submitted by Z. T. Walter in partial fulfilment of the requirements of the degree of Master of Arts, Graduate School, University of Missouri, 1928.

[2] John L. Nierman, *J. Phys. Chem.*, **24**, 192 (1920); Clarence F. Scholl, THIS JOURNAL, **42**, 889 (1920).

[3] S. C. Lind, J. E. Underwood and C. F. Whittemore, *ibid.*, **40**, 465 (1918); H. A. Doerner and William M. Hoskins, *ibid.*, **47**, 662 (1925).

[4] L. M. Henderson and Frank C. Kracek, *ibid.*, **49**, 738 (1927).

[5] H. N. McCoy, U. S. Patent 1,103,600 (1914).

[6] Frank E. E. Germann, THIS JOURNAL, **43**, 1615 (1921).

which contained approximately a total of 26 × 10^{-5} g. of radium element. This material had previously been used in radioactive researches at the University of Missouri. Before its use in this study it was converted to radium–barium bromide by first making radium–barium carbonate. This carbonate was then treated with hydrobromic acid and the pure crystals of radium–barium bromide were obtained upon the evaporation of the hydrobromic acid solution.

(B) **Method of Treatment.**—The purified radium–barium bromide was taken into solution and the solution made up to exactly one thousand grams. This solution was then analyzed for both its radium and its barium content. The radium in the solution was determined by the emanation method in carefully calibrated electroscopes. The barium in the solution was determined by the sulfate method. This solution throughout this paper is called the stock solution.

(C) **Method of Growth and Separation of Crystals.**—A suitable quantity of this stock solution was weighed into a fused quartz evaporating dish. The solution was then evaporated on the water-bath until it was saturated. The crystals were then grown from the solution by removal of water with slow evaporation, the process requiring two to four hours depending upon the quantity of crystals removed from the solution. During the separation of the crystals the solution was continuously stirred. When the desired quantity of crystals had been separated, the dish was weighed and the loss of weight during evaporation was obtained. A sample of mother liquor was next decanted from the liquor above the crystals, weighed and made up to 1000 g. for analysis for radium content.

The next step in the process consisted in the complete removal of all mother liquor from the crystals. The usual plant process at this point is merely to decant all of the mother liquor that can be conveniently poured from the crystals, thus leaving them wet with impoverished liquor. The procedure used in this investigation was to centrifuge the crystals in a hand centrifuge. The manner in which the crystals were completely separated from the mother liquor is considered to be the distinctive feature of this work, for in previously reported papers this point had not been given sufficient attention. The dry crystals were finally weighed as the hydrate, $\text{Ra–BaBr}_2\cdot 2\text{H}_2\text{O}$.

Now from the previously determined content of the stock solution and from the values of the radium content of the mother liquor and quantity of barium bromide separated, the value for K, the partition constant, may easily be obtained.

(D) **Data Expressed in Terms of Doerner and Hoskins' Equation.**—In Table I all of the information necessary for the calculation of the partition constant, K as defined by Doerner and Hoskins, is given. The equation given by them is as follows: $K = (\log y/a)/(\log n/b)$, where y

is the total radium (element) remaining in the mother liquor left after fractionation and separation of crystals; a equals the quantity of radium (element) in the sample of stock solution used in the fractionation; n represents the quantity of anhydrous radium–barium bromide remaining in the mother liquor after fractionation; b is the quantity of anhydrous barium bromide in the sample of stock solution fractionated. All weights are expressed in grams.

TABLE I

EXPERIMENTAL DATA FOR THE DOERNER-HOSKINS FORMULA

Expt.	Crystals sepd., %	y	a	n	b	K
1	5.36	35.01×10^{-6}	47.76×10^{-6}	35.47	37.48	5.63
2	8.85	31.73×10^{-6}	47.76×10^{-6}	33.76	37.48	3.91
3	10.98	11.11×10^{-6}	23.88×10^{-6}	16.68	18.74	6.58
4	17.55	58.62×10^{-7}	23.88×10^{-6}	15.45	18.74	7.27
5	18.12	38.45×10^{-7}	13.06×10^{-6}	9.87	12.05	6.13
6	24.55	46.2×10^{-7}	23.88×10^{-6}	14.14	18.74	5.83
7	30.65	33.83×10^{-7}	23.88×10^{-6}	13.00	18.74	4.35
8	35.79	9.98×10^{-7}	13.06×10^{-6}	7.74	12.05	5.83
9	45.25	5.93×10^{-7}	13.06×10^{-6}	6.59	12.05	5.13
10	45.75	5.75×10^{-7}	26.12×10^{-6}	13.08	24.10	6.25
11	54.59	3.07×10^{-7}	13.06×10^{-6}	5.47	12.05	4.75

(E) **Data Expressed in Terms of the Equation of Chlopin and Nikitin.**[7]—Another equation has been developed by Chlopin and Nikitin in which a relation is expressed between the concentration of radium per unit volume of crystals separated and the concentration per unit volume of mother liquor. Chlopin and Nikitin state that none of the equations previously given expresses very closely the experimental results. The equation favored by Chlopin and Nikitin is modeled after the Nernst–Berthelot distribution or partition equation. In this equation, K, the partition coefficient, has a somewhat different meaning than is usually given to it. Here it is the ratio of the concentration of radium per unit volume of crystals separated to the concentration of radium per unit volume of mother liquor. The equation follows: $XS_1/m = K(1 - X)S_0/q$. X is the fraction of radium in the crystals separated; $1-X$, fraction of radium remaining in mother liquor; S_0, density of mother liquor, 1.63; S_1, density of the crystals separated, 3.58; m is the weight of the crystals separated; and q is the weight of the mother liquor remaining after fractionation.

In order to apply the equation of Chlopin and Nikitin to our experimental results, it was necessary to determine the density of the mother liquor and thus calculate the volume of the solution obtained after the crystals were removed. The value used for the density of barium bromide crystals (hydrate) was taken from "International Critical Tables." The

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[7] W. Chlopin and B. Z. Nikitin, *Z. anorg. allgem. Chem.*, **166**, 311 (1927).

experimental results expressed in the symbols employed by Chlopin and Nikitin are given in Table II.

TABLE II

EXPERIMENTAL RESULTS EXPRESSED IN SYMBOLS OF THE CHLOPIN-NIKITIN EQUATIONS

Expt.	Crystals sepd., %	q	m	X	$(1-X)$	K
1	5.36	80.00	2.01	0.267	0.733	31.91
2	9.93	78.62	3.315	.336	.664	28.24
3	10.98	38.99	2.311	.521	.479	40.40
4	17.55	36.51	3.688	.748	.252	64.40
5	18.12	20.72	2.45	.706	.294	44.5
6	24.55	34.24	5.16	.807	.193	60.8
7	30.65	31.76	6.44	.858	.142	77.8
8	35.79	16.59	4.83	.924	.076	91.4
9	45.25	14.46	6.11	.950	.050	106.4
10	45.75	27.64	12.36	.977	.023	218.9
11	54.59	12.24	7.55	.977	.023	148.2

(F) Data Expressed in Terms of Schlundt's Exponential Equations.[8]—The calculation of the values of K, the partition constant, as given in Schlundt's exponential equation is comparatively simple. The equation is, $Q_1 = Q_0e^{-Kp}$, where p is the fraction of the crystals separated, K is the distribution or partition coefficient; e is the natural log base; Q_1 is the fraction of radium remaining in mother liquor, and Q_0, the initial quantity of radium, may here be taken as unity. The values of K as calculated by this equation are given in Table III.

TABLE III

EXPERIMENTAL RESULTS IN TERMS OF EXPONENTIAL EQUATION

Expt.	Crystals sepd., %	Q_1	K	Expt.	Crystals sepd., %	Q_1	K
1	5.36	0.733	5.80	7	30.65	0.142	6.37
2	8.85	.664	4.60	8	35.79	.076	7.19
3	10.98	.479	6.70	9	45.25	.050	6.62
4	17.55	.252	7.86	10	45.75	.023	8.24
5	18.12	.294	6.74	11	54.59	.023	6.91
6	24.55	.193	6.70				

Discussion

From an examination of the experimental tables it will be noticed that the Chlopin-Nikitin equation definitely does not express a true partition coefficient, for the values of K increase as larger fractions of the crystals are removed from the stock solution. It will also be noticed that, while the values for the partition coefficient as expressed by the Doerner-Hoskins equation and the Schlundt exponential equation do not coincide, they do express a fairly exact relation between the radium in the crystals separated

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[8] Herman Schlundt, "Mesothorium," Technical Paper 265, U. S. Bureau of Mines, 1922.

and the salt remaining in the mother liquor. The average value for the partition constant, *K*, Schlundt equation, is 6.66, while the Doerner and Hoskins constant is 5.64. The corresponding values for the distribution of radium in other systems using the Doerner-Hoskins equation are: for the radium–barium sulfate system *K* is equal to about 1.8; for the radium–barium chloride system *K* is equal to 2.74.[9] It is evident that of these three systems the radium–barium bromide system gives by far the most efficient enrichment of radium by fractional crystallization, and indeed it has been found so in practice, but these results show that it can be made more than twice as efficient as the chloride system.

Summary

1. The theories which attempt to explain the mechanism of fractional crystallization are outlined.

2. Three equations are cited to show the mathematical expressions advanced in the literature to represent the partition of radium salts between mother liquor and crystals separated in the process of fractionation.

3. A method of completely freeing the crystals from mother liquor by use of a centrifuge is described.

4. The average value for the partition coefficient in the Schlundt equation was found to be 6.66.

5. The average value for the partition coefficient in Doerner and Hoskins' equation was found to be 5.6.

6. Both the Schlundt and the Doerner-Hoskins equations seem to express equally well the partition relation, namely, that in the process of fractionation the distribution of radium between crystals and mother liquor takes place continuously in constant ratio.

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[9] Unpublished experiments by Dr. G. F. Breckenridge, University of Missouri.