[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Contamination of Precipitated Barium Sulfate by Univalent Cations[1]

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Previous investigations of the contamination of precipitated barium sulfate by univalent cations[4] have done much toward establishing the conditions affecting this contamination, but have been incomplete in at least two important respects: (1) establishing the composition of the precipitates by complete analyses, and (2) studying the physical properties of the precipitates as a function of the amount of contamination. It has been the primary purpose of this research to investigate the nature of this contamination, particularly from the standpoint of possible solid solution formation as demonstrated by X-ray measurements.[5] Toward this end, we have, first, attempted to limit the system under study so that the contamination by cations alone might be investigated, and, secondly, we have made complete analyses so that we might know the entire composition of our precipitates.

The structures studied in this paper are to be considered the product of localized kinetic processes occurring during precipitation, and would not represent equilibrium systems.

Experimental

In order to limit our system so as to study only the cationic contamination of barium sulfate, we have made use of the fact that salicylate ion and hexammine cobaltic ion are not coprecipitated by barium sulfate in significant amounts. The use of large ions that do not coprecipitate for the purpose of limiting coprecipitation is not new,[6] but the opportunities offered by this device have not been greatly appreciated.

Most of the contaminated precipitates were prepared by the slow addition of neutral solutions of barium salicylate (from 0.1 to 0.5 M) to neutral solutions of different concentrations of alkali sulfate (from 0.25 to 3.5 M), with vigorous motor stirring and at temperatures between 92 and 98°. For a barium ion concentration of 0.25 molar, a rate of addition of 9 ml. per minute was adopted. Where the concentration of barium salicylate solution was varied, the rate of addition was correspondingly changed so that the rate of formation of the precipitates was approximately the same in every case. The total amount of barium solution added was such that only from 10 to 20% of the original amount of sulfate was precipitated, keeping the sulfate concentration fairly constant.

"Pure" reference barium sulfate 601 was prepared by the slow addition of 0.25 M barium salicylate solution to 0.005 M hexammine cobaltic sulfate solution acidified with 1 ml. of concd. sulfuric acid per liter. The word "pure" as used in this paper is a convenient designation rather than a claim.

For the few precipitates prepared differently, the method of preparation is indicated in Table II.

All contaminated precipitates were digested in their mother liquors for three and one-half hours, motor stirring and temperatures of 90 to 100° being maintained. The "pure" reference precipitate 601 was decanted five times with hot water immediately after precipitation, then digested in water for the remaining period of time.

After digestion, all precipitates were washed with hot water five times by decantation, transferred to a Büchner funnel, washed until washings were free from salicylate ion by chemical test, and then ten times more. Washings totalled about five liters in each case.

Drying conditions varied. The majority of precipitates were subjected to vacuum treatment for from one to ten hours, in most cases at 110°. The reference precipitate 601 was vacuum-dried over concentrated sulfuric acid at room temperature until constant weight was attained.

Analytical reagent grade chemicals were considered to be of sufficient purity for the work.

To determine NH_4^+ in the precipitates, 1-g. samples were digested in a Kjeldahl distillation apparatus with 150 ml. of a boiling solution containing 12 g. sodium hydroxide and 30 g. sodium carbonate for one and one-half hours, the ammonia being distilled into 0.1 M hydrochloric acid. The excess acid was back-titrated with alkali, using methyl red indicator. Blank tests were run on the reagents used.

A short direct method of analysis was devised for the determination of total K^+, Na^+ and Li^+. It was found that the total alkali metal contaminant could be recovered quantitatively by igniting 0.5 to 1 g. samples of precipitate to constant weight at 900 to 1000°, leaching out the contaminant with a few ml. of hot distilled water (containing one drop of concentrated sulfuric acid), filtering, evaporating the filtrate and igniting the residue at 500 to 600° to constant weight as the alkali sulfate. This entire cycle was then repeated; amounts of alkali sulfate recovered by the second set of leachings were from 0.0 to 1.0 mg. The temperatures used were experimentally found not to volatilize potassium, sodium or lithium sulfate

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(4) (a) E. F. Allen and J. Johnston, THIS JOURNAL, **32**, 588 (1910); (b) J. Johnston and L. H. Adams, *ibid.*, **33**, 829 (1911).

(5) (a) L. Vegard and H. Schelderup, *Physik. Z.*, **18**, 93 (1917); (b) L. Vegard, *Z. Physik*, **5**, 17 (1921), and succeeding papers.

(6) G. A. Hulett and L. H. Duschak, *Z. anorg. Chem.*, **40**, 196 (1904).

in amounts over 0.1 mg. for the ignition periods employed. Work by Kolthoff and MacNevin[7] would suggest the practicability of such an analytical method for limited systems, although we were not familiar with their work at the time our method was devised.

Analysis for alkali-ion content by the method of Allen and Johnston,[4] consisting of dissolving the sample in concentrated sulfuric acid, re-precipitating the barium sulfate by pouring into water, then filtering and evaporating the filtrate, gave results about 10% higher than the ignition and extraction method. The discrepancy may be due to a slight solubility of barium sulfate in solutions of such high acid concentration.

Analysis of the total barium and sulfate contents of three precipitates, using the digestion method of Wolesensky given below, made after the removal of the contaminant by ignition and leaching, gave in each case a mole ratio of unity; this shows that the ignition and leaching process does quantitatively remove the contaminant.

Using the short direct method of analysis, the results obtained in the determination of Li^+, Na^+ and K^+ are given in Table II, together with the NH_4^+ results by Kjeldahl analysis. Except for precipitates 29, 33, 39, 42 and 43 (where the amount of sample was rather limited) the values given represent the mean of two analyses and their average deviation. Loss on ignition data is also included in Table II.

For determination of total barium and total sulfate content, the sodium carbonate fusion method for metathesizing barium sulfate was not found practical for this research, since the precipitates contained volatile sulfate, some of which was lost during the fusion. Therefore, total barium and total sulfate content determinations were made with 0.5-g. samples using the sodium carbonate digestion method of Wolesensky[8] to effect decomposition of the barium sulfate. After filtration the filtrate was acidified with hydrochloric acid and the sulfate ion precipitated by the rapid addition of 0.05 *M* barium chloride solution in excess. The barium carbonate was dissolved on the filter with hot dilute hydrochloric acid in excess. (A small amount of barium sulfate was usually found suspended in this solution containing barium ion; the solutions were always digested for several days and re-filtered to recover this small amount, which was subtracted from the original sample weight.) The barium ion was re-precipitated by pouring the solution into 300 ml. of hot water containing 2 ml. of concd. sulfuric acid. All analytical precipitates were fumed with 2 drops of concd. sulfuric acid before final ignition. Blank tests were run on the reagents used. The use of dilute barium chloride solution, rapid addition to the sulfate ion solution, and volumes of about 400 ml. for the latter, would tend to minimize errors due to coprecipitation of sodium chloride.

Results of analysis for total sulfate and total barium, expressed as the mole ratio, are given for eighteen precipitates in Table I. The extreme deviation was 0.6%. For precipitates having ionic contamination, we have included in the table the $SO_4^=/Ba^{++}$ mole ratios calculated from the alkali-ion and NH_4^+ analyses on the assumptions that the contaminating ion is present in the precipitate either completely as the sulfate or the bisulfate.

Results obtained by the direct method of alkali-ion and NH_4^+ analysis, when computed to the bisulfate, agree reasonably well (Table I) with analyses of the total barium and total sulfate contents for ten precipitates containing NH_4^+, K^+ and Na^+. For Li^+ there is a distinct trend toward the normal sulfate, in highly-contaminated precipitates.

Tests for the presence of salicylate ion were conducted as follows: Samples of 1 to 5 g. were dissolved in concd. sulfuric acid without the application of heat, or with only gentle warming on the steam-bath. The barium sulfate was re-precipitated by pouring the acid solution into 150 ml. of water, and filtered off. The filtrate was shaken with ether, and the ether extract evaporated. The ether residue (no visible residue was ever obtained) was dissolved in 2 ml. of ethyl alcohol, diluted to 50 ml. with water, and 0.5 ml. of 4 *M* acetic acid and 0.5 ml. of 0.1 *M* ferric chloride solution added. The color reaction with salicylate ion is sensitive to one part per million,[9] and as used would detect over 0.01 weight % salicylate ion in the precipitate. Of nine precipitates tested, none contained over 0.01 weight % of salicylate ion.

A test on ppt. 601 to detect the presence of cobalt as a contaminating ion gave negative results, and is substantiated by the work of others.[10]

Analysis of the water content was made by determining the loss of weight on ignition to constant weight at 900 to 1000°. For precipitates contaminated with NH_4^+ the loss on ignition represents the loss of water and the loss of NH_4HSO_4, the latter being quantitatively volatilized by this procedure.[4a] The water content may then be obtained by subtracting the weight of ammonium bisulfate found by analysis from the total loss on ignition. For precipitates containing K^+ or Na^+ the loss on ignition represents a loss of water and a loss of sulfuric acid from the decomposition of the alkali metal bisulfate. The water content is thus obtained by subtracting from the loss on ignition the amount of sulfuric acid corresponding to the bisulfate of the alkali-ion analysis. In the case of Li^+, this ion is apparently present partly as the normal sulfate and partly as the bisulfate (see Table I). By analysis for total lithium,

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(7) I. M. Kolthoff and W. M. MacNevin, *J. Phys. Chem.*, **44**, 921 (1940).

(8) E. Wolesensky, *Ind. Eng. Chem.*, *Anal. Ed.*, 1, 29 (1929).

(9) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. I, D. Van Nostrand Co., New York, N. Y., 1936, p. 163.

(10) L. Waldbauer, F. W. Rolf and H. A. Frediani, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 888 (1941).

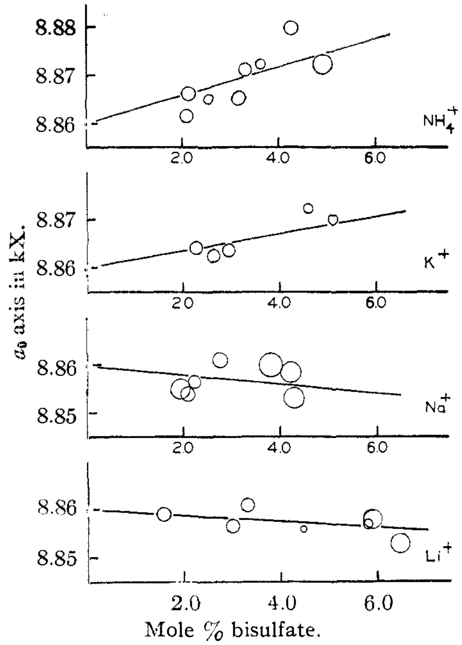

Fig. 1.—a_0 axis *vs.* composition.

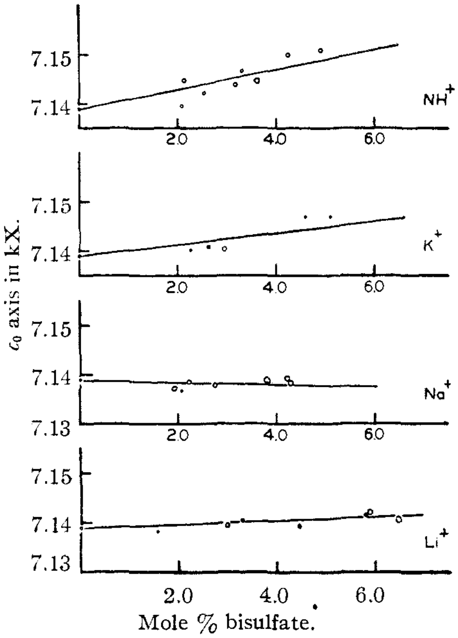

Fig. 3.—c_0 axis *vs.* composition.

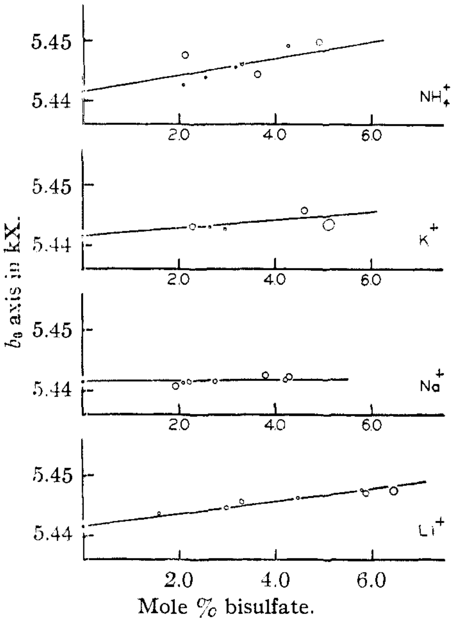

Fig. 2.—b_0 axis *vs.* composition.

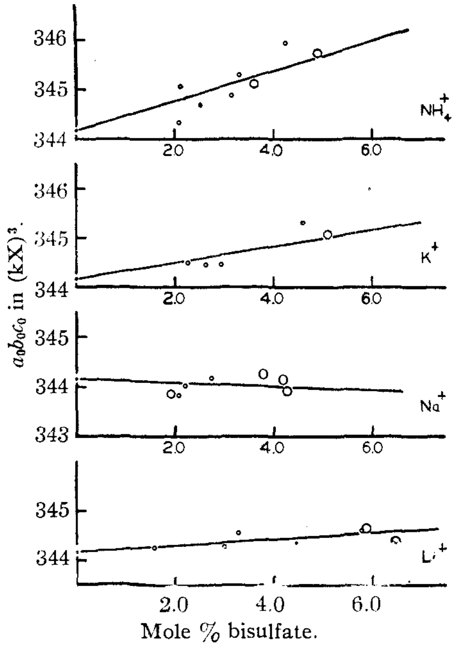

Fig. 4.—Unit cell volume *vs.* composition.

total barium, and total sulfate, the proportion of lithium present as the bisulfate can be found, and thus the amount of sulfuric acid corresponding thereto. Subtracting this computed amount of sulfuric acid from the total loss on ignition will give the water content.

The precision measure shown for the water content in Table II reflects the probable errors in both loss on ignition and alkali-ion analyses.

A less accurate estimation of the water content may be obtained by adding together the weight of barium ion, sulfate ion and alkali ion (all found by analysis), plus the weight of hydrogen ion equivalent to the amount of bisulfate present. This total weight should be that of the original sample, minus the amount of water present. This method agrees reasonably well with the amount of water as found by the alternative method, but is burdened with the errors in the barium and sulfate analyses.

Density measurements were made using the method of Jette and Foote.[11] To ensure that sur-

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[11] E. R. Jette and F. Foote, *J. Chem. Phys.*, **1**, 29 (1929).

face effects were not significantly affecting the results, measurements were made using both bromobenzene and isobutyl alcohol as the hydrostatic liquid, these liquids having different wetting properties for barium sulfate.

Precision powder photograms of the precipitates were made with the same apparatus used by Walden and Cohen,[12] except for a few mechanical improvements. Calcium radiation was used; the wave length employed in the calculations was $K_{\alpha_1} = 3.35169$ kX.[13] Lattice constants were computed by the method of least squares developed by Cohen.[14]

For each ionic contaminant, lattice constants and unit cell volume have been plotted against the amount of contaminant expressed as the bisulfate (Figs. 1, 2, 3 and 4), the radii of the circles representing the probable errors of the individual parameters. Numerical values of the unit cell volume are given in Table II. An average of 17 pairs of lines was measured per film, no fewer than 12 being measured in any case. The parameters computed from different films for the same substance agreed within their probable errors. The ranges of the probable errors on the individual films were a_0 0.008 to 0.03%; b_0 0.004 to 0.02%; c_0 0.004 to 0.009%.

All X-ray exposures were made between 23 and 30°.

Computations

An example of the method of obtaining the calculated $SO_4^=/Ba^{++}$ mole ratios for Table I is given here for ppt. 37: *as alk. Sulfate*

(1) For a 1.000 g. sample, the loss on ignition = 0.0107 ± 0.0001 g., and the amount of alkali ion sulfate recovered = 0.0117 ± 0.0003 g. K_2SO_4. Therefore

$$\begin{array}{ll} 0.0117 \pm 0.0003 & \text{g. } K_2SO_4 \\ +0.0107 \pm 0.0001 & \text{g. water and sulfuric acid (total loss on ign.)} \\ \hline 0.0224 \pm 0.0004 & \text{g. of total contamination in 1 g. ppt.} \end{array}$$

(2) Subtracting from the total sample

$$\begin{array}{ll} 1.000 & \text{g. total sample} \\ -0.0224 \pm 0.0004 & \text{g. total contaminant} \\ \hline 0.9776 \pm .0004 & \text{g. barium sulfate} \end{array}$$

$$(0.9776 \pm .0004)\,\frac{0.4115}{96.06} = 0.004187 \pm 2 \times 10^{-6} \text{ mole } Ba^{++} \text{ and moles } SO_4^= \text{ as barium sulfate}$$

(3) To find total moles of $SO_4^=$

$$\frac{(0.0117 \pm .0003)}{174.3} = 0.000067 \pm 2 \times 10^{-6} \text{ mole } SO_4^= \text{ as } K_2SO_4$$

$$\begin{array}{ll} 0.004187 \pm 2 \times 10^{-6} & \text{mole } SO_4^= \text{ as barium sulfate} \\ +0.000067 \pm 2 \times 10^{-6} & \text{mole } SO_4^= \text{ as } K_2SO_4 \\ \hline 0.004254 \pm 3 \times 10^{-6} & \text{total mole } SO_4^= \end{array}$$

(4) Mole ratio $SO_4^=/Ba^{++}$ calcd. as K_2SO_4

$$\frac{0.004254 \pm 3 \times 10^{-6}}{0.004187 \pm 2 \times 10^{-6}} = 1.016 \pm 0.001 \ \frac{\text{moles } SO_4^=}{\text{moles } Ba^{++}} \text{ as alk. sulfate}$$

for Ppt. 37 *as alkali bisulfate*

(1) Repeating steps (1) and (2) above, gives

$0.004187 \pm 2 \times 10^{-6}$ mole Ba^{++} and $SO_4^=$ as barium sulfate

(2) To find moles $SO_4^=$ present as $KHSO_4$

$$(0.0117 \pm .0003)\,\frac{272.3}{174.3} = 0.0183 \pm 0.0005 \text{ g. } KHSO_4 \text{ equivalent to potassium sulfate found}$$

$$\frac{(0.0183 \pm 0.0005)}{136.2} = 0.000134 \pm 4 \times 10^{-6} \text{ mole } SO_4^= \text{ present as } KHSO_4$$

(3) Total moles $SO_4^=$ and mole ratio

$$\begin{array}{ll} 0.004187 \pm 2 \times 10^{-6} & \text{mole } SO_4^= \text{ as } BaSO_4 \\ +0.000134 \pm 4 \times 10^{-6} & \text{mole } SO_4^= \text{ as } KHSO_4 \\ \hline 0.004321 \pm 5 \times 10^{-6} & \text{total mole } SO_4^= \end{array}$$

$$\frac{0.004321 \pm 5 \times 10^{-6}}{0.004187 \pm 2 \times 10^{-6}} = 1.032 \pm 0.002 \ \frac{\text{mole } SO_4^=}{\text{mole } Ba^{++}} \text{ as alkali bisulfate}$$

An example of the method of obtaining the moles H_2O/moles Li_2SO_4 ratios for Table III is given here for ppt. 29:

(1) For a 1.0000-g. sample, the loss on ignition = 0.0129 ± 0.0001 g. and the amount of Li_2SO_4 recovered = 0.0153 ± 0.0003 g. For ppt. 29 also, the $SO_4^=/Ba^{++}$ mole ratios are as follows: Experimental ratio = 1.048 ± 0.002, mole ratio calcd. as sulfate = 1.034 ± 0.001, and as bisulfate = 1.067 ± 0.001.

(2) The fractions of total lithium existing as sulfate and as bisulfate are

$$\begin{array}{l} 1.067 \pm 0.001 \\ -1.048 \pm 0.002 \\ \hline 0.019 \pm 0.0022 \end{array} \qquad \begin{array}{l} 1.067 \pm 0.001 \\ -1.034 \pm 0.001 \\ \hline 0.033 \pm 0.0014 \end{array}$$

$$\frac{(0.019 \pm 0.0022)}{(0.033 \pm 0.0014)} = 0.58 \pm 0.06 \text{ fraction of total lithium as } Li_2SO_4$$

and 0.42 ± 0.06 fraction of total lithium as $LiHSO_4$

(3) Amounts of Li_2SO_4, $LiHSO_4$ and H_2SO_4 in 1.-g. sample

$(0.0153 \pm 0.0003)\ (0.58 \pm 0.06) = 0.0089 \pm 0.0010$ g. Li_2SO_4

$(0.0153 \pm 0.0003)\ (0.42 \pm 0.06)\ (208.0/110.0) = 0.0121 \pm 0.0017$ g. $LiHSO_4$

$(0.0121 \pm 0.0017)\ (98.10/208.0) = 0.0057 \pm 0.0008$ g. H_2SO_4

(4) Amounts of total water and water "associated" with Li_2SO_4 contamination

Loss on ignition	0.0129 ± 0.0001 g.
H_2SO_4 from $LiHSO_4$ decomp.	0.0057 ± 0.0008 g.
Total water	0.0072 ± 0.0008 g.

Total water	0.0072 ± 0.0008 g.
Water present as water of hydration[16]	0.0045 ± 0.0002 g.
"associated" water	0.0027 ± 0.0008 g.

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[12] G. H. Walden, Jr., and M. U. Cohen, THIS JOURNAL, **57**, 2591 (1935).

[13] "Intern. Tab. Kryst. Best.," Vol. II.

[14] M. U. Cohen, *Rev. Sci. Instruments*, **6**, 68 (1935); *Z. Krist.*, **A94**, 288 (1936).

(5) Moles of Li_2SO_4 and "associated" water, and mole ratio

$$(0.0089 \pm 0.0010)/110.0 = (81 \pm 9) \times 10^{-6} \text{ mole } Li_2SO_4$$
$$(0.0027 \pm 0.0008)/18.0 = (150 \pm 40) \times 10^{-6} \text{ mole "assoc." water}$$
$$\frac{\text{mole "assoc." water}}{\text{mole } Li_2SO_4} = 1.85 \pm 0.49$$

Discussion of Results

Chemical Constitution.—For precipitates containing NH_4^+, K^+ or Na^+ the data in Table I would seem to indicate the presence of the contaminant as the bisulfate, rather than the normal sulfate, from the agreement between the experimental mole ratio and the mole ratio calculated as the bisulfate. The composition of such precipitates may thus be expressed as barium sulfate, plus ammonium, potassium, or sodium bisulfate, plus water, confirming the suggestion advanced by Allen and Johnston.[4a] Since these three ions are all of size comparable to the barium ion, if they replaced barium ion in the barium sulfate lattice to form a solid solution a substitution of *one* such univalent cation for *one* barium ion could take place with only minor effects upon the crystal lattice. Such a structure would also demand the simultaneous introduction of a proton to preserve electrical neutrality, the contaminant thus being present as a bisulfate. The chemical evidence would seem to be consistent with such a possible structure. A substitution of *two* ammonium, potassium or sodium ions for *one* barium ion, if they replaced the latter in the lattice of barium sulfate, would demand a more extreme adjustment in the lattice. This would require the contaminant to be present as the normal sulfate, which would not be consistent with the chemical data for these three cations in Table I.

TABLE I

$SO_4^=/Ba^{++}$ MOLE RATIOS

	Ppt. no.	Exptl. ratio	Calculated ratio	
			As alk. sulfate	As alk. bisulfate
NH_4^+	57	1.030	1.014 ± 0.001	1.027 ± 0.001
	59	1.042 ± 0.002	1.017 ± .001	1.035 ± .002
	30	1.040 ± .001	1.019 ± .001	1.038 ± .001
	51	1.048	1.025 ± .001	1.051 ± .001
K^+	53	1.029 ± 0.001	1.013 ± .001	1.025 ± .002
	37	1.027 ± .001	1.016 ± .001	1.032 ± .002
	32	1.058	1.028 ± .001	1.057 ± .001
Na^+	61	1.018	1.012 ± .001	1.024 ± .001
	60	1.024	1.014 ± .002	1.029 ± .002
	33	1.036	1.020 ± .001	1.041 ± .001
Li^+	63	1.030	1.017 ± .001	1.033 ± .001
	42	1.032	1.026 ± .001	1.051 ± .001
	29	1.048 ± .002	1.034 ± .001	1.067 ± .001
	28	1.047 ± .003	1.034 ± .001	1.068 ± .001
	54	1.043	1.039 ± .001	1.078 ± .001
	52	1.043	1.040 ± .001	1.080 ± .001
	55	1.043	1.042 ± .001	1.084 ± .001
"Pure"	601	1.005 ± .002		1.005 ± .002

For precipitates containing Li^+, the chemical data in Table I would seem to show that the contaminating cation is present both as the bisulfate and normal sulfate, depending upon the total amount of lithium present in the precipitate, since the experimental $SO_4^=/Ba^{++}$ mole ratio varies from that corresponding to the bisulfate to that corresponding to the normal sulfate. The composition of precipitates containing Li^+ may thus be expressed as barium sulfate, plus lithium bisulfate, plus lithium sulfate, plus water. The lithium ion is small compared to the barium ion, and if it were to replace barium ion in the barium sulfate lattice to form a solid solution, either *one* or *two* lithium ions could take the place of *one* barium ion, so far as space is concerned, with only minor effects on the crystal lattice even for the latter possibility. For precipitates having low lithium contents, the chemical data in Table I are consistent with the presence of lithium as the bisulfate, as for NH_4^+, K^+ and Na^+ and consistent with a solid solution structure in which *one* lithium ion replaces *one* barium ion with the simultaneous introduction of a proton. For precipitates having high total lithium contents, the chemical data in Table I are consistent with the presence of lithium as the normal sulfate, and consistent with a solid solution structure in which *two* lithium ions replace *one* barium ion. At intermediate concentrations of lithium ion, the chemical data indicates the presence of both normal sulfate and bisulfate, and are consistent with the presence of both the above structures.

The radius of the lithium ion is approximately only half that of the barium ion; the possible substitution of two lithium ions for one barium ion would be spatially reasonable, although open to objection on electrostatic grounds.

In precipitates having high lithium contents, Table III shows that two moles of water appear to accompany each mole of Li_2SO_4 present as the normal sulfate in the precipitate. In terms of a possible solid solution structure, this would indicate that one pair of water molecules accompanies the entrance into the lattice of one pair of lithium ions as the normal sulfate. This information affords an interesting suggestion that an alternative structure could be the substitution of *two* lithium ions for *two* closely-situated barium ions (only one in each lattice space), with the simultaneous substitution of the two water molecules for the one sulfate ion which is now chemically extraneous. This mechanism is spatially reasonable, expresses correctly the entire chemical and density evidence, and is not open to objection from an electrostatic point of view.

The analogy may be extended to the case of nitrate contamination investigated by Walden and Cohen[12] where two nitrate ions substitute for one sulfate ion. Here *two* nitrate ions could replace *two* sulfate ions, one of the allied barium ions being simultaneously replaced by water to maintain electrical neutrality. When the intricate packing arrangement of the sulfate groups in the barium sulfate lattice is considered, the mechanism here suggested is seen to be spatially reasonable, and

TABLE II[a]

	Ppt. no.	Wt. % alkali bisulfate		Wt. % loss on ignition	Wt. % water	Unit cell vol. in $(kX)^3$	"Dry" basis expt. density
NH_4^+	45	1.07 ± 0.06		1.17 ± 0.005	0.10 ± 0.06	345.09 ± 0.05	4.416 ± 0.014
	64	1.08 ± .02		1.41 ± .04	.33 ± .05	344.35 ± .05	
	57	1.29 ± .01		1.48 ± .01	.19 ± .02	344.70 ± .04	4.369 ± .011
	63	1.60 ± .01		1.65 ± .02	.05 ± .03	344.89 ± .05	
	50 a	1.71 ± .05		1.99 ± .02	.28 ± .05	345.29 ± .05	4.365 ± .012
	25	1.87 ± .02		2.10	.23	345.12 ± .09	
	30 a	2.00 ± .02		2.01	.01		
	47	2.14		2.05 ± .10	.0	345.96 ± .05	
	51	2.48 ± .02		2.41 ± .02	.0 ± .03	345.76 ± .08	4.436 ± .011
K^+	53	1.39 ± .04		0.83 ± .005	.33 ± .02	344.52 ± .05	4.424 ± .011
	35 a, s	1.67 ± .03		1.20 ± .02	.65 ± .03	344.47 ± .05	
	37 s	1.83 ± .04		1.07 ± .01	.41 ± .02	344.47 ± .05	
	34	2.83 ± .03		1.30 ± .02	.28 ± .03	345.32 ± .04	4.346 ± .012
	32 a	3.11 ± .03		1.32	.20	345.09 ± .08	4.357 ± .011
Na^+	39 s	1.08		1.09	.65	343.86 ± .09	
	62	1.13 ± .02		0.85 ± .01	.39 ± .02	343.84 ± .05	
	61	1.20 ± .01		0.86 ± .01	.37 ± .02	344.03 ± .05	4.386 ± .013
	60	1.47 ± .05		0.83 ± .02	.23 ± .03	344.18 ± .05	4.413 ± .013
	33 a	2.04		1.05	.22	344.25 ± .10	4.365
	49 a	2.21 ± .02		0.86 ± .01	.0 ± .02	344.16 ± .09	
	38	2.25 ± .05		0.93 ± .01	.01 ± .03	343.94 ± .09	4.377 ± .013
		% $LiHSO_4$	% Li_2SO_4				
Li^+	43 s	0.77 ± 0.15	0.0	1.07	.70	344.25 ± 0.05	
	65	1.42 ± .20	0.0	0.94 ± .01	.40 ± .07	344.27 ± .05	4.380 ± .035
	66	1.14 ± .15	0.23 ± 0.11	0.99 ± .01	.45 ± .07	344.55 ± .05	
	42	0.62	0.84	1.02 ± .02	.72 ± .10	344.35 ± .04	4.366
	29 a	1.21 ± .17	0.89 ± .10	1.29 ± .02	.72 ± .08	344.59 ± .05	4.336 ± .034
	28	1.12 ± .27	0.97 ± .14	1.28 ± .04	.75 ± .13	344.63 ± .09	4.386 ± .045
	54	0.44 ± .20	1.54 ± .11	1.23 ± .02	1.02 ± .09	344.37 ± .09	4.378 ± .043
	52	0.28 ± .21	1.69 ± .11	1.14 ± .01	1.01 ± .10		
	55	0.11 ± .22	1.86 ± .12	1.14 ± .01	1.09 ± .10		
"Pure"	601	....	....	0.45 ± .02	0.45 ± .02	344.17 ± .03	4.472 ± .011

[a] Values given here for precipitates containing Li^+ are the results of both direct alkali-ion and SO_4^{--}/Ba^{++} analyses. *a* indicates that the sulfate solution was acidified before precipitation with 5 ml. of concentrated sulfuric acid per liter. *s* indicates precipitation by the method of simultaneous rapid addition of equal amounts of equimolar solutions of barium and sulfate reagents.

TABLE III[a]

WATER ASSOCIATED WITH LITHIUM CONTAMINATION

Ppt. no.	Total % H_2O X	"Associated" % H_2O (X-0.45%)	Wt. % Li_2SO_4	Moles H_2O per mole Li_2SO_4
42	0.72 ± 0.10	0.27 ± 0.10	0.84 ± 0.11	1.96 ± 0.70
29	0.72 ± .08	.27 ± .08	0.89 ± .10	1.85 ± .49
28	0.75 ± .13	.30 ± .13	0.97 ± .14	1.88 ± .85
54	1.02 ± .09	.57 ± .09	1.54 ± .11	2.24 ± .39
52	1.01 ± .10	.56 ± .10	1.69 ± .11	2.02 ± .37
55	1.09 ± .10	.64 ± .10	1.86 ± .12	2.10 ± .34

[a] The precision measures shown take account of the combined errors in the alkali-ion, loss on ignition, and SO_4^{--}/Ba^{++} mole ratio analyses. The most probable value for the "associated" water and its precision measure is: moles H_2O/moles Li_2SO_4 = 2.06 ± 0.13.

free from the objection of having two similarly-charged ions occupying the same lattice space. Sufficient data on the water contents of Cohen's precipitates are unfortunately lacking, so the alternative structure indicated here for nitrate contamination cannot be supported experimentally at this time.

Since, as will be shown later in this paper, the X-ray evidence definitely indicates the formation of a solid solution structure for the contaminations studied here, it appears that at least the coprecipitation of sodium and lithium by this mechanism would seem to violate the classical rules of Goldschmidt regarding crystalline miscibility.[15] However, the systems studied here are the result of localized kinetic processes occurring during precipitation, whereas Goldschmidt's rules apply to equilibrium systems. For the non-equilibrium process which gives the structures studied here, unstable solid solution formation regardless of ion size or solubility would not be an unreasonable expectation.

From the facts and discussion given above, and the powerful re-crystallization effect noted for coprecipitated lithium in another paper,[16] it is obvious that lithium behaves somewhat uniquely as a contaminant of barium sulfate. The effect mentioned above, where precipitates containing co-

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[15] Stillwell, "Crystal Chemistry," McGraw-Hill Book Co., New York, N. Y., 1938, pp. 324-325.

[16] George Walton and George H. Walden, Jr., THIS JOURNAL, **68**, 1750(1946).

precipitated lithium also exhibit an increase in water content with increase in ionic contamination, this additional water (above the 0.45% present as the variable water of hydration which is discussed in another paper[16]) being associated with the presence of lithium as the normal sulfate, is not shown by the other univalent cations studied. In stable mineral systems, lithium is commonly found at the center of an octahedron whose six corners are occupied by oxygen atoms; the same type of grouping, in 6-fold coördination with oxygen, is shown by magnesium, iron, manganese, cobalt, nickel and chromium which are similar in size to lithium. Sodium and potassium, being larger, are ordinarily found in 7-fold to 12-fold coördination with oxygen, as are also barium, strontium and calcium; the size of the ammonium ion would also place it with this latter type of grouping. Although close analogy to stable mineral systems could not be implied for the non-equilibrium structures studied here, it does appear that the unique behavior of lithium ion as a contaminant of barium sulfate is related to its small size and lower coördination numbers. In the barium sulfate lattice, barium ion is in 12-fold coördination with oxygen.

X-Ray Measurements

The X-ray data show that for the series of precipitates prepared for each of the contaminating ions except Na^+, there occurs a definite orderly variation of lattice parameters and unit cell volume with amount of contaminant present (Figs. 1, 2, 3 and 4). This is strong evidence that these precipitates are solid solutions of NH_4^+, K^+, and Li^+ with barium sulfate.

The percentage expansion of the unit cell, 100 $\Delta V/V$, produced by the introduction of equivalent amounts (4 mole %) of contaminating ions has been plotted against the difference in radius between the univalent cation and the barium ion divided by the radius of the barium ion ($r_{X^+} - r_{Ba^{++}}/r_{Ba^{++}}$). The relation is shown in Fig. 5. The values used for the ionic radii are those of Pauling,[17] corrected to the value for 12-coördination[18]: $Ba^{++} = 1.35$ kX, $NH_4^+ = 1.61$ kX, $K^+ = 1.41$ kX, $Na^+ = 1.07$ kX.

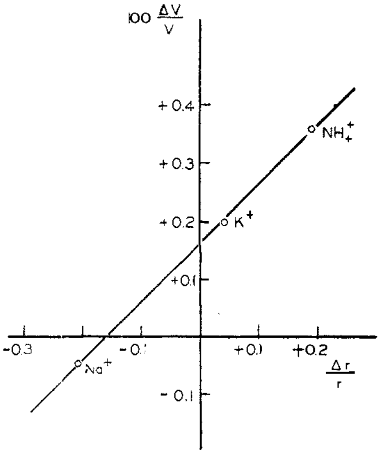

Fig. 5.—Percentage expansion of unit cell *vs.* percentage change in ionic radii.

It is apparent that the small changes produced by the coprecipitation of Na^+ are a result of ionic size, and that the structure produced must also be a solid solution, as for NH_4^+, K^+ and Li^+.

Presumably the lattice changes observed are the net result of contamination by both alkali ions and water. However, the method of preparation used was such as to originally include the same amount of water in all the precipitates, except those few prepared by simultaneous addition; and we have repeatedly observed that the vacuum drying of contaminated precipitates has no effect on the lattice parameters.

Visual comparison of two excellent films of "pure" reference barium sulfate 601 and of heavily-contaminated 32, taken in a Debye–Scherrer camera, showed *all* lines to be common to both films and no observable changes in the relative intensity of any line. This indicates that there exists no ordered arrangement of contaminant in the lattice.

Density

It is common practice in solid solution studies to establish the type of solid solution by computing densities from the X-ray measurements for each of the possible types, and comparing these with directly-measured experimental values. It has not been possible to do this previously with barium sulfate precipitates due to the fact that this material contains water which is completely removed only by rather drastic heat treatment, giving anomalously low densities. In another paper,[16] we have found that this tightly-bound water is present as a substitutional solid solution in which the water occupies its normal molecular volume, and that on removal it escapes from the barium sulfate lattice leaving "holes" which are inaccessible to the hydrostatic liquid. This discovery was not made until after the precipitates prepared for this research had been subjected to drying *in vacuo* at 110°, which removed a part of the "bound" lattice water.

To correct the experimental densities for the effect of lattice water it is necessary to know: (1) how much water was initially present, and (2) how much was removed. To determine the first of these factors, two additional precipitates were prepared under the usual conditions of slow precipitation. The first of these was precipitated in the absence of any alkali contaminant; it was found to contain 0.45% water after drying to constant weight in a desiccator over concentrated sulfuric acid, a procedure which was shown to remove none of the bound water. The second precipitate was made in the presence of potassium

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(17) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 330.

(18) L. Pauling, *ibid.*, p. 348.

sulfate, and contained 0.40% water after similar drying procedure. It should be noted also from Table II that no precipitate produced by the usual slow precipitation method contained over 0.45% water (except where water is taken in with lithium sulfate). These data, as well as the experience of others,[19] show that under fixed conditions of precipitation the bound water content of barium sulfate is quite reproducible, unless a coprecipitating ion such as Li^+ carries additional water with it. NH_4^+, K^+ and Na^+ do not behave this way (Table II) in influencing the amount of water retained.

In view of these facts we have made what seems to us the reasonable assumption that all of the precipitates made by slow addition and not containing Li^+ had the same initial water content of 0.45%. Their water content when the density measurements were made is given in Table II. We have, accordingly, corrected these measured densities to a "dry" basis, *i. e.*, the density they would have had if they had been originally precipitated in the anhydrous condition, by assuming that the water actually present is in the form of a substitutional solid solution with water displaying its normal molecular volume, and that the difference between this content of water and 0.45% has left its volume of empty space, inaccessible to the hydrostatic liquid. These corrected experimental values are given in Table II, and plotted in Fig. 6 against the weight per cent. of contaminant. The precision measures given in the table reflect the errors of the experimental density measurement and of the measurement of the water content.

The densities of the precipitates containing Li^+ may not be corrected in this way, since here the initial water content depends upon the amount of Li^+ present. However, while other barium sulfate precipitates lose their water of hydration under vacuum at 110° at the rate of about 0.05% of the weight of the precipitate per hour, the rate of loss for those containing Li^+ is much slower. Accordingly, the water contents as found by analysis have been taken as equal to the initial water content, and the densities of these precipitates corrected to the "dry" basis on this assumption.

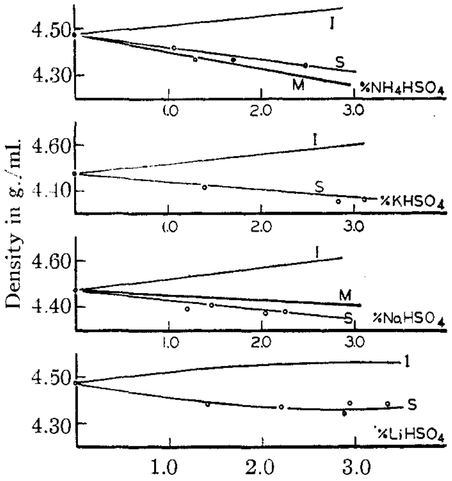

Fig. 6.—Density *vs.* composition.

Based on the X-ray measurements and chemical analyses, theoretical density curves calculated on the assumptions of interstitial (curve I) and substitutional (Curve S) solid solution formation, and mechanical mixture (curve M for NH_4^+ and Na^+) have been included in Fig. 6, to be compared with the measured corrected density values plotted thereon. It can be seen that the experimental values lie closer to the curves calculated on the assumption of substitutional solid solution than they do to the curves calculated for the other structures. The average deviation of the experimentally-based points from the mechanical mixture curve is twice as large as the average deviation of the same points from the substitutional solid solution curve in the case of NH_4^+, and three times as large in the case of Na^+. Moreover, except for one point, the experimental density values lie always toward one side of the calculated mechanical mixture curve; they show a more reasonable distribution with respect to the curve calculated on the assumption of solid solution. The comparison is not extended to K^+ because the difference in density between the two structures would be too small for any valid decision (due to similarity of size of the barium and potassium ions), nor to Li^+ because the additional quantity of water in this case makes the effect of cation substitution less important toward the density.

Granting the X-ray evidence of solid solution, the densities establish the type of solid solution as substitutional, the univalent cations replacing barium ion in the barium sulfate lattice.

Coprecipitation of Oxonium Ion.—Efforts to study the coprecipitation of oxonium ion were, except in one case, rather unsuccessful because we were unable to prepare, by the methods used, precipitates containing a significant amount of contaminant. Although it is possible to obtain a significant contamination of barium sulfate by oxonium ion, our experimental procedure, which involved washing the precipitates with hot water until free from acid by test, invariably gave us precipitates for which the $SO_4^{=}/Ba^{++}$ mole ratio was unity. The one exception was precipitated in, and washed with, iced water. It contained 1.56 ±0.10 wt. % sulfuric acid and 1.92 ± 0.10% water; the b_0 parameter for this precipitate (5.4449 ± 0.0003 kX) showed an expansion, and the a_0 parameter (8.8590 ± 0.0009 kX) a contraction, as compared with a precipitate containing only a comparable amount of water (a_0 = 8.8639 ± 0.0007 kX; b_0 = 5.4422 ± 0.0002 kX). The c_0 axes were the same within experimental error.

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[19] D. Balarew and G. Kandilarow, *Z. anorg. Chem.*, **162**, 344 (1927).

The substance may have been a solid solution of barium sulfate and hydrated sulfuric acid. However, even at room temperature, the surface of the precipitate showed the presence of sulfuric acid after several days, so it was concluded that the relative instability of oxonium ion as a contaminant rendered it unsuitable for further study at this time.

Summary

1. X-Ray measurements show that barium sulfate precipitates containing coprecipitated NH_4^+, K^+, Na^+ or Li^+ are solid solutions of barium sulfate with these univalent cations. Density measurements show the type of solid solution to be substitutional.

2. The number of univalent cations present is equal to the number of sulfate ions in excess over the number of barium ions, for precipitates containing NH_4^+, K^+ or Na^+. These precipitates may be formally described as substitutional solid solutions of barium sulfate plus ammonium, potassium, or sodium bisulfate, plus water.

3. For precipitates having low lithium content, the number of excess sulfate ions is equal to the number of lithium ions present. For precipitates having higher total lithium content, more than one lithium ion is present for each excess sulfate ion, the ratio approaching two as an upper limit. Precipitates contaminated with Li^+ can be formally described as substitutional solid solutions of barium sulfate plus lithium bisulfate, plus lithium sulfate, plus water.

4. Associated with coprecipitated lithium present as the normal sulfate, one molecule of water per lithium ion is taken into the barium sulfate lattice in addition to the variable water of hydration. Extensive vacuum drying at 110° does not remove this water.

5. No superstructure formation is indicated. Substitution of the contaminating ions in the lattice is therefore random.

6. Possible structures are suggested for barium sulfate precipitates contaminated by lithium.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Nature of the Variable Hydration of Precipitated Barium Sulfate[1]

BY GEORGE WALTON[2] AND GEORGE H. WALDEN, JR.[3]

Barium sulfate prepared by precipitation from aqueous solution always contains a quantity of water which is held with remarkable tenacity.[4,5] This water is not given up by the precipitate upon exposure to dry air at room temperature, and is indeed removable with extreme slowness by vacuum desiccation over a good dehydrating agent or even by vacuum treatment at 110°; its complete removal from the precipitate requires the application of temperatures above 500°.[6,7] It can be shown, by following the loss in weight with time while drying the moist precipitate *in vacuo* over concentrated sulfuric acid, that such water is not held by external surface sorption; the curve obtained (Fig. 1) has a sharp break at the point where the surface moisture has been removed, but a precipitate thus dried may still contain an appreciable amount of water (as can be seen by comparison with its weight upon total drying). The amount of water retained is known to be reproducible for a given method and rate of precipitation.[4]

During an investigation of the contamination of barium sulfate by univalent cations,[8] a number of precipitates were prepared which did not have any significant chemical contamination, but which did contain differing amounts of water after drying to remove surface moisture. These precipitates were shown by analysis to have barium and sulfate ions present in equivalent amounts (Table I), the absence of other ions being established by chemical tests. Their composition may thus be expressed simply as barium sulfate plus water, the water being released during ignition, and the loss on ignition being taken as a direct measure of their water content.

Since the nature of the variable hydration of barium sulfate has never been conclusively established, it became of interest to apply the methods of X-ray analysis[9] to this problem. Accordingly, precision measurements of the lattice parameters of these precipitates were made. They showed (Fig. 2) a regular increase in the a_0 and c_0 axes and the volume of the unit cell with increase in water content. This may be taken as proof that the tightly-held water forms a solid solution with the precipitated barium sulfate.

It should be emphasized here that the phenome-

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(9) (a) L. Vegard and H. Schelderup, *Physik. Z.*, **18**, 93 (1917); (b) L. Vegard, *Z. Physik*, **5**, 17 (1921).