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

Structural Changes Taking Place During the Aging of Precipitates. X. The Distribution Coefficient of Lead between the Surface of Barium Sulfate and Solution. The Determination of the Specific Surface of Barium Sulfate

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In the present study the distribution coefficient K of lead between the surface of barium sulfate and solution has been determined.

$$\frac{\text{Pb Surface}}{\text{Pb Solution}} = K \frac{\text{Ba Surface}}{\text{Ba Solution}} \qquad (1)$$

In this expression Pb Solution and Ba Solution denote the activities of the lead and barium ions in the solution. In our calculations concentrations have been used instead, since the only salts present in the solution were barium and lead (or thorium B) nitrates, which are strong electrolytes and whose mean activities in dilute solutions are the same. By the addition of sodium nitrate the ionic strength of the solution could be changed, but it has been shown that the value of the distribution coefficient was not changed noticeably by such an addition. Thus the use of concentrations instead of activities under the conditions specified is experimentally justified.

In a previous study[1] it has been shown that upon shaking of barium sulfate with a thorium B or an active lead solution, a rapid exchange occurs and that simultaneously lead is removed slowly as a result of recrystallization of the barium sulfate. In order to minimize the effect of recrystallization as much as possible, barium sulfate was used which had been subjected to a drastic aging process. In this way fairly perfect crystals were obtained whose surface has been measured with the aid of the microscope (Ba Surface).

The knowledge of K is of practical significance since it permits the determination of the specific surface of various products of barium sulfate. In dealing with fine products of barium sulfate which are not quite perfect, the great difficulty is encountered that the curve representing the total removal of active lead with time is a result of the two processes mentioned. An extrapolation of the experimental figures to a zero time of shaking, therefore, would yield an uncertain value of the amount of exchange. In order to improve the situation either of the two following alternatives may be applied: (1) After exchange equilibrium in the surface has been attained, a fairly large excess of barium nitrate is added to the solution which will extract all of the lead from the surface layer[1] without affecting the lead in the recrystallizate. Thus by determining after various times of shaking the ratio of active lead left in the solution and that removed, we find the ratio (Pb Surface + Pb recrystallizate)/(Pb Solution). After addition of the large excess of barium nitrate, the activity is redetermined and Pb Surface/Pb Solution is calculated. This method yields useful results with fine but well aged products of barium sulfate. With fresh or relatively fresh precipitates, however, the recrystallization may continue fairly rapidly after the addition of the large excess of barium salt. (2) The speed of recrystallization is affected by a change of the medium. In a previous communication[1] it has been shown that the speed of recrystallization of aged barium sulfate is reduced drastically in 50% ethanol, the time–adsorption curve becoming almost flat after the attainment of exchange equilibrium in the surface. Since the procedure in 50% ethanol is of practical significance in the determination of the specific surface of barium sulfate, we have determined the value of the distribution constant K using 50% ethanol as a solvent instead of water. The method is simpler than that proposed in 1, since it does not require an extraction of the exchanged lead in the surface. On the other hand, it has been shown in this work that a difficulty is introduced by working in 50% ethanol. The adsorption of barium salts from aqueous medium by finely divided, well-aged barium sulfate has been found negligibly small. Hence (Ba solution) (eq. 1) corresponds to the amount of barium salt added to the solution. This is no longer true in 50% ethanol as a solvent, the adsorbability being relatively great, especially from dilute solutions of barium salts. In the present work the amount of barium salt adsorbed has been determined and corrected for.

Experimental

Determination of K in Aqueous Medium.—The coarse product B[1] was subjected to a drastic aging in 2 N hydrochloric acid at 175°, washed

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[1] I. M. Kolthoff and W. MacNevin, THIS JOURNAL, **58**, 499 (1936).

and made air dry. The average diameter of the product was determined by measuring the dimensions of about one thousand particles with the aid of the microscope. The "surface average particle diameter"[2] was calculated from the ratio $\Sigma nd^3/\Sigma nd^2$ and found to be 6.92 microns.[3] From this value a total surface of 1926 square centimeters per gram of barium sulfate was calculated. Assuming the particles to be cubic, it is calculated that the specific surface of the product corresponds to

$$\frac{1926}{\left(\frac{233.4}{4.5 \times 6.06 \times 10^{23}}\right)^{2/3}} = 1.0 \times 10^{18}$$

barium sulfate molecules or barium ions on the surface of 1 gram; 4.5 being the density of barium sulfate.

One-gram samples of the product were shaken for one-half, one and four hours, respectively, with 49.5 cc. of solution containing thorium B and being 0.002 molar in nitric acid and 4×10^{-5} molar in barium nitrate, the final barium concentration in the solution being 4.25×10^{-5} molar as a result of dissolved barium sulfate. The amounts of thorium B expressed in per cent. removed after the indicated period of shaking were found to be 8.6, 9.2 and 10.7%, respectively. The experiments were repeated, but at the end of the indicated periods of shaking a large excess of barium nitrate was added and the whole shaken for five minutes[1] in order to find the percentage of thorium B removed by exchange with barium ions in the surface. In this way it was found that 0.2, 0.5 and 1.9% of the thorium B, respectively, was removed in an irreversible way and 8.4, 8.7 and 8.8%, respectively, by exchange with barium ions in the surface. Thus, we have the necessary data to calculate the ratio ThB Surface/ThB Solution = R in expression (1); this ratio being 8.4/91.4 = 0.092, 8.7/90.7 = 0.096 and 8.8/89.3 = 0.098, respectively, yielding an average value of R of 0.095. By graphical extrapolation of the original adsorption data for thorium B to a time zero, where no thorium B is incorporated within the lattice, a value of R = 8.4/91.6 = 0.092 is found. Taking the average of these two values in the calculation of K it is found that

$$K = \frac{\text{ThB Surface}}{\text{ThB Solution}} \cdot \frac{\text{Ba Solution}}{\text{Ba Surface}} = \frac{0.0935 \times 49.5 \times 4.25 \times 10^{-3} \times 6.06 \times 10^{23}}{1.0 \times 10^{18}} = 0.12$$

Determination of K in 50% Ethanol.—In a previous paper[1] it was shown that in a medium of 50% ethanol the recrystallization of barium sulfate is strongly inhibited and that exchange between barium and lead is virtually complete after one hour. Two grams of the barium sulfate was shaken for one hour with 48.5 cc. of a 50% ethanol solution 4.0×10^{-5} molar in barium nitrate, 2.0×10^{-3} in normal nitric acid and containing thorium B; the adsorption of thorium B was found to be 10.3% (R = 0.115). By special experiments, it was shown that the adsorption of barium nitrate from 50% ethanol by this coarse precipitate was negligible. Substituting the above data in the general formula

$$K\ (50\%\ \text{ethanol}) = \frac{0.115 \times 48.5 \times 10^{-3} \times 4.0 \times 10^{-5} \times 6.06 \times 10^{23}}{2 \times 1.0 \times 10^{18}} = 0.067$$

The ratio of the two constants in 50% ethanol and water for the coarse product is 0.067/0.118 = 0.57.

Determination of the Specific Surface of the Fine Barium Sulfate (Product A).—It is now possible to calculate the specific surface of the "fine" precipitate A[1]. When 0.2 g. was shaken for one hour with 49.5 cc. of a 50% ethanol solution containing 2×10^{-4} molar barium nitrate, 2×10^{-3} normal nitric acid and thorium B, 30.0% of the barium nitrate and 14.6% of the thorium B were found to be adsorbed. Substituting these values in equation (1) yields

$$\text{Ba Surface} = \frac{14.6 \times 48.5 \times 10^{-3} \times 1.4 \times 10^{-4} \times 6.06 \times 10^{23}}{85.4 \times 0.2 \times 0.0674} =$$

5.21×10^{19} Ba atoms on the surface per gram of "fine" barium sulfate

Without knowing the specific surface of the fine product, it is possible to determine the ratio of $K_{50\%\ \text{ethanol}}$ to K_{water}.

$$K_{50\%\ \text{ethanol}} = R_{50\%\ \text{ethanol}} \frac{(\text{Ba Solution})\ \text{ethanol}}{\text{Ba Surface}}$$

$$K_{\text{water}} = R_{\text{water}} \frac{(\text{Ba Solution})\ \text{water}}{\text{Ba Surface}}$$

Hence

$$\frac{K_{50\%\ \text{ethanol}}}{K_{\text{water}}} = \frac{R_{50\%\ \text{ethanol}}}{R_{\text{water}}} \frac{(\text{Ba Solution})\ \text{ethanol}}{(\text{Ba Solution})\ \text{water}}$$

From the reversibility experiments for the fine precipitate reported in Table IX in a previous paper[1] an average value of R_{water} of 0.22 was found at a (Ba Solution) water of 2×10^{-4} molar, the total volume being 49.5 cc. From these and the above experiments in 50% ethanol, it is found that

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(2) Perrott and Kinney, *J. Am. Ceram. Soc.*, **6**, 417 (1923).

(3) For details concerning the size groups the reader is referred to the doctor's thesis of the Junior author.

$$\frac{K_{50\%\ \text{ethanol}}}{K_{\text{water}}} = \frac{\frac{14.6}{85.4} \times 1.4 \times 10^{-4}}{0.22 \times 2 \times 10^{-4}} = 0.55$$

For the coarse product, having a specific surface 52 times smaller than the fine one, a ratio of 0.57 was found. The agreement between the two ratios is as good as can be expected and gives support to the reliability of the reported figures of K and to the interpretation of the previous data.

Effect of Varying Mol Percentage of Lead in the Surface upon the Value of K. A. Experiments in 50% Ethanol.—In the experiments described above thorium B was the only source of lead used, its total amount being so small that (Ba Surface) remained constant, even if all of the thorium B were removed by exchange. This is no longer true when the total amount of lead in the system is increased by addition of inactive lead to the thorium B solution. From the experimentally determined percentage of lead removed by exchange and the original amount of lead in the solution, the number of lead ions in the surface of the barium sulfate can be calculated (Pb Surface). Since each adsorbed lead ion replaces a barium ion from the surface, the number of barium ions after establishment of exchange equilibrium is equal to the original number minus Pb Surface, whereas Ba Solution will be equal to the amount of barium added to the solution plus the amount replaced by exchange (Pb Surface). Thus it is possible to calculate the value of K

$$K = \frac{\text{Pb Surface}}{\text{Pb Solution}} \times \frac{\text{Ba Solution}}{\text{Ba Surface}}$$

with increasing mole percentage of lead in the surface. One-gram samples of the fine barium sulfate (product A) were shaken for one hour with 48.5 cc. of a 50% ethanol solution 2×10^{-4} molar in barium nitrate, 2×10^{-3} molar in nitric acid and containing the concentration of radioactive lead nitrate reported in the first column of Table I. The adsorption was determined "radio-actively." As an example the calculation of K is given in the case in which the original lead nitrate concentration was equal to 10^{-4}.

$$K = \frac{42.3 \times 3.28 \times 10^{18}}{57.7 \times 5.09 \times 10^{19}} = 0.047$$

The objection might be raised that it has been assumed that all of the lead removed had taken part in the kinetic exchange and that none was adsorbed in the form of lead nitrate. Previously it has been stated that in a medium of 50% ethanol a distinct adsorption of barium nitrate on barium sulfate is found. Therefore, a slight adsorption of lead nitrate may be expected to occur. If this were the case, all the data in Table I would have to be corrected for the amounts of lead adsorbed in the form of nitrate. The result would be that the values of K which were found to decrease with increasing mole percentage of lead in the surface would become even smaller than those reported in Table I. The conclusion, therefore, is that the value of K decreases with increasing mole percentage of lead in the surface and that the actual data may be smaller than those reported. The first part of this conclusion is fully substantiated by the experimental work of G. Noponen in this Laboratory, who determined the distribution coefficient of lead sulfate throughout the entire precipitate and who found decreasing values with increasing mole percentage of lead sulfate in the barium sulfate.

B. Experiments in Aqueous Medium.—Five-gram samples of the coarse barium sulfate (digested at 175° previously mentioned in this paper) were shaken for one hour with 49.9 cc. of an aqueous solution, containing 5×10^{-5} molar barium nitrate (solubility of barium sulfate in this medium corresponds to 0.23×10^{-5} molar), 2×10^{-3} molar nitric acid and varying concentrations of radioactive lead nitrate. The amount of lead adsorbed was determined "radio-actively." A summary of all the results is given in Table II. Again it is found that the value of K decreases

TABLE I

CHANGE OF K WITH INCREASING MOLE PERCENTAGE OF LEAD IN THE SURFACE OF BARIUM SULFATE (50% ETHANOL)

Original concn. of lead nitrate molar	Pb adsorbed in %	Pb Surface number of ions	Ba Solution number of ions	Ba Surface number of ions	Pb Surface in mol. percentage	K
0 (ThB)	63.2	....	2.05×10^{18}	5.21×10^{19}	0.0	0.067
10^{-7}	63.1	....	$2.05 \times$ —	$5.21 \times$ —	.0	.067
10^{-5}	59.3	0.18×10^{18}	$2.23 \times$ —	$5.19 \times$ —	.35	.062
10^{-4}	42.3	$1.24 \times$ —	$3.29 \times$ —	$5.09 \times$ —	2.4	.047
2×10^{-4}	34.7	$2.04 \times$ —	$4.09 \times$ —	$5.01 \times$ —	3.9	.043
4×10^{-4}	26.2	$3.08 \times$ —	$5.13 \times$ —	$4.90 \times$ —	6.3	.037

TABLE II

CHANGE OF K WITH INCREASING MOLE PERCENTAGE OF LEAD IN THE SURFACE OF BARIUM SULFATE (AQUEOUS MEDIUM)

Original concn. of lead nitrate m	Pb adsorbed in %	Pb Surface number of ions	Ba Solution number of ions	Ba Surface number of ions	Pb Surface in mol percentage	K
0 (ThB)	26.8	....	1.58×10^{18}	5.00×10^{18}	0.0	0.116
10^{-7}	27.0	....	$1.58 \times$ —	$5.00 \times$ —	0.0	.117
10^{-5}	21.6	0.065×10^{18}	$1.64 \times$ —	$4.94 \times$ —	1.3	.091
2×10^{-5}	19.4	$.117 \times$ —	$1.70 \times$ —	$4.88 \times$ —	2.3	.084
4×10^{-5}	15.1	$.183 \times$ —	$1.76 \times$ —	$4.82 \times$ —	3.7	.065
5×10^{-5}	14.1	$.213 \times$ —	$1.79 \times$ —	$4.79 \times$ —	4.3	.062
7×10^{-5}	13.5	$.285 \times$ —	$1.86 \times$ —	$4.72 \times$ —	5.7	.061

with increasing mole percentage of lead sulfate in the surface. The values of K reported in Table II are more pertinent than those in Table I, since the adsorption of barium as well as of lead nitrate from aqueous medium was found to be negligible.

Discussion

By making certain assumptions Imre[4] derived mathematically that

$$K = e^{(E_{\mathrm{Pb}} - E_{\mathrm{Ba}})/RT}$$

in which E_{Pb} is the adsorption energy of lead ions and E_{Ba} that of barium ions on barium sulfate. The adsorption energy E according to Imre can be calculated from the expression

$$E = -L/N$$

in which L is the heat of solution of the salt and N the number of ions constituting it. In this way Imre calculated a value of K equal to 0.64 (20°). From his own experimental work on the change of the adsorption of thorium B on barium sulfate with the temperature, Imre calculates a value of K equal to 0.21–0.39. In a previous paper[1] it has been mentioned that we do not agree with the interpretation Imre has given of his own experimental work. In the present paper we find by direct measurements a value of K in aqueous medium of 0.12 which is much smaller than the average figure calculated by Imre.

In his fundamental paper on the application of radioactive indicators in kinetic exchange experiments Paneth[5] assumed that K would be equal to the ratio of the solubilities of barium and lead sulfate. Taking the solubility of barium sulfate equal to 1.1×10^{-5} and that of lead sulfate to 1.4×10^{-4} a value of K is calculated of 0.08, which is smaller but of the same order as that found in our work (0.12). Our own value is based upon the value of the specific surface calculated from the microscopic measurements which involves an uncertainty of about 10% when dealing with a heterodisperse precipitate.

From the fact that the value of K was found to decrease from 0.12 to 0.067 with a change of the medium from water to 50% ethanol it may be concluded that the solubility of barium sulfate decreases about twice as much as that of lead sulfate in 50% ethanol as a solvent instead of water.

Summary

1. The value of the distribution coefficient K of lead sulfate between water and barium sulfate was found to be 0.12, and between 50% ethanol and barium sulfate 0.067 (25°).

2. In both media the value of K decreases with increasing mole percentage of lead sulfate in the surface of barium sulfate.

3. The specific surface of aged barium sulfate can be determined by the radioactive method, either by working in a medium of 50% ethanol and correcting for the amount of barium salt adsorbed or by working in aqueous medium and deriving Pb surface from reversibility experiments.

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[4] L. Imre, *Z. physik. Chem.*, **A171**, 239 (1934).

[5] F. Paneth, *Physik. Z.*, **15**, 924 (1914).