

Nomenclature

Q = heat added to system, B. t. u.
 M = mass of material in system, lb.
 v = sp. vol. of system, cu. ft./lb.
 T = abs. temp., ° Rankine
 p = abs. pressure, lb./sq. ft.
 C_p = sp. heat at constant pressure, B. t. u./lb./° F.
 l = latent heat of vaporization, B. t. u./lb.
 x = quality of two-phase mixture, mass fraction in gas phase
 J = mechanical equivalent of heat, B. t. u./ft-lb.

Subscripts:

1 = initial state
 2 = final state
 s = condition of saturation

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RECEIVED May 9, 1935.

New Method for Barium Chloride

BARIUM compounds of commerce are obtained either from witherite or barytes. Since the most plentiful barium mineral is barytes, this ore is employed to a greater extent than the carbonate. The process used for the manufacture of soluble barium compounds is first to form barium sulfide by calcining the barytes with coke, leaching the sulfide with hot water, and then treating the solution with the proper chemical to obtain the desired barium salt. In carrying out this procedure it is necessary to resort to different methods of purification in order to obtain a technically pure product. This is especially true in the manufacture of blanc fixe where such impurities as iron, sulfur compounds, etc., have a great tendency to lessen the value of the blanc fixe as a pigment. With these facts in mind it seemed worth while to investigate the preparation of water-soluble compounds of barium from barytes without going through the intermediate stage of converting the barytes to barium sulfide.

Previous Work

Different methods, in addition to the use of coke, have been used to decompose barium sulfate. Mosttowitsch (13) de-

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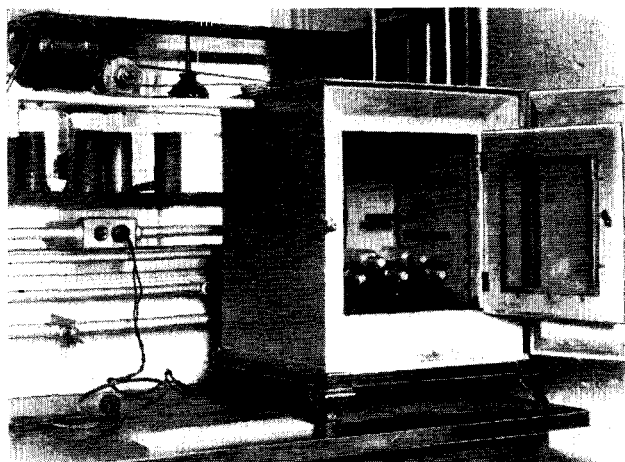


FIGURE 1. OVEN WITH ROTATING CYLINDERS

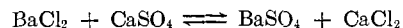
Decomposition of Barium Sulfate by Calcium Chloride in Aqueous Solution

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composed barium sulfate by heating it with silica at 1000° C. Marchal (9) studied the dissociation pressure of barium sulfate at 1800° C. and a mixture of barium sulfate and silica at 1250° C. Bundikov and Shilov (3) claimed to have obtained a 97.7 per cent decomposition of barium sulfate by heating it with silica in an electric furnace at 1000° C.

M. Asselin reported to Arth (1) that he had prepared aqueous solutions of barium aluminate by heating barium sulfate with bauxite at high temperatures. Others who studied the reaction between barium sulfate and alumina in the presence of coke were Gaudin (5), Martin (10), Hershman (6), and Morey (11). Booth and Ward (2) studied the reaction between barium sulfate and alumina between 100° and 1450° C. with satisfactory results. Newberry and Barret (14) produced barium oxide by heating barium sulfate with magnesia at 1500° C. Kharmandar'yan and Brodovich (8) claimed to have obtained a small yield of 99.6 per cent barium chloride by chlorinating barytes at 600° C. for 2 hours in the presence of the catalysts alumina and carbon.

Still (15), while investigating, under the direction of the senior author, the chemistry of Farr's process (4) for the manufacture of finely divided barium sulfate by heating barytes with strong calcium chloride solutions, found that, under the conditions of high concentration of calcium chloride in aqueous solution and high temperature, the reaction



might be reversed. In order to study this reversion, it was necessary to remove the barium chloride formed from the

reaction products in a non-ionized state. To accomplish this, at the suggestion of Farr, Still used methanol to extract the barium chloride from the calcium sulfate formed. While the methanol used by this investigator was a poor solvent, it enabled this investigator to prove conclusively that the reaction was reversible. Recently Ipatieff and Freitag (?) reported the transformation of heavy spar into barium carbonate by heating under pressure with a sodium carbonate solution.

Present Experiments

In the investigation of the reaction, $\text{BaSO}_4 + \text{CaCl}_2 \rightleftharpoons \text{BaCl}_2 + \text{CaSO}_4$, it was first necessary to devise a means of separating the barium chloride formed from the calcium sulfate present, in order to determine the extent to which the reaction approached completion. It was obvious that some inert organic solvent, or a system of organic solvents, must be used to dissolve the barium chloride from the reaction products and leave undissolved the calcium sulfate. While it would be advantageous to find a solvent which would remove only the barium chloride, any solvent, or mixture of solvents, which would remove the barium chloride and any excess calcium chloride present, leaving insoluble the calcium sulfate formed, was considered satisfactory. Ethylene glycol was found to be satisfactory, but as the amount of barium chloride in a given volume of ethylene glycol was increased, the solution became increasingly more viscous until a point was reached where the solution was too viscous for practical handling. The mobility of the solution of barium chloride in the glycol was raised materially, without affecting its dissolving power beyond practical purposes, by diluting the ethylene glycol with three volumes of methanol. This mixture not only dissolved out the barium chloride, leaving calcium sulfate as an insoluble residue, but also dissolved any unreacted calcium chloride used to carry out the reaction.

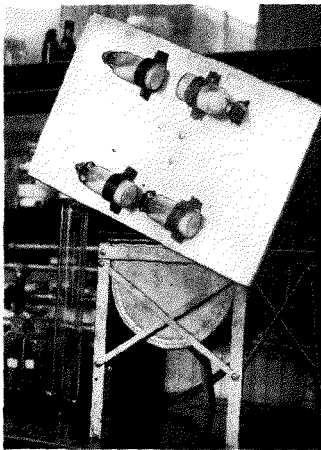
Method of Analysis

Using synthetic mixtures consisting of barium sulfate, calcium sulfate, calcium chloride, and barium chloride, these mixtures were extracted with the methanol-glycol solvent, and an aliquot of the clear extract was tested for the presence of the sulfate ion and analyzed for the percentage of barium chloride present. The best results were obtained when the method outlined by Morse (12) was followed. An aliquot of the clear extract, equivalent to 0.2-0.3 gram of barium chloride, was dissolved in

250 cc. of distilled water, 6 drops of acetic acid (specific gravity, 1.065) were added, and the solution was heated to boiling. Fifteen cubic centimeters of a 10 per cent ammonium chromate solution were added dropwise, with constant stirring, and the solution was allowed to stand for at least one hour. The supernatant liquor was decanted through a prepared Gooch crucible, using care to retain as much of the precipitate as possible in the beaker. Using a clean filter flask, 20 cc. of hot nitric acid (5 per cent solution) were poured through the Gooch crucible to dissolve any barium chromate which had collected there, and the hot acid filtrate was poured into the beaker containing the barium chromate, which precipitate gradually went into solution. The filter flask was washed out with water into the original precipitating beaker, and the solution of barium nitrate was diluted to 250 cc. with distilled water. After heating the solution to just below the boil-

In strong concentrated aqueous solutions it has been proved that calcium chloride decomposes barium sulfate, giving barium chloride and calcium sulfate. The discovery of this fact and the study of this reaction was possible only through the use of organic or non-ionizing solvents. In particular, ethylene glycol with the addition of methanol is excellent for removing the barium and calcium chlorides from the reaction product. This process indicates a probable new commercial method for the making of barium chloride.

FIGURE 2.
MECHANICAL
EXTRACTOR



ing point, it was made slightly alkaline with ammonium hydroxide and then slightly acid with acetic acid; 15 cc. of 10 per cent ammonium chromate solution were then added. The precipitated solution was allowed to stand at least one hour; the barium chromate was filtered into a weighed Gooch crucible, dried at 200° C. to constant weight, and from the weight of barium chromate found, the amount of barium chloride in the sample was calculated. The separation of barium and calcium chromates obtained by this procedure are as follows (in grams):

	1		2		3		4	
	Taken	Found	Taken	Found	Taken	Found	Taken	Found
BaCl ₂	0.1329	0.1322	0.1707	0.1711	0.2047	0.2050	0.1333	0.1360
CaCl ₂	0.3960	0.3660	0.6687	0.4000

Chemicals and Apparatus

The barium sulfate employed for the data in Table I and in the curves was of c. p. grade, prepared especially for x-ray work. Before use the samples were heated to redness in a platinum dish to drive off any moisture present, ground, and screened through a 50-mesh screen. The calcium chloride was

of the analytical reagent grade. The ethylene glycol and absolute methanol were also of c. p. grade.

The reactions were carried out in a Dekhotinsky constant-temperature oven, constant within $\pm 1^\circ \text{C}$. This oven, shown in Figure 1, was specially equipped with motor-driven cylinders revolving at 20 r. p. m. The mixtures were sealed in heavy Pyrex bombs measuring approximately 6×0.75 inch in size (15.2×1.9 cm.) and 50 cc. in volume. In carrying out an experiment, a glass rod 0.25 inch in diameter was put into each bomb after charging and before sealing, to insure good mixing of the reacting substances; this is most essential. The sealed bombs were revolved in a horizontal position at 20 r. p. m. throughout the reaction time. After the reaction had been allowed to proceed for a specified time at the desired temperature, the bombs were removed from the reaction oven, cooled to room temperature (30°C .), and opened, and the contents were washed into 4-ounce (0.12-liter) tincture bottles using 100 cc. of the methanol-ethylene glycol solvent. The bottles and their contents were shaken mechanically on the machine shown in Figure 2 until all of the barium chloride and calcium chloride in the mixture had been dissolved. The bottles with their con-

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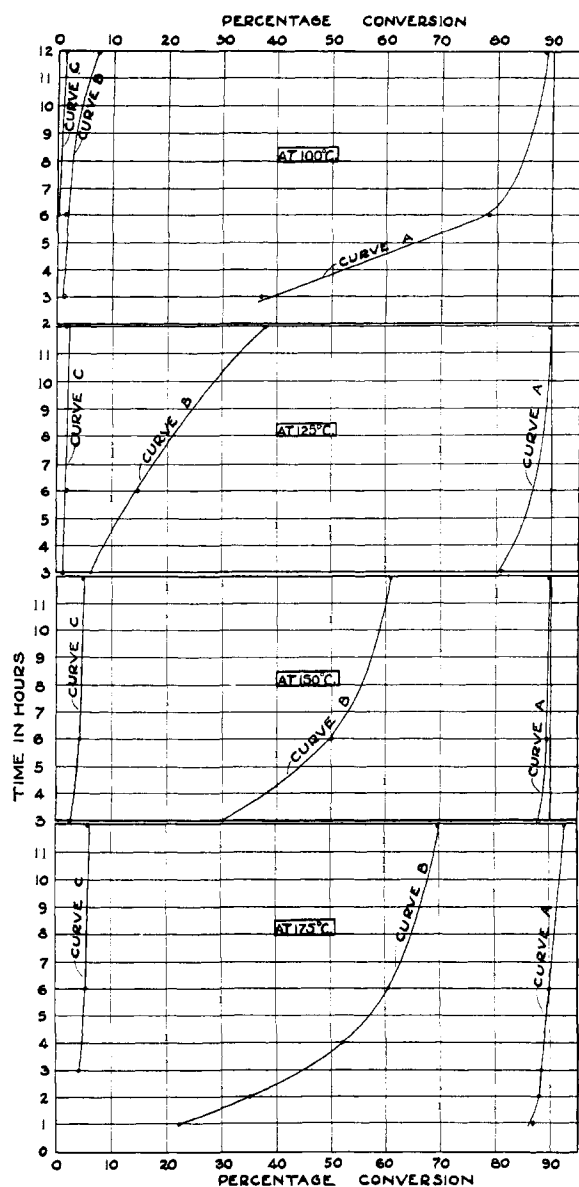


FIGURE 3. DECOMPOSITION OF BARIUM SULFATE WITH CALCIUM CHLORIDE AT VARIOUS TEMPERATURES

tents were then analyzed for the percentage of barium chloride present in the reaction product.

Procedure

The reaction $\text{BaSO}_4 + \text{CaCl}_2 \rightleftharpoons \text{BaCl}_2 + \text{CaSO}_4$ was experimentally studied at 100°, 125°, 150°, and 175° C. for periods of 3, 6, and 12 hours. Three grams of barium sulfate were used in 4.5 grams of water for all mixtures, and the concentration of the calcium chloride solution was varied by varying the weight of calcium chloride added to each mixture. The time recorded for each decomposition represents the actual time the bomb remained in the reaction oven. All experiments were run in duplicate.

It was found by trial that all barium chloride and calcium chloride present in the reaction product was in solution in the methanol-glycol solvent within 2 hours when shaken mechanically. All samples were agitated for 2 hours on the mechanical shaker and allowed to settle for a few minutes, and then an aliquot of the clear supernatant liquid was taken, filtered

through a dry Gooch by suction, and analyzed for barium chloride.

The composition of the mixtures was as follows (in grams):

	A	B	C
BaSO ₄	3	3	3
CaCl ₂	6	5	4
H ₂ O	4.5	4.5	4.5
H ₂ O/CaCl ₂	0.75	0.90	1.125

Conversion at 100°, 125°, 150°, and 175° C.

Table I gives the experimental results obtained by averaging two closely agreeing duplicates when reacting mixtures A, B, and C at the temperatures and elapsed time indicated. These experiments were carried out in sealed tubes or bombs under continuous rotation. In a reaction of this kind it was found that efficient stirring was most essential.

Figure 3 shows the results indicated in Table I when plotted. Figure 4 plots the conversion of the different mixtures against temperature; each curve represents a given mixture for a specified time and indicates how the conversion varies with increasing temperature. In all these curves the letters A, B, or C refer to the mixtures of the composition represented under A, B, or C given above.

TABLE I. CONVERSION OF BARIUM SULFATE TO BARIUM CHLORIDE

Time Hours	Mixt. A %	Mixt. B %	Mixt. C %	Mixt. A %	Mixt. B %	Mixt. C %
	At 100° C. ^a			At 125° C.		
3	37.16	1.47	..	80.82	3.015	1.39
6	78.70	1.51	..	85.76	14.46	1.55
12	88.43	7.17	..	89.88	37.64	1.69
	At 150° C.			At 175° C.		
1	86.88	22.14	..
2	88.08	35.41	..
3	87.57	30.47	3.56	88.51	52.33 ^b	4.65
6	89.42	49.67	4.13	89.78	60.36	5.55
12	89.87	60.81	4.62	92.73	70.03	5.73

^a Conversion for mixture C was under 0.5 per cent even for 12 hours.
^b 3.5-hour run.

Decomposition of Barium Sulfate with Aqueous Calcium Chloride, when Boiled and Evaporated to Dryness

Three grams of barium sulfate, 5 grams of calcium chloride, and 6.75 grams of water were put into a 125-cc. Pyrex bottle and heated on a hot plate until all water was evaporated. The resulting mass was extracted with the methanol-ethylene glycol solvent and then analyzed for barium chloride. The results showed that 88.25 per cent of barium sulfate was converted to barium chloride. Following the same procedure but using theoretical amounts of barium sulfate and calcium chloride, the amount of conversion was found to be 73.55 per cent.

Decomposition of Barium Sulfate Fused with Inorganic Salts

Using the molecular ratios, fusions were made with barium sulfate and calcium chloride, barium sulfate and sodium chloride, barium sulfate and magnesium chloride, barium sulfate and aluminum chloride. After obtaining a clear fusion, when possible, the mass was cooled, extracted with the methanol-ethylene glycol solvent, and analyzed for barium chloride present. The results obtained are as follows:

Mixture	Conversion of BaSO ₄ to BaCl ₂ %	Remarks
NaCl + BaSO ₄	No reaction	Clear fusion
CaCl ₂ + BaSO ₄	95.40	Clear fusion
MgCl ₂ ·6H ₂ O + BaSO ₄	37.30	Hard to fuse; not a clear fusion
AlCl ₃ + BaSO ₄	36.00	Very poor fusion

Commercial Application

The decomposing action of calcium chloride solutions on ground mineral barytes has been amply proved according to the procedures outlined in the Farr patent (4).

The barium chloride formed, and any excess calcium chloride used, are easily removed by the organic solvent. A semi-commercial method for carrying out the described procedures for the manufacture of barium chloride is now under way. Solvents other than the methanol-ethylene glycol mixture will be investigated, as well as recoveries of solvents used. However, it is not anticipated that any great difficulty will be met in the recovery of the solvent. In the commercial application of this reaction there is also no great difficulty in separating the barium chloride and calcium chloride by aqueous crystallization, especially when using only the small molecular excess of calcium chloride needed when the mixture is heated sufficiently long to evaporate off all the water. This heating can be continued, if necessary, to incipient infusion.

Summary

The decomposition of barium sulfate with calcium chloride in aqueous solution was investigated at 100°, 125°, 150°, and 175° C. varying the time up to 12 hours, using the following weight concentration ratios:

Mixture	BaSO ₄	CaCl ₂	H ₂ O
A	1	2	1.5
B	1	1.67	1.5
C	1	1.33	1.5

Using the most concentrated mixture, A, conversions up to about 90 per cent were obtained even at 100° C., provided sufficient time (about 12 hours) was allowed to elapse. The most dilute mixture, C, gave conversions under 5 per cent. By fusing calcium chloride with barium sulfate, conversions up to 95 per cent resulted.

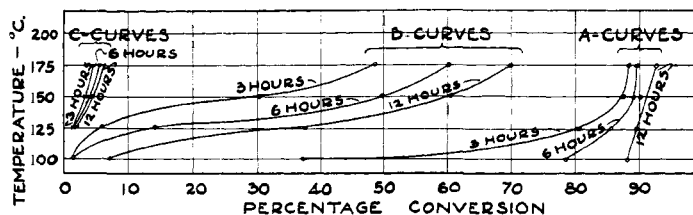


FIGURE 4. DECOMPOSITION OF BARIUM SULFATE WITH CALCIUM CHLORIDE FOR VARIOUS PERIODS

protecting these processes is now on file with the United States Patent Office.

Acknowledgment

It is a pleasure to acknowledge the continued helpful suggestions and advice from H. V. Farr, and the courtesy of the furnishing of chemicals and apparatus on the part of the Mallinckrodt Chemical Works.

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RECEIVED May 6, 1935. Presented before the Division of Industrial and Engineering Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935. Part of a thesis submitted by W. N. Pritchard, Jr., in partial fulfillment of the requirements for the degree of doctor of philosophy at Purdue University.

Composition of Nitrogenous Fertilizer Salts Sold in the American Market

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THE following compilation of analyses of nitrogenous fertilizer salts is offered as a contribution to assembled and recorded information concerning the more exact and detailed composition of fertilizer ingredients as currently distributed in the American trade. Such information, of course, is fundamental to an understanding of questions arising in fertilizer chemistry and technology as well as in the agronomics of fertilizer use.

Nitrogenous compounds, unlike potash salts, show a wide variation in the forms in which the nitrogen is present. The form is generally understood, but little information is readily available concerning the associated components. The value of such information can be appraised only in terms of the use to be made of it.

The analyses here reported are "complete" in the sense

that the constituents whose presence is suspected have been determined. The fact that the sum of these constituents approximates 100 per cent indicates that none of importance has been overlooked. The results are reported in the elemental form, not only to conform with the official method of reporting nitrogen but also to avoid the injection of uncertainties of interpretation. Since conventional combinations as acidic and basic radicals and their salts are generally understood, they are omitted as superfluous.

The samples were secured through the esteemed collaboration of state agricultural chemists from those already collected during 1934, incidental to the routine sampling of fertilizers being offered for sale, under the appropriate state fertilizer control laws.

Samples were sought of the six states—Maryland, Virginia,

This work is being continued, using inorganic salts to react with the barium sulfate. Also other barium compounds will be tried. Similar work is well under way on analogous strontium salts under the direction of the senior author. Patent application protecting these processes is now on file with the United States Patent Office.