# XL.—*On Calcium Hydrosulphides.*

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## *Calcium Hydrosulphide.*

WE have succeeded, after many trials, in establishing the existence of normal calcium hydrosulphide by getting it in the solid state. Although often referred to in connection with the recovery of sulphur from alkali-waste, and with the purification of coal-gas by lime, this substance has remained unknown till now except in dilute solution.

Pelouze (*Compt. rend.*, **62**, 108; *Handw. Ch.*, **2**, 353) endeavoured to prepare it by treating calcium hydroxide in the form of milk of lime with a current of hydrogen sulphide gas, and concluded that a solution could only be obtained in this way which held no more than 7 per cent. of it. He also found that he could prepare more concentrated solutions by using calcium sulphide or a solution of sugar-lime. We find, on the other hand, that calcium sulphide acts much more slowly than lime in yielding concentrated solutions of the hydrosulphide.

Böttger's directions (*Annalen*, **29**) for preparing calcium hydrosulphide for use as a depilatory, which are copied into many works on chemistry and pharmacy, are misleading, as, according to them, hydrogen sulphide is to be passed into thin milk of lime until the mass acquires a bluish-grey colour. The production of this colour is due to the formation of ferrous sulphide, and this must take place as soon as any soluble sulphide is present, and before, therefore, any quantity of lime has been acted upon by the hydrogen sulphide. As to the mass thus obtained, which is to be smeared upon hides as a depilatory, the little true hydrosulphide in it is in solution in the liquid part of it. Only last year a similar misapprehension appeared in a paper by Lewis T. Wright (*J. Soc. Chem. Ind.*, **2**, 122), in which he states that he prepares calcium hydrosulphide by saturating moist calcium hydroxide with hydrogen sulphide, and then uses the product in the place of soda-lime in the determination of nitrogen in nitrates. The product he uses cannot contain any solid calcium hydrosulphide. Gas-lime, too, is not calcium hydrosulphide, as commonly described.

Calcium sulphide has long been known to yield some calcium hydrosulphide in solution when heated with water, and to yield it in the drainings from soda-waste heaps. From the interior of a heap of waste, which had been lying for months, Kraushaar (*Chem. Soc. J.*, **34**, 171; *Dingl. polyt. J.*, **226**, 412) dissolved out by cold water more than 3 per cent. of the sulphur, and found nine-tenths of this to be in the form of hydrosulphide. This, however, must have been partly in the form of sodium salt. By heat under pressure, according to Kraushaar (*loc. cit.*), confirmed by Curphey, most of the sulphur of soda-waste can thus be dissolved out; but according to Schaffner (*Lunge's Alkali Manuf.*, **2**, 658—659), Chance (*J. Soc. Chem. Ind.*, **2**, 11), and Weldon (*ibid.*), the solution is only partial unless very much water is employed.

## *Preparation of Calcium Hydrosulphide.*

Nothing can be simpler in the abstract than the preparation of calcium hydrosulphide, consisting, as it does, in treating calcium hydroxide with hydrogen sulphide in presence of a sufficiently small quantity of cold water, and then crystallising the solution. But the details of the process require much attention, and this fact probably explains how it is that the hydrosulphide has not hitherto been obtained. The difficulties of its preparation depend upon its instability and exceeding solubility in water.

If hydrogen sulphide is forced through a semi-solid mass of calcium hydroxide and water, the whole will become liquefied and increased in volume. To this clear solution much lime has still to be added, and dissolved by hydrogen sulphide, before a saturated solution is obtained. This lime might be added as hydroxide, but it is practically requisite to use the oxide, as, unless the hydroxide were dry, too much water would be yielded by it, and if it were not in fine powder troublesome lumps would form from it, and the operations of drying and pulverising thus required would probably be attended with carbonatisation by the atmosphere. Quicklime prepared from precipitated calcium carbonate is almost necessary for preparing the hydrosulphide. That made from calcite may, after grinding, be used for making a moderately concentrated solution, but it is too difficult of dissolution by hydrogen sulphide to be convenient for making a saturated solution.

The preparation of a crystallising solution of calcium hydrosulphide takes days to complete, and all through the process air must of course be excluded. In hot weather it is hardly possible to prepare it without cooling down, and at all seasons cooling with snow or ice facilitates the process.

The lime we used was made by igniting, in platinum crucibles, calcium carbonate which had been precipitated from an alkaline alcoholic solution of fused calcium chloride. It was always found free from sulphate and carbonate, but was never so pure as to dissolve in the large proportions required without leaving some small residue. We believe, indeed, that dissolution to saturation by hydrogen sulphide will be found a more delicate wet test of the purity of lime than any other.

We tried hydrogen sulphide prepared from several sources, but ended by using the ordinary gas from iron sulphide, washed, and filtered through a column of cotton, and sometimes dried with calcium chloride.

The vessels we finally employed for making crystallising solutions were formed out of tubing 18—20 mm. in diameter. The body of the tube was about 1½ decimetres in length, and ended in long drawn-out limbs of about 5 mm. in diameter. One of these was bent acutely just beyond its origin in the main part of the tube. The tube being fixed in a nearly vertical position, with its bent limb below, the gas could be sent through this limb up from the very bottom of the liquid, and thus made to keep the undissolved lime well agitated. Occasionally when working with almost finished solutions, a stout platinum wire was, without stopping the current of gas, pushed down the upper straight limb of the tube into the solution to detach adhering matters. Except at these moments, and when adding more lime, the exit-tube was always in connection with a wash-bottle, serving as a guard against the entrance of air.

Before setting the solution to crystallise, it had to be left to clarify by the subsidence of excess of lime and of the impurities always present in small quantities. It had then to be decanted into a crystallising tube. This was done in a stream of hydrogen sulphide, after the tube had been turned to the horizontal position to avoid bubbling of the gas and disturbance of the sediment. The two tubes were connected by black rubber tubing during the decantation. The mouths of the crystallising tube were afterwards closed by caoutchouc caps coated with paraffin, but, except for the few moments occupied in transferring, the solution touched glass only.

In order to prepare a solution of the necessary concentration, between two and three parts only of water must be used with one of calcium oxide. But as large a proportion as that may be added, and yet through evaporation from the hot mass, nearly dry calcium hydroxide be obtained. Evidently, therefore, the addition of this amount of lime to the water must be made gradually. To start with, 1 part of lime dropped into somewhat less than 4 parts of hot water gives, from the purity and fine division of the lime, about the stiffest paste of hydroxide that can be worked with. The mixing must be done in the preparation-tube itself. Thin milk of lime may be used instead, but in that case a larger quantity of lime will have to be added afterwards. In the thick paste dissolution of the hydroxide proceeds, with evolution of heat, and with comparative rapidity, along the channels which the hydrogen sulphide works out for itself in forcing its way through the paste. Admixture of the undissolved mass of the hydroxide with the concentrated solution thus formed, is attended with evolution of heat, and the replacement of hydroxide by so abundant a crystalline precipitate of hydrated sulphide as to render the whole very thick again.

Dissolution of the first quantity of lime having become complete, fresh lime is added to the clear thin liquid. The lime reacts more mildly with the solution than with simple water. If very well agitated, the lime passes gradually into a slimy matter, consisting probably of very fine crystals, before it passes into solution. Often, however, some crystalline lumps form, which, however, very slowly, even if left at rest, break down into the slimy matter. When calcite-lime is used, hard crystalline masses generally form, which are afterwards practically irreducible, so that such dense lime is hardly to be used successfully. The lime dissolves best when added gradually, and is then less likely to choke up the tube with hard crystalline sulphide. We have found it necessary to make additions of lime about four times, in order to reach the point of saturation, and leave some excess in proof of having done so. We have already described the decantation of the formed solution from this excess and the small unavoidable impurities.

If the liquid is kept cold during the passage of the gas, in order to favour reaction, crystals of the hydrosulphide at last form in abundance; but this is not the case at ordinary temperatures. Saturation to the crystallising point being reached, the current of gas is stopped, and the liquid left in the tube to clarify, very carefully sealed up, at the ordinary, or a slightly warm temperature, in order that most of the crystals which may have formed in the cold shall redissolve. After decantation, the clear solution is again kept in ice, when it crystallises, and the more abundantly the better it has been saturated at a low temperature.

The calcium hydrosulphide thus obtained is separated from its mother-liquor by draining and blowing a current of hydrogen sulphide through the mass of crystals, the tube being all the while immersed in snow. They cannot be removed from an atmosphere of hydrogen sulphide without undergoing change, and admit therefore of no further drying, except by a momentary swinging of the tube to expel adhering liquid centrifugally. In warm weather, the crystals evolve hydrogen sulphide even in an atmosphere consisting of that gas.

## *Properties of Calcium Hydrosulphide.*

Calcium hydrosulphide forms colourless prismatic crystals. It melts on a slight rise of temperature, in its water of crystallisation, but not without decomposition beginning, even in an atmosphere of hydrogen sulphide. Most probably, it never itself undergoes oxidation by the air, but decomposes into other compounds before that change can take place.

It is exceedingly soluble in water and in alcohol, so much so indeed, that a fourth of its weight of water at ordinary temperatures appears to be more than sufficient to hold it in solution. The addition of four or five drops of water to 10 c.c. of saturated solution entirely destroys its power of crystallising when cooled in ice. There is, however, nothing singular in this, as all salts with much water of crystallisation show the same behaviour in close vessels at temperatures near that of their aqueous fusion.

An almost saturated solution, even when warm, loses no water, or scarcely any, in a current of dry hydrogen sulphide. Thus, gas previously dried, passed in a steady stream for four hours through a slightly warm solution, gave only $4\frac{1}{3}$ mgrms. increase in weight to a calcium chloride tube, through which it passed on leaving the solution.

The specific gravity of one solution, which proved on analysis to hold 32 per cent. anhydrous, or 64 hydrated, salt, was found to be 1·255 at 23° C., and that of another holding $37\frac{1}{2}$ per cent. anhydrous, or $75\frac{1}{2}$ per cent. hydrated, salt in solution, 1·310 at $23\frac{1}{2}°$. The solutions are colourless, and similar in degree of liquidity to other concentrated saline solutions.

Other properties of calcium hydrosulphide are described in the succeeding sections of this paper.

### *Composition of Calcium Hydrosulphide.*

The existence of calcium hydrosulphide in solution has long been admitted, and is sufficiently established by the qualitative reactions of the solution. The nature of the crystals now described is equally well shown by the same means. Their free solubility in water and alcohol proves the absence of hydroxide. The absence of colour proves the absence of polysulphides. The precipitation of all the sulphur by zinc salts, and the solubility of the crystals in alcohol, already adduced, prove the absence of oxidised sulphur salts. The liberation of hydrogen sulphide by manganous salts proves the presence of basylous hydrogen and the solubility in alcohol, by showing the absence of calcium oxide, hydrated or not, proves that the hydrogen is in equivalent amount to the calcium. All this stands true without seeking support from the analogy to other compounds and reactions. We have not, however, failed to recognise the importance of quantitative determinations, and have made a number of analyses both of solutions and of crystals. Our difficulty has been to prepare samples for analysis.

A mixture of sulphur-free potassium hydroxide and potassium hypobromite was used as the oxidising agent. The solution was weighed by difference, directly into potassium hydroxide solution, the weighings being made in a Sprengel's specific gravity tube. The crystals were weighed in the tube in which they had been made. The oxidation by the hypobromite was immediate and complete in the cold, but as a precaution heat was applied. The calcium was precipitated as oxalate, and the sulphur as barium sulphate.

0·836 gram of a solution of specific gravity 1·255 at 23° gave calcium 11·96 per cent., and sulphur 19·26 per cent. Two atoms of sulphur to one of calcium, taking this as 11·96, would be 19·14.

Of another solution, specific gravity 1·310 at $23\frac{1}{2}$°, 0·594 gram gave calcium 13·76 per cent., and 0·818 gram gave sulphur 22·85 per cent. It was difficult to weigh off these solutions with a high degree of accuracy, so that calcium and sulphur would better have been estimated in the same portion. The results, however, give to 100 atoms of calcium 207 of sulphur, leaving therefore no room to doubt as to the facts.

The attempt to remove mother-liquor from some good crystals by rapidly effected pressure between blotting-paper, gave results which were sufficiently definite in their indication, but which showed only a little more than 7 atoms of sulphur instead of 8, to 4 of calcium. The analysis was made upon only 0·2566 gram, and yielded quantities corresponding to calcium 20·07 per cent., and sulphur 28·32 per cent.

A quantity of good crystals from another preparation was weighed while still wet with mother-liquor. It amounted to 3·275 grams, and gave calcium 16·47 per cent., and sulphur 26·11 per cent., making 33 atoms calcium to 65 atoms sulphur. To have been 2 atoms to 1 calcium, the sulphur should have been found 26·35 per cent. instead of 26·11 per cent.

Other analyses made, were only for the determination of the water of crystallisation. The crystals, dried on blotting-paper, and partly decomposed in consequence, had given results already stated, which correspond to $6H_2O$. Calculation for a mixture of $99(CaH_2S_2,6H_2O)$ with $13CaH_2O_2$, gives exactly 20·07 per cent. calcium as found, and 28·39 per cent. sulphide instead of 28·32 per cent. as found. The water here shown present may be safely taken as not less than the water of crystallisation; for, by an experiment, also already described, it had been proved that a cold saturated solution does not evaporate in a current of dry gas, and from this it stands still more certain that the water of the crystals will not escape at common temperatures.

By a determination of calcium in another preparation of good crystals, successfully drained while ice-cold, we obtained, using 0·9455 gram, 17·54 per cent., which corresponds with about $6\frac{4}{5}$ molecules of water. The adoption of $7H_2O$ as expressing the water of crystallisation, would need the assumption that the crystals, wet as they were, had lost much hydrogen sulphide, and this cannot be admitted. On the other hand, the adoption of $6H_2O$ makes more than 5 per cent. of water of solution to be present with the crystals, corresponding with perhaps as much as 15 per cent. solution at or near 0°, and this assumption may be admitted as quite probable.

We conclude, therefore, from our experiments, that calcium hydrosulphide crystallises almost certainly with 6 mols. of water, and is therefore formulated by $CaH_2S_2,6H_2O$.

### *Calcium Hydroxyhydrosulphide; its Preparation.*[*]

The decomposition of a solution of calcium hydrosulphide was stated by Berzelius to yield calcium sulphide, and by Pelouze to yield hydroxide. Both observations will have been correct, the calcium sulphide

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[*] *Hydrated Calcium Sulphide.*—The remarkable results of Lunge and Naef's investigation of the constitution of the chlorides of lime and of lithia (*Annalen*, **219**, 129) have placed Odling's formula for the lime compound, ClO.CaCl, quite beyond the region of legitimate doubt, as against the formula $CaCl_2,CaO_2Cl_2$, and

being understood to be hydrated. The hydrosulphide becomes the hydroxyhydrosulphide in concentrated solutions, hydroxide in weak ones, and mixtures, or possibly compounds of the two, when the solutions are of medium strength, while the hydroxyhydrosulphide itself becomes hydroxide by the action of water. These decompositions proceed only when the hydrogen sulphide produced can escape or become diluted, and are much more rapid and complete in hot solutions than in cold solutions.

Nothing else, we believe, has been published concerning calcium sulphide formed in the wet way, besides Berzelius' statement of its occurrence in acicular crystals. As we find it to be hydrated, and different in its behaviour with water from true calcium sulphide, we follow all analogy in describing it as calcium hydroxyhydrosulphide, symbolised by Ca(SH)(OH). It is certainly of common, though unrecognised occurrence in the arts.

Calcium hydroxyhydrosulphide is formed from the hydrosulphide by the reaction of this salt with water:—

$$CaS_2H_2 + OH_2 = Ca(SH)(OH) + SH_2,$$

or with calcium hydroxide:—

$$CaS_2H_2 + CaO_2H_2 = 2Ca(SH)(OH).$$

It is also formed by the union of water with calcium sulphide, as in the interior of heaps of soda-waste, and by the reaction between calcium hydroxide and hydrogen sulphide, as in coal-gas purification. The first of these modes of formation may also be properly regarded as a process of dissociation, as the water yielding the hydroxyl is already a part of the crystals of the hydrosulphide.

Even in a closed vessel, when an ice-cold saturated solution of calcium hydrosulphide, having crystals of the salts lying in it, is merely allowed to rise to a summer temperature, it effervesces a little from this decomposition, the crystals at the same time melting. But when exposed to the air, calcium hydrosulphide begins at once to change rapidly into the hydroxyhydrosulphide. Its crystals

there can therefore be, as regards the bivalent nature of calcium, no hesitation in adopting for the hydrated calcium sulphide the constitutional formula HS.Ca.OH.

According to Sabatier (*Compt. rend.*, **89**, 234; *Chem. Soc. J.*, **36**) the admixture of a solution of the hydroxide with one of the hydrosulphide of potassium or sodium is not accompanied by evolution of heat, unless indeed the solutions are very concentrated, and then only to a slight extent. The so-called monosulphides of these metals in the form of hydrated crystals seem therefore to have no sufficient claim to their title, and should rather be regarded as combinations of hydroxide with hydrosulphide under the influence of forces of crystallisation—

$KSH,KOH$, rather than $K_2S,H_2O$.

retain their shape for a time, but quickly grow dull and crusted on the surface. Beneath the crust they deliquesce, and thus become a liquid mass enclosed in a pasty shell. Although, as already mentioned, they lose no water by evaporation, they yet decrease in weight very quickly during deliquescence by evolving hydrogen sulphide.*

Decomposition of concentrated solutions of calcium hydrosulphide exposed to the air, is not less remarkable than that of the crystals. The solution becomes almost instantly crusted over with crystals, and if a current of air is passed through it an abundant precipitation of crystals, which as well as those of the crust are calcium hydroxyhydrosulphide, is the result. The simultaneous oxidation which occurs is relatively slight, while absorption of carbon dioxide appears not to take place at all. (See a subsequent section of this paper.) All oxidation may, however, be avoided by exposing the solution to an atmosphere of hydrogen, or to a stream of this gas instead of air.

The reaction of a solution of calcium hydrosulphide with calcium hydroxide has already been referred to in describing the preparation of the hydrosulphide. Where the lime used has been prepared from precipitated carbonate, and it is kept well agitated in the solution, it becomes rapidly converted into a crystalline translucent precipitate, much more bulky than itself. With insufficient agitation, this lime may at first form crystalline lumps, but these are not permanent. When, however, dense calcite-lime is taken, the reaction proceeds very slowly, and if this lime be left lying in the solution, it is gradually replaced by relatively large prismatic crystals of the hydroxyhydrosulphide, some of which shoot up into the liquid above. This mass of crystals is permanent in the mother-liquor.

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* This is the second salt made known by one of us that *deliquesces with loss of weight* when exposed to air, and from the same cause, decomposition with liberation of water. The other salt is normal ammonium carbonate, which decomposes into ammonia, acid ammonium carbonate, and water for the most part liquid—$CO_3(NH_4)_2,OH_2 = NH_3 + CO_3H.NH_4 + OH_2$ (*Chem. Soc. J.*, **23**, 185).

The resemblance between barium hydrosulphide and calcium hydrosulphide is very close, except perhaps in the property of stability. Both crystallise on cooling their solutions in prisms having water of crystallisation,—how much in the case of the barium salt is unknown. Crystals of the barium salt are stated to effloresce in the air, and their solution, when heated, to lose hydrogen sulphide; probably, therefore, the efflorescence, like that of the calcium salt, is due not to loss of water, but of hydrogen sulphide. Yet solid barium hydrosulphide is said to lose water when heated, and only at an incipient red heat to lose hydrogen sulphide, and become the sulphide. The correctness of this statement may, however, fairly be doubted, when the action of water upon this salt and upon the hydroxyhydrosulphide is considered.

### *Properties of Calcium Hydroxyhydrosulphide.*

Calcium hydroxyhydrosulphide occurs in colourless four-sided prisms, which are sometimes of size, but are generally in exceedingly minute needles, detached or crusted together, or, when they have been formed by a graduated exposure of the solution to the atmosphere, arranged in stellate groups. Deprived quickly of their mother-liquor, the crystals may be obtained dry with scarcely any appearance of change. They gradually, however, become opaque from decomposition, although they retain their silky lustre for a comparatively long time. Calcium hydroxyhydrosulphide slowly evolves hydrogen sulphide in the air, and becomes yellow by absorption of oxygen. It also takes up carbon dioxide from the air, but not very freely at first. It contains water of crystallisation, which it loses when heated, but not without partial decomposition.

It dissolves readily in water, but the solution almost immediately decomposes into hydroxide, which is precipitated, and hydrosulphide, which remains in solution. It is insoluble in a moderately concentrated solution of calcium hydrosulphide, and unaffected by it. It is insoluble in alcohol, and is slowly decomposed by this liquid, as by water, hydrosulphide becoming dissolved out. From the readiness with which calcium hydroxyhydrosulphide is converted into hydroxide, preparations of it are apt to be largely mixed—or possibly combined—with hydroxide.* Such preparations often show very little appearance of having become so much changed in composition.

In describing the preparation of the hydrosulphide, we have already indicated that the hydroxyhydrosulphide reacts with hydrogen sulphide to reproduce the hydrosulphide.

### *Composition of Calcium Hydroxyhydrosulphide.*

The decomposition of the hydroxyhydrosulphide by water into

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* A tube containing a nearly saturated solution of calcium hydrosulphide, and having its ends closed by caoutchouc caps coated with paraffin, was left aside during the winter months. The solution had then become, for the most part, converted into transparent colourless crystals of hydroxyhydrosulphide and a non-crystalline pellicle on its surface and on the walls of the tube. The residual solution was only moderately yellow, so that very little oxidation had occurred, while, on opening the tube, air rushed in, showing that the tube had become partly vacuous. The gas remaining in it was hydrogen sulphide. The pellicle was a very singular body. It was insoluble in water, and apparently only slowly affected by washing. It had a porcellanous whiteness and translucency, and was remarkably tough, more like an animal membrane than an inorganic salt. Washed and dried at a moderate heat, it still preserved much of its tenacity, and when moistened, again assumed its membranous character. When ignited in a tube, it lost some water and hydrogen sulphide, but still retained its form. A qualitative examination of it satisfied us that it was a basic hydroxyhydrosulphide.

hydrosulphide and hydroxide, its freedom from colour, mode of formation, transparent solution in hydrochloric acid, and the complete precipitation of its sulphur by manganous salts, prove it to be a compound (or mixture) of hydroxide and hydrosulphide. All that is further necessary, therefore, is the quantitative estimation of the sulphur and the calcium.

Some calcium hydrosulphide solution was exposed for an hour or more to the air, and the crust of crystals which formed during this exposure was lifted off with a spatula, washed quickly with only a little water, and analysed without drying. An unweighed quantity gave 0·0644 gram calcium and 0·0515 gram sulphur, quantities which are in the atomic proportions of these elements.

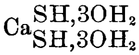
Two other preparations were separately made, and as the mother-liquor of the hydroxyhydrosulphide is only a solution of hydrosulphide, any portion of which adhering to the crystals must become hydroxyhydrosulphide also, while washing with water decomposes the crystals, these preparations were simply drained on porous tiles without any washing, and with great success, judging from their appearance. The analyses, made upon 1·5993 grams and 0·6630 gram, gave—

| | I. | II. | $CaSH.OH,3H_2O$. |
|---|---|---|---|
| Calcium ..... | 27·48 | 27·85 | 27·78 |
| Sulphur ..... | 21·49* | 22·05 | 22·22 |
| Water ...... | — | — | 50·00 |
| | | | 100·00 |

An analysis was made of the cleanest crystals we could prepare by the reaction between solid calcium hydroxide (or oxide?) and solution of the hydrosulphide; but, in accordance with what we have stated concerning this method of preparing the hydroxyhydrosulphide, we had to use the dense calcite-lime in order to get a growth of crystals, and the crystals thus obtained proved to be impure, two-sevenths of the calcium being, not hydroxyhydrosulphide, but, for the most part, still hydroxide.

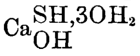
It will be seen from our analyses of the hydrosulphide and the hydroxyhydrosulphide, that the two salts may be written thus:—

Hydrosulphide.



$$\mathrm{Ca}\begin{matrix}\mathrm{SH,3OH_2}\\ \mathrm{SH,3OH_2}\end{matrix}$$

Hydroxyhydrosulphide.[†]



$$\mathrm{Ca}\begin{matrix}\mathrm{SH,3OH_2}\\ \mathrm{OH}\end{matrix}$$

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[*] A slight loss of barium sulphate occurred in this case.

[†] Barium hydroxyhydrosulphide is well known, but under the designation of hydrated barium sulphide, just as the hydroxide was once styled the hydrated oxide. Like the calcium salt, barium hydroxyhydrosulphide occurs in minute crystals having water of crystallisation, and dissolving in water, with subsequent

### *Calcium Monosulphide.*

True calcium monosulphide, as distinguished from the hydroxyhydrosulphide, can be obtained, but mixed with some hydroxide, by gently heating the hydrosulphide in a current of hydrogen sulphide. Thus produced it is a white amorphous solid. It dissolves without much difficulty in water, differing therein from the sulphide of the furnace, in consequence, no doubt, of less density, and fine state of division. In dissolving, it must be assumed to pass into the hydroxyhydrosulphide. The first stage of the decomposition of the hydrosulphide by heat, as already pointed out, is into hydroxyhydrosulphide. This, then, if enough water is present, changes into hydroxide, but in the absence of water into sulphide—

$$\text{1st.} \quad CaS_2H_2 + H_2O = CaSH.OH + H_2S$$

$$\text{2nd.} \left\{ \begin{array}{l} CaSH.OH + H_2O = CaO_2H_2 + H_2S, \text{ or} \\ CaSH.OH = CaS + OH_2. \end{array} \right.$$

Both forms of the second stage occur in the decomposition of the crystals of hydrosulphide, as shown by the experiment we now describe, in which about one-fifth of the calcium became hydroxide, and the rest sulphide.

Having prepared some crystals of hydrosulphide in a tube, the tube with its contents was weighed, and, by deducting the weight of the empty tube afterwards, the weight of the salt was ascertained to be 0·9455 gram. A stream of well-dried hydrogen sulphide was then passed through the tube and maintained to the end of the experiment. The tube was heated for a time at 65°, and then to 100°, at which it was kept for three hours. The residue was amorphous and very white, except at the edges, where it was yellow from oxidation. This oxidation had occurred for the most part during the preparation of the crystals. The calcium and sulphur in it were both determined. It agreed closely in composition with a mixture expressed by the formula $5CaS + \frac{1}{10}CaS_4 + CaO_2H_2$, the polysulphide being due to accidental atmospheric oxidation—

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conversion into hydroxide and hydrosulphide. This shows how improbable it is that the hydrosulphide can without any decomposition lose its water of crystallisation by heat. Its composition is expressed by the formula $BaOH(SH),5H_2O$. Like the calcium compound, it forms combinations, or mixtures easily taken for combinations, with various proportions of the hydroxide. It loses its water of crystallisation by heat, being at the same time partly decomposed, thus resembling the calcium salt. Anhydrous barium sulphide produced at temperatures below a red heat has not been described.

| | Calculated. | Found. |
|---|---|---|
| Calcium ............ | 54·1 | 54·1 |
| Sulphur ............ | 38·3 | 38·2 |
| Hydroxyl............ | 7·6 | — |
| | 100·0 | |

It is mentioned in the opening section of this paper that we have found ignited calcium sulphide less ready in forming hydrosulphide with hydrogen sulphide than lime itself. The cause of this evidently lies in the activity of the lime towards water, by which hydroxide is first formed. We are inclined to believe from our observations that calcium sulphide does not directly unite with hydrogen sulphide, but first changes to hydroxyhydrosulphide by taking up water.

Our attempt to form pure calcium sulphide by strongly igniting lime in a mixture of carbon dioxide and carbon bisulphide, following Schöne, gave us, after three hours' ignition, a mixture of 11CaS with 5CaO.* Air was excluded during the cooling. Sabatier also did not succeed by Schöne's method.

### *Hydrogen Sulphide decomposes Calcium Carbonate.*

Carbon dioxide decomposes the calcium hydrosulphides. It would be needless to mention this, were it not that we have to call attention to the complementary reaction. We find that hydrogen sulphide decomposes calcium carbonate, so that in the precipitated form this salt becomes dissolved by hydrogen sulphide passed in a quick current through the water in which it is suspended.†

Carbon dioxide mixed with sufficient excess of hydrogen sulphide, may be sent through lime-water and yet not cause a precipitate,

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* This symbolic expression, like analogous ones in other parts of this paper, means what it legitimately ought to do, according to the first principles of chemistry, 11CaS = 11 × 72 parts of calcium sulphide, and 5CaO = 5 × 56 parts of calcium oxide. The very prevalent custom of using symbols as mere abbreviations of names, without any quantitative signification, is much to be regretted in the interests of science. No doubt there will appear to many a justification for this practice, in its serving to distinguish two substances confused together under one name, between, for example, [$CO_2$] and [$CO_3H_2$], either of which is often called "carbonic acid." To those who feel this, I would propose the adoption of square brackets, as here just used, when formulæ are written as distinctive abbreviations. In any case, it would be better to avoid altogether the use of an ambiguous name like "carbonic acid," than to attempt to remedy confusion in nomenclature by confusion in notation.

† Barium carbonate in the precipitated state is slightly dissolved by hydrogen sulphide in the presence of much water (*Miller's Chemistry*), thus behaving like the calcium compound.

calcium hydrosulphide being formed. Here, then, is a case in which lime-water fails to detect the presence of carbon dioxide.

### *Hydrogen Sulphide decomposes Calcium Polysulphides.*

Odling has pointed out, in his *Manual of Chemistry*, that hydrogen sulphide is liberated when a solution of calcium hydrosulphide is boiled with sulphur. Boiling alone will liberate hydrogen sulphide always, but with sulphur dissolving the evolution is greatly increased. We are able greatly to enlarge Odling's statement. Concentrated solutions of the hydrosulphide react with sulphur almost as energetically as hydrochloric acid solutions upon marble. To see this to advantage, the solutions of hydrosulphide should be a little warm, and the sulphur in powder. Ground roll is better than flowers, because it is free from acid and more easily moistened. The sulphur dissolves to an orange-red solution, and hydrogen sulphide escapes with very brisk effervescence.

Dissolution of sulphur in calcium hydrosulphide solution is attended with a distinct fall in temperature, as the following experiment shows. About 40 c.c. of a moderately strong solution contained in a deep tube surrounded with cotton-wool, was treated with powdered sulphur, and the mixture stirred with a thermometer. A fall of $2\frac{1}{2}°$ C. was observed, namely from the temperature of the atmosphere, $26\frac{1}{2}°$, to 24°.

By aiding the dissolution of the sulphur in the hydrosulphide by the heat of a water-bath until reaction ceases, that is, until the remaining sulphur stops effervescing with the solution and sinks to the bottom, the decomposition of the hydrosulphide becomes almost perfect, only a minute quantity remaining in the liquid. The calcium is converted, with the exception indicated, into pentasulphide.* When the decomposition is incomplete, all the calcium which is not hydrosulphide is pentasulphide. We would emphasise this statement, because Schöne (*Jahresb.*, **15**, 129; *Pogg. Ann.*, **117**, 58) has shown that when calcium monosulphide and sulphur are boiled in water together, there may be formed tetrasulphide as well as pentasulphide when the sulphur is not in excess. We find that although more than five atoms of sulphur to one of calcium may enter into solution during the reaction of sulphur upon the hydrosulphide (or the hydroxide), still when a pure pentasulphide solution has once cooled and deposited, as it does, the excess over five atoms, it cannot again be made to take up a perceptible quantity of additional sulphur by boiling this with it.

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* Rose obtained barium polysulphide by heating solution of the hydrosulphide with sulphur, but evidently not under the condition of absence of hydroxide, and without this, that fact had not the special significance we find in the analogous one here described.

The reaction between calcium hydrosulphide and sulphur is made still more remarkable by being, as we have found it to be, reversible; that is, we find that hydrogen sulphide decomposes calcium pentasulphide readily, and, under suitable conditions, completely. Hydrogen sulphide bubbled through the pentasulphide solution produces a copious precipitate of pure sulphur, as freely as it would precipitate arsenic or selenium from solution. The calcium becomes hydrosulphide, and if the solution is cold and sufficiently dilute, all polysulphide is destroyed, as seen from the bleaching of the solution. In more concentrated solutions the conversion to hydrosulphide cannot be finished even in a freezing mixture. As when the reaction proceeds the other way, so here, the solution contains at any intermediate stage only hydrosulphide and pentasulphide.

We think these remarkable reactions may be attributed to the formation of hydrogen pentasulphide as a transition product. When hydrogen persulphide is dropped into a concentrated solution of calcium pentasulphide, it is resolved, with a strong effervescence such as a concentrated acid would cause, into hydrogen sulphide and sulphur. If now, with this "catalytic" decomposition in mind, we conceive in the reaction between calcium pentasulphide and hydrogen monosulphide, hydrogen pentasulphide to be constantly forming, and as constantly decomposing till the reaction is over, we may write for its formation—

$$CaS_5 + 2H_2S = CaS_2H_2 + H_2S_5;$$

and if, in the same way, hydrogen pentasulphide should be formed and decomposed continuously when calcium hydrosulphide and sulphur come into reaction, we may also write—

$$CaS_2H_2 + 8S = CaS_5 + H_2S_5,$$

and thus the matter becomes cleared up. To speak more generally, we have only to admit than when sulphur and hydrogen monosulphide meet, either one of them being free and the other in feeble combination, then hydrogen pentasulphide forms, and undergoes dissociation immediately afterwards.*

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* Calcium pentasulphide is decomposed, by boiling its solution, into hydrogen sulphide, lime, and sulphur, a fact of which we have convinced ourselves by careful testing, although it had already been observed by others. We see in this evidence that calcium pentasulphide may be a hydroxyhydropentasulphide—

$$Ca{}^{S_5H}_{OH},$$

and, in favour of this view, we may note that the only solid polysulphide of alkaline earth-metals known, barium and strontium tetrasulphides, contain water (Schöne). The division of the calcium between the weak sulphur acid and water is in accordance, too, with Berthelot's thermochemical views.

With this constitution of calcium pentasulphide adopted, a modification of the

We have still to give the essential details of our experiments. All along care was taken to keep air away from the solutions. The proof that sulphur can completely decompose calcium hydrosulphide was a qualitative one. Having heated the sulphur with the hydrosulphide just to the point when effervescence ceased, in a gentle current of hydrogen, maintained only to assist in keeping air out, the solution was cooled and then precipitated with manganese sulphate. The sulphur and manganous sulphide having been filtered off, the mother-liquor, relatively concentrated as it otherwise was, gave only a few flocks of precipitate—at first only a brown colour—with either copper or silver solution. Before adding these, however, the odour of hydrogen sulphide was quite distinct in it. We might have heated our pentasulphide solution a longer time than we did, probably with advantage, but we apprehended the decomposition of pentasulphide which hot water ultimately effects.

The evidence for the completeness of the decomposition of calcium pentasulphide by hydrogen sulphide was still more simple, and has been already mentioned, namely, the bleaching of the solution, a severe test, as will be admitted, when the great tinctorial power of alkaline polysulphides is remembered.

explanation given in the text is open to us of the remarkable reactions there described, as well as of the decomposition of the pentasulphide by water. The displacement of sulphur by water, and the displacements of sulphur and hydrogen sulphide, one by the other, are seemingly odd reactions, so to speak. Now if the pentasulphide is hydroxyhydropentasulphide, such displacements do not take place, and the reactions are then hardly peculiar in nature, thus—

$$CaOH(S_5H) + OH_2 = CaO_2H_2 + S_5H_2 (= 4S + SH_2)$$
$$CaOH(S_5H) + 2SH_2 = CaS_2H_2 + S_5H_2 + OH_2.$$

When sulphur is put into calcium hydrosulphide solution, it is also brought into contact with the products of the decomposition of the hydrosulphide with water. It then acts, not upon the hydrosulphide, but upon one of these products—the hydroxyhydrosulphide,—and by converting this into the pentasulphide, leaves room for a further decomposition of the hydrosulphide by water which, liberating more hydrogen sulphide, and again more, gives rise to the free escape of this gas. We need only formulate the first reaction, that between the sulphur and calcium hydroxyhydrosulphide:—

$$CaOH(SH) + 4S = CaOH(S_5H).$$

The nature of the reaction of hydrogen pentasulphide with calcium hydroxyhydropentasulphide is also more easy of interpretation than that of its reaction with the calcium pentasulphide. In the equation—

$$CaOH(S_5H) + S_5H_2 = CaS_2H_2 + 8S + OH_2,$$

two not improbable assumptions are made, one being that calcium hydroxide reacts with hydrogen pentasulphide, and the other that the di-pentahydrosulphide, $Ca(S_5H)_2$, dissociates to the hydrosulphide, and the thiosulphuric anhydride, $2S_4$ or $2SS_3$.

Quantitative tests were made to determine the composition of intermediate solutions. Solutions were prepared by boiling calcium hydrosulphide solution with sulphur, and then leaving them to cool, all in an atmosphere of hydrogen sulphide. One portion of solution for analysis was weighed out into zinc acetate solution and used for estimating the sulphur thus precipitated in the free state. The zinc sulphide was dissolved out with hydrochloric acid, and the free sulphur weighed, and tested for purity. Another quantity was weighed into potassium hydroxide, and oxidised by hypobromite. This was used for the estimation of the total sulphur and the calcium. Subtracting sulphur precipitated free by zinc acetate, from the total sulphur, gave us that precipitated as zinc sulphide. Subtracting from this a quantity chemically equivalent to the calcium, and dividing the remainder by 16, gave us the hydrogen combined with sulphur. The quantities of solution weighed out for analysis varied in amount from 1·615 grams to 0·810 gram.

*First Preparation.*—This was made from a solution of calcium hydrosulphide which had become a little yellow through atmospheric oxidation. In consequence of this, no doubt, the results of the analysis showed a slight deficiency in the sulphur of the polysulphide. They corresponded with the composition, calculated from the calcium, of $CaS_2H_2 + 3CaS_5$, but with about one-fourteenth part of the pentasulphide assumed to be changed into thiosulphate:—

| | Calculated for $CaS_2H_2 + 3CaS_5$. | Found. |
|---|---|---|
| Calcium | 10·47 | (10·47) |
| Sulphur, precipitated combined | 10·47 | 10·36 |
| Sulphur, precipitated free | 25·13 | 23·87 |
| Sulphur, total | 35·60 | 34·23 |

*Second Preparation.*—This gave results agreeing with the calculation for $25CaS_2H_2 + 22CaS_5$:—

| | Calculated. | Found. |
|---|---|---|
| Calcium | 7·57 | (7·57) |
| Sulphur, precipitated combined | 9·28 | 9·35 |
| Sulphur, precipitated free | 11·34 | 11·45 |
| Sulphur, total | 20 62 | 20·80 |

### *The Formation of Calcium Thiosulphate.*

The conversion of calcium hydrosulphide into thiosulphate by oxidation is not uncommonly represented by the equation—

$$CaS_2H_2 + 2O_2 = CaS_2O_3 + OH_2,$$

but the correctness of this is more than doubtful.

Calcium hydrosulphide, as already described, undergoes saponification, or change into acid and base, to an extent limited only by the non-removal, as formed, of the hydrosulphuric acid. Calcium hydroxyhydrosulphide is an intermediate product, unless much water is present, and saponification proceeds more and more slowly in consequence of the formation of this less soluble salt, though it is not thereby arrested. When freely exposed to the air, the hydrosulphide, both in the solid state and in solution, rapidly and visibly changes so far as to lose half its sulphur as hydrogen sulphide, and by the time that this has happened very little thiosulphate has formed. Oxidation does not become considerable even during the conversion of the calcium to hydroxide and carbonate, provided that contact with fresh air is maintained. In illustration of the slowness of the oxidation, we may describe some experiments other than those referred to in previous sections.

For six hours we passed moist air deprived of its carbon dioxide in a rapid stream through a small volume of solution of calcium hydrosulphide, thus bringing the solution in contact with an enormous excess of fresh air. Very much hydroxyhydrosulphide (and hydroxide) separated out, but the quantities of thiosulphate and pentasulphide were so small that we did not proceed with their exact estimation.*

Another experiment was made simultaneously with the other, and like it, except for the modification of adding calcium hydroxide in order to convert as much as possible of the hydrosulphide at once to hydroxyhydrosulphide. It gave essentially the same results as the other, and certainly did not show greater oxidation. From this it will be seen that the evidence of the occurrence of material oxidation in the case of the basic salt is no stronger than in that of the normal salt. In order to get the formation of any considerable quantity of thiosulphate, the hydrosulphide or hydroxyhydrosulphide must be preserved in a limited space, the atmosphere in which can only slowly renew itself.

All the experiments we have made fairly lead us to the conclusion that it is hydrogen sulphide which oxidises, and then, by its products reacting with the hydroxyhydrosulphide, forms the thiosulphate. The oxidation of hydrogen sulphide, though slow, is probably not more so, under favourable circumstances, than the formation of thiosulphate, well known to be slow, and is here no doubt quickened by the influence

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* After adding zinc acetate solution, the filtrate from the very large precipitate, scarcely diluted with washings, gave with barium chloride and bromine only a very slight precipitate on heating. The zinc precipitate was partly (apparently more than half) soluble in acetic acid and in hydrochloric acid, left only a small amount of flocculent sulphur.

of the basic substance—calcium hydroxyhydrosulphide. The equation—

$$Ca\genfrac{}{}{0pt}{}{SH}{OH} + 2O_2 + SH_2 = Ca\genfrac{}{}{0pt}{}{S}{O}SO_2 + OH_2,$$

probably gives a correct view of the reaction, so far as it is yet understood. Here we may remark that, from the point of view of the constitution of a thiosulphate, the equation $CaS_2H_2 + 2O_2 = CaS_2O_3 + OH_2$ is not easy to follow.

Of the occurrence of oxidation of the hydrogen sulphide with the formation of sulphur, there is the strongest evidence in the considerable production of calcium pentasulphide from the very commencement of the oxidation. Any explanation of the production of thiosulphate is insufficient that leaves out of consideration the simultaneous production of pentasulphide. The latter has received a separate explanation in which the sulphur necessary to combine with calcium monosulphide is derived from the oxidation of another part of the calcium sulphide, into lime and sulphur: the soundness of the form of oxidation here assumed to take place can hardly be sustained. Calcium sulphide when dry does not oxidise at common temperatures, and when heated it oxidises to sulphite and sulphate. When moist it only slowly yields oxidation-products, and then not without hydrolysis into hydrogen sulphide and lime. Calcium sulphide does not combine with sulphur even when heated with it, if dry, and if moist only by previous hydrolysis also, and actual escape of hydrogen sulphide.

The lixiviation of soda-waste, and especially that carried on experimentally by Kraushaar, serves to show that with a very limited supply of air, the oxidation of the hydrogen sulphide, which we hold to take place, yields unoxidised sulphur which then forms polysulphide, while a further admission of air produces oxidised sulphur for the production of thiosulphate.

The fact that pentasulphide always accompanies thiosulphate, suggests the question whether the formation of pentasulphide precedes and leads to that of thiosulphate. We have tested the point to some extent by experiments, without getting decisive results; but it seems to us more probable from them than not, that the formation of thiosulphate does not depend upon that of pentasulphide.

We thought it worth testing whether atmospheric oxidation might possibly be essential to the production of pentasulphide and thiosulphate when sulphur and lime are boiled together in water, and found that this reaction went on just as well in an atmosphere of coal-gas as in air. Lime and sulphur seem to be without distinct action upon each other in cold water.

We tried the effect of lime upon calcium pentasulphide. In the cold no thiosulphate was formed in a day. When the two substances were boiled together, with exclusion of air, a very slight formation of thiosulphate occurred, but this fact has no significance, because the pentasulphide by itself very slowly yields thiosulphate in a boiling solution. Whether the nascent sulphur of oxidising hydrogen sulphide can act upon lime in the cold, in the same way as free sulphur acts upon it in boiling water, we cannot tell.

Calcium pentasulphide is stated to yield thiosulphate both by reaction with water and with the oxygen of the air. Schöne observed that potassium pentasulphide boiled with water yielded a little thiosulphate. By long boiling of calcium pentasulphide solution out of contact with air, very small quantities only of thiosulphate are formed, provided evaporation does not proceed so far as to cause the separation of much solid matter. When, however, the solution is boiled down until much sulphur and lime have separated out (and hydrogen sulphide escaped), a not inconsiderable amount of thiosulphate is produced. We do not think that these experiments, or those of Schöne, prove that any direct conversion of pentasulphide into thiosulphate by water takes place:—

$$CaS_5 + 3OH_2 = CaS_2O_3 + 3SH_2$$

(*Watts's Dict.*, 1st Suppl., p. 957), for after lime and sulphur have separated out these substances can react to form thiosulphate in the known way, and before they have done so to a visible extent the minute quantities of thiosulphate found may arise from a slight entrance of air, or even from a slight formation of lime and sulphur at the surface or edges of the liquid. To accept the above equation is to admit that water can oxidise sulphur like the oxide of a metal.

As is well known, calcium pentasulphide by the action of the air yields sulphur and calcium thiosulphate. From experiments which we have made, the change that occurs would seem to be not so simple as is supposed. A wide-mouthed glass jar of about 26 litres' capacity was prepared by placing some fully slaked lime in it in a thin layer over the bottom, and leaving it tightly closed up for a day in order to remove carbon dioxide from the enclosed air. Then it was opened, a watch-glass holding pure concentrated solution of pentasulphide quickly inserted, and the cover replaced. In a day the solution had crusted over. The bottle was again opened, and the air in it tested and found still to contain much oxygen. This air was, however, partly replaced by oxygen-gas, for fear that it might not in itself contain enough. The bottle was reclosed and left for six days more, and then finally opened. The air within could still rekindle a glowing taper. The pentasulphide solution was still yellow and clear, but had a thick crust on its surface. There was no odour observable in the bottle, and the lime showed no sign of discoloration on its surface. Throughout the experiment there was condensed water on the walls of the bottle, and no sensible loss in volume by the solution was noticeable. The crust on the solution was found to be sulphur, neither carbonate nor other calcium salt being found in it. The solution, in spite of its yellow colour, contained very little sulphide, and nothing else but a very great abundance of thiosulphate.

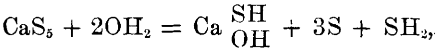
Some solution of pentasulphide exposed to the air in a watch-glass gave essentially the same result, but, in the first place, it dried up in a few days (when the water was renewed and again dried up in a few more days); in the second place, all sulphide was decomposed; and, in the third place, much calcium carbonate was found with the sulphur, and the thiosulphate was not so abundant as in the exposure in the bottle. Some solution of pentasulphide was also exposed to the air in a watch-glass, but mixed with lime, and gave results the same as before, except that a very little sulphide had escaped change, and that the solution reacted strongly alkaline from the presence of lime.

These experiments are in entire conformity with the requirements of the equation—

$$CaS_5 + 3O = CaS_2O_3 + 3S,$$

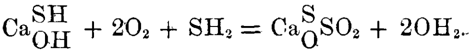
and we should have described them more briefly but for the result of another form of the experiment. We passed for several hours a rapid stream of air deprived of its carbon dioxide through a small quantity of pentasulphide solution, and found that the air was always carrying away with it small quantities of hydrogen sulphide, and that the solution gradually deposited crystals of sulphur and of Schöne's hydroxytetrasulphide of calcium, a compound of hydroxide with tetrasulphide of calcium. As when boiled, therefore, saponification of some of the pentasulphide had occurred, and then the lime had decomposed some more pentasulphide into sulphur and tetrasulphide, and combined with the latter. We treated the whole with zinc acetate and tested for thiosulphate as usual. We found no more thiosulphate apparently than the minute quantity we had found the solution to contain before treatment—that is to say, we found that either no thiosulphate at all, or as we prefer to put it, only a trace had been produced.

We cannot but regard this experiment as a proof that direct oxidation of pentasulphide by the air does not happen, and that the oxidation is that of hydrogen sulphide. Hydrogen sulphide is slowly liberated from the pentasulphide, and if this is rapidly removed as it forms, the remaining penta- and tetra-sulphides undergo no oxidation by free oxygen. When solution and air are left in contact at rest, the oxidation of the hydrogen sulphide keeps pace with its liberation, and its oxidised products then react upon the pentasulphide to form thiosulphate and sulphur. We may suppose the reaction with water to be that expressed by—



$$CaS_5 + 2OH_2 = Ca\genfrac{}{}{0pt}{}{SH}{OH} + 3S + SH_2,$$

and then with oxygen, as before represented—



$$Ca\genfrac{}{}{0pt}{}{SH}{OH} + 2O_2 + SH_2 = Ca\genfrac{}{}{0pt}{}{S}{O}SO_2 + 2OH_2.$$