

Summary

1. Adsorbed wool violet strongly inhibits the aging of barium sulfate.

2. The presence of much gelatin in the aqueous suspension inhibits the aging of barium sulfate only slightly, although it is strongly adsorbed on barium sulfate. This is explained by

the hydrophilic character of the adsorbed gelatin.

3. The aging of barium sulfate is strongly inhibited in a medium of 50% ethanol.

4. Precipitates of barium sulfate prepared at boiling temperature are very imperfect. Aging of precipitates at higher temperature promotes the perfection process considerably.

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

Studies on Aging of Fresh Precipitates. XXI. Properties of Barium Sulfate Precipitated from Ammonium Acetate Medium and the Coprecipitation of Lead

BY I. M. KOLTHOFF AND G. E. NOPONEN

A study of the properties of barium sulfate precipitated from ammonium acetate medium is not only of theoretical but also of practical importance in connection with the problem of separating barium and lead, and of the extraction of lead sulfate from the mixed sulfates with ammonium acetate solution.¹ In the present work the coprecipitation of lead with barium sulfate, when the latter is precipitated from a medium containing much ammonium acetate, has been investigated. In a previous study² it has been shown that under equilibrium conditions the amount of lead in the solid phase can be calculated from the distribution expression. It should be realized that the value of the distribution constant, K , found previously,² decreases considerably when the liquid phase contains much acetate, as the activity coefficient of the lead ions is decreased much more than that of the barium ions as a result of complex formation. But the value of K does not decrease to zero; therefore, it is impossible to have pure barium sulfate in equilibrium with a solution containing lead and ammonium acetate. All one can hope for in analytical work is to find conditions under which the barium sulfate precipitate contains a minimum amount of lead and the solid phase is far removed from the state of equilibrium with the liquid phase.

Experimental

In the following work experiments were carried out under such conditions that the lead, if present alone in the solu-

tion, would not precipitate in the form of lead sulfate. In order to know these conditions, the solubility of lead sulfate was determined by shaking pure samples of the salt for three to four hours at room temperature ($26 \pm 1^\circ$) with the solutions containing varying amounts of ammonium acetate and sodium sulfate. The lead content of the saturated solution was found by precipitation as lead chromate from hot acetic acid solution with potassium dichromate and iodimetric determination of the chromate in the precipitate. The results are given in Table I.

TABLE I
SOLUBILITY OF LEAD SULFATE IN AMMONIUM ACETATE-SULFATE SOLUTIONS AT $26 \pm 1^\circ$

Concn. ammonium acetate, M	Concn. sodium sulfate, M	Concn. of lead, moles/liter
0.6 ^a	0.01	0.0052
.6	.005	.0089
1.5	.005	.0288
2	.01	.0390
3	.005	.0697
3	.01	.0692

^a Solution was also 0.6 M in acetic acid.

Coprecipitation of Lead with Barium Sulfate from Ammonium Acetate Medium.—In the following experiments the concentration of ammonium acetate, after making up to a volume of 100 ml. was 2 M . In the first series the barium sulfate was precipitated by adding the sulfate to a mixture of barium and lead in ammonium acetate, in the second series the barium was added to a mixture of lead and sulfate in ammonium acetate. Series I: to 20 ml. of 0.05 M barium nitrate was added 10 ml. of 0.10 M lead nitrate and 34 ml. of 6 M ammonium acetate. The mixture was shaken while 20 ml. of 0.10 M sodium sulfate was added from a buret in four to five minutes. The volume was then made up to 100 ml. and the suspension placed on a shaker. After various periods of shaking the suspensions were centrifuged and 50 ml. of the centrifugate analyzed for lead by adding 2 to 3 ml. of 6 M acetic acid, heating to the boiling point and adding 10 ml. of 0.05 M

(1) Cf. J. Majdel, *Z. anal. Chem.*, **83**, 36 (1931); F. Feigl and L. Weidenfeld, *ibid.*, **84**, 220 (1931); W. W. Scott and S. M. Alldredge, *Ind. Eng. Chem., Anal. Ed.*, **3**, 32 (1931); J. W. Marden, *This Journal*, **38**, 310 (1916).

(2) I. M. Kolthoff and G. E. Noponen, *ibid.*, **60**, 197 (1938).

potassium dichromate. The heating was continued until the precipitate had become crystalline and then ammonium hydroxide was added until the solution was neutral. After cooling the lead chromate was filtered on a sintered glass crucible and determined iodometrically. Series 2: the experiments were carried out as in Series I, except that the sulfate, lead and ammonium acetate solutions were mixed and the barium nitrate was added from a buret. The results are reported in Table II.

TABLE II

COPRECIPITATION OF LEAD WITH BARIUM SULFATE FROM AMMONIUM ACETATE SOLUTION

Time of shaking of ppt., hours	Sodium sulfate as precipitant		Barium nitrate as precipitant	
	Pb in ppt., millimoles	Pb in ppt., %	Pb in ppt., millimoles	Pb in ppt., %
0	0.0482	4.82	0.317	31.7
1	.0496	4.96	.300	30.0
24	.0552	5.52	.295	29.5

Although the supernatant liquids in both series of experiments had approximately the same composition, the lead content of the precipitates obtained with sodium sulfate as precipitant was much smaller than that of those with barium nitrate as precipitant. This result is in excellent agreement with the coprecipitation rules derived³ in a theoretical way. Evidently the precipitates obtained in both series of experiments consist of heterogeneous mixed crystals of barium and lead sulfate which are not in equilibrium with the solution. The precipitates obtained in Series I contain too little lead and, on aging, become richer in lead. The precipitates obtained in Series II contain too much lead and become poorer in lead on aging. It is seen from the results in Table I that in none of the two cases the state of equilibrium is reached, even after very long periods of aging. From these results it may be concluded that the barium sulfate obtained at room temperature from relatively concentrated ammonium acetate solution is fairly perfect. Upon shaking of highly imperfect barium sulfate with lead solutions distribution equilibrium is attained after a reasonable time.³ On the other hand, the rate of recrystallization of the relatively perfect, heterogeneous mixed crystals obtained from ammonium acetate medium is small. Actually these crystals, when observed with the microscope, show a large size and appearance of perfection, as compared to the individually invisible particles obtained in the absence of ammonium acetate. Moreover, the former are readily filterable. Apparently ammonium acetate not only increases the solubility of lead sulfate, but also that of barium sulfate, and the formation of larger crystals from ammonium acetate medium may be expected on the basis of von Weimarn's⁴ rule giving the relation between degree of dispersion and supersaturation.

Since the mixed crystals obtained from ammonium acetate medium age very slowly, it may be expected that the amount of lead occurring in the precipitate will be greatly dependent upon the speed of addition of the precipitant. This should be especially true when sodium sulfate is the precipitating agent. When the latter is added

slowly to the barium-lead acetate solution, the mixed crystals formed will approach heterogeneous equilibrium with the mother liquor of varying composition during the precipitation much closer than when the sulfate is added quickly. In the former case the distribution of lead between solid and solution will be governed approximately by the logarithmic Doerner and Hoskins⁵ expression and the precipitate should be poorer in lead than when the sulfate is added rapidly. The reverse is true when barium nitrate is the precipitating agent. Under these conditions the ratio of lead to barium in the solution during precipitation is very large and especially upon slow addition of barium a large incorporation of lead may be expected, yielding a distribution according to the Doerner and Hoskins expression.

The following experiments on the effect of the rate of addition of precipitating agent were performed. To 50 ml. of 4 M ammonium acetate, 10 ml. of 0.1 M lead nitrate and 20 ml. of 0.05 M barium nitrate in an Erlenmeyer flask was added from a buret, 20 ml. of 0.1 M of sodium sulfate. The contents of the flask were shaken by a rotary shaker during the addition of the sulfate. In one series of experiments the sulfate was added in twenty seconds, in another series during a period of ten minutes. After the addition of precipitant, the suspensions were shaken for various periods of time and the liquid phases analyzed for lead. The experiments were repeated except that the barium nitrate was used as precipitating agent. The results are given in Table III.

TABLE III

EFFECT OF RATE OF ADDITION OF PRECIPITANT UPON COPRECIPITATION OF LEAD

Time of shaking of ppt., hours	Sodium sulfate as precipitant		Barium nitrate as precipitant	
	Added in 20 sec.	Added in 10 min.	Added in 20 sec.	Added in 10 min.
0	0.220	0.0661	0.219	0.379
1	.222	.0661	.221	.373
20	.226	.0663	.237	.344

It is seen that the effect of rate of addition of precipitant is very great and that the precipitates, again, recrystallize very slowly upon aging in the mother liquor. The most extreme differences are found, as was expected, in the two series in which the precipitants were added slowly. Upon fast precipitation the same amounts of lead were found in the precipitates, independent of the order of precipitation. Upon aging, the lead content increases slowly after slow precipitation with sulfate, whereas a slow decrease is noticed upon aging after slow precipitation with barium. The speed of recrystallization is increased greatly when the aging is performed at higher temperatures. The suspensions formed under conditions given in Table III were heated to boiling temperature, the flasks closed, placed in an oven at 95° and allowed to digest for twenty hours. At the end of this time, the mixtures were cooled, filtered and the filtrates analyzed for lead. It is seen from Table IV that in all cases the same state of equilibrium is approached, which, however, is different from that at room temperature as the complex

(3) I. M. Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932).

(4) P. P. von Weimarn, "Die Allgemeinheit des Kolloiden Zustandes," Th. Steinkopff Verlag, Dresden, 1925.

(5) H. A. Doerner and W. M. Hoskins, *THIS JOURNAL*, **47**, 662 (1925).

constant of the lead acetate complex varies with the temperature.

TABLE IV
EFFECT OF DIGESTION AT 95° UPON COPRECIPITATION OF LEAD

Precipitant	Time of addn. of precipitant	Millimoles of Pb in ppt. after digestion	Millimoles of Pb co-precipitated at boiling temp.,
Na ₂ SO ₄	20 sec.	0.111	0.16
Na ₂ SO ₄	10 min.	.092	.029
Ba(NO ₃) ₂	20 sec.	.19	.43
Ba(NO ₃) ₂	10 min.	.18	.39

Some experiments similar to those of Table III also were carried out by adding the precipitant to the boiling solutions. Immediately after the precipitation the suspensions were cooled and the filtrates analyzed for lead. The results are given in the last column of Table IV. From a practical viewpoint it is of interest to mention that the least coprecipitation of lead is found when the barium-lead mixture in ammonium acetate is precipitated at boiling temperature with sulfate added slowly, and the suspension cooled and filtered immediately.

Aging of Barium Sulfate Precipitated from Ammonium Acetate Medium.—In the experiments described so far the lead was coprecipitated with the barium sulfate. In the following experiments lead nitrate was added to the suspension after precipitation of barium sulfate and the rate of entrance of lead into the precipitate determined. To 25 ml. of 4 *N* ammonium acetate and 5 ml. of 0.1 *M* barium nitrate was added quickly 10 ml. of 0.1 *M* sodium sulfate. Immediately after the precipitation 10 ml. of 0.01 *M* lead nitrate was added, the suspension shaken for various periods of time, filtered and the filtrates analyzed for lead. The results are given in Table V.

TABLE V
SPEED OF PENETRATION OF LEAD INTO BARIUM SULFATE

Time of shaking with Pb soln.	1 hour	3 hours	9 hours	1 day	2 days	4 days
% of added lead in precipitate	9.7	10.3	12.9	29.0	27.3	46.6

It is apparent that the barium sulfate precipitated from ammonium acetate medium is far from being perfect, at least much less perfect than the mixed crystals with lead sulfate obtained under similar conditions (compare Tables III and IV). In the interpretation of the results of Table V it should be realized that the speed of penetration of the lead in the above experiments cannot be compared with that carried out in the absence of ammonium acetate,³ as the latter increases the rate of recrystallization and the precipitate obtained from acetate medium is much more perfect. This is shown by experiments in which the rate of penetration of chromate⁶ into the barium sulfate was used as an indicator of the degree of perfection of the precipitate. In the first place it was ascertained that the distribution coefficient *K* of the chromate between the solid phase and the solution is not affected by ammonium acetate. Barium sulfate was precipitated and shaken with chromate and sulfate⁶ in a medium of 2 *N*

ammonium acetate. Distribution equilibrium was attained after one to two days of shaking, a value of *K* of 1.14 being found. In the absence of ammonium acetate *K* was found to be equal⁶ to 1.1.

In the following experiments barium sulfate was precipitated in the presence of ammonium acetate. In one series chromate was added to the suspension and the latter shaken, the final concentration of ammonium acetate being 2 *M* of sodium sulfate 0.01 *M* and of sodium chromate 0.01 *M*. In the other series of experiments the barium sulfate suspension was centrifuged immediately after precipitation and the supernatant liquid containing the ammonium acetate poured off. The precipitate was washed with water and suspended in a solution 0.01 *M* in sodium sulfate and 0.01 *M* in sodium chromate, but containing no ammonium acetate. After various periods of shaking samples were removed, centrifuged and the solution analyzed for chromate

TABLE VI
EFFECT OF AMMONIUM ACETATE UPON SPEED OF PENETRATION OF CHROMATE

Time of shaking with chromate	% of added CrO ₄ in ppt. (in 2 <i>M</i> Am. Ac.)	% of added CrO ₄ in ppt. (no Am. Ac.)
10 min.	0.60	0.35
30 min.	..	.40
1 hour	.9	..
2 hours
18 hours	6.6	.50
26 hours	..	2.3
7 days	36.4	..
12 days	..	4.4
29 days	37.0	..

From a comparison of the results of Table VI with those of a previous paper⁶ it follows that the barium sulfate precipitated in the presence of much ammonium acetate is much more perfect than when prepared in the absence of acetate. It is clear from the results in Table VI that barium sulfate prepared in the presence of ammonium acetate and aged in a 2 *M* solution of the latter salt perfects itself much faster than a precipitate obtained under similar conditions but aged in the absence of acetate. This increased rate of recrystallization of the barium sulfate in the acetate solution is attributed to an increased solubility of the precipitate in the ammonium acetate.

Summary

1. The amount of coprecipitation of lead with barium sulfate when the latter is precipitated from acetate solution depends greatly upon the speed of addition of precipitant. With very fast addition of the latter the amount of coprecipitation at room temperature is practically independent of the order of mixing the reagents.

2. The heterogeneous mixed crystals of barium and lead sulfate formed on precipitation from acetate medium age very slowly in the supernatant liquid at room temperature but very markedly on digestion at 95°.

(6) I. M. Kolthoff and G. E. Noponen, *THIS JOURNAL*, **60**, 39 (1938).

3. The least coprecipitation of lead is obtained when sodium sulfate is added very slowly to the boiling mixture of barium and lead.

4. Barium sulfate precipitated at room temperature from fairly concentrated ammonium ace-

tate solutions is much more perfect than when precipitated in the absence of acetate. The further perfection of the former precipitate is promoted on aging in a solution containing ammonium acetate.

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The Influence of Temperature and Pressure on the Volume and Refractive Index of Benzene

BY R. E. GIBSON AND JOHN F. KINCAID

Introduction

The influence of pressure on the refractive index of liquids has been measured in the past by two methods. In the first¹ the refractive index changes produced by small pressure changes of the order of one atmosphere were measured with an interferometer. The initial value of dn/dP was obtained in such experiments but not the effect of pressure on dn/dP . In the second method² a steel apparatus for withstanding high pressures was used. It was fitted with glass windows mounted so that the liquid between them formed a 30° prism. The refractive index of the liquid was determined from the angle of the prism and the angle of minimum deviation. Readings were made at pressures up to 13,500 atmospheres. This second method has the disadvantage that the windows are an essential part of the light path and what happens to the optical properties of the glass under such conditions is still quite an open question.

In this paper we shall describe a method which has not been used hitherto for measuring the effect of pressure on the refractive indices of liquids, and give results for benzene. The method has limitations but they are obvious. In order to discuss the specific refraction of benzene under different conditions we shall also include new data on the compressions of benzene at different temperatures together with derived thermodynamic quantities and also the densities and

(1) (a) W. C. Röntgen and L. Zehnder, *Ann. Physik*, **44**, 24 (1891); (b) F. Himstedt and I. Wertheimer, *ibid.*, **67**, 395 (1922); (c) I. Eisele, *ibid.*, **76**, 396 (1925).

(2) T. C. Poulter, C. Ritchey and C. A. Benz, *Phys. Rev.*, **41**, 366 (1932). The effect of pressures up to 1800 atm. on the refractive indices of water, alcohol, and their mixtures, and of carbon bisulfide, has been determined recently, but so far only abstracts of the papers describing this work have been published. See F. E. Poindexter and J. S. Rosen, *Phys. Rev.*, **45**, 760 (1934), and Poindexter, *ibid.*, **47**, 202 (1935).

rough values of the compressions of three optical glasses.

Experimental

Our method of measuring the effect of pressure on the refractive index of a liquid consists of adjusting the pressure at a constant temperature so that the liquid has the same refractive index as a piece of optical glass immersed in it. The apparatus is shown diagrammatically in Fig. 1. The win-

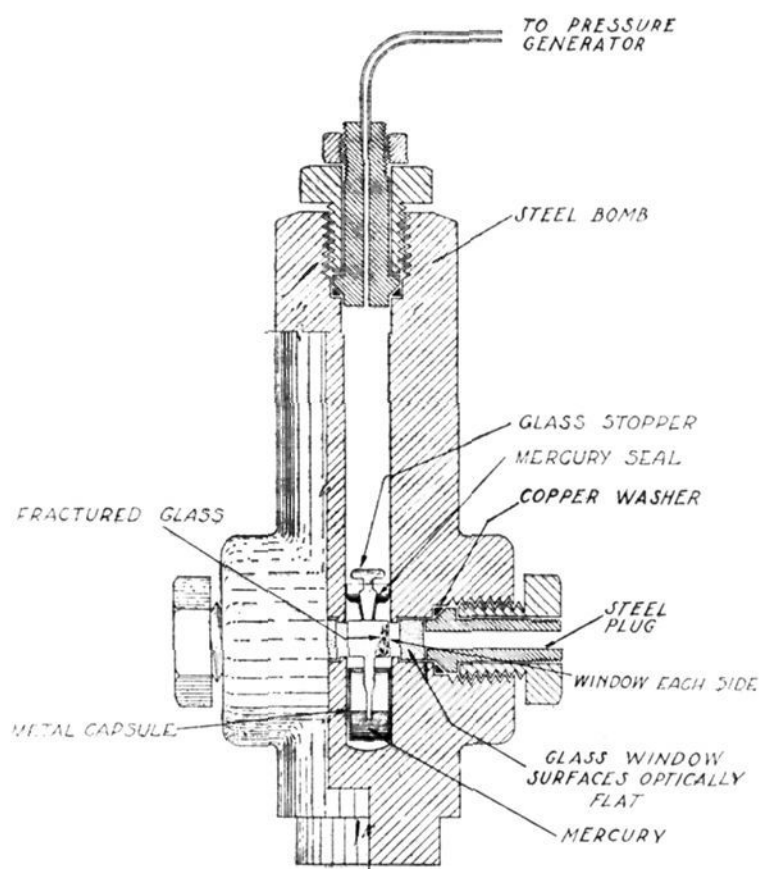


Fig. 1.—Diagram of apparatus for the comparison of the refractive indices of a liquid and a glass under high pressure.

dow bomb itself already has been described.³ The benzene was contained in a small vessel provided with plane parallel windows. The opening at the

(3) R. E. Gibson, *THIS JOURNAL*, **59**, 1521 (1937).