LV.—*On some Sulphur Compounds of Calcium.*

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Introductory.

THOUGH the sulphides of calcium form an integral part of two important industries, viz., the Leblanc soda process and the purification of coal-gas, yet up to the last few months these substances have received but little attention at the hands of investigators.

It appeared worthy of interest, with a view to a particular study of the chemical changes involved in the latter industry, to determine the composition of the substances formed (1) by the action of hydrogen sulphide on calcium hydroxide, and (2) of carbon disulphide on the resultant material.

Historical.

Calcium Sulphide.—Berzelius, in his monograph on the sulphides of the alkali metals (*Schweigger's Journal*, **34**, 12), describes a process for the preparation of calcium sulphide by passing hydrogen sulphide over red-hot lime (free from water and carbonic anhydride). The

equivalent weights of the water and calcium sulphide formed in accordance with the equation—

were found to be in the proportion of 87 : 89, or practically 1 : 1.

In another memoir Berzelius (*Pogg. Ann.*, **6**, 442) obtained by the evaporation of the liquid formed by the continued action of hydrogen sulphide on calcium hydroxide, crystalline needles of hydrated calcium sulphide, to which, in accordance with more modern views, the name calcium hydroxyhydrosulphide is assigned.

On the other hand, Rose (*Pogg. Ann.*, **55**, 443) states that calcium sulphide, when boiled with water, yields the hydrosulphide which dissolves, and the hydroxide which remains undissolved. From the solution on evaporation acicular crystals separate out, to which Rose ascribes a composition $\text{Ca}_6\text{S}_5\text{O}_3 \cdot 20\text{H}_2\text{O}$, presumably calcium hydroxy-hydrosulphide, with a slight excess of calcium oxide, and formed according to the equation—

While this work was in progress, there appeared a most important and interesting communication by Divers and Schmidzu (*Trans.*, 1884 278), on the preparation and properties of crystalline calcium hydrosulphide and hydroxyhydrosulphide, and of the amorphous sulphide; this has thrown considerable light on the constitution of these compounds, and materially assisted the author in the later part of his investigations.

Short notices of oxygenated sulphur compounds of calcium have also been published by Folkard (*Chem. News*, **49**, 258; *Abstr.*, 1884, 892) and W. Foster (*Journal of Gas Lighting*, September 30, 1884).

Calcium Sulphocarbonate or Thiocarbonate.—In another memoir (*Pogg. Ann.*, **6**, 444), Berzelius describes the preparation of this salt by digesting together calcium sulphide, water, and carbon disulphide, at a temperature of 30°, air being excluded throughout the experiment. The sulphide is gradually dissolved, with production of a deep red liquid, from which, on evaporation in a vacuum, there separated a red confusedly crystalline red mass. With hydrochloric acid, the solution of the salt gave a red oil, described also by Zeise, probably thiocarbonic acid. A solution of calcium thiocarbonate gives with solution of salts of the heavy metals, dark brown precipitates, with nickel and manganese salts, olive-green solutions, with ferrous salts a deep wine-red coloration, and with zinc-salts a golden white precipitate. These various substances emit carbon disulphide when heated, leaving a residue of the sulphide, oxide, or carbonate, according to the nature of the metal. Calcium thiocarbonate on exposure

to the air is slowly converted into the carbonate, a change immediately effected by heating to 60–80°; in concentrated solutions it gives off carbon disulphide, leaving a residue of calcium sulphide.

D. Walker (*Chem. News*, **30**, 28) describes a calcium thiocarbonate, $\text{CaCS}_3 \cdot 2\text{Ca}(\text{OH})_2 + 6\text{H}_2\text{O}$, prepared by agitating milk of lime with carbon disulphide; it is described as crystallising in light orange-yellow needles, soluble to a small extent in cold water, yielding an orange-yellow solution, from which, on addition of hydrochloric acid, yellow oily drops of thiocarbonic acid separate out. These several investigations will be alluded to in the course of the present paper.

Preparation of Calcium Sulphide in the Dry Way.

The method of preparing calcium sulphide described by Berzelius, which consists in passing hydrogen sulphide over calcium oxide or hydroxide, was adopted in outline, and it was thought that a better insight might be gained into the nature of the change if the weights of calcium hydroxide used, and of calcium sulphide and water formed, could be determined accurately.

In the first experiment, selected transparent crystals of Iceland spar were used for the preparation of the calcium oxide, but further investigations showed that even the best specimens contained traces of ferric oxide, alumina, and silica. To eliminate these impurities, the crystals were dissolved in dilute hydrochloric acid, and the solution evaporated to dryness to separate out silica; the chloride was then redissolved, a few drops of nitric acid added, and the iron precipitated as ferric oxide, together with the alumina. The filtrate from this was fractionally precipitated by ammonium carbonate, the first portions containing invariably traces of iron (derived possibly from the carbonate), together probably with small quantities of barium and strontium. The carbonate was then washed free from chloride by decantation. In order to convert the carbonate into oxide, it was heated either in a porcelain tube, in a current of hydrogen or steam, those portions of the material at the two ends of the tube being invariably rejected; or the carbonate was placed within a platinum crucible, enclosed within a fireclay crucible, the space between them being packed with crude lime, and the whole heated in a gas furnace. The presence of lime prevents the reabsorption of carbonic anhydride on cooling, and also the formation of hard non-friable masses, which were occasionally produced when the products of the combustion of the coal-gas came into direct contact with the carbonate. The product contained only the smallest traces of carbonate, and dissolved perfectly when it was suspended in water and hydrogen sulphide passed in. In the course of the work, most marked evidence was obtained as to

the delicate nature of this test for the purity of calcium oxide, as suggested by Divers. In fact it was this test alone which caused the substitution of calcium oxide prepared by the process described above for that prepared from Iceland spar. The resultant oxide contained only the smallest traces of carbonate.

Hydration of the Oxide.—The hydration of the oxide, under conditions precluding contact with carbonic anhydride, was effected as follows:—A watch-glass containing a weighed sample of the oxide was placed at the top of a glass cylinder, with both ends open; over this was inverted another cylinder of rather larger diameter, and the two placed in a beaker containing a hot solution of sodium hydroxide. The apparatus was kept for some time in a warm place, until the oxide was converted into the hydroxide, the excess of water being removed by drying over calcium chloride.

In order to show the accuracy of this process, the following results may be cited:—

Weight of CaO taken.	Weight of Ca(OH) ₂ formed.	Ratio of $\frac{\text{Ca(OH)}_2}{\text{CaO}}$.	
		Found.	Theory.
3.5734	4.7314	1.3242	1.3216
3.5776	4.7324	1.3215	—
3.8574	5.0679	1.3136	—
3.9473	5.190	1.3145	—
Mean....		1.3144	1.3216

The calcium hydroxide was then transferred as quickly as possible into a cylindrical tube, tapering gradually at the lower end, then bent at a right angle; on the limb is blown a bulb, beyond which it is bent through an angle of 180°, and drawn off at its lower extremity into a fine point. This apparatus was found to be the most suitable for the elimination of the water, which was apt to form damp masses of the sulphide, and thus choke up the tube.

A ground glass stopper fitted with a limb bent at right angles with a stopcock closed the upper end, and the lower or tapering end was partially closed with a loosely fitting glass bulb, to prevent the hydrate from falling into the limb of the tube. This apparatus will for brevity sake be designated "the lime tube." The upper limb of this tube was connected with a T-piece, through one arm of which could be passed hydrogen, and through the other hydrogen sulphide, each arm being fitted with a stopcock. The hydrogen was purified and dried by passing it through potassium chromate solution, strong sulphuric acid, sticks of solid potash, and calcium chloride, whilst the hydrogen sulphide (from iron pyrites and hydrochloric acid) was purified by

washing with water, passing it through damp iron sulphide to stop traces of oxygen, and finally dried. The water formed in the reaction was collected in a U-tube filled with calcium chloride, the form being that used in combustion analysis, with one limb bent up, into which passed the drawn-out extremity of the lime tube. As a necessary precaution, the calcium chloride in the hydrogen and hydrogen sulphide apparatus, and in the collecting tube, was always taken simultaneously from the same sample. During the passage of the hydrogen sulphide, the lime tube was heated to a temperature of 60° , in a square copper box filled with water; through a cork at the bottom of this passed the drawn-out extremity of the lime tube. The temperature of the water was maintained constant by means of the automatic mercury and oil gas regulator, described at length in a former paper* (Trans., 1883, 371); water was also supplied from a water level regulator.

Method of Analysis used.—Sulphur was determined by Carius' method for the determination of sulphur in organic substances.

Calcium was estimated by oxidation by nitric acid in the above process, and precipitating the calcium sulphate by ammonium oxalate, or (2) by evaporating the substance with dilute sulphuric acid to which was added a little nitric acid, and weighing the sulphate formed; water and carbon, if present, by the usual processes of organic analysis.

Preliminary experiments showed that at first, on passage of the hydrogen sulphide, the calcium hydroxide gained considerably in weight, and but small quantities of water were eliminated; but on continuing the process the weight of the product was approximately equal to the original hydroxide. This result would accord with the conversion of the hydroxide, $\text{Ca}(\text{OH})_2$, into the sulphide CaS , the molecular weights of which are in the ratio of 74 : 72.

Series I.

Constant temperature 60° . In this series the water evolved was not estimated.

Conditions of experiment.	Time.	Weight of contents of lime tube.	Difference.
— ..	—	5.0596	—
Hydrogen sulphide passed..	3 days	5.0242	— 0.0304 gr.
„ „ „ ..	12 hours	5.0242	<i>nil.</i>

* In order to show the degree of constancy obtainable by the regulator, I may mention that an instrument supplied to Professor Moseley's Anatomical Department for an incubating apparatus has maintained the temperature constant within one degree for two years.

Analysis of Resultant Material.

	Found.	Mean.
Calcium as CaSO_4 ..	53.44, 53.42 per cent.	53.43
Sulphur as BaSO_4	43.13 ,,	43.13
Water	3.2 ,,	3.20
		<hr/> 99.76

Atomic proportion of calcium to sulphur 1 : 1.009.

The substance is thus calcium monosulphide, CaS , containing a small proportion of water. On comparing the analytical and synthetical numbers, supposing that 3.2 per cent. of the water is retained by the resultant sulphide, then the following results obtain:—

	Theory.	Experiment.
Calcium hydroxide	5.0246	5.0246
Calcium sulphide	4.8793	4.8638

The error is less than 1 per cent, the small difference arising doubtless either from slight oxidation of the sulphide, or from a small quantity of the hydroxide escaping transformation into the sulphide.

The experiments were repeated at the same temperature of 60° ; owing to a temporary block, the temperature was raised for a short time to drive forward the water.

Series II.

Conditions of experiment.	Temp.	Time.	Weight of contents of lime tube.	Diff.	H_2O collected.
—	—	—	4.240	—	—
Hydrogen sulphide passed	60°	36 hours	4.250	+ 0.01	1.9477
„	90	1 hour			
„	70	14 hours			
„	60	20 „	4.215	— 0.045	0.035
Net results			—	— 0.035	+ 1.0827

Analysis of Resultant Material.

	Found.
Calcium as CaSO_4	54.21 per cent.
Sulphur as BaSO_4	43.57 ,,
Water.....	1.97 ,,
	<hr/> 99.75 ,,

Atomic proportion of calcium to sulphur 1 : 1.004.

The reaction is thus practically represented by the equation—

If the 2 per cent. found by analysis of the sulphide be transferred to the water collected in the tube, then the synthetical and analytical results will compare as follows:—

	Theory.	Experiment.
Calcium hydroxide..	4·24	4·24
Calcium sulphide } obtained }	4·121	4·125 { reckoned in the anhydrous state.
Water formed	2·071	2·053

These numbers are within the limits of experimental error.

Conditions of Formation in the Dry Way.

In the course of this investigation it was observed that perfectly dry calcium oxide was unaltered by perfectly dry hydrogen sulphide; this result is analogous to the well-known fact, often demonstrated as a lecture experiment, that dry calcium oxide does not absorb dry carbonic anhydride. But the former case is the more remarkable, in that it would appear more *a priori* probable that the elimination of an infinitesimally small quantity of water would cause the reaction to proceed to its final completion. Another example is thus afforded of the necessity of the intervention of a third substance to bring about the reaction of two others.

It was noticed that the excess of hydrogen sulphide was retained with considerable pertinacity, probably owing to the solution of calcium oxide in the water, and formation of calcium hydrosulphide, or the direct combination of the calcium sulphide with hydrogen sulphide, thus:

Properties of Calcium Sulphide.

Anhydrous calcium sulphide when freshly prepared is a white powder, emitting a considerable odour of hydrogen sulphide when exposed to the air; if moistened, it turns of a pale yellow tint, probably due to the formation of oxidised products (cf. Divers, *supra*). The various samples of calcium sulphide prepared by Divers and the author were quite colourless, but there appears to be some misapprehension regarding the colour of these substances, for they are described in various text-books as possessing a blue tint, and even recently in the *Journal of Gas Lighting*, September 30th, 1884,

A. Foster mentions a greyish-blue calcium oxysulphide. Some small quantity of a bright blue material, obtained in the course of the dissolution of calcium oxide prepared from Iceland spar, was examined qualitatively. It was washed at first several times with cold water, and then repeatedly with hot water; the residue dissolved in hydrochloric acid with evolution of hydrogen sulphide. The solution contained aluminium, silica, and calcium in some quantity, and traces of iron, derived from impurities contained in the calcium oxide.

Preparation of Calcium Hydrosulphide in the Wet Way

has been made the subject of an extensive research by Divers, whose experiments would not have been repeated, had it not appeared that the process might offer a convenient method for the preparation of the thiocarbonate, and to decide whether the calcium oxide is completely converted into calcium hydrosulphide by the hydrogen sulphide, supposing the resultant solution to be sufficiently dilute. An apparatus similar to that described by Divers was used, and his method of procedure followed closely, although it was found eventually more convenient to add the calcium oxide in small quantities at a time, so as to prevent the formation of the hard masses. It was found when hydrogen sulphide was passed into 1 part of calcium oxide, suspended in 4 parts of water, that the oxide completely dissolved, as observed by Divers, due presumably to the complete conversion of all the calcium oxide into hydrosulphide. For *à priori* it is exceedingly improbable that calcium oxide should dissolve in water containing hydrogen sulphide simultaneously as the hydroxide and the hydrosulphide. In order to bring further evidence on this point, a tube containing water saturated at about 13° with hydrogen sulphide was weighed, and to it was gradually added a known weight of calcium oxide, which was completely dissolved; the water evaporated by the passage of this gas was collected in a calcium chloride tube. The tube and its contents were again weighed, and the difference in weight before and after the experiment, less that of the calcium oxide added, represents the amount of hydrogen sulphide absorbed.

The following results were obtained:—

	Calcium oxide.	Hydrogen sulphide required.	Percentage.
Theory	2·5103	3·048	100
Experiment	2·5103	2·880	94·48

As a further confirmation the atomic ratio of the calcium to the sulphur in the resultant solution was found to be $\text{Ca} : \text{S} = 1 : 1.191$;

it is thus shown both by synthetical and analytical processes that the calcium oxide is practically converted entirely into calcium hydrosulphide. The same point was more fully investigated in a repetition of the above experiment. 20 c.c. of water were saturated with hydrogen sulphide at the ordinary temperature; the results are given in the following table.

I. Weight of water + H ₂ S + CaO added.	II. Gain.	III. Weight of water collected.	IV. Total gain.	V. Lime added.	VI. Difference of IV - V = H ₂ S absorbed.	VII. Percentage proportion of that required by theory.
20·0272	—	—	—	—	—	—
22·9478	2·9206	0·0546	2·9751	1·3484	1·6258	99·41
22·9343	2·9071	0·0641	2·9675	<i>nil</i>	—	—
25·9416	5·9144	0·0934	6·0078	2·7368	3·271	95·41
27·9874	7·9602	0·14	8·0011	3·7450	4·2561	94·01
30·1256	10·0904	0·1779	10·2643	4·7311	5·5332	94·85

These results show that even if the solution is comparatively strong, nearly the theoretical proportion of hydrogen sulphide is absorbed. Thus, both by the dry and wet method, calcium oxide is completely converted into sulphide or hydrosulphide as the case may be. The molecular combinations of calcium and sulphur described by Folkard (*vide supra*) are in all probability mixtures of calcium sulphide with unaltered oxide.

It will be remembered, in connection with calcium hydrosulphide, that it has been proposed to make a solution of this substance on a large industrial scale, viz., by treating a mixture of the alkali waste and water with hydrogen sulphide; the solution is then evaporated to drive off the hydrogen sulphide, and there is formed, according to the experiments of V. Miller and Opl, a crystalline form of pure calcium hydrate, thus: $\text{Ca}(\text{SH})_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + 2\text{H}_2\text{S}$ (*Dingl. polyt. J.*, **253**, 350, Abstr., 1884, 1442). There seems, however, to be some little doubt as to the entire practical realisation of this change.

Calcium Thicarbonate.

Lime, over which coal-gas containing hydrogen sulphide has been passed, technically known as "foul lime," is a well-known absorbent of carbon disulphide. In practice, the gas engineers have found that this absorption is best effected when the lime is moistened with water to such a degree that it can easily be moulded with the fingers; this material, when fouled, is mixed with an equal weight of slaked lime.

It has further been shown that the absorption of the carbon disulphide stops at a stage at which only one-third of the sulphide would be converted into the thiocarbonate or sulphocarbonate, if the change be assumed to be as follows:—

The product is a greyish-blue mass, in which nodules of a red-dish-yellow colour are interspersed. On exposing this material for a short time to the air, it is again rendered effective for the removal of carbon disulphide.

A more minute study of the composition of the substance resulting from the action of carbon disulphide on calcium sulphide, and of the conditions of its formation, present several points of theoretical and technical importance.

Preliminary experiments were made, in which pure and dry hydrogen, saturated with the vapour of carbon disulphide by bubbling through that liquid, was passed into the lime tube containing nearly anhydrous calcium sulphide. No alteration in weight was observable even on passage for several days at the ordinary temperature, and at 45° and 60°, so that perfectly dry calcium sulphide is not the absorbent of carbon disulphide. A little water was then added to the tube, and the passage of the gas recontinued; the contents of the tube became at first pale yellow, then yellowish-red masses were observed. Treatment of the contents of the tube with cold water indicated that the red compound was soluble in water, leaving probably the calcium sulphide for the most part undissolved.

This suggested the *modus operandi*; the sulphide treated with carbon disulphide was quickly introduced into a flask filled with hydrogen, and some recently boiled cold water added. The flask was fitted with a plug through which passed two tubes bent at right angles, one of which served as an inlet for the hydrogen, while the other, or outlet tube, was connected with another similarly fitted flask. The sulphide was allowed to digest for some time in the cold, a continuous current of hydrogen being passed through the apparatus during the operation; when it appeared that the greater part of the substance was dissolved, the outlet tube of the flask was pushed down into the liquid, while the inlet tube was raised; by this means the solution was forced over by the current of hydrogen gas into the second flask, thus separating it from the undissolved sulphide without contact of air.

As a preliminary experiment, the proportion of calcium to sulphur was determined in about 1 c.c. of this liquid. The following results were obtained:—

1st portion—

Calcium oxide	=	0.101	grams
Barium sulphate	=	0.8496	„
Ratio of calcium to sulphur.	=	1 : 2.023	„

2nd portion—

Calcium oxide	=	0.157	grams
Barium sulphate	=	0.3418	„
Ratio of calcium to sulphur.	=	1 : 2.017	„

The liquid presumably does not contain the colourless calcium hydrosulphide; the ratio of calcium to sulphur = 1:2 would also be satisfied by substances having the composition $\text{CaS}, \text{CaCS}_3$ or $\text{Ca}(\text{OH})_2, 2\text{CaCS}_3$, of which the latter, as the sequel will show, is the more probable.

In order to isolate the substance in question, further experiments were made in which the nearly anhydrous calcium sulphide was placed under a small quantity of water, and hydrogen, saturated with carbon disulphide vapour, passed into the mixture; the superincumbent water turned gradually to a red tint, and the solution was separated from the sulphide by the method indicated above. The liquid was then placed under the air-pump; after a few days red prismatic needles appeared, from which the adherent water was drained as far as possible, and they were again dried under the air-pump. The crystals thus obtained were exceedingly deliquescent, and on contact with air lost their red colour, and became yellow and less soluble in water. An analysis was made by the processes enumerated above.

	Found.	Calculated for $\text{Ca}(\text{OH})_2, \text{CaCS}_3, 7\text{H}_2\text{O}$.
Calcium.....	22.68	22.99
Sulphur.....	27.77	27.58
Carbon	3.65	3.42
Water	41.90	41.42
Oxygen (by difference).	4.00	4.59
	100.00	100.00

The substance is thus a basic calcium thiocarbonate, crystallising with 7 mols. H_2O . An aqueous solution of this substance gave with hydrochloric acid a red oil, and with solutions of various metallic salts the same precipitates and colorations observed by Berzelius (*vide supra*); it was decolorised readily by passage of carbonic anhydride with formation of calcium carbonate.

In order to prepare this substance in rather larger quantities,

hydrogen gas was first blown into a solution of calcium hydrosulphide prepared by Divers' process until a considerable quantity of crystals of calcium hydroxyhydrosulphide were precipitated. An analysis of the liquid containing these crystals in suspension showed that the ratio of calcium to sulphide was a little more than 1 : 1. The hydrogen was then made to bubble through carbon disulphide, and the liquid at first turned pale yellow, while the suspended crystals appeared to dissolve. But after a time the liquid became nearly solid from formation of a yellow crystalline substance. Hydrogen sulphide was evolved continuously throughout the process, a result in accordance with the observations of gas engineers that the passage of coal-gas containing carbon disulphide over damp foul lime caused the evolution of hydrogen sulphide, which is absorbed by a so-called check box containing damp ferric oxide. This was drained as far as possible from the mother-liquor, washed twice with freshly-distilled water, and then dried in a vacuum. The following results were—

	Found.	Calculated for $2\text{Ca}(\text{OH})_2, \text{CaCS}_3, 10\text{H}_2\text{O}$.	Calculated for $10\text{Ca}(\text{OH})_2, 6\text{CaCS}_3, 50\text{H}_2\text{O}$.
Calcium....	25·14	25·20	25·12
Sulphur....	22·31	20·17	22·73
Carbon	2·75	2·52	2·82
Water.....	44·04	45·38	43·10
Oxygen (by difference)	5·76	6·73	6·33
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The compound is thus probably $2\text{Ca}(\text{OH})_2, \text{CaCS}_3, 10\text{H}_2\text{O}$, containing a slight excess of calcium thiocarbonate; it resembled in appearance and properties the basic calcium thiocarbonate described by Walker (*vide supra*).

On a repetition of these latter experiments, the same succession of phenomena was observed; at first, on passage of the hydrogen with carbon disulphide vapour into the solution of calcium hydrosulphide, there separated out the white crystals of calcium hydroxyhydrosulphide accompanied by a copious evolution of hydrogen sulphide; on continuing the passage of the gas the crystals became yellow, and as the liquid turned to the consistency of a paste, about four times its volume of water was added, and the passage of the gas continued. Then there separated out the yellow crystalline substance noticed above, which subsequently dissolved to form the red liquid, yielding on evaporation in a vacuum the long red prismatic needles obtained in the former experiments. There was also slow evolution of hydrogen sulphide throughout the latter part of the experiment.

A sufficient quantity was not obtained for analysis, but the solution agreed in all its properties with former solutions and with those described by Berzelius.

From these results some conclusions can be drawn regarding the particular sulphur compound of calcium which is effective in the removal of carbon disulphide from the coal-gas. For, firstly, dry calcium sulphide does not, but moist calcium sulphide does absorb carbon disulphide; secondly, the conversion of calcium hydrosulphide into the hydroxyhydrosulphide precedes the absorption of any appreciable quantity of carbon disulphide; and thirdly, calcium hydroxyhydrosulphide suspended in water absorbs carbon disulphide. Thus the last-named substance is the absorbent formed either (i) from calcium sulphide, (ii) from calcium hydrosulphide, in accordance with the equations—

As the evolution of hydrogen sulphide is always concomitant with the absorption of carbon disulphide, and a basic calcium thiocarbonate is the resultant, the change can in all probability be represented as follows:—

This result would be in accordance with Rose's experiments (*vide supra*), which showed that the products formed by heating calcium sulphide with water were calcium hydroxyhydrosulphide and hydroxide, both of which would take part in the formation of the basic calcium thiocarbonate.

Further experiments showed that the material obtained by passing the vapour of carbon disulphide into calcium sulphide was partially decomposed with evolution of carbon disulphide by the passage of hydrogen sulphide, a result in accordance with the observations of the gas engineers, who have noticed that as the quantity of hydrogen sulphide passing into the calcium sulphide purifier was greater or less, the efficiency of the purifier was inversely diminished or increased (cf. Jones, "On the Purification of Coal-gas:" *Proc. Inst. C.E.*, **61**, Part ii). The author is continuing investigations regarding the effective value of calcium sulphide for the removal of carbon disulphide, with especial reference to the purification of coal-gas.

Summary.—The main points of the above paper are as follows:—

(I.) By the action of hydrogen sulphide on solid calcium hydroxide

there is formed a calcium monosulphide in accordance with the equation $\text{Ca}(\text{OH})_2 + \text{H}_2\text{S} = \text{CaS} + 2\text{H}_2\text{O}$.

(II.) By the action of hydrogen sulphide on calcium hydroxide in aqueous solution there is formed calcium hydrosulphide in accordance with the equation $\text{Ca}(\text{OH})_2 + 2\text{H}_2\text{S} + x\text{Aq} = \text{Ca}(\text{SH})_2 + 2\text{OH}_2 + x\text{Aq}$.

(III.) Calcium hydroxyhydrosulphide, $\text{CaSH}\cdot\text{OH}$, absorbs carbon disulphide with formation of unstable basic calcium thiocarbonates, decomposed slowly by hydrogen sulphide, and readily by carbonic anhydride.

In conclusion, the author wishes to return his best thanks to Mr. Vernon Harcourt for much valuable assistance and advice in the course of the inquiry.