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THE DECOMPOSITION OF ALKALINE EARTH SULPHATES.

BY

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THE DECOMPOSITION OF ALKALINE EARTH SULPHATES

By *L. A. Bhatt and H. E. Watson.*

The decomposition of calcium sulphate as a source of sulphur compounds is a matter of considerable industrial importance, particularly in India and countries where no extensive deposits of sulphur or pyrites exist. There are two main methods of breaking down the sulphate, the first by reduction to calcium sulphide, and the second by heating to a high temperature preferably in contact with siliceous materials.

In the former case the sulphide is usually treated with magnesium chloride to liberate hydrogen sulphide and this gas is oxidised to sulphur dioxide, which can be used for the production of sulphuric acid. The sequence of operations is thus more complicated than in the second case where sulphur dioxide is produced directly; but here the high temperatures required, said to be about 1400° , constitute a large item of expense.

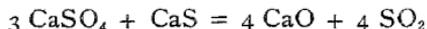
The experiments to be described were conducted with the object of studying the decomposition in rather more detail than has hitherto been done, and of investigating the possibilities of obtaining a larger yield of sulphur dioxide at a lower temperature.

The literature of the subject is considerable, some of the more important data being as follows.¹ Hofman and Mostovitch (*Trans. Amer. Inst. Mining Eng.*, 1909, **39**, 628) find that calcium sulphate when heated alone begins to decompose at 1200° and fuses at 1360° , it is not entirely decomposed at 1400° . On adding one, two or three molecular proportions of silica, sulphur dioxide is evolved at 100° and decomposition is complete at 1300° . An equimolecular mixture of calcium sulphate and ferric oxide fuses at 1250° with partial decomposition. J. W. Cobb, (*J. S. C. I.*, 1910, **29**, 72) gives the temperature of initial decomposition of calcium sulphate in dry air as 125° to 1230° . One to three per cent. is decomposed in an hour at 300° and decomposition is rapid at 1380° to 1390° . The effect of moisture is not appreciable. On addition of silica decomposition begins at 1005° , this temperature being independent of the quantity of silica. Mlle. Germaine Marchal (*Compt. rend.*, 1923, **177**, 1300)

¹ *c. f.* also E.P. 227,175 of 1919; G.P. 301,712, 1915; 302,433, 334,247, 1916; 310,070, 1917; 314,414, 1919.

finds that the reaction between calcium sulphate and silica begins at 870° and that the velocity of reaction is very great at 1230°. It is calculated that the pressure of the evolved gases reaches one atmosphere at 1273°, an equilibrium being attained if the system is a closed one. If alumina is used instead of silica, decomposition begins at 940–950° and the pressure becomes atmospheric at 1363°.

Hofman and Mostovitsch (*Bull. Amer. Inst. Mining Eng.*, 1910, 47, 917) also investigated the reduction of calcium sulphate and showed that reduction with carbon or carbon monoxide begins at 700° and that the reaction



takes place slowly at 800° and energetically between 850° and 900°. Basset (F. P. 428,019, 1910) also states that the decomposition of gypsum with alumina is facilitated by addition of powdered carbon.

The two papers last mentioned suggest the possibility of decomposing the sulphate at comparatively low temperatures by admixture with both silica and carbon, and the following experiments were designed with the object of ascertaining the nature of the reactions which take place under these conditions.

EXPERIMENTAL.

The mixture to be investigated (4 gms.) was heated in an electric tube furnace, usually in a current of nitrogen, and the gases evolved were absorbed and estimated. The residue was removed from the furnace after cooling, and analysed.

For temperatures up to 1100° a quartz tube 2.5 cm. in diameter and 54 cm. long, wound with No. 16 s.w.g. nichrome wire embedded in a mixture of chromite and alundum cement was used. This was placed in a large box of magnesia and the ends of the tube were water-cooled to avoid burning the rubber stoppers with which they were closed. These stoppers were further protected with a covering of asbestos paper. The temperature variation along the central 10 cm. of the tube where the large porcelain boat containing the charge was placed, was not more than 10°. When the furnace temperature did not exceed 1000° the nichrome wire lasted for a considerable time, but at 1100°, it usually broke after heating for about 15 hours and frequent rewinding was necessary. The temperature was measured with a nickel-nichrome couple contained in a quartz tube and calibrated at intervals against a standard couple

An attempt was made to reach higher temperatures by means of a vertical tube furnace similar to the Hirsch furnace. A quartz tube (2.5 cm. external diameter) was fitted inside a fireclay tube lined with alundum cement in such a way that the gap between the two tubes was 9 mm. for 20 cm. in the centre, gradually increasing to 25 mm. at the ends, the total length being 50 cm. The space was filled with powdered graphite resistance material and by gently tapping the tube the powder could be made to fill any small gaps caused by gradual oxidation. Iron rings embedded in the graphite served as leads for current and the whole was packed in a drum filled with magnesia. A temperature of 1400° could be readily obtained, but the quartz tube invariably cracked even after a few heatings at 1200°. Further experiments were consequently abandoned.

PREPARATION OF MATERIALS.

Calcium, barium and strontium sulphates were prepared by precipitation and completely dehydrated before use. *Calcium sulphide* was made by reducing calcium sulphate with hydrogen at 850° and allowing the product to cool in the gas. Analysis showed the composition of the product to be, CaS, 95.2; CaO, 2.8; and CaSO₄, 1.7 per cent.

Calcium sulphite was obtained from solutions of sodium sulphite and calcium chloride, the precipitate after washing being dried in a vacuum. It contained CaSO₃, 94.3; and CaSO₄, 5.7 per cent. In this case and the preceding, no attempt was made to prepare a very pure material.

Silica of high purity was dehydrated at 900° before use. *Charcoal* was prepared from wood, ground to pass through a 60-mesh sieve and dried at 110° for 3 hours. It contained 3.65 per cent. of ash, the chief constituents of which were CaO, 68.3; SiO₂, 14.1; and Fe₂O₃, 8.2 per cent.

Iron from a sample of reduced iron was further reduced with hydrogen until the product contained 94.6 per cent. of the metal. *Nitrogen* prepared by passing air and ammonia over hot copper was washed with sulphuric acid and alkaline pyrogallol and stored in a gas-holder. It was again washed with pyrogallol and dried with concentrated sulphuric acid before use.

ANALYSIS OF THE PRODUCTS.

In addition to carbon monoxide and dioxide, the gaseous products of the reaction were sulphur trioxide, sulphur dioxide, sulphur and sometimes hydrogen sulphide in small quantities. These were passed

through a U-tube containing moistened glass wool and then through two wash-bottles containing sodium hydroxide. At the end of an experiment the whole absorption apparatus was washed out and the solution made up to 250 c.c. Sulphur dioxide and hydrogen sulphide were estimated together by means of iodine; the latter gas was precipitated with ammoniacal zinc chloride solution and the sulphur dioxide estimated in the filtrate. Sulphur was separated by filtration and estimated after oxidation to sulphate. Sulphur trioxide was usually determined by oxidising a portion of the solution with bromine water, estimating the total sulphur and subtracting the amount due to sulphur dioxide and hydrogen sulphide.

The residue in the boat consisted of calcium silicate, sulphate and sulphide, carbon and silica. Sulphide was estimated by adding a portion to a measured amount of standard acidified iodine solution and titrating the excess of iodine with thiosulphate. Owing to absorption of iodine by the carbon it was necessary to wait for some time after the apparent end-point was reached for this iodine to be liberated. The total sulphur was estimated by oxidation and the amount of sulphate obtained by difference.

CALCIUM SULPHATE.

A few preliminary experiments were made with calcium sulphate alone, as Hofman and Mostovitsch (*loc. cit.*) have stated that there is no decomposition below 1150°, while Budnikoff and Syrkin (*Chem. Ztg.*, 1923, 47, 22) found 0.21 per cent. decomposition at 1000°.

Three grams of calcium sulphate were heated for three hours at different temperatures, and the products examined with the following results:—

TABLE I.
Effect of Heat upon Calcium Sulphate alone.

Experiment No.	Temperature	Percentage of original sulphur as		Total
		CaSO ₄	SO ₂ + SO ₃	
1	900	99.9	0.0	99.9
2	1000	99.8	0.2	100.0
3	1150	99.1	0.8	99.9

Budnikoff and Syrkin's results are thus confirmed,

REDUCTION WITH CARBON.

In order to form an idea as to the nature of the reaction between calcium sulphate and carbon under the conditions of the present experiments, these two substances were heated together in different proportions in an atmosphere of nitrogen for varying times. Table II shows the results obtained.

TABLE II.

Reduction of Calcium Sulphate with Carbon.

Experiment No.	Temperature	Time of heating, hours	Ratio CaSO ₄ : C	Percentage of original sulphur as			Total
				CaSO ₄	CaS	SO ₂ + SO ₃	
4	720	3	1 : 4	94.6	5.3	...	99.9
5	720	5	1 : 4	88.3	11.9	...	100.2
6	720	5	1 : 4	88.2	12.0	...	100.2
7	720	8	1 : 4	71.7	28.2	...	99.9
8	860	5	1 : 4	14.9	85.0	...	99.9
9	860	5	1 : 4	14.0	86.0	...	100.0
10	950	5	1 : 1	53.6	39.7	6.6	99
11	950	5	1 : 1	51.1	38.9	10.0*	...
12	950	5	2 : 1	78.3	19.6	1.6	99.5
13	1150	2	1 : 2	12.3	65.1	22.6*	...

* By difference.

From the above it may be seen that the results of duplicate experiments agree as closely as can be expected in view of the fact that the substances reacting are solids and that exact reproducibility of the temperature conditions is difficult.

The reaction is very slow at 720° and does not go to completion in 5 hours at 860° even with a large excess of carbon. At 950° reaction appears to take place between the sulphide and sulphate with liberation of sulphur dioxide, but only a small proportion of the total sulphur is thus eliminated in 5 hours. Even at 1150°, this reaction is not rapid enough to be of practical value. An analysis of the gases evolved in expt. 11 showed the ratio of CO₂ to CO to be 70 : 1.

ACTION OF SILICA.

Some experiments were made in which calcium sulphate was heated with silica alone, air being passed at the rate of about 1 litre per hour. The results are given in Table III.

TABLE III.
Action of Silica on Calcium Sulphate.

Experiment No.	Temperature	Time of heating, hours	Atmosphere	Ratio $\text{CaSO}_4 : \text{SiO}_2$	Percentage of original sulphur as			Total
					CaSO_4	SO_2	SO_3	
14	900	5	dry air	1 : 1	99.1	0.7		99.8
15	1000	5	„	1 : 1	90.4	6.5	3.2	100.1
16	1100	1	„	1 : 1	48.6	42.2	9.1	99.9
17	1100	1	„	2 : 1	64.8	18.2	17.0	100.0
18	1100	1	„	1 : 2	30.2	45.2	24.7	100.1
19	1150	1	„	1 : 1	13.6	70.2	16.2	100.0
20	1100	1	moist air	1 : 1	70.5	23.2	6.2	99.9
21	1100	1	„	1 : 1	70.4	26.1	3.5	100.0
22	1100	1	„	1 : 1	68.8	25.1	5.8	99.7
23	1100	1	„	1 : 2	60.0	30.1	9.8	99.9
24	1100	5	dry air	1 : 1	42.2	30.9	26.9	100.0
25	1100	4*	„	1 : 1	17.7	50.8	31.5	100.0
26	1100	4	„	1 : 2	3.5	60.9	35.6	100.0
27	1100	4*	„	1 : 2	0.0	64.4	35.3	99.7

* Four 1 hr. periods; material reground.

These figures agree in general with those of previous observers. Mlle. Marchal (*loc. cit.*) gives the vapour pressure of the evolved gases as 1.05 cm. at 940° and 2 cm. at 1000°. The decomposition in expt. 15 corresponds approximately with the amount of sulphur dioxide at 6 mm. pressure which would be removed from 2.7 gms. of calcium sulphate by the quantity of air passed in 5 hours, and is thus distinctly less than the quantity to be expected from her results.

Expts. 16, 17 and 18 show that the influence of the quantity of silica is considerable, while from the results 20 to 23 it appears that the reaction does not take place so readily in the presence of moisture.

In expt. 20, air saturated with water vapour at 25° was used and in the next three experiments the air was bubbled through water at 60° before entering the furnace.

Expt. 24 when compared with No. 16 shows that the reaction tends to come to a standstill after some time when equimolecular proportions of the materials are used. In No. 25 the mixture was removed from the furnace every hour and reground, and a considerable increase in the amount of decomposition resulted. With two molecules of silica the reaction is nearly complete in 4 hours at 1100° as shown by expt. 26. Hourly grinding as conducted in No. 27 produces a quantitative decomposition.

ACTION OF CARBON AND SILICA.

Mixtures containing various proportions of calcium sulphate, carbon and silica were heated in a current of nitrogen passing at approximately 1 litre per hour, with results shown in Table IV.

TABLE IV.

Action of Carbon and Silica on Calcium Sulphate in Nitrogen.

Experiment No.	Temperature	Time of heating, hours	Ratio. CaSO ₄ : C : SiO ₂	Percentage of original sulphur as					
				CaSO ₄	CaS	SO ₂	SO ₃	H ₂ S	Total
28	720	5	1 : 4 : 0.23	94.2	3.9	2.0*			100.1
29	720	8	1 : 4 : 0.23	90.9	6.7	2.2*			99.8
30	860	5	1 : 4 : 1	23.5	58.2	11.8	6.2		99.7
31	950	5	1 : 4 : 1	0.9	78.7	12.0	7.9		99.5
32	950	5	1 : 1 : 1	59.9	21.4	11.8	6.7		99.8
33	950	5	2 : 1 : 1	68.1	16.6	13.9	1.5		100.0
34	950	5	2 : 1 : 1	66.2	17.6	13.1	2.1		100.0
35	1,000	3	1 : 4 : 1	1.2	71.4	20.9	5.2	1.4	100.1
36	1,000	3	1 : 4 : 1	0.9	70.1	21.7	5.1	2.1	99.9
37	1,000	3	1 : 2 : 1	30.7	50.0	12.9	6.1		99.7
38	1,000	3	1 : 2 : 1	30.5	51.8	11.4	6.2		99.9
39	1,000	3	1 : 2 : 0.5	18.0	61.4	19.6	0.9		99.2
40	1,100	1	1 : 2 : 0.5	4.1	48.8	29.6	17.4		99.9
41	1,100	3	1 : 2 : 0.5	4.0	49.7	30.8	15.5		100.0

* SO₂ + SO₃

At 720° the reduction is slower than with carbon alone, only 9.1 per cent. of calcium sulphate being decomposed in 8 hours as compared with 28.3 per cent. in expt. 7. At the same time small quantities of sulphur dioxide are evolved, which is not the case with silica or carbon alone.

A similar state of affairs is found at the higher temperatures. For example in expt. 32, 40.1 per cent. of sulphate is decomposed instead of 48 per cent. in expts. 10 and 11, while volatile sulphur is 18.5 per cent. as compared with 6.6 per cent. with carbon alone and about 3 per cent. with silica alone as estimated from expts. 14 and 15. Expt. 32 and 33 show that halving the amount of silica reduces the volatile sulphur only from 18.5 to 15.4, while decreasing the amount of carbon has a much larger effect (31-34), the reason being that the reaction with carbon is nearly complete and depends on the quantity, while the reaction with silica has by no means reached its final stage under the conditions of these experiments. At 1100° the reaction is nearly quantitative with regard to both materials.

It seems probable that the decreased decomposition when silica is present is largely caused by mechanical action; it is possible that the increase in the amount of sulphur trioxide liberated is partly due to the formation of an intermediate compound which is more readily acted upon by silica than is calcium sulphate. It will be observed that in experiments 33 and 34, the amount of carbon is only sufficient to reduce 25 per cent. of the calcium sulphate to sulphide whereas actually 33 per cent. has been decomposed. The difference is rather more than would be decomposed by silica alone at this temperature. The production of calcium sulphite might give rise to the conditions observed and consequently a few experiments were made with this substance.

DECOMPOSITION OF CALCIUM SULPHITE.

Calcium sulphite was heated for 5 hours at 950° in an atmosphere of nitrogen with the results shown in Table V.

TABLE V.
Decomposition of Calcium Sulphite in 5 hours at 950°.

Experiment No.	Substances heated	Percentage of original sulphur as						Total
		CaSO ₃	CaSO ₄	CaS	SO ₂	SO ₃	S	
42	CaSO ₃	4.8	68.5	22.8	4.0 ¹			100.1
43	CaSO ₃ + C	0.0	29.4	63.2	7.7 ²		...	100.3
44	CaSO ₃ + SiO ₂	0.4	38.6	2.1	44.9	1.6	12.7	100.3
45	CaSO ₃ + 2 SiO ₂	0.6 ²	61.1		29.0	0.6	8.4	99.7
46	„	0.7 ²	60.1		29.3	0.6	9.0	99.7

¹ SO₂ + SO₃.

² CaSO₃ + CaS.

Expt. 42 shows that calcium sulphite decomposes at 950° mainly in accordance with the equation $4\text{CaSO}_3 = 3\text{CaSO}_4 + \text{CaS}$. Addition of carbon, as might be expected, merely increases the proportion of sulphide. The presence of silica, however, appears to inhibit almost entirely the formation of sulphide. This would occur if silica acted on the sulphide, but it is shown subsequently that silica has no appreciable action on calcium sulphide at 950° although it reacts at 1100° with liberation of sulphur; hence it appears that the low yield of sulphide is not due to this cause. If the direct reaction $\text{CaSO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{SO}_2$ took place more readily than the decomposition to sulphate and sulphide there should be very little formation of sulphate. This is by no means the case, and in fact the quantity of calcium sulphate is nearly as great when silica is present in bimolecular proportion as when there is none. The reason for the diminished yield of sulphate with one molecule of silica is not apparent. The most probable explanation for the low yield of sulphide seems to be that the sulphide is acted upon by silica at a lower temperature when it is being formed from sulphite than when it is first made and then heated with silica. Additional evidence for this is to be found in the fact that appreciable quantities of elementary sulphur are produced, just as they are when silica acts on calcium sulphide at 1100°.

ACTION OF SILICA ON CALCIUM SULPHIDE.

A sample of calcium sulphide containing 1.7 per cent. of sulphate was heated in nitrogen for one hour with the results shown in Table VI.

TABLE VI.

Action of Silica on Calcium Sulphide.

Experiment No.	Substances heated	Temperature	Percentage of original sulphur as				Total
			CaS	CaSO ₄	SO ₂	S	
47	CaS	950	98.9	1.0	trace		99.9
48	CaS + SiO ₂	„	97.3	1.0	1.2	trace	99.5
49	„	1100	82.5	0.4	5.6	11.2	99.7
50	„	„	82.3	0.4	5.9	11.4	100.0
51	CaS	„	98.5	0.2	1.1	0.0	99.8
52	CaS + SiO ₂	„	80.1	0.3	6.6	12.8	99.8
53	CaS	„	99.0	0.1	0.9	0.0	100.0

The experiments are given in the order in which they were performed. When small quantities of sulphate (in excess of the original amount) and sulphur dioxide were found, the nitrogen used was re-purified and great care taken to avoid any leakage of air into the apparatus. In spite of this, sulphur dioxide was always given off when silica was present and the quantity of sulphur was approximately twice that of the dioxide. Moisture might have this effect but the gases were well dried and there was very little action in absence of silica. The silica itself was practically anhydrous. The formation of silicide would explain the presence of sulphur dioxide, but this reaction appears to be highly improbable and no silicide was detected. At present there appears to be no satisfactory explanation and further work is required in this direction.

ACTION OF IRON.

According to Kestner (*Compt. rend.*, 1884, **99**, 876) two parts of calcium sulphate and one part of ferric oxide when heated to bright redness ('rouge blanc') give off sulphur dioxide and oxygen and a mixture of lime and ferric oxide remains. This experiment has been repeated at temperatures of 950°, 1000° and 1100°. At 1000° 0.4 per cent. of the sulphur was evolved in 3 hours and 5.4 per cent. at 1100°. These quantities are somewhat greater than in the case of calcium sulphate alone, but the effect of ferric oxide is much less than that of silica.

Martin and Fuchs (*Z. anorg. Chem.*, 1922, **125**, 307) have made a lengthy study of the action of iron upon calcium sulphate and have shown that the sulphate is rapidly reduced at 750° forming iron sulphide. At higher temperatures sulphur dioxide is evolved, it being theoretically possible to obtain 80 per cent. of the sulphur in that form.

A few experiments have been made to determine the effect of adding silica to the reaction-mixture. A specimen of reduced iron was used, freshly reduced in hydrogen before mixing with the other ingredients. A convenient and accurate method of estimating the metallic iron in this was to add a weighed quantity to copper sulphate and determine the precipitated copper electrolytically after solution in nitric acid.

The reaction-mixture fused to a black mass containing iron and calcium sulphides and calcium sulphate. At the temperature of the experiments ferric sulphate is presumably completely decomposed so that the total sulphate has been given as CaSO_4 . The mixed sulphides were determined by estimating the hydrogen sulphide evolved with acid,

Table VII shows the effect of heating various mixtures at 950° for 5 hours in an atmosphere of nitrogen.

TABLE VII.

Action of Iron and Silica on Calcium Sulphate at 950°.

Experiment No.	Mixture	Percentage of original sulphur as					Total
		CaSO ₄	CaS + FeS	SO ₂	SO ₃	S	
54	3CaSO ₄ + 8 Fe	46.8	13.4	28.5	2.5	8.6	99.8
55	„	46.4	14.5	27.8	2.5	8.6	99.8
56	3CaSO ₄ + 8 Fe + 3 SiO ₂	49.0	4.5	44.8	0.9	0.2	99.4
57	3CaSO ₄ + 8 Fe + 11 SiO ₂	64.1	7.9	24.4	0.9	2.4	99.7

The addition of silica in molecular proportion to calcium sulphate slightly increased the amount of sulphate but reduced the quantity of sulphides so that considerably more sulphur dioxide was evolved. A large excess of silica appeared to have an inhibiting action.

As these experiments did not appear likely to lead to results of value they were not extended.

DISCUSSION OF RESULTS.

It is evident from the foregoing tables that the addition of carbon to a calcium sulphate-silica mixture increases the amount of sulphur liberated as gas at 1000°, but at the same time calcium sulphide is formed and is acted upon by silica less readily than the sulphate, so that the temperature necessary for a quantitative decomposition is raised. The increased liberation of gases appears to be due to the reduction taking place in two stages, the intermediate compound, possibly calcium sulphite reacting at the moment of its formation, more readily with silica than does calcium sulphate.

The reaction between calcium sulphate and calcium sulphide appears to take place at a higher temperature than the reaction between calcium sulphate and silica.

The addition of iron as a reducing agent in addition to silica does not seem likely to be of value, again owing to formation of sulphides, and consequently it appears that a high yield of sulphur in the gaseous form is best obtained by heating with silica in absence of a reducing agent. For a quantitative decomposition under experimental conditions

a temperature of 1100° is required and under manufacturing conditions a distinctly higher temperature would be necessary in order to bring about the reaction in a reasonable time.

DECOMPOSITION OF MAGNESIUM, STRONTIUM AND BARIUM SULPHATES.

A few experiments were conducted with the above materials for comparison with calcium sulphate. The relative decomposition points were determined by heating in the tube furnace in a current of air with the temperature slowly rising until the gases just began to redden blue litmus paper. The values obtained were :—

	Alone	With 1 mol. SiO ₂
MgSO ₄	740
SrSO ₄	1100	780
BaSO ₄	>1100	850

The value for magnesium sulphate agrees with the determination by Reidenbach (*Diss. Kusel*, 1910) who states that decomposition begins at 750°, although le Chatelier (*Bull. Soc. chim.*, 1887, (2) 47, 300) gives the temperature as 1160°. The experiments recorded in Table VIII show the effect of silica on magnesium sulphate at different temperatures.

TABLE VIII.

Action of Silica on Magnesium Sulphate.

Substances heated	Temperature	Time, hours	Percentage of original sulphur as			Total
			MgSO ₄	SO ₂	SO ₃	
MgSO ₄	900	2	97.1	2.5	0.4	100.0
„	1000	1	95.3	3.8	0.7	99.8
„	1100	2	6.3	71.1	22.6	100.0
MgSO ₄ + SiO ₂	900	1	93.7	5.2	1.1	100.0
„	1000	1	80.1	15.5	4.1	99.7
„	1100	1	0.2	74.3	25.6	100.1

From these it appears that silica accelerates the decomposition of magnesium sulphate but not as much as might be expected from comparison with calcium sulphate. The effect of a rise in temperature from

1000° to 1100° is very marked. Similar experiments with strontium sulphate resulted in only 2·3 per cent. decomposition with 1 mol. of silica in one hour at 1100°. In the case of barium sulphate the decomposition under these conditions was 5·4 per cent.

SUMMARY.

1. The behaviour of calcium sulphate, sulphide and sulphite on heating alone and in presence of silica has been studied.

2. The effect of adding reducing agents to the calcium sulphate-silica mixture has been examined and it has been found that although sulphur dioxide is liberated at a lower temperature under these conditions, the temperature required for complete decomposition is higher owing to the formation of calcium sulphide.

3. A quantitative decomposition of calcium sulphate may be obtained on the small scale in 4 hours at 1100° with excess of silica in a slow current of air, but in commercial practice it would be desirable to work at a temperature 100–150° higher.

4. Measurements have been made of the amount of decomposition of magnesium, strontium and barium sulphates alone and with silica at different temperatures.

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