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Studies on Aging of Fresh Precipitates. XVII. The Equilibrium between Mixed Crystals of Barium–Lead Sulfate and Solutions

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Barium and lead sulfate form a series of mixed crystals. A study of the distribution of lead between the mixed crystals and solutions under conditions of equilibrium is complicated by the fact that the mixed crystals separating upon addition of sulfate to a mixture of a barium and lead salt are heterogeneous and not in equilibrium with the supernatant liquid. From studies on the aging of fresh precipitates carried out in this Laboratory it was expected that homogeneous mixed crystals in equilibrium with the liquid phase could be obtained in either of the following ways. Method A, lead solution is added to a fresh and highly imperfect precipitate of barium sulfate and the suspension shaken in the presence of an excess of barium until the composition of the solid and liquid phases becomes constant. Method B, a precipitate consisting of mixed crystals of barium and lead sulfate obtained upon addition of sulfate to a mixture of a barium and lead salt is shaken with the supernatant liquid until the composition of the solid and liquid phases becomes constant.

The repeated recrystallizations during the aging of the primary imperfect precipitates ultimately results in the formation of mixed crystals in equilibrium with the liquid phase. If the primary precipitate is not highly imperfect, or if it perfects itself too rapidly during the aging, the time of attainment of distribution equilibrium may be very great and equilibrium may not be reached even after long periods of shaking. Consequently, one is faced with the uncertainty whether the true state of equilibrium is reached after long periods of shaking when the composition of the solid and liquid phases does not change appreciably upon further shaking. Application of both methods A and B mentioned above is decisive regarding the question whether true equilibrium is attained.

In the following work the distribution coefficient K has been calculated from the expression[2]

$$K = \left(\frac{\text{moles Pb}^{++}}{\text{moles Ba}^{++}}\right)_{\text{crystal}} \times \left(\frac{\text{moles Ba}^{++}}{\text{moles Pb}^{++}}\right)_{\text{solution}} \quad (1)$$

Experimental

Procedure.—The general procedure was to add measured volumes of solutions from a pipet to a glass bottle. After mixing, the bottle was stoppered and placed in a mechanical shaker which gave the bottle a vertical throw of about 10 cm. at a speed of 150 phases per minute. The temperature of the room in which the shaker was located was 26 ± 1°. When the shaking was carried out at 95° the bottle was put into an oven equipped with a rotator turning the bottle end over end every five seconds. After a given period of shaking, the bottle and its contents were centrifuged, and samples of the centrifugate analyzed for lead and barium. Centrifuging was resorted to because barium sulfate precipitated quickly at room temperature under the conditions of this work is usually of such small size that it passes through the finest filter paper. Lead was determined volumetrically in the centrifugate after precipitation as chromate using a modified procedure given by Brown, Moss and Williams.[3] To the neutral sample was added 2 to 3 ml. of 20% perchloric acid and the volume made up with water to about 100 ml. The solution was brought to the boiling point and 10 ml. of 0.05 *M* potassium dichromate added. The precipitate was digested until it became reddish-orange and crystalline in appearance. After standing for five to six hours at room temperature the lead chromate was collected by filtration on a sintered glass crucible, washed, dissolved in hydrochloric acid and the chromate determined iodometrically. When the amount of lead was greater than 0.25 millimole the lead chromate could be filtered immediately after precipitation. The results were found to be reliable to 0.2% with samples containing 0.05 millimole or more of lead.

The concentration of barium in the supernatant liquid could not be calculated accurately from the composition of the reacting mixtures as the precipitates contained an excess of occluded barium. For this reason the barium was determined gravimetrically as barium sulfate in the centrifugate after removal of the lead as sulfide.

Experiments at Room Temperature (26 ± 1°)

Time Required for the Establishment of Equilibrium.—The experiments reported in Table I were carried out in the following way. To 25 ml. of 0.11 *M* barium nitrate was added from a pipet 25 ml. of 0.10 *M* sodium sulfate. Immediately after the precipitation 10 ml. of 0.10 *M* lead nitrate was added and the mixture shaken for various periods of time. The maximum which occurs after about eighteen hours of shaking is explained easily by the fact that the mixed crystals formed during the early stages of aging are heterogeneous and too rich in lead. As a result of the replacement of barium by lead in the precipitate the barium concentration in the solution increases, caus-

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[1] From a thesis submitted to the Graduate School of the University of Minnesota by G. E. Noponen in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] *Cf.* also H. C. Yutzy and I. M. Kolthoff, THIS JOURNAL, **59**, 916 (1937); H. Flood, *Z. anorg. allgem. Chem.*, **229**, 76 (1936).

[3] D. J. Brown, J. A. Moss and J. B. Williams, *Ind. Eng. Chem., Anal. Ed.*, **8**, 134 (1934).

TABLE I

TIME REQUIRED FOR THE ESTABLISHMENT OF EQUILIBRIUM (METHOD A)

Time of shaking	5 min.	1 hr.	4 hrs.	18 hrs.	24 hrs.	4 days	1 wk.	1 mo.	$2^1/_2$ mos.
Total lead in ppt., %	9.4	16.7	20.4	20.9	20.5	19.3	16.2	14.4	14.1

TABLE II

TIME REQUIRED FOR THE ESTABLISHMENT OF EQUILIBRIUM (METHOD B)

Time of shaking	5 min.	1 hr.	24 hrs.	4 days	8 days	14 days	1 month
Total lead in ppt., %	67.6	59.0	32.0	24.1	17.3	14.8	13.7

ing a less favorable distribution of the lead in the precipitate during the later stages of aging. From the results in Table I it is seen that at least a month of shaking is required to establish distribution equilibrium. It is questionable, however, whether true equilibrium is reached, as the speed of recrystallization after a month of aging may have become extremely small. For this reason the experiments were repeated using method B, in which the sodium sulfate solution was added to a mixture of barium and lead nitrate. As may be seen from Table II the primary precipitate is very rich in lead, and the lead content of the solid decreases continuously upon aging. It is gratifying to note that the amount of lead found in the precipitate after a month of shaking agrees within 3% with that obtained after two and one-half months of shaking using method A (Table I). This indicates that true equilibrium is attained after one to two months of shaking.

Distribution Coefficient K as a Function of the Mole Fraction of Lead in the Mixed Crystals.—The results reported in Table III were obtained by using method A. In some cases the order of mixing was reversed or method B was applied. In all cases 25 ml. of 0.11 M barium nitrate and 25 ml. of 0.10 M sodium sulfate were used.

TABLE III

DISTRIBUTION OF LEAD AT VARYING MOLE FRACTIONS IN THE PRECIPITATE

Expt.	Lead nitrate added Ml.	Concn. M	Volume of suspension, ml.	Time of shaking, months	Total lead in ppt., %
1	50	0.1	100	2	8.0
2	35	.1	85	1	9.6
3	25	.1	75	1	10.9[a]
4	20	.1	70	1	11.9
5	15	.1	65	1	13.3
6	10	.1	60	2	14.1[b]
7	5	.1	55	2	17.5
8	25	.01	75	2	23.0
9	10	.01	60	2	29.8

[a] A value of 10.8% was obtained using method B. [b] When the sulfate was added to the barium (reverse precipitation) and then the lead added, a value of 13.8% was obtained after one month. Using method B a value of 13.7% was found after one month.

From the results of Table III and the barium determination in the supernatant liquids the distribution coefficient K (equation 1) can be calculated. The results are given in Table IV.

TABLE IV

DISTRIBUTION COEFFICIENT K OF LEAD BETWEEN MIXED CRYSTALS AND SOLUTION (26 ± 1°)

Expt.	Pb in soln., mmol.	Ba in soln., mmol.	Pb in ppt., in mole %	K
1	4.60	0.581	16.0	0.0241
2	3.16	.507	13.5	.0249
3	2.23	.471	10.9	.0258
4	1.76	.431	9.52	.0257
5	1.30	.400	7.98	.0267
6	.86	.352	5.64	.0245
7	.413	.304	3.50	.0267
8	.193	.277	2.30	(.0342)
9	.070	.252	1.19	(.0432)

It is seen that the value of K is constant and equal to 0.0255 ± 0.01 over the range of 16 to about 3 mole per cent. of lead in the mixed crystals. At lower mole per cent. than three the value of K seems to increase. However, it is not quite certain that the values in experiments 8 and 9 correspond to true equilibrium. It was found that the speed of attainment of equilibrium decreases with decreasing mole percentage of lead in the precipitate. This is to be expected as the solubility of the mixed crystals and, therefore, also the rate of recrystallization increases with increasing mole per cent. of lead in the precipitate. The fact that the value of K between 3 and 16 mole per cent. of lead is constant may be considered as conclusive. In order to obtain another independent check some experiments were carried out under other conditions. To 26 ml. of 0.30 M barium nitrate was added 25 ml. of 0.30 M sodium sulfate followed immediately by 10 ml. of 0.1 M lead nitrate. After shaking for thirty-five days the lead content in the precipitate remained constant and corresponded to 29.5% of the total lead, or to a mole percentage of 3.94 and a value of K of 0.0264. The latter is in good agreement with the values given in Table IV.

In the derivation of equation (1) it was assumed that the ratio $(f_{\text{Ba}}/f_{\text{Pb}})_{\text{solution}}$ is independent of the ionic strength if the electrolyte present does not form complex or slightly dissociated compounds with barium or lead. The experiments reported so far were carried out with solutions which were about 0.05 to 0.1 M in sodium nitrate. In order to test the above assumption experiments were carried out with suspensions 1.1 M in sodium nitrate. At a mole percentage of 6.40 of lead a value of K of 0.0262 was found, indicating that the assumption was justified. If the experiments were carried out in the presence of acetate the value of K decreased materially as a result of the complex formation between lead and acetate.

In the experiments reported in Tables III and IV the suspensions had a volume of 55 to 100 ml. It was found that the speed of attainment of equilibrium decreases when the suspensions are diluted with water, the effect being more pronounced at smaller mole fractions of lead in the precipitate. Apparently, the speed of recrystallization decreases with decreasing electrolyte content of the solution and decreasing mole percentage of lead in the precipitate.

In the following experiments the volume of the suspension was 250 ml. The results are given in Table V.[4]

TABLE V

EFFECT OF DILUTION UPON SPEED OF DISTRIBUTION OF LEAD

Time of shaking, months	Pb in ppt., mole %	Apparent K	K (Table IV)
1	16.2	0.0252	0.0241
2	7.7	.0413	.025
1	2.7	.0445	.030
1	2.3	.0866	(.034)
1	0.93	.0910	(.045)

Effect of Ethanol upon the Distribution Coefficient.—Quite generally, the activity products of barium and lead sulfate are affected differently by a change of the medium; therefore, the value of the distribution coefficient may be expected to change when the medium is varied. Two sets of experiments were carried out in which the percentages of ethanol in the liquid phases were 29 and 50, respectively. In each case two series of experiments were performed, one in which the alcohol was added immediately after precipitation of the barium sulfate before the addition of lead nitrate (method C) and the other in which the alcohol was present during the precipitation (method D). These two methods of precipitation yield different precipitates. The experiments in 29% ethanol were made with the following suspensions. Method C: to 50 ml. of 0.11 *M* barium nitrate was added in order 50 ml. of 0.1 *M* sodium sulfate, 50 ml. of absolute ethanol and 25 ml. of 0.1 *M* lead nitrate. After one week of shaking 13.3% of all the lead was in the precipitate, after one month 12.8%. The experiments made by method D were carried out in a similar way, except that the ethanol was added to the barium nitrate before the sulfate was added. After one week of shaking 13.8% of all the lead was in the precipitate, after one month 13.0%. The experiments in 50% ethanol were made with the following suspensions. Method C: to 25 ml. of 0.11 *M* barium nitrate were added 25 ml. of 0.10 *M* sodium sulfate, 75 ml. of absolute ethanol and 25 ml. of 0.1 *M* lead nitrate After one week of shaking 6.08% of all the lead was in the precipitate, after one month 6.47%. Applying method D yielded 8.04% of the lead in the precipitate after one week and one month of shaking.

From the above figures and the determined barium content of the supernatant liquids the values of the distribution coefficient were calculated. These are given in Table VI.

TABLE VI

EFFECT OF ETHANOL UPON THE VALUE OF DISTRIBUTION COEFFICIENT

Alcohol in %	Medium during pptn.	Lead in ppt., mole %	K
29	Water	6.40	0.021
29	Ethanol–water	6.50	.022
50	Water	6.48	.010
50	Ethanol–water	7.99	.014

Apparently equilibrium had been attained in the experiments in 29% ethanol, but in 50% alcohol equilibrium was only approached. Comparison of the figures with those of Table IV shows that ethanol decreases the distribution coefficient, the value in 50% ethanol being about one-half of that in water. A similar result was arrived at in an entirely different way by Kolthoff and MacNevin,[5] who determined the distribution of radioactive lead between the surface of barium sulfate and a liquid phase.

Experiments at 95 ± 1°.—It was hoped that equilibrium distribution would be obtained more quickly at higher temperatures because of more rapid recrystallization. The general procedure was to mix the solutions at room temperature and then to place the suspensions immediately in a boiling water-bath. After four to five minutes of preheating, a stopper was tied on the bottle and the latter rotated in an oven at 95°. After a certain period of shaking at 95° the bottle with contents was cooled quickly, centrifuged and the mother liquor analyzed for lead and barium in the manner already described.

Time of Establishment of Equilibrium at 95°.—When the lead content of the solid phase is relatively great equilibrium seems to be approached quickly.

Method A.—To 25 ml. of 0.1 *M* sodium sulfate was added 25 ml. of 0.11 *M* barium nitrate and 25 ml. of 0.1 *M* lead nitrate. The results are given in Table VII. It seems that distribution equilibrium is already attained after ten minutes of shaking. An attempt was made to attain the same state of equilibrium by using method B, in which the sulfate is added to a mixture of barium and lead. The results are found in Table VIII. In this case it takes a much longer time before equilibrium is established than when method A is used. The primary precipitate obtained by method B contains much lead; hence, it is much more soluble and for this reason much more perfect than the precipitate obtained by method A. As repeated recrystallizations are necessary to obtain homogeneous distribution of the lead, it is evident that the time required for establishment of equilibrium is greater for the precipitate obtained by method B than for the much less perfect precipitate obtained by method A.

When the amount of lead in the final precipitate decreases the time for attainment of equilibrium increases and the difference between results by methods A and B becomes greater. Thus, when in the experiments reported in Tables VII and VIII, 10 ml. of 0.01 *M* lead nitrate instead of 25 ml. of 0.1 *M* was used, 59.2% of the lead was found in the precipitate after ten minutes of shaking, 42.5% after one day and 41.5% after four days (method A), whereas with method B 70.2% was found after three days and 70.0% after five days. These results make it appear that a true equilibrium state cannot be obtained at 95° within a few days in systems in which there is a small amount of lead.

Distribution Coefficient *K* at 95°.—In the following experiments 25 ml. of 0.1 *M* sodium sulfate was added to 25 ml. of 0.11 *M* barium nitrate, followed by a measured volume of lead nitrate (method A). The results are given in an abbreviated form in Table IX.

The values obtained in the first two experiments corre-

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[4] A detailed description of these experiments is found in the thesis of the junior author.[1]

[5] I. M. Kolthoff and W. M. MacNevin, THIS JOURNAL, **58**, 725 (1936).

TABLE VII

TIME REQUIRED FOR ESTABLISHMENT OF EQUILIBRIUM AT 95° (METHOD A)

Time of heating	10 min.	20 min.	30 min.	1 hr.	2 hrs.	4 hrs.	8 hrs.	16 hrs.
Total lead in ppt., %	13.1	13.0	13.1	13.2	13.0	13.1	13.1	13.0

TABLE VIII

TIME REQUIRED FOR ESTABLISHMENT OF EQUILIBRIUM AT 95° (METHOD B)

Time of heating	10 min.	30 min.	1 hr.	3 hrs.	7 hrs.	20 hrs.	2 days	3 days
Total lead in ppt., %	21.3	20.3	19.4	17.3	15.3	14.0	14.0	13.9

TABLE IX

APPARENT DISTRIBUTION COEFFICIENT AT 95°

Lead nitrate added		Time of shaking, hours	Lead in ppt., mole %	Apparent K
Ml.	Concn., M			
50	0.1	46	16.7	0.026
35	.1	46	14.3	.027
25	.1	8	13.1	.036
20	.1	19	11.8	.038
10	.1	25	7.72	.041
25	.01	96	3.44	.065
25[a]	.01	138	1.97	.072
10	.01	96	1.66	.075

[a] Suspension diluted with water to 250 ml. before heating and shaking.

spond to equilibrium conditions as the same figures could be obtained by method B. Comparison of these figures with those in Table IV reveals that the value of K at relatively high mole percentages of lead hardly changes when the temperature is changed from 26 ($K = 0.0255$) to 95° ($K = 0.0265$).

It is doubtful whether the values of K in Table IX at smaller mole percentages of lead in the precipitate actually correspond to equilibrium conditions. In order to check this point various experiments were made in which after the addition of lead a measured volume of perchloric acid was added. The solubility of the precipitate in acid is greater than in water and the acid, therefore, promotes the repeated recrystallizations. From what has been said in previous sections it is to be expected that the perchloric acid does not affect the values of K. Some of the results are given in Table X. From a comparison with the values obtained in the absence of perchloric acid (taken from Table IX) it is evident that the figures of the "apparent K" in Table IX at lower mole percentages of lead are too high and do not correspond to the true equilibrium conditions. From the results in Table X it may be inferred that the value of K increases with decreasing mole percentage of lead in the precipitate. A similar conclusion was arrived at from the results obtained at room temperature (Table IV).

TABLE X

APPARENT DISTRIBUTION COEFFICIENT AT 95° IN THE PRESENCE OF PERCHLORIC ACID

Concn. of $HClO_4$, M	Time of shaking	Lead in ppt., mole %	Apparent value of K Presence of $HClO_4$	Absence of $HClO_4$
0.575	20 hours	14.3	0.026	0.027
.575	18 hours	11.8	.030	.038
.575	22 hours	3.08	.054	.065
.23	5.5 days	1.65	.053	.072
.18	5 days	1.32	.035	.075

Experiments with Thorium B at 95°.—As indication was obtained that the value of K increases with decreasing mole percentage, an attempt was made to determine the distribution coefficient at zero mole percentage of lead by carrying out the experiments with thorium B. To 10 ml. of 0.1 M sodium sulfate were added 10 ml. of 0.11 M barium nitrate, enough perchloric acid to make the concentration in the suspension 0.005 N and 10 ml. of a thorium B solution of known activity. The suspension was preheated and shaken in the oven. Blank experiments showed that under the conditions mentioned no thorium B was adsorbed on the glass. The results are given in Table XI. Apparently, equilibrium is reached after eighteen hours of shaking. From the results in Table XI and the barium determination a distribution coefficient of 0.088 was calculated. Although there is no certainty that the true state of equilibrium was attained, it is of interest to compare this figure with the value of 0.12 obtained by Kolthoff and MacNevin[6] at room temperature from exchange experiments in the *surface* of barium sulfate. The latter value involves an uncertainty in the microscopic measurement of the specific surface. Considering the small temperature coefficient of the distribution coefficient the order of agreement is very gratifying and lends support to the conclusion that the value of the distribution coefficient increases with decreasing mole percentage of lead in the mixed crystal. A similar result was obtained conclusively by the above authors in their exchange experiments.

TABLE XI

DISTRIBUTION OF THORIUM B AT 95°

Time of shaking, hr.	1	2	4	18	26	41
ThB in ppt., %	63	59.5	56.0	49.2	49.3	48.9

Experiments at 185°.—As the rate of recrystallization increases with the temperature an attempt was made to determine the distribution coefficient at 185°. The experiments were carried out in 2.5-cm. heavy-walled Pyrex glass tubes. The end of a tube was drawn out, the various reagents added, the tube was sealed, thoroughly shaken by hand and placed in an electric Carius oven in which the temperature was kept at 185°. After the heating period the tube was removed and allowed to cool. The contents of the tube were then centrifuged and analyzed for lead and barium.

In the following experiments 25 ml. of 0.11 M barium nitrate was added to 25 ml. of 0.1 M sodium sulfate followed by addition of 25 ml. of 0.1 or 0.01 M lead nitrate. A similar set of experiments was carried out in which 10 ml. 2.3 N perchloric acid was added after the lead. Again it is seen that at high mole percentages of lead distribution equilibrium is reached easily. The values of K found in

TABLE XII

APPARENT DISTRIBUTION COEFFICIENT AT 195° IN PRESENCE AND ABSENCE OF PERCHLORIC ACID

Lead nitrate added		Time in oven,	Absence of $HClO_4$		Presence of $HClO_4$	
Ml.	M	days	Lead in ppt., mole %	Apparent K	Lead in ppt., mole %	Apparent K
25	0.1	1	13.0	0.036	12.7	0.034
25	.1	5	12.4	.033	12.7	.034
25	.01	1	3.85	.081	3.26	.060
25	.01	5	3.85	.081	3.26	.060

the first two experiments were virtually the same in the presence and absence of perchloric acid. It may be mentioned that these experiments show that perchloric acid has no effect upon the distribution coefficient. It is also seen that the value of K (0.034) at 185° at relatively high mole percentages of lead differs little from that at room temperature (0.0255). At smaller mole percentages only apparent equilibrium is reached in the absence of perchloric acid and it is even questionable whether the value obtained in the presence of perchloric acid corresponds to true equilibrium.

Experiments with Thorium B at 185°.—The experiments were carried out by adding to 10 ml. of 0.1 M sodium sulfate 10 ml. of 0.11 M barium nitrate and 10 ml. of a thorium B solution or 10 ml. of a radioactive lead solution of known lead content. The results are given in Table XIII.

TABLE XIII

DISTRIBUTION OF RADIOACTIVE LEAD AT 185°

Concn. of lead (m. p. l.)	ThB	ThB	ThB	ThB	2.5×10^{-6}	2.5×10^{-6}	2.5×10^{-6}	2.5×10^{-6}	2.5×10^{-4}	2.5×10^{-4}	2.5×10^{-4}	2.5×10^{-4}
Time of heating, hours	22	41	45	54	30	41	45	53	22	41	45	53
Lead in ppt., %	59.4	54.5	67.4	61.4	55.5	59.8	60.8	57.7	55.6	54.0	60.8	62.0

Taking from the results in Table XIII an average value of 59%, a value of K is calculated equal to 0.10. Again, this value compares favorably with that found by Kolthoff and MacNevin[5] at room temperature.

Conclusions and Summary

1. The value of the distribution coefficient K of lead between mixed crystals of barium and lead sulfate and solutions was found to be 0.0255 at mole percentages of lead varying from 3 to 16 in the solid at 26°. At a mole percentage of about 13, K was found to be equal to 0.0265 at 95° and to 0.034 at 185°, showing that the change of K with the temperature is very small.

2. The mixed crystals do not behave as ideal solid solutions. In the first place definite indication was obtained that the value of K becomes larger at all temperatures when the mole fraction of lead becomes small. Moreover, if the solid solutions were ideal the value of K should be equal to the ratio of the solubility products of barium and lead sulfate. Taking the former equal to 1.2×10^{-10} and the latter to 2×10^{-8}, the calculated value of K is 0.006. Actually at zero mole percentage of lead in the precipitate a value of K of 0.09 (95°) to 0.12 (185°) was found. The deviation from the calculated value becomes greater with decreasing mole fraction of lead in the solid.

3. At relatively high mole percentages of lead in the precipitate distribution equilibrium is reached in short periods of time at all temperatures. At small mole fractions of lead a long time is required for attainment of equilibrium and it is questionable whether the figures presented in this paper at low mole percentages of lead correspond to true equilibrium conditions. Addition of perchloric acid favors the speed of distribution of the lead because the acid increases the solubility and consequently also the speed of recrystallization of the precipitate.

4. The value of K decreases with increasing ethanol content of the suspension.

5. Large amounts of sodium nitrate and perchloric acid, *i. e.*, of electrolytes which do not form complex or undissociated compounds with barium and lead, do not affect the value of the distribution coefficient.

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