

cubic metre of space in the vessel gave 3000 cubic metres of hydrogen, so that there was no difficulty in making vessels large enough for that process. With six small vessels of about 12 gallons each they could make about 1000 cubic metres of hydrogen a day and they could get vessels which were about 20 times that size.

The cost of the hydrogen differed according to the quantity produced; it would be about  $\frac{1}{3}$ d. a cubic metre at atmospheric pressure, and in large plants cheaper. The analyses of coal which he had given were calculated free of ash. The quantities of ash were different.

Mr. E. GRANT HOOPER asked whether Dr. Bergius had distilled the coal made in his experiments and what were the distillation products of the coal he had produced?

Dr. BERGIUS said they had heated some and found aromatic compounds. They could not say exactly all the compounds that were in the tar. Carbon monoxide only existed in extremely small quantities in the peat and there was no carbon monoxide in the gas from the cellulose. The amount of inorganic matter in the peat varied from 1 per cent. to 40 per cent., therefore they must calculate free of ash, and the material in their experiments had 3 or 4 per cent.

For avoiding the attack of the vessels by the water, there were different ways. They chose special qualities of steel. But, apart from that, there were other means of getting round this difficulty.

### Scottish Section.

Meeting held at Glasgow on Tuesday, 25th March, 1913.

DR. THOMAS EWAN IN THE CHAIR.

#### THE FIXATION OF NITROGEN BY MIXTURES OF BARIUM OXIDE AND CHARCOAL.

BY THOMAS EWAN, M.Sc., Ph.D., AND THOMAS NAPIER.

In 1860 Margueritte and de Sourdeval (*Comptes rend.*, 50, 1100, 1860) announced, without further detail, that a mixture of baryta and carbon, when calcined in presence of atmospheric air, combines very readily with nitrogen. The reaction was again studied by Mond in 1879 (*this J.*, 1889, 505). He found that the formation of cyanide requires a temperature of at least 1200° C. and proceeds most readily at 1400° and that 40 per cent. of the barium may be cyanised without difficulty. Barium cyanide is not acted on by carbon monoxide but is destroyed by carbon dioxide at high temperatures. At the temperature of the reaction barium carbonate fuses and must be mixed with sufficient carbon to form an infusible mixture.

Hempel (*Ber.*, 1890, 23, 3388) made a few experiments on the effect of pressure on the reaction, by heating a mixture of barium oxide and charcoal electrically in nitrogen at pressures varying from 1 to 60 atmospheres. The percentage of the barium cyanised increased rapidly with the pressure.

A considerable improvement in the technology of the process was made by J. B. Readman (*Eng. Pat.* 6021, 1894) by the application of the electric furnace for the production of the high temperature required. The process in this form was worked by the Scottish Cyanide Co. for some years.

The discovery that a large part of the nitrogen fixed is in the form of barium cyanamide,  $\text{BaCN}_2$ , was first published by Frank and Caro (*Eng. Pat.* 25,475, 1898).

The recent experiments of Kühling (*Ber.*, 1907, 40, 310) and of Kühling and Berkhöld (*Ber.*, 1908, 41, 28) have shown that the action of nitrogen on a mixture of barium

carbonate and charcoal begins at about 950° C., the quantity of nitrogen fixed increasing rapidly with the temperature. The addition of small quantities of barium chloride to the mixture has little or no effect on the fixation of nitrogen whilst large quantities diminish it. According to N. Caro (*Ger. Pat.* 212,706, 1907) alkali or alkaline earth fluorides accelerate the reaction and make it possible to work at 900°—1100° C., and a similar claim is made for potassium carbonate by Snodgrass in a Transvaal patent of 1907.

Our experiments were begun early in 1909 in order to find out whether, with the help of a suitable catalyst, it is possible to fix nitrogen by the barium process without resorting to the very high temperatures hitherto employed. We began by studying the behaviour of pure barium carbonate, in very much the same way as Kühling and Berkhöld, with whose work we were not, however, acquainted at the time.

A mixture of 2 parts of pure barium carbonate and 1 part of well burned wood charcoal, made by grinding the constituents together in a mortar, was placed in an iron boat which was heated in a porcelain tube in a current of dried nitrogen. The supply of nitrogen was regulated so that 2 litres of gas were collected at the exit end of the porcelain tube in 2 hours. The regulation and measurement of the temperature of the boat were very troublesome. In the early experiments the porcelain tube was heated in a gas-fired furnace in which different parts of the tube differed in temperature by 50° C. or more; by exploring the tube with a thermocouple before each experiment it was possible to find a region of fairly even temperature in which the boat and thermocouple were placed. The platinum-rhodium couple, enclosed in a quartz tube, was placed inside the porcelain tube and as near the boat as possible; the quartz, however, soon becomes porous under the combined action of the high temperature and of vapours containing barium compounds and the platinum wires are then acted on becoming very brittle. The E.M.F. of the couple changes rapidly and requires frequent calibration. These difficulties were overcome by using a Heraeus electric furnace in which the distribution of temperature along the tube does not change from day to day. The thermocouple was placed in the annular space between the porcelain tube and the tube on which the platinum foil resistance is wound. The boat occupied the central 2 inches of the heated tube, which was 12 ins. long; the greatest difference of temperature in the central 2 ins. was 9° and the couple outside the tube read 5° higher than inside. The melting points of antimony, 624°, sodium chloride, 798°, sodium carbonate, 852°, and potassium sulphate, 1066°, were used in standardising the pyrometer.

In the experiments, the results of which are given in Table I., the current of nitrogen was passed for 2 hours from the time at which the required temperature was reached, the boat was then allowed to cool off in an atmosphere of nitrogen. About 3 minutes were required to raise the temperature from 900°, at which the absorption of nitrogen just begins, to the experimental temperature. The whole of the gas collected, consisting essentially of carbon monoxide and nitrogen, was analysed, and also the contents of the boat. The analysis of the product was made by placing the boat in a corked flask full of water until everything was dissolved, after which the solution was filtered quickly and made up to a known volume. In suitable portions of the solution the total quantity of soluble barium compounds and the cyanide were estimated by titration with normal hydrochloric acid and silver nitrate respectively. Cyanamide was estimated in a third portion of the solution by neutralising it with nitric acid and boiling for about 20 minutes in order to expel the greater part of the hydrocyanic acid; after cooling and adding a few drops of ammonia, excess of silver nitrate is added and the precipitate of silver cyanamide filtered off and washed thoroughly. It is then dissolved in very dilute, cold nitric acid and the solution titrated with ammonium sulphocyanide and iron alum. The barium carbonate in the insoluble residue is dissolved in hydrochloric acid, preferably after burning off the charcoal, and then precipitated with ammonium carbonate, filtered off, washed and titrated with hydrochloric acid.

The results of a number of experiments made in this way are contained in the following table.

excess of nitrogen (interpolated from Table I.). The addition of quantities of potassium carbonate up to 11 per

TABLE I.

No.	Average temp. of boat.	Time hrs.	Grams BaCO <sub>3</sub> used.	Gas collected.		Mols. N <sub>2</sub> used to 1 mol. BaCO <sub>3</sub>	Percentage of the BaCO <sub>3</sub>			Per cent. of N <sub>2</sub> fixed as cyanamide.	Per cent. of the N <sub>2</sub> absorbed
				% CO.	c.c. N <sub>2</sub>		combined with N.	converted into BaO.	unchanged.		
3	860	2	2.784	14.5	1690	5.6	0	13.0	87.0	0	0
38	933	2	3.105	23.8	1445	3.8	1.03	34.5	64.5	0.0	0.25
35	960	2	0.505	6.0	1850	28.0	40.7	40.6	12.7	5.6	1.4
34	955	2	0.566	8.8	1812	26.0	37.3	50.7	12.0	10.4	1.4
28	960	2	1.110	19.7	1582	11.0	30.4	59.3	10.3	1.2	2.5
30	960	2	1.291	20.3	1566	10.1	27.6	59.0	13.4	4.0	2.6
20	963	2	1.340	20.2	1576	9.8	29.0	54.0	16.1	5.0	3.0
26	961	2	1.416	22.5	1512	8.9	21.9	63.0	15.1	2.1	2.4
27	960	2	1.577	23.2	1504	7.9	16.8	62.0	21.2	5.3	2.1
4	971	2	2.624	40.4	1148	3.6	14.0	68.8	17.2	8.0	3.9
8	969	2	2.787	38.4	1212	3.6	10.1	65.8	24.1	7.0	2.8
33	961	2	1.335	58.2	88	0.55	1.7	22.7	75.6	0.0	3.0
25	1000	2	2.786	30.8	1172	3.5	39.3	44.3	16.3	5.0	11.2
30	1000	1½	2.308	30.7	1266	4.6	36.3	46.5	14.6	13.8	7.2
2	1070	2	2.720	30.4	1188	4.4	45.0	38.8	16.2	11.0	10.3

The most interesting result of these experiments is that the percentage of the barium cyanised in the same time and at the same temperature is a function of the quantity of nitrogen passed over it. Kühling and Berkhold used the same quantities of barium carbonate and of nitrogen in each of their experiments, and therefore failed to observe this connection. In our experiments at 960° the quantity of nitrogen passed over the mixture varied from 0.55 to 28.9 molecules per mol. of barium carbonate used, the corresponding increase in the percentage of the barium combined with nitrogen being from 1.7 to 40.7, the percentage of carbon monoxide in the gas collected after passing over the barium carbonate on the other hand decreased from 85.2 to 6.9. This led us to suspect that the reaction is reversible, the small amount of change when little nitrogen is used being simply due to the reaction being stopped by the accumulation of carbon monoxide.

In other respects our results agree closely with those of Kühling and Berkhold. They may be summarised briefly as follows:—1. The absorption of nitrogen begins between 900° and 930°. 2. The amount absorbed under the same conditions increases very rapidly with the temperature, for example if 4 mols. of nitrogen are passed over 1 mol. of BaCO<sub>3</sub> in 2 hours about 1 per cent. of the barium will combine with it at 930, about 14 per cent. at 960 and about 40 per cent. at 1000°. 3. The greater part of the nitrogen fixed is in the form of cyanide. 4. At 960°, about 2½ per cent. of the nitrogen used is fixed, at 1000° about 10 per cent. (under the conditions of our experiments).

The results of a few experiments in which potassium carbonate was added to the mixture of barium carbonate and charcoal may be given here as they were made in exactly the same way as those included in Table I.

cent. seems to improve the results but the improvement is no more than would be produced by a difference of 10° or 20° in the temperature, a quantity which falls within the limits of accuracy of the measurements since these experiments were made with the gas-fired furnace.

The conditions under which the reaction occurs in the experiments just described are really rather complicated, the composition of the gas in contact with the mixture changing continuously during the run, so that it is impossible to draw any very certain conclusions about the nature and course of the reactions which take place. The state of affairs is brought out clearly by a set of four experiments in which equal quantities of the barium carbonate-charcoal mixture were heated for ½, 1, 1½ and 2 hours respectively in a current of nitrogen of constant speed. The gas escaping during each 10 to 15 minutes was collected and analysed, and the solid product was also analysed at the end of each run. The temperature was the same in all four experiments, about 950°. The results are given in diagram 1, in which the curves marked CO and H<sub>2</sub> represent the percentages of carbon monoxide and hydrogen in the gases collected at the exit end of the tube and those marked BaO and Ba(CN)<sub>2</sub> represent the percentages of the barium carbonate which are converted into barium oxide and into barium cyanide and cyanamide at any time during the progress of the experiment. It will be seen that carbon monoxide is evolved very rapidly at first. That the maximum quantity is not found at the beginning of the run is due to the arrangement of the apparatus. The boat containing the barium carbonate and charcoal was placed in the centre of a porcelain tube which was initially full of pure nitrogen, and about 10 minutes were required for the gases evolved from the boat to reach the exit end of the tube. The hydrogen found is derived partly from the charcoal, which usually contains

TABLE II.

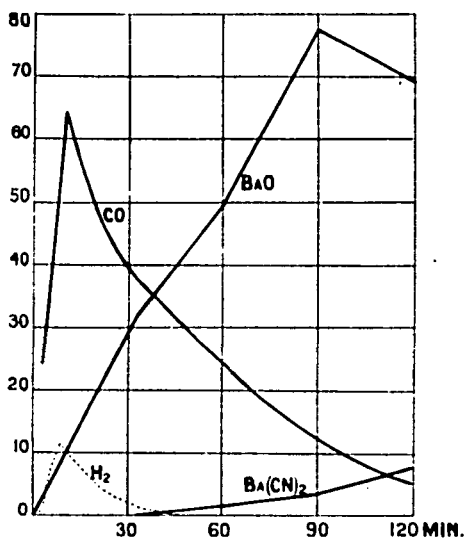
No.	Average temp. of boat.	Time hrs.	Mols. N <sub>2</sub> used to 1 mol. BaCO <sub>3</sub>	% CO in gas collected.	% K <sub>2</sub> CO <sub>3</sub> in the mixture of K <sub>2</sub> CO <sub>3</sub> + BaCO <sub>3</sub>	% of the Ba combined with N <sub>2</sub> .		% of the N <sub>2</sub> absorbed.
						observed.	calculated.	
9	957	2	5.6	35.2	4.7	20.2	10.0	3.6
14	963	2	4.3	39.4	7.4	19.4	12.5	4.5
7	964	2	5.0	20.9	10.0	26.0	14.7	5.4
15	960	2	4.3	44.7	11.5	18.7	12.5	4.4
10	966	2	5.6	38.9	16.7	13.2	16.2	2.4
16	960	2	6.9	31.8	40.0	8.4	10.7	1.2

The figures in the column headed "per cent. of the Ba combined with N<sub>2</sub>, calculated" are the results which would be obtained with pure barium carbonate using the same

about 1 per cent. of it, and partly from the barium carbonate which, as Finkelstein (Ber. 1900, 39, 1585) has observed, retains small quantities of water very tenaciously.

No cyanide is produced until some 30 per cent. of the barium carbonate has been converted into oxide and the quantity of carbon monoxide in the gas has fallen to about 30 per cent. and the percentage of carbon monoxide falls steadily as the formation of cyanide progresses.

DIAGRAM I.

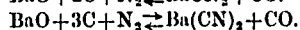
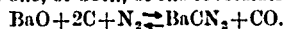


The results above described indicate, as already mentioned, that the absorption of nitrogen by barium oxide and charcoal is reversible. Direct proof of this was obtained by trying the action of pure carbon monoxide on a mixture of barium cyanide and cyanamide which was made by heating dry barium ferrocyanide *in vacuo* at about 1000°. The mixture was placed in an iron boat in a porcelain tube which was evacuated and then filled with pure carbon monoxide and heated at 960° for 2 hours. After cooling, the gases were pumped out and analysed and found to contain 18.2 per cent. of CO and 81.8 per cent. of N<sub>2</sub>. The compositions of the mixture used and of the product (calculated in grm.-molecules per 100 grms. of mixture) were:—

	Initial mixture.	Final mixture.	Increase.
Ba(CN) <sub>2</sub> .....	0.158	0.184	+0.006
BaCN <sub>2</sub> .....	0.182	0.032	—0.150
BaO .....	0.087	0.220	+0.133

The principal change which has occurred is obviously  $\text{BaCN}_2 + \text{CO} = \text{BaO} + 2\text{C} + \text{N}_2$ . A little cyanamide has also been converted into cyanide,  $\text{BaCN}_2 + \text{C} = \text{Ba(CN)}_2$ . It does not necessarily follow, however, that carbon monoxide acts on the cyanamide only, because, as will be shown later, cyanide and cyanamide (in presence of carbon) tend towards an equilibrium the relative quantities depending on the quantity of barium oxide present.

We may assume, therefore, that the fixation of nitrogen is due to one, or both, of the reversible reactions



If barium oxide, cyanide, cyanamide, and charcoal did not mix, but remained as separate phases, then when equilibrium was attained at any given temperature the ratio of the partial pressures of carbon monoxide and nitrogen in the gaseous phase would be independent of the relative quantities of the solid or liquid substances; and if a mixture of barium oxide and charcoal were heated in an atmosphere of carbon monoxide and nitrogen containing less than the equilibrium quantity of carbon monoxide the reaction would go on until the whole of the barium oxide was converted into cyanide or cyanamide. If, on the other hand, the barium compounds do mix the ratio of the partial pressures of carbon monoxide and nitrogen in the gas when equilibrium is attained at any given temperature will depend on the relative quantities

of cyanide, cyanamide and oxide in the mixture. The latter appears to be the actual state of affairs and we have attempted to determine the relation between the composition of the solid (or fused) mixture and that of the gaseous phase at three different temperatures (1000°, 1100° and 1150°).

The method finally adopted was to heat the barium mixture in a current of gas containing carbon monoxide and nitrogen until the gas escaping from the apparatus had the same composition as that entering it. To make sure that equilibrium was really attained two experiments were made with each mixture of carbon monoxide and nitrogen, one in which the initial material contained no combined nitrogen and a second in which it contained much more combined nitrogen than the final product.

For the experiments with nitrogen-free raw material a mixture of pure barium carbonate, charcoal and reduced iron was heated in a vacuum at the temperature of the subsequent experiment so long as gas was evolved; the product always contained a little undecomposed carbonate. The nitrogenous raw material was made by heating a mixture of dry barium ferrocyanide and charcoal (sometimes with a little reduced iron) in a current of nitrogen at about 1000°. Analyses of the products so obtained are given in Tables III. and IV. The addition of iron to the mixtures was intended to accelerate the attainment of equilibrium between the cyanide and cyanamide as explained later.

The mixture was placed in a wrought-iron boat (lined with magnesia at the highest temperatures to prevent the fusion of the iron in contact with the charcoal) and heated in a porcelain tube in the electric furnace. The temperature was usually kept constant within 2°. A definite mixture of carbon monoxide and nitrogen (freed from oxygen, carbon dioxide and moisture by passing it first over red-hot copper and then through a concentrated solution of caustic potash and finally strong sulphuric acid) was passed over the boat until the composition of the gas was no longer affected. In several cases the product, after cooling, was reground and retreated in order to make sure that no unattacked substance had been enclosed in the fused or semi-fused mass.

In the first experiments the boat was left to cool off, after the experiment, in the stagnant mixture of carbon monoxide and nitrogen left in the tube. We overlooked the fact that the equilibrium changes as the temperature falls and that carbon monoxide is absorbed on cooling. The results of the experiments made in this way are therefore affected by a small error, it is not very serious because the principal change during cooling is the conversion of barium oxide into carbonate. To avoid this error we first tried to obtain more rapid cooling by pushing the boat quickly into the cold end of the porcelain tube; still more rapid cooling was attained by attaching a water-cooled, quartz tube to the end of the porcelain tube, by pushing the boat into this, at the end of the experiment, it could be cooled below the reaction temperature in a few seconds. Finally we arranged the porcelain tube vertically and placed the mixture in a small iron gauze basket which was enclosed in a perforated steel capsule supported by an iron rod which passed through a packed gland at the upper end of the tube. The lower end of the tube was fixed into a wide-necked flask containing mercury. At the end of the experiment the capsule and its contents were pushed down under the surface of the cold mercury; in this way the material was cooled in one or two seconds and also removed from contact with the carbon monoxide.

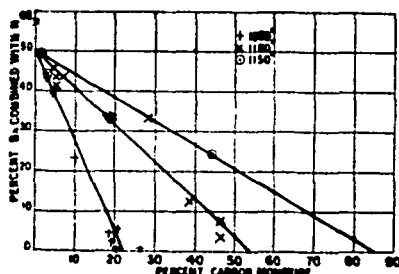
In order to estimate the error produced by the absorption of carbon monoxide in cooling, analyses of the gas left in the tube were made in three experiments with the following results:—

No.	Boat cooled.	% CO in gas.		Temp.	c.c. CO absorbed.
		Before cooling.	After cooling.		
97	In cold end of porcelain tube	4.0	4.0	1100	0
100	"	46.2	32.5	1100	16.8
101	In quartz tube	44.1	37.4	1151	8



In diagram 2 the percentages of the barium combined with nitrogen after equilibrium is reached are plotted against the corresponding percentages of carbon monoxide.

DIAGRAM II.



It will be seen that with one or two exceptions the experimental points lie very nearly on three straight lines which converge towards a point representing the conversion of one-half of the barium oxide into cyanide and cyanamide in contact with pure nitrogen. It is improbable that these straight lines represent the true form of the curves below one per cent. of carbon monoxide. Our experiments show that equilibria in which less than 50% of the barium is combined with nitrogen are attained rapidly and easily, but that, for some reason, the speed of fixation of further quantities of nitrogen is extremely small. When, for example, a mixture of barium carbonate and charcoal is heated in a current of nitrogen at 1100° over 45 per cent. of the barium combines with nitrogen in two hours, whilst a further 80 hours are required to carry the conversion to 57 per cent. (No. 110, Table IV.). It is therefore possible that true equilibrium in presence of pure nitrogen will only be attained when the whole of the barium is combined with nitrogen.

We have made many attempts to find a theoretical interpretation of these results but without success. An accurate knowledge of the mutual solubility of the compounds is necessary for a proper understanding of the equilibrium and we have not found time to investigate this. The arrest of the reaction at half conversion appears, however, to be most readily explained by the assumption that a compound,  $\text{BaO} \cdot \text{Ba}(\text{CN})_2$ , is formed in which the barium oxide is very much less active than the uncombined substance. This would also explain the fact that up to 1150° the mixtures lose nothing by volatilisation, whereas barium cyanide itself, as is mentioned later, is readily volatile at much lower temperatures.

Two experiments may be quoted here in order to give some indication of the rate of absorption of nitrogen by a mixture of barium oxide and charcoal. An intimate mixture of 2 grms. of barium carbonate and 1 gm. of charcoal was first heated at 1100° *in vacuo* until no further evolution of carbon monoxide occurred. It was then treated with a steady current of nitrogen at the same temperature and the carbon monoxide produced collected at short intervals and measured. The total quantity of nitrogen fixed was then estimated by analysis of the product. The quantity of carbon monoxide evolved agreed fairly well with the quantity of nitrogen fixed and its rate of evolution therefore afforded a fairly accurate indication of the progress of the reaction. The results were as follows:—

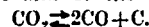
TABLE V.

Time of passage of nitrogen (minutes).	a.		b.	
	Per cent. of the barium combined with N.	Per cent. combined per minute.	Per cent. of the barium combined with N.	Per cent. combined per minute.
10	13.2	1.32	21.7	2.17
20	21.7	0.85	32.0	1.60
30	27.0	0.90	37.5	1.25
40	30.4	0.76	41.5	1.04
60	34.5	0.58	46.0	0.77
80	36.0	0.45	48.2	0.60
100	38.8	0.39	49.5	0.49
120	40.0	0.33	50.2	0.42

In *a* the quantity of nitrogen supplied per minute was sufficient to combine with 7.5 per cent. of the barium, in *b* it was equivalent to 17.5 per cent. per minute. The great increase in velocity produced by an increase in the supply of nitrogen shows very clearly that the reaction itself is a fast one. The diminution of speed which accompanies the conversion of the barium oxide is due partly to the diminution of the available barium oxide and probably partly to the formation of a protective glaze of a readily fusible mixture of barium cyanide and oxide over the surface of the unattacked particles.

Side by side with the main reaction between barium oxide, nitrogen and carbon which has been discussed, two other reactions take place:  $\text{BaCO}_3 + 2\text{C} \rightleftharpoons \text{BaO} + 3\text{CO}$  and  $\text{Ba}(\text{CN})_2 \rightleftharpoons \text{BaCN}_2 + \text{C}$ .

The pressure of carbon monoxide in equilibrium with barium carbonate and carbon at any temperature may be calculated from a knowledge of the dissociation pressure of barium carbonate and of the equilibrium



The initial dissociation pressure of barium carbonate (when less than 10 per cent. of it is decomposed) as determined by Finkelstein (Ber. 39, 1585, 1906) is given by the

$$\text{expression } \log_{10} p_{\text{CO}_2} = \frac{-13860}{T} + \log_{10} T + 8.197, \text{ where } T$$

is the absolute temperature and  $p_{\text{CO}_2}$  the pressure of  $\text{CO}_2$  in mm. Hg. The pressures of carbon monoxide and dioxide in equilibrium with carbon have been measured very accurately by Rhead and Wheeler (J. Chem. Soc., 1911, 1140). They have expressed their results by an equation\* which, after some numerical transformation becomes

$$\log_{10} \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{8263}{T} - 0.00067T - 10.581, \text{ where } p_{\text{CO}_2} \text{ and } p_{\text{CO}}$$

are the partial pressures of carbon dioxide and carbon monoxide respectively in mm. of mercury and  $T$  is the absolute temperature. Combining these two expressions we obtain the pressure of carbon monoxide (in mm. of mercury) which is in equilibrium with a mixture of barium carbonate (very little decomposed) and carbon at the absolute temperature  $T$ ,

$$\log_{10} p_{\text{CO}} = -\frac{11062}{T} + 0.5 \log_{10} T + 0.00033T + 9.389.$$

From this expression the following table is calculated:—

Temperature (C°)	$p_{\text{CO}}$ in mm.
800	0.2
900	7.5
1000	479
1100	2312
1200	9078

From these figures it appears, in accordance with our experience, that the decomposition of barium carbonate must take place to a considerable extent before any barium cyanide can be formed. As Finkelstein has shown the dissociation pressure of barium carbonate falls rapidly as decomposition proceeds owing to dilution or combination with barium oxide and apparently barium cyanide has a similar effect since when mixed with oxide and cyanide some barium carbonate can remain undecomposed even at 1180° when the pressure of carbon monoxide in contact with it has fallen to a few millimetres.

\* This equation represents the experimental results very exactly; it does not, however, appear to us to have the theoretical significance which the authors ascribe to it. They write Le Chatelier's general equation in the form  $\log_{10} \frac{C_1}{C_2} + \log_{10} P + \frac{1}{T} \int L \frac{dT}{T^2} = \text{const.}$

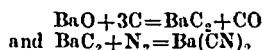
Reference to Le Chatelier's original memoir (Ann. des Mines, 1888 [8], 13, 157) shows that the quantity under the sign of integration should be  $L \frac{dT}{T^2}$ ,  $L$  being the heat absorbed by the reaction

$2\text{CO} = \text{C} + \text{CO}_2$  at constant pressure and not that evolved at constant volume as Rhead and Wheeler have taken it to be. By introducing the value  $L = 38055 + 2.02T - 0.0031T^2$  into the erroneous formula and neglecting the integration entirely they

obtain the formula  $\frac{38055 + 2.02T - 0.0031T^2}{T} + \log_{10} P + \log_{10} \frac{C_1}{C_2} = K$  which represents their results very well, and has therefore been used in our calculations.

We are unable to give any explanation of the curious fact that the quantity of carbonate remaining undecomposed under otherwise similar circumstances increases with the excess of charcoal present in the mixture (compare Nos. 106 and 99 with 104 and 107, Table IV., also Nos. 102 and 103, Table IV.).

It has been assumed that the absorption of nitrogen is preceded by the formation of barium carbide thus:—



As far as we know this hypothesis was first made in the analogous case of the formation of potassium cyanide from potassium carbonate, carbon and nitrogen by F. R. Hughes (Graham, Report of Juries, Exhibition of 1851, 1, 95) and again independently by Berthelot in 1868 (Comptes rend., 67, 1141). N. Caro (Chem. Ind., 1895, 14, 289) appears to have been the first to extend the hypothesis to the alkaline earths. We are not aware that any experimental evidence exists showing that barium carbide is really formed under the conditions in which nitrogen is fixed. We therefore heated an intimate mixture of 2 parts of barium carbonate and 1 part of charcoal in an iron boat in a porcelain tube, which was connected to a Töpler pump and to a pressure gauge. The temperature of the boat was gradually raised to 1100° the gases evolved being continuously pumped out: after about an hour the quantity of gas collected indicated almost complete decomposition of the carbonate, the pressure was about 3 mm. and it showed little tendency to increase when pumping was discontinued. The temperature was then raised to 1200° and the pumping continued at intervals for 9½ hours, the pressure fell gradually to about 1 mm. of mercury and on lowering the temperature to 1100° it was too small to be read on the gauge. The material left in the boat gave off acetylene when dissolved in water, a quantitative analysis showed that 15.9 per cent. of the barium carbonate used had been converted into carbide. 8.3 per cent. of it had remained unchanged and the remainder had been converted into oxide. It appears, therefore, that at 1200° the equilibrium pressure of the reaction  $\text{BaO} + 3\text{C} \rightleftharpoons \text{BaC}_2 + \text{CO}$  is about 1 mm. of mercury when only a small quantity of carbide is present, with more carbide it might be smaller but would not be greater.

The approximate equation which Nernst has deduced from his thermodynamic theorem may be used in order to show that this result is at least not improbable. For the case under consideration Nernst's equation becomes

$$\log_{10} p_{\text{CO}} = -\frac{Q}{4571T} + 1.75 \log_{10} T + 3.6$$

where  $p_{\text{CO}}$  is the equilibrium pressure of carbon monoxide in atmospheres at the absolute temperature  $T$  and  $Q$  is the heat evolved by the reaction  $\text{BaC}_2 + \text{CO} = \text{BaO} + 3\text{C}$ . Introducing the values of  $p_{\text{CO}}$  and  $T$  above measured  $Q$  is found to be 74,000 cal., from which we obtain the heat of formation of barium carbide from its elements,  $\text{Ba (metal)} + \text{C}_2 (\text{amorph.}) = \text{BaC}_2 + 23,400 \text{ cal.}$  The heat of formation of barium carbide has not been measured, but that of calcium carbide is 19,700 cal. and the following comparison of the heats of formation of some calcium and barium compounds indicates that the difference between them has quite a possible value.

#### Heat of formation of Ba—Heat of formation of Ca-compound.

Hydride	..	— 8.7 Cal. per atom metal.
Carbide	..	+ 3.7 " " "
Nitride	..	+ 12.4 " " "
Oxide	..	— 25.5 " " "
Fluoride	..	— 16 " " "
Chloride	..	+ 6.1 " " "
Bromide	..	+ 10 " " "
Sulphide	..	— 11 " " "
Carbonate	..	— 6 " " "

Using the above value of  $Q$ , and calculating  $p_{\text{CO}}$  in mm. of mercury instead of in atmospheres, Nernst's equation becomes:—

$$\log_{10} p_{\text{CO}} = -\frac{16250}{T} + 1.75 \log_{10} T + 5.48$$

from which the following table is calculated:—

$t$	$T$	$p_{\text{CO}}$ (mm.)	$p_{\text{CO}}$ (atmos.) $\times 100$
950	1223	0.004	0.00056
1000	1273	0.014	0.0018
1100	1373	0.138	0.018
1200	1473	1.0	0.129

The figures in the last column are the same as the maximum percentage of CO which if mixed with nitrogen at 1 atmosphere pressure could exist in presence of barium carbide at the temperatures given in the first column. It is clear, therefore, that barium carbide could not be formed at all in presence of the mixtures of carbon monoxide and nitrogen from which the latter is freely absorbed by barium oxide and carbon, and it cannot be regarded as an intermediate product in the reaction.

It is, however, quite probable that in the analogous reaction with calcium oxide the carbide is a necessary intermediary. For the reaction  $\text{CaC}_2 + \text{CO} \rightleftharpoons \text{CaO} + 3\text{C} + 103,200 \text{ cal.}$ , Nernst's equation becomes:—

$$\log_{10} p_{\text{CO}} (\text{atmos.}) = -\frac{103200}{4571T} + 1.75 \log_{10} T + 3.6$$

The substantial accuracy of this equation has been verified by Rothmund (this J., 1902, 761). The equation gives:—

$$p_{\text{CO}} = 1 \text{ atmosphere at } 2117^\circ \text{ C}$$

$$p_{\text{CO}} = \frac{1}{2} \text{ " " at } 2037^\circ \text{ C}$$

The Cyanid Gesellschaft (Eng. Pat. 16,298, 1902) states that "nitrogen has no action on a mixture of lime and carbon at 1100° and the reaction  $\text{CaO} + 2\text{C} + \text{N}_2 = \text{CaCN}_2 + \text{CO}$  takes place best at a temperature of 2000°, at this temperature only a little of the nitrogen is unabsorbed."

The last statement indicates that at 2000° the partial pressure of the carbon monoxide evolved is about 1 atmo., which agrees very well with the above calculation.

We have finally to consider the relation between barium cyanide and cyanamide and carbon. Our results may be arranged under the headings:—

- Behaviour of pure barium cyanide when heated.
- Behaviour of barium ferrocyanide when heated.

(c) Composition of products obtained by the action of nitrogen on mixtures of barium carbonate and charcoal.

#### a. Behaviour of pure barium cyanide when heated.

Barium cyanide was prepared by A. Joannis (Ann. Chim. phys., 1882 [5], 26, 484) by treating crystallised baryta,  $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ , with dry hydrocyanic acid until the crystals nearly disappeared, a small excess of the acid was then added to the concentrated solution, which was evaporated *in vacuo* in the cold until the hydrate  $\text{Ba(CN)}_2 \cdot 2\text{H}_2\text{O}$  was left. This was then heated very gradually *in vacuo* to 100°. An analysis of the product gave 72.04 per cent. Ba and 27.21 per cent. CN, which corresponds with 99.29 per cent.  $\text{Ba(CN)}_2$ , 0.18 per cent.  $\text{Ba(OH)}_2$  and 0.53 per cent. water. By following Joannis' directions exactly we always obtained a product containing about 92 per cent. of  $\text{Ba(CN)}_2$  and 8 per cent. of  $\text{Ba(OH)}_2$ . Even when a cold solution, an analysis of which showed it to contain Ba and CN in the correct proportions, was evaporated *in vacuo* at a few degrees above zero, the salt deposited contained about this proportion of hydroxide. It is obvious that the saturated solution is hydrolysed to a considerable extent and the free hydrocyanic acid escapes in a vacuum. The impure crystals of the dihydrate can, however, be dried without much further change. This observation led us to a fairly easy method of preparation of the anhydrous salt. Pure, recrystallised barium

hydroxide is dried *in vacuo*, yielding a very fine, dry powder of  $\text{Ba}(\text{OH})_2$ . This is suspended in dry petroleum ether and an emulsion of anhydrous hydrocyanic acid and petroleum ether added to it in about theoretical quantity. In this way the solid hydrate is obtained without evaporation  $\text{Ba}(\text{OH})_2 + 2\text{HCN} = \text{Ba}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ . The crystals, when dried *in vacuo* at a gradually rising temperature, yield a product with only 5 per cent. of barium hydroxide and by shaking this with a small excess of dry hydrocyanic acid and petroleum ether and again drying *in vacuo* a product was obtained containing 97.33 per cent.  $\text{Ba}(\text{CN})_2$ , 0.37 per cent.  $\text{Ba}(\text{OH})_2$ , 1.42 per cent.  $\text{BaCO}_3$ .

The dry salt fuses at about  $600^\circ$ , it is distinctly volatile even at its melting point, for example a sample lost 42 per cent. of its weight when heated for 1 hour at  $650^\circ$  *in vacuo*, and 65 per cent. of its weight when heated for  $1\frac{1}{2}$  hours at  $800^\circ$  in an atmosphere of nitrogen. From Joannis' determinations of the heat of solution of the anhydrous salt and of the heat of neutralisation of baryta by hydrocyanic acid the following heats of reaction may be calculated:—



The following table contains the results of a number of experiments in which dry barium cyanide was heated.

an excess of finely divided iron (made by reducing ferric oxide in coal gas) was added to the cyanide. The increased quantity of cyanamide formed is very striking; the only other experiments in which anything approaching to this quantity of cyanamide is formed are those in which a considerable quantity of the material volatilised, if the volatile material is barium cyanide the relatively large quantity of cyanamide in the residue would be easily understood. In the last four experiments in Table VI., iron was excluded as far as possible. The effect of iron on the change is clearly seen by comparing the four experiments in each of which the barium cyanide was heated for 4 hours at  $620^\circ$ .

No.	Mols. $\text{BaCN}_2$ in 100 mols. of $(\text{BaCN}_2 + \text{Ba}(\text{CN})_2)$ .	Conditions.
69	13.6	Iron boat lined with $\text{MgO}$ .
71	12.9	Carbon boat.
64	29.0	Iron boat.
70	63.4	Iron boat; excess spongy iron added.

It is evident that the greater the surface of iron in contact with the barium cyanide the greater is the quantity of it converted into cyanamide under otherwise similar

TABLE VI.

Composition of product.

No.	Temp.	Time of heating. hrs. min.	Composition of product. Mols. per 100 mols. $\text{Ba}(\text{CN})_2 + \text{BaCN}_2$			Remarks.
			$\text{BaCN}_2$	$\text{BaCO}_3$	$\text{BaO}$ .	
68	500	17 50	8.2	< 11	0	$\text{N}_2$ : nothing volatilised: fritted.
60	550	1	3.2	9.6	0	vacuum: nothing volatilised: caked but not fused:
62	600	1	11.6	?	?	$\text{N}_2$ : nothing volatilised: semi-fused.
63	620	2	25.4	14.0	7.5	$\text{N}_2$ : nothing volatilised: semi-fused.
64	620	4	20.0	15.4	4.5	$\text{N}_2$ : nothing volatilised: almost completely fused.
70	620	4	63.4	< 19.3	6.9	$\text{N}_2$ : spongy Fe added: fused.
61	650	1	46.2	1.4	about 8.5	vacuum: about $\frac{1}{2}$ volatilised: completely fused.
66	700	1	30.7	8.8	10.2	$\text{N}_2$ : nothing volatilised: porous fused mass.
67	700	3 30	30.5	8.4	18.0	$\text{N}_2$ : nothing volatilised: porous fused mass.
59	800	1	41.4	5.2	?	vacuum: about $\frac{1}{2}$ volatilised: completely fused.
65	800	1 15	29.5	12.5	18.4	$\text{N}_2$ : about $\frac{1}{2}$ volatilised: completely fused.
58	1000.	1	53.4	?	?	vacuum: about $\frac{1}{2}$ volatilised: fused.
69	620	4	13.6	?	4.8	$\text{N}_2$ : Iron boat lined $\text{MgO}$ : fritted to hard mass.
71	620	4	12.9	?	2.5	$\text{N}_2$ : Carbon boat: charcoal added:
72	700	2	12.9	?	7.0	$\text{N}_2$ : $\text{MgO}$ boat:
73	705	2	25.0	?	3.0	$\text{N}_2$ : carbon boat: charcoal added:

Of the above experiments the first 12 were made in iron boats; in every case the product was dark coloured, owing to the separation of carbon, but it was noticed that the greater part of the carbon had separated in contact with the iron boat. This led us to try experiment 70 in which

circumstances. A comparison of Nos. 62, 63 and 64 or of Nos. 60 and 68 shows that the formation of barium cyanamide is very slow, especially at low temperatures; it is therefore probable that the iron merely accelerates this change catalytically.

TABLE VII.

No.	Time of heating. (Hours.)	Temp.	Grams charcoal per gram $\text{Ba}_2\text{FeCy}_2$	Per cent. of the barium in the product in the form of					mols. $\text{BaCN}_2$	mols. $\text{BaO}$ .
				$\text{Ba}_2\text{FeCy}_2$	$\text{Ba}(\text{CN})_2$	$\text{BaCN}_2$	$\text{BaO}$	$\text{BaCO}_3$	per 100 mols. $\text{Ba}(\text{CN})_2 + \text{BaCN}_2$	
1	2	580	0	33.7	21.0	43.4	0	1.0	66.5	0
2	2	850	0	0	30.4	43.7	19.9	0.0	54.7	24.8
3	1	1000	0	0	30.2	41.8	20.0	2.0	53.6	25.6
4	2	1000	0	0	37.4	7.3	50.2	5.0	16.3	112.3
5	1	bright red	0.17	0	31.2	33.9	22.1	12.7	52.1	33.9
6	1	"	0.17	0	30.8	30.6	27.9	10.7	50.0	45.4
7	2	850	0.2	0	29.8	16.2	46.2	7.7	35.2	100.4
8	2	850	0.36	0	21.7	12.8	36.2	29.2	37.1	104.9
9	1	700	0.52	0	15.9	2.2	38.2	43.7	12.2	211
	2	850								

There is no evidence in these experiments that the reaction  $\text{Ba}(\text{CN})_2 = \text{BaCN}_2 + \text{C}$  is reversible. In Nos. 71 and 73 excess of charcoal was mixed with the barium cyanide, but the conversion into cyanamide went as far (or further) than in the parallel experiments 69 and 72 with no charcoal.

(b.) *Products obtained by heating barium ferrocyanide.*

Barium ferrocyanide is most easily made by mixing hot, concentrated solutions of equivalent quantities of barium chloride and sodium ferrocyanide (if potassium ferrocyanide is used a double potassium barium ferrocyanide crystallises out). The salt loses the greater part of its water of crystallisation at  $160^\circ$ , but, as Drechsel (*J. pr. Chem.*, 1880 (2) 21, 77) observed a little water is retained even at this temperature. By heating 3.323 grms. of the salt, previously dried at  $160^\circ$ , in vacuo at  $1050^\circ$  until decomposition was complete we obtained 26.5 c.c. of hydrogen (at  $19^\circ$  and 1 atmo.) which corresponds with 0.6 per cent. of water in the dried salt. When the dry salt is heated in a vacuum or in an atmosphere of nitrogen decomposition begins at about  $500^\circ$ , nitrogen is evolved and a mixture of carbon, iron and barium cyanide and cyanamide remains behind. Drechsel had already observed, qualitatively, the formation of barium cyanamide and attributed it to the action of water on barium cyanide, but the quantities produced are much too large to be explained in this way. The compositions of the products which we have obtained by heating barium ferrocyanide, either alone or mixed with charcoal, are given in Table VII.

TABLE VIII.

No.	Temp.	Time of Heating (Hours).	Mols. $\text{BaCN}_2$ per 100 mols. $\text{BaCN}_2 \times \text{Ba}(\text{CN})_2$ in the product.	Mols. $\text{BaO}$ per 100 mols. $\text{BaCN}_2 \times \text{Ba}(\text{CN})_2$ in the product.
38	933	2	0.0	3350
35	960	2	5.6	114
34	955	2	10.4	136
28	960	2	1.2	195
30	960	2	4.0	214
29	963	2	5.0	180
26	961	2	2.1	287
27	960	2	5.3	370
4	971	2	8.0	493
8	969	2	7.0	650
33	961	2	0	1340
25	1000	2	5.0	112
39	1000	1	13.8	128
2	1070	2	11.0	87

TABLE IX.

No.	Time of Heating (Hours).	Temp.	Mols. $\text{BaCN}_2$ per 100 mols. $\text{BaCN}_2 \times \text{Ba}(\text{CN})_2$ in product.	Mols. $\text{BaO}$ per 100 mols. $\text{BaCN}_2 \times \text{Ba}(\text{CN})_2$ in product.
100	4.5	1000	13.0	98
95	4.5	1001	4.5	136
96	6	1002	5.6	128
108	6.2	1000	10.8	209
105	5.2	1000	6.1	1640
107	4.1	1000	40.0	1390
110	82.2	1100	62.9	36
97	4.0	1100	9.4	103
91	5.2	1101	21.2	111
92	6.1	1100	21.4	106
84	2.0	1101	9.4	111
87	2.0	1102	7.4	150
88	4.0	1100	8.2	148
89	4.7	1100	16.0	160
98	3.6	1100	3.3	174
85	2.0	1101	47.6	401
93	6.0	1100	74.0	1030
94	3.3	1100	60.0	2030
100	3.8	1100	14.3	1020
103	4.4	1150	10.6	70
102	2.5	1151	4.3	115
101	3.0	1151	7.4	253

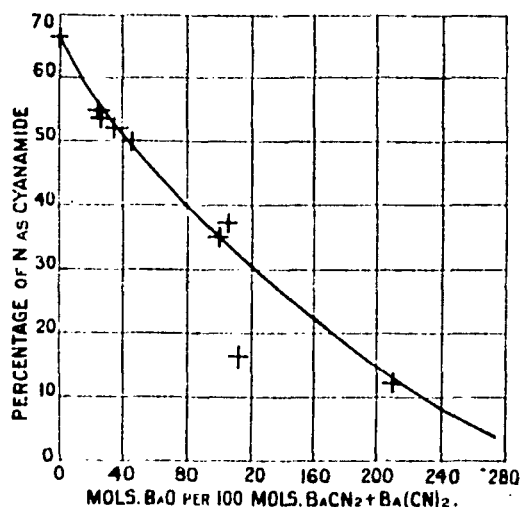
In experiments 1—3 of Table VII. the barium ferrocyanide was heated alone in a vacuum: in No. 4 the product of No. 3 was heated in pure carbon monoxide. In the remaining experiments (5—9) well-roasted charcoal was mixed with the ferrocyanide and the heating was done in an atmosphere of nitrogen.

(c.) *Composition of products obtained by the action of nitrogen on mixtures of barium carbonate and charcoal.*

Tables VIII. and IX. contain the relative quantities of barium cyanide, cyanamide and oxide contained in the products obtained in the various experiments tabulated in Tables I., III., and IV. A few results are omitted because the actual quantities of cyanamide were too small to be estimated accurately.

The results collected in Tables VI.—IX. are best considered together: at first sight they appear to be perfectly chaotic. There is, however, some relation between the percentage of the combined nitrogen which is in the cyanamide form and the quantity of barium oxide in the mixture. This comes out most clearly when the figures in Table VII. are plotted graphically. (Diagram III.) As the mixture is diluted more and more

DIAGRAM III.



with barium oxide the combined nitrogen passes more and more into the form of cyanide. This seems to be quite independent of the temperature at which the barium ferrocyanide was heated. This regularity does not appear at all in the composition of the synthetic mixtures (Tables VIII. and IX.). The percentage of the nitrogen in the form of cyanamide in these mixtures appears to have no relation to the quantity of barium oxide present, it is also hardly affected by the temperature. Time may, however, be an important factor; the one experiment in which the mixture was heated for a very long time (82.2 hours in No. 110) gave a result which falls nearly on the curve in Diagram III., and the same remark applies to the experiment in which barium cyanide was heated with finely divided iron (No. 70, Table VI.). In the other experiments with barium cyanide the change was obviously incomplete and no regularity could, therefore, be expected.

It may be pointed out that a definite relationship between the quantities of barium cyanide, cyanamide and oxide present in a mixture could only be expected if the three substances were completely miscible and if the reaction  $\text{Ba}(\text{CN})_2 = \text{BaCN}_2 + \text{C}$  were reversible. If the reaction is reversible and either barium cyanide or barium cyanamide forms a solid phase, then there is no necessary connection between the quantities of them present in a mixture because the absolute quantity of a solid phase may vary to any extent without affecting the equilibrium. Our want of knowledge of the mutual solubilities of the nitrogen and oxygen compounds of barium again makes it impossible to give a satisfactory explanation of this reaction. We regret that lack of time makes it necessary for us to leave the question in this unsatisfactory position.

The experiments described were made in the laboratory of the Casel Cyanide Co., Ltd., and our thanks are due to the directors of the company for permission to publish them.