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.

NEW YORK, N. Y. RECEIVED JANUARY 14, 1946

[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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(1) From a Thesis submitted by George Walton in partial fulfillment of the requirements for the degree of Doctor of Philosophy from the Faculty of Pure Science at Columbia University in 1941.

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

(5) P. R. Averell and G. H. Walden, Jr., THIS JOURNAL, **59**, 906 (1937).

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

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

(8) George Walton and G. H. Walden, Jr., THIS JOURNAL, **68**, 1742 (1946).

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

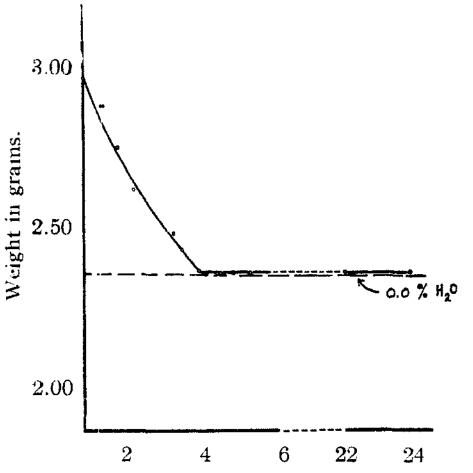

Fig. 1.—Weight of preparation 601 dried over concd. sulfuric acid.

non studied would be the result of localized kinetic processes occurring during precipitation, and would not in any way imply a similar structure to an equilibrium system of barium sulfate and water.

It was realized that the X-ray evidence did not necessarily require all of the water to be present in the form of a solid solution. Also, the X-ray evidence by itself could not distinguish between the various possible types of solid solutions which might be formed, such as the interstitial, or simple or complex substitutional types. However, the densities of the contaminated precipitates would vary with the type of solid solution formed, just as in the case of alloy systems. Therefore, to indicate the type of solid solution, density measurements were made on four of the precipitates.

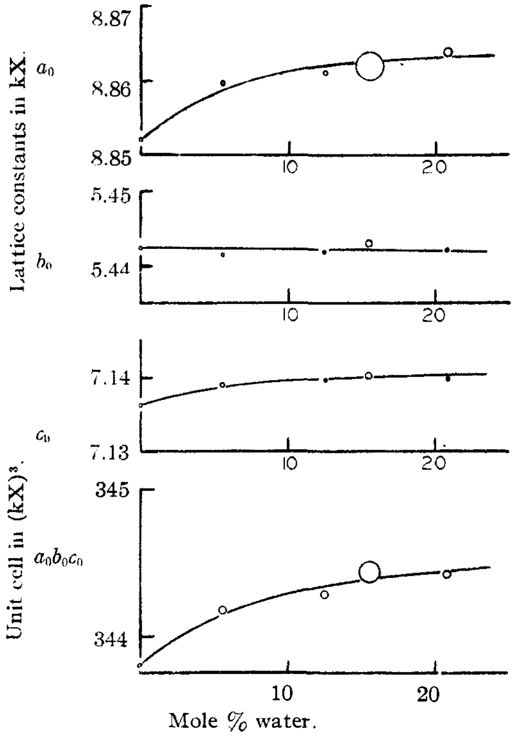

Fig. 2.—Lattice constants and unit cell volume *vs.* composition.

For material which had been dried as above to constant weight over sulfuric acid, the measured density agreed very well (Table II) with the density calculated from the observed lattice parameters and the water content, assuming for the calculations that the water retained its normal density and that it replaced an equal volume of barium

TABLE I[a]

CONSTITUTION AND UNIT CELL VOLUME OF PRECIPITATES

Ppt. no.	Exptl. SO_4^{--}/Ba^{++} mole ratios	Wt. % water	Mole % water	$a_0b_0c_0$ in $(kX)^3$
28 IGN.	0.997 ± 0.001	0.00 ± 0.01	0.0 ± 0.1	343.81 ± 0.02
601	1.005 ± .002	0.45 ± .02	5.5 ± .2	344.17 ± .03
204	1.001	1.09 ± .02	12.5 ± .2	344.28 ± .03
21	1.002	1.40 ± .03	15.5 ± .3	344.43 ± .08
26	0.998 ± .001	1.99 ± .02	20.8 ± .2	344.42 ± .03

[a] 28 IGN. is the product obtained by the ignition (at 950 ± 50°) and leaching of ppt. 28 (or any lithium-contaminated precipitate) as described under methods of analysis in another paper.[8] Barium sulfate 601 was prepared by the slow addition of 0.25 molar barium salicylate solution to 0.005 molar hexammine cobaltic sulfate solution acidified with 1 ml. concentrated sulfuric acid per liter. The precipitates 21, 26, 204 were prepared by the slow addition of 0.1 to 0.25 molar barium salicylate solutions to 0.05 to 2.0 molar sulfuric acid solutions. These precipitates and 601 were subjected to long-continued digestion and washing to reduce ionic contamination.

TABLE II

DENSITY OF PRECIPITATES IN GRAMS/ML.

Ppt. no.	Exptl. density	Calculated density		
		Substit.	Interst.	Mech.
28 IGN.	4.448 ± 0.010	4.480 ± 0.005	4.480 ± 0.005	4.480 ± 0.006
601	4.407 ± .010	4.410 ± .005	4.495 ± .005	4.405 ± .006
204	4.326 ± .009	4.316 ± .005	4.523 ± .005	4.312 ± .007
204 IGN.	4.312 ± .009	4.269 ± .004	4.473 ± .005	4.475 ± .007
21	4.284 ± .013	4.273 ± .005	4.535 ± .005	4.267 ± .008
21 IGN	4.244 ± .014	4.213 ± .005	4.472 ± .005	4.474 ± .008

sulfate. These assumptions hold true for a mere mechanical mixture of barium sulfate, such as would result from the water being held by "inclusion" of mother liquor, "inner or outer surface" sorption, or similar possible mechanisms; however, they also hold true for a substitutional solid solution in which a group of three water molecules is substituted for one barium sulfate group in the lattice. Since one barium sulfate group occupies about 86 (kX)[3] (one-quarter of the unit cell) and three water molecules occupy about 90 (kX)[3,10] such a complex type of substitution becomes very plausible from a spatial viewpoint; it would demand an increase in unit cell volume upon coprecipitation of barium sulfate with water, which is in accord with experiment.

Although the measured densities definitely eliminate the possibility that this water exists as an interstitial solid solution, they cannot of themselves decide between a mechanical mixture and a substitutional solid solution of the complex type suggested above. However, measurements of the densities for two of the precipitates (21 and 204) both before and after the removal of the water by ignition give a novel and interesting indication that the solid solution structure is the correct one. Although water (d. 1.0) was being removed from barium sulfate (d. 4.4) the density of the latter material was found to be decreased by this procedure. The decrease in density was proportional to the weight of water removed. One precipitate showed the same effect after partial removal of the water by extensive vacuum drying at 110°. All experimental means to obtain a higher density were without effect, although these included boiling the precipitate with the hydrostatic liquid, boiling under reduced pressure, subjecting the precipitate to vacuum and admitting the hydrostatic liquid before breaking the vacuum, and working with another liquid having different wetting properties with regard to barium sulfate.

If the coprecipitated water, or any major fraction of it, were present in such a structure that the space occupied by it would be accessible to the hydrostatic liquid when the water was removed, then an increased density would result; this does not check with the experimental evidence.

The density values obtained experimentally could be explained only on the basis that removal of the water left "holes" to which the hydrostatic liquid did not have access. This can be interpreted to indicate that the water was present as a substitutional type of solid solution, and that upon its removal the structure became a "subtraction lattice," into which the hydrostatic liquid did not penetrate. This type of lattice is experimentally found in other systems,[11] and demands certain structural features which the barium sulfate lattice is known to fulfill.[12]

Computations of the lattice parameters of two of the precipitates both before and after removal of the water by ignition showed no significant change[12a] although a slight but definite broadening of the lines was observed on the X-ray photogram. This shows that the slightly-expanded "subtraction lattice" left by the removal of coprecipitated water is quite resistant to collapse. Since the barium sulfate lattice is a structure of large ions in close packing,[14,15] this is a reasonable expectation.

The manner in which the water escapes from the precipitate without shattering the crystalline particles cannot be clarified at this time. The slight line-broadening observed may in fact indicate that this does occur to some extent; however, since shattering during removal of the water would leave material with the high density of uncontaminated barium sulfate, which is shown here to be contrary to the observed density change, it could occur only to a very limited extent, if at all.

The results obtained here quite naturally give rise to the question as to what are the actual density and lattice parameters of barium sulfate containing neither lattice water nor "holes." During our investigation of the properties of precipitates of barium sulfate contaminated with univalent positive ions,[8] it was found that ignition of barium sulfate containing coprecipitated lithium bisulfate, besides permitting the quantitative recovery of lithium as the normal sulfate, left a residue consisting of remarkably perfect crystals of barium sulfate. The effect is similar to that noted by Kolthoff[7] for the "thermal aging" of impure barium sulfate. Determination of the lattice parameters of this material showed a unit cell volume smaller by 0.11 ± 0.01% than that of any other uncontaminated barium sulfate samples which we had examined. Moreover, the measured density of this compact material agrees reasonably well with the density calculated for a pure barium sulfate having the observed lattice constants and having no "holes" which might be inaccessible to the hydrostatic liquid (see ppt. 28 IGN., Table II). It appears that this ignition product is a very close approach to ideal crystalline barium sulfate, and its lattice parameters ($a_0 = 8.8522 \pm 0.0002$, $b_0 = 5.4424 \pm 0.0002$ and $c_0 = 7.1363 \pm 0.0002$ kX) have therefore been used as the parameters of the anhydrous reference barium sulfate in Fig. 2.

When hydrated barium sulfate is fused with lithium sulfate or lithium bisulfate some recrystallization does take place, but to no such extent as observed for the case where the lithium is originally

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[10] Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[11] Gunnar Hägg, *Nature*, **131**, 167 (1933).

[12] Gunnar Hägg, *Z. Krist.*, **91**, 114 (1935) (English).

[12a] This is quantitative support for Cohen's (ref. 13) observation that drying precipitates at 110° had no visible effect on the X-ray pattern obtained.

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

[14] Linus Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 355.

[15] W. L. Bragg and West, *Proc. Roy. Soc.* (London), **A114**, 450 (1927).

present as a contaminant. Coprecipitated potassium or sodium bisulfate also effect a similar but incomplete recrystallization. It is not apparent, as yet, why such a recrystallization process should take place upon ignition of barium sulfate contaminated with the alkali metal ions, nor why the effect should be so pronounced in the case of coprecipitated lithium.

Experimental

Methods of Analysis.—The methods of chemical, X-ray, and density analysis employed were the same as described in another paper.[8] Density measurements were made between 24 and 30°; their average deviation is given in Table II. Density calculations for the several possible types of structures were based on the methods given in Clark[16]; the precision measures given for the calculated density values in Table II take into account the experimental precision measures of the X-ray, water content and SO_4^{--}/Ba^{++} mole ratio analyses.

Results of Analysis.—Analytical results for total sulfate and total barium, expressed as the mole ratio, are given in Table I. Analytical results for the water content are also included in the table both as weight and mole per cent.

Values for the lattice parameters of the precipitates are given graphically in Fig. 2, the individual parameters and the unit cell volume being plotted against water content. The circles represent the probable errors of the individual parameters, as determined from the least squares solution of the film data. Unit cell volumes and their probable errors are given numerically in Table I.

Results of density measurements on four of the precipitates are given in Table II, measurements having been taken on two of them (21, 204) both before and after ignition. For comparison, the density values calculated from the water content and X-ray data, assuming that the water is present as a substitutional solid solution in which $(H_2O)_3$ groups replace barium sulfate groups and leave "holes" upon their removal, are given in the third column (Substit.). The densities calculated on the assumption of interstitial solid solution, where the water would occupy the interstices of the lattice without displacing either barium or sulfate ions, are given in the fourth column (Interst.). Values for the densities calculated on the assumption of a mechanical mixture of barium sulfate and water, where the space occupied by the water is accessible to the hydrostatic liquid after the water is removed, are given in the fifth column (Mech.).

Summary

1. X-Ray measurements show that the variable water of hydration of barium sulfate precipitated from aqueous solution is present as a solid solution.

2. Density measurements on the precipitates indicate that the solid solution formed is complex substitutional, a group of three water molecules replacing one barium sulfate group in the lattice.

3. The removal of the water from these hydrated precipitates leaves cavities to which the hydrostatic liquid does not have access. This indicates formation of a stable "subtraction" lattice.

NEW YORK, N. Y.

RECEIVED JANUARY 14, 1946

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[16] G. L. Clark, "Applied X-Rays," McGraw-Hill Book Co., New York, N. Y., 1932, p. 289.

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The Measurement and Calculation of Hydrogen Ion Concentrations in Saline Acetate and Phosphate Buffers[1]

BY DAVID I. HITCHCOCK AND ROZANNE PETERS[2]

In spite of recent revisions of the *p*H scale[3,4,5] it is still true that *p*H is an arbitrarily defined quantity for solutions in general. The *p*H values of the widely used phosphate and acetate buffers, as shown by Brönsted[6] and by Cohn,[7] cannot be calculated from mass action equations, even when the ionic strength is kept constant, without the introduction of variable activity coefficients. It was pointed out by Guggenheim[8] that either C_H or $C_H f_\pm^2$ would be a more useful measure of acidity than $C_H f_H$, even if the latter could be measured with certainty, because one of the former quantities is often the determining factor in an acid-base equilibrium.

The object of the present work was to find a series of buffers, of ionic strength comparable to that of physiological fluids, having hydrogen ion concentrations which could be measured by means of a cell without liquid junction and calculated by simple mass law equations without the introduction of activity coefficients. These conditions were fulfilled by acetate and phosphate buffers, 0.025

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[1] A brief report of this work was presented before the American Society of Biological Chemists and published in *Federation Proc.*, **1**, 115 (1942).

[2] Aided by a grant from the Fluid Research Funds of the Yale University School of Medicine, 1940–1941.

[3] MacInnes, Belcher and Shedlovsky, THIS JOURNAL, **60**, 1094 (1938).

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[5] Hamer and Acree, *J. Research Natl. Bur. Standards*, **23**, 647 (1939); Hamer, Pinching and Acree, *ibid.*, **36**, 47 (1946).

[6] Brönsted, *J. Chem. Soc.*, **119**, 574 (1921).

[7] Cohn, THIS JOURNAL, **49**, 173 (1927); Cohn, Heyroth and Menkin, *ibid.*, **50**, 696 (1928).

[8] Guggenheim, *J. Phys. Chem.*, **34**, 1758 (1930).