

VIII. *On the products of the action of Potassium on Cyanide of Ethyl.* By H. KOLBE, PH. D. and E. FRANKLAND, Esq.

Professor Bunsen, in his investigation on the isolation of Cacodyl,\* points out two important conditions, which, in the separation, by means of metals, of the organic radicals from their liquid combinations, it is essentially necessary to observe. Firstly, the decomposition must be effected at a lower temperature than that at which the substance to be decomposed boils; and, secondly, the metallic compound produced must not be insoluble in the newly-formed radical.

These remarks induced us to make an experiment upon the separation of ethyl from its cyanide by means of potassium, as we conceived that this metal would exert its affinity for cyanogen at a temperature below the boiling point of that liquid.

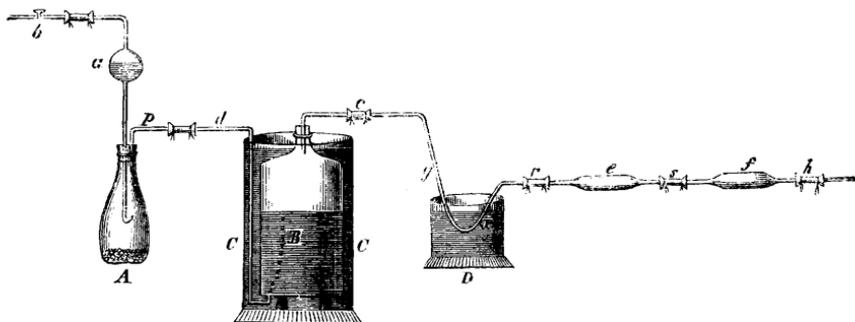
This expectation appeared to be fully realized. For, not only did the potassium act energetically upon the cyanogen compound, even at ordinary temperatures, but the cyanide of potassium which was formed in large quantity, was so completely dissolved in the sur-

\* *Annalen der Chemie*, Bd. 42, S. 45.

rounding liquid, that the metal retained a bright surface to the last. At the same time, an inflammable gas, insoluble in water, and possessing a faint ethereal odour, was evolved. We at first imagined this gas to be the radical sought, and we therefore resolved to follow out the investigation.

We employed the following apparatus, Fig 1, for the preparation of

FIG. 1.



the gas. In the flask *A*, which was capable of containing about 60 cubic centimetres, was placed a number of small pieces of potassium, previously freed from the adhering rock oil; the neck was fitted with a cork, through which were inserted, on the one side, the gas-delivering tube *p*, and on the other, the tube *a* having a bulb blown upon it, the lower end being recurved and drawn out to a capillary orifice; the upper extremity was connected by a caoutchouc joint with the stop-cock *b*. The bulb served to contain the cyanide of ethyl, which, by the cautious opening of the stop-cock *b*, could afterwards be allowed to fall in drops upon the potassium.

For the collection of the gas, the receiver *B*, inverted in the glass cylinder *C*, was employed, its lower edge resting upon two strips of glass. The gas-delivering tube *g*, proceeding from the tubulure of the bell-jar was slightly drawn out at *x*, and then connected by caoutchouc joints with the wider tubes *e*, *f*, which served to contain the gas for eudiometric purposes. To the extremity of the last of these was attached a caoutchouc tube *h*, containing a piece of glass rod, by means of which the aperture could be perfectly closed.

Immediately before the experiment, and previous to the gas-delivering tube *d* being introduced under the bell-jar *B*, a quantity of boiled water, still warm, was poured into the outer cylinder *C*, and suction being applied to the open extremity at *h*, the entire system of tubes from *B* to *h* was filled with it. The caoutchouc tube

surrounding the small piece of glass rod above mentioned, was then rendered perfectly air-tight by being tied with silk cord.

The first few drops of cyanide of ethyl, which, by the momentary opening of the stop-cock *b* were allowed to fall upon the potassium, exhibited generally a very violent action, which was not unfrequently attended by flashes of light, and accompanied, especially at the commencement, by a very rapid evolution of gas, which soon expelled all atmospheric air from the apparatus. As soon as the last traces of air had been displaced from the apparatus, the conducting tube *d* was inserted under the edge of the receiver *B*, which then became slowly filled with gas, as the pieces of potassium gradually disappeared on the addition of cyanide of ethyl and were converted into a tenaceous mass of a yellowish colour. Towards the end of the process, the decomposition was promoted by the application of a gentle heat. The experiment was interrupted as soon as the evolution of gas perceptibly diminished, the potassium being then, in most instances, quite consumed.

It appeared desirable to allow the gas collected in the bell-jar to stand over water for several hours, or even for a whole day, that the vapour of cyanide of ethyl, with which it was still contaminated, might be perfectly absorbed; we therefore took the precaution to cover the outer surface of the water with a layer of oil, in order to prevent the possibility of diffusion taking place between the enclosed gas and the atmosphere. The cylinder was afterwards quite filled with water, and the caoutchouc tube at *h* opened until all the water was expelled from the system of tubes, and its place was occupied by the gas acting under the pressure of the outer column of water.

The caoutchouc connectors *h*, *s*, and *r*, were then tied with silk cord, the two last doubly, and these being cut through between the ligatures, the tubes *e* and *f* were taken asunder. To make the four ends perfectly gas-tight, they were immersed in melted wax; by taking this precaution, gases may be preserved for a twelvemonth without any diffusion taking place; this method was preferred to fusing them before the blow-pipe, as it was to be feared that the heat necessary in the latter case might decompose the gas.

The rest of the gas was employed for the determination of its specific gravity, and for combustion with oxide of copper. For the first purpose we used a glass flask, containing about 200 cubic centimetres, the neck of which was contracted before the blow-pipe, until its diameter was reduced to that of a stout straw. This could be closed air-tight by means of a small ground-glass stopper.

In order to dry the gas, several pieces of fused potash were intro-

duced and fixed to the bottom of the flask by a gentle heat; it was then filled with mercury, inverted in the vessel *D* containing the same metal, and its open mouth held over the extremity of the gas-delivering tube, previously cut off at the point *x*. To overcome the pressure of the mercury, the gas in the receiver *B* was more strongly compressed by pouring a proportionate quantity of quicksilver into the outer cylinder. The gas was allowed to pour into the flask until the mercury in the neck stood only  $10^{\text{mm}}$  above that in the vessel; the flask was then brought, with its mouth still immersed in the liquid metal, into a room of a constant temperature, where it was allowed to remain for upwards of an hour. Whilst the gas assumed the temperature of the surrounding air, which was ascertained by a delicate thermometer, it was at the same time perfectly dried by means of the pieces of fused potash. The height of the internal column of mercury was measured by a pair of compasses, and determined in millimeters. The flask was then carefully stopped under mercury and weighed, without bringing the hand in contact with it; it was afterwards filled with dry air, and lastly, with mercury, the weight being taken after each operation.

The following results were obtained:

Temperature of room . . . . .	19.7° C.
Height of barometer . . . . .	748.0 m. m.
Height of mercury in flask above that in outer vessel	17.2 m. m.
Weight of flask filled with gas . . . . .	53.591 grms.
Temperature in balance case . . . . .	20.3° C.
Weight of flask filled with dry air . . . . .	53.5775 grms.
Temperature of balance case . . . . .	20.9° C.
Capacity of flask . . . . .	210.2 c. c.

From which the specific gravity was calculated at 1.075.

For ascertaining the relative proportions of carbon and hydrogen, we allowed an indefinite volume of the gas to stream over ignited oxide of copper contained in a combustion tube, which was connected at one extremity with a chloride of calcium tube and potash apparatus, both previously weighed, and at the opposite end with another chloride of calcium tube connected with the gas apparatus *B* by the caoutchouc tube *c*. Thus the gas was freed from moisture before passing over the ignited oxide of copper. By carefully depressing the receiver *B*, a perfectly regular stream of gas was obtained, the velocity of which was indicated by the liquid in the potash apparatus.

When a sufficient quantity of water and carbonic acid had been formed, the caoutchouc tube *c* was divided, and the gases remaining in the combustion tube were drawn through the potash bulbs by

suction, in the usual manner. On re-weighing the chloride of calcium tube, it was found to have increased by 0.1794 grms.; the weight of the potash apparatus had increased 0.2915 grms. The gas consequently contained 0.0795 parts by weight of carbon to 0.0199 parts of hydrogen; numbers which closely correspond with the proportion  $C : H = 2 : 3$ .

The eudiometric analysis should confirm this result, and at the same time indicate the degree of condensation. For this purpose the gas contained in one of the tubes *ef* was employed, filled as before described, and transferred under mercury into the eudiometer and exploded with oxygen. For the details of the methods of observation in eudiometrical researches, and the precautions necessary to be used, we refer to the "Handwörterbuch der Chemie," article "Eudiometrie," vol. II. p. 1050.

## I.

	Observed vol.	Temp. C.	Height of mer- cury above that in trough.	Barom.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Volume of gas used (moist) . . . .	117.2	15.7	456.5 <sup>mm</sup>	743.9 <sup>mm</sup>	30.37
After admission of O (moist) . . . .	348.9	15.7	216.3 ,,	743.5 ,,	169.55
After combustion (moist) . . . .	224.5	16.1	286.1 ,,	743.1 ,,	94.00
After absorption of CO <sub>2</sub> (dry) . . . .	121.6	16.2	451.5 ,,	744.4 ,,	33.74
After admission of H (dry) . . . .	323.3	16.3	241.4 ,,	744.0 ,,	153.37
After combustion (dry)	167.4	16.1	404.0 ,,	744.9 ,,	53.90

## II.

Volume of gas used (moist) . . . .	68.7	15.2	500.7 ,,	744.1 ,,	15.00
After admission of O (moist) . . . .	331.9	15.3	229.1 ,,	743.6 ,,	157.65
After combustion (moist) . . . .	281.6	15.3	280.9 ,,	744.1 ,,	120.07
After absorption of CO <sub>2</sub> (dry) . . . .	231.6	15.3	333.1 ,,	747.7 ,,	90.92
After admission of H (dry) . . . .	539.0	15.4	21.5 ,,	746.8 ,,	370.05
After combustion (moist) . . . .	247.2	15.4	316.7 ,,	745.5 ,,	97.30

It appears from the above analyses that 1 volume of the gas requires  $3\frac{1}{2}$  volumes of oxygen for combustion, and generates 2 volumes of carbonic acid.

	Volume of gas used.	Oxygen consumed.	Carb. acid generated.
I.	30·37	106·02	60·26
=	1	: 3·49	: 1·99
II.	15·00	51·74	29·15
=	1	: 3·45	: 1·94

The above facts prove that the unknown gas has the composition and the state of condensation of the hitherto hypothetical radical methyl. The determination of its specific gravity, already detailed, gave the number 1·076, which agrees sufficiently near with the calculated specific gravity (1·037) when we consider that the gas, at the time the experiment was made, probably contained a little of the comparatively heavy cyanide of ethyl vapour.

1 vol. Carbon vapour	=	0·82922
3 vols. Hydrogen	=	0·20730
1 vol. Methyl gas	=	<u>1·03652</u>
By experiment		1·076

Methyl is a colourless gas, not condensable at a temperature of  $18^{\circ}$  C. ( $65^{\circ}\cdot 5$  F.), insoluble in water, and possessing a slight ethereal odour. One volume of alcohol absorbs 1·13 volumes of this gas; agitated with an equal volume of previously boiled alcohol over mercury, it disappeared, with the exception of a small bubble, which did not amount to  $\frac{1}{2}$  per cent. Concentrated sulphuric acid had no action upon methyl, nor did it combine with sulphur or iodine when those elements were heated in the gas.

It appeared important to ascertain whether methyl, like hydrogen, would combine immediately with chlorine to form chloride of methyl. For this purpose we again filled some dried tubes, similar to those marked in the figure *ef*, and joined them with flexible connectors; to these a chloride of calcium tube was attached, connected with the caoutchouc tube *c*, which last was closed by a silken cord, while the receiver *B* was being filled with gas; the ligature was then loosed, and by pressing down the bell-jar, the gas was driven through the system of tubes. As the volume of gas in the receiver amounted to nearly twenty times the capacity of the tubes to be filled, we took for granted that all atmospheric air had been expelled from the apparatus. The tubes were then taken

asunder at the caoutchouc connections, in the manner before described.

Another tube, of the same dimensions as one of those above mentioned, was now filled with dry chlorine, and then connected as quickly as possible by a strong india-rubber joint, with a similar tube containing methyl, and the two gases were thus allowed to communicate with each other. After remaining for twenty-four hours, carefully preserved from the light, they perfectly intermingled, but were otherwise unchanged. On exposure to diffused daylight, the colour of the chlorine gradually disappeared, a proof that combination had taken place. After twenty-four hours more, the two tubes were hermetically sealed before the blow-pipe, and reserved for further experiments.

On breaking off the end of one of the tubes under mercury, it did not appear that any condensation had taken place, yet the new product could not be chloride of methyl, since a few bubbles of the gas which were allowed to escape contained a large quantity of hydrochloric acid.

To determine the quantity of hydrochloric acid present, we transferred the gas into a small eudiometer, and after carefully noting the volume, a ball of tribasic phosphate of soda was introduced, and afterwards one of caustic potash, which was allowed to remain until all traces of hydrochloric acid were absorbed; the volume was again read off, and the residual gas transferred to a large eudiometer, furnished in the usual manner with platinum wires, in which it was then exploded with oxygen, and yielded the following results.

## ESTIMATION OF HYDROCHLORIC ACID.

	Observed volume.	Temp. C.	Height of mer- cury above that in trough.	Barom.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Volume of gas used (dry) . . . .	103·6	18°·9	47·2 <sup>mm</sup>	752·5 <sup>mm</sup>	68·35
After absorption of H Cl (dry) . . .	55·1	18°·8	95·0 ,,	755·1 ,,	34·00

## EXAMINATION OF THE GAS FREED FROM HYDROCHLORIC ACID.

Gas used (moist) . .	116·1	18°·8	439·2 ,,	755·0 ,,	32·50
After admission of O (moist) . . . .	362·5	19°·0	186·6 ,,	754·8 ,,	187·05

	Observed volume.	Temp. C.	Height of mer- cury above that in trough.	Barom.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
After explosion* (moist)	281·5	19°·1	269·8 ,,	753·7 ,,	123·00
After absorption of CO <sub>2</sub> (dry) . . .	186·1	19°·8	367·3 ,,	753·2 ,,	66·95
After admission of H (dry) . . . . .	462·3	20°·0	86·5 ,,	752·4 ,,	286·90
After explosion (moist)	240·2	20°·0	311·6 ,,	752·0 ,,	94·70

Owing to the great difficulty of obtaining the tubes for the methyl and chlorine of precisely the same size, and further, as in connecting them together it is impossible to prevent a small quantity of atmospheric air from being included, absolute correctness cannot be

\* The heat developed by the explosion was so great, that a portion of mercury was volatilized and the interior of the eudiometer was partially covered with a black film of the metal. At the same time a large quantity of free chlorine was evolved, which caused the residual gas to assume a deep yellow colour; it was, however, rapidly and perfectly absorbed by the mercury, converting the black film above mentioned into white bichloride of mercury.

According to Bunsen (*Annalen der Chemie*, Bd. 46, S. 33), the hydrogen of combustible gases containing chlorine should not be estimated by explosion with oxygen, since the hydrochloric acid evolved is partially decomposed with the separation of chlorine. If, as the results prove, a complete combustion has taken place in the above analysis, then the cause of this phenomenon unquestionably depends upon the high temperature accompanying the explosion of the gas. The following eudiometrical experiments show how very much the combustibility of hydrochloric acid is augmented by an increase of the heat developed during combustion; in these experiments hydrochloric acid was exploded with a mixture of oxygen and hydrogen, procured from the decomposition of water by voltaic agency, and free oxygen, in different proportions.

## FIRST EXPERIMENT.

	Observed vol.	Temp. C.	Height of mer- cury above that in trough.	Barom.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Oxygen gas (dry) . . .	172·3	21°·2	382·4 <sup>mm</sup>	748·9 <sup>mm</sup>	63·1
After admission of the gases composing water (dry) .	285·5	21°·2	265·9 ,,	748·0 ,,	137·6
After admission of H Cl (dry)	362·2	21°·2	187·4 ,,	746·9 ,,	202·7
After explosion (moist) .	237·7	21°·2	316·5 ,,	746·9 ,,	102·3
After admission of water (moist) . . . . .	170·0	21°·2	367·0 ,, ( + 1·5 <sup>mm</sup> = 21 <sup>mm</sup> pressure of water. )	746·9 ,,	61·2

The explosion by means of the electric spark was in the above instance very slight, and the small quantity of chlorine separated could scarcely be distinguished by the colour it imparted to the gas. In the next experiment, where a smaller volume of

expected in the above analysis. The results, however, furnish data which enable us safely to fix the atomic constitution of the new chlorine compound.

It follows, then, that the mixture consisted of equal volumes of hydrochloric acid gas and of the other product. The explosion of the gas remaining after the absorption of carbonic acid with hydrogen, showed that it contained 2·8 vols. of nitrogen, the conversion of which into nitric acid during the explosion must have reduced the observed volume; the quantity of atmospheric air due to the above amount of nitrogen is 3·5 vols., which being deducted from 32·50, leaves 29·0 vols. of the true combustible gas; this, according to the analysis, consumed 90·5 vols. oxygen, forming with it 56·0 vols. carbonic acid.

Thus it has been shown, that 1 vol. of methyl gas with 1 vol. of chlorine is decomposed into 1 vol. of hydrochloric acid ( $= \frac{1}{2}$  vol. H +  $\frac{1}{2}$  vol. Cl) and into 1 vol. of another gas; the last must therefore evidently consist of  $\frac{1}{2}$  vol. chlorine and 1 vol. methyl, minus  $\frac{1}{2}$  vol. hydrogen, and its specific gravity must be 2·226.

hydrochloric acid gas was ignited with a much larger volume of the elements of water and less excess of oxygen than before, the explosion was attended with a much greater development of heat; there was at the same time a sublimation of the mercury and a copious separation of chlorine.

## SECOND EXPERIMENT.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Constituents of water (dry) .	305·4	21°·4	251·2 <sup>mm</sup>	746·8 <sup>mm</sup>	140·4
After admission of O (dry) .	353·0	21°·5	199·8 „	746·2 „	178·8
After admission of H Cl (dry)	405·6	21°·4	146·1 „	745·8 „	225·6
After explosion (moist) .	119·6	21°·5	435·2 „	742·9 „	32·0
After admission of water (moist) . . . . .	111·1	21°·5	419·8 „ (+ 2 <sup>mm</sup> = 26 <sup>mm</sup> ) (pressure of water)	742·9 „	31·3

Although no absolutely exact results could be expected from these experiments, on account of the last reading being performed over water, yet they sufficiently demonstrate the point above alluded to.

By the first experiment, in which 65·1 vols. of hydrochloric acid were burnt with 74·5 vols. of the elements of water and 63·1 vols. of oxygen, only 1·9 vols. of this last disappeared. There were thus only 7·6 out of 65·1 vols. of hydrochloric acid decomposed. In the second experiment, 46·8 vols. of hydrochloric acid were mixed with 140·4 vols. of the constituents of water and 38·4 vols. of oxygen. On the explosion taking place, 7·1 vols. of oxygen disappeared. Out of 46·8 vols. of hydrochloric acid, only 18·4 vols. escaped decomposition. In the first instance, scarcely  $\frac{1}{3}$ ; in the second, above  $\frac{2}{3}$  of the volume of the acid gas was consumed.

1 vol. Carbon vapour . . .	·82922
$2\frac{1}{2}$ vols. Hydrogen . . .	·17270
$\frac{1}{2}$ vol. Chlorine . . .	1·22445
	2·22637
Condensed to 1 vol. =	

This is the composition and state of condensation of chloride of ethyl, 1 vol. of which, according to calculation, requires 3·25 vols of oxygen for complete combustion, and generates 2 vols. of carbonic acid; the above analysis sufficiently coincides with this calculation, 3·15 vols. of oxygen being consumed, and 1·93 vols. of carbonic acid generated by 1 vol. of the combustible gas.

Although this gas agrees closely with chloride of ethyl in its composition, in the state of condensation of its elements, and consequently in its specific gravity, yet it is not the same body, but a compound isomeric with it. For whilst chloride of ethyl becomes liquid at 12° C. and crystallizes at - 18° C., this gas, freed from hydrochloric acid by a ball of phosphate of soda, and from moisture by one of potash, retains its gaseous condition unchanged at the latter temperature. The two bodies also differ, though less decidedly in their relative solubility in water, which takes up an equal volume of chloride of ethyl, but absorbs at a temperature of 19° C. and a pressure of  $\frac{7}{8}$ m, nearly twice its volume of this gas.

It can scarcely be doubted, that this isomerism in a body having the rational composition of chloride of ethyl, is caused by the anomalous grouping of its atoms. It is possible that the new gaseous body is a conjugate compound of one atom of methyl with another atom of the same gas in which 1 eq. of hydrogen is replaced by chlorine  $C_2 H_3 + C_2 \left( \begin{smallmatrix} H_2 \\ Cl \end{smallmatrix} \right)$ . But how far this hypothesis is correct, further investigations must determine.

On the other hand, this gas exhibits several points of agreement with chloride of ethyl; it possesses a similar odour, burns with a green flame, generating hydrochloric acid vapour, and by exposure to sunlight with excess of chlorine, it is transformed like that compound into a substance resembling camphor, which is, without doubt sesquichloride of carbon  $C_2 Cl_3$ . Owing to the want of material, we have not further studied its properties.

#### KYANETHINE.

When 1 atom of methyl is obtained from 1 atom of cyanide of ethyl, the elements  $C_2 H_2 Cy$  remain, and must evidently be contained

in the tenaceous yellow mass, which in the preparation of methyl is left in the place of the potassium.

We have not, however, yet succeeded in ascertaining the combination into which this body, or at least the group  $C_2 H_2$  enters. When the residue is treated with water, a large quantity of cyanide of potassium is dissolved, and a white insoluble substance remains, which, as the following observations show, has no connection with the compound sought for.

This insoluble substance, which on account of its remarkable relations to cyanide of ethyl, had the first claim upon our attention, was freed from cyanide of potassium and cyanide of ethyl by washing with cold water, and then dissolved in boiling water. On cooling, small crystalline scales, of a pearl-like lustre were deposited; these dried at  $100^\circ C.$  exhibited the following composition.

- I. ·3557 grms. burnt with oxide of copper\* gave ·856 grms. carbonic acid, and ·300 grms. water.  
 II. ·2055 grms. gave ·495 grms. carbonic acid, and ·171 grms. water.

The determination of the nitrogen was effected, according to Bunsen's method, by igniting an indefinite quantity of the substance with oxide of copper and metallic copper in a hermetically sealed glass tube, previously freed from nitrogen and exhausted.

By this process the following data were obtained :

	Observed vol.	Temp. C.	Height of mer- cury above that in trough.	Barom.	Corrected vol. at $0^\circ C.$ and $1^m$ pressure.
Volume of mixed gases					
$CO_2 + N$ (moist) .	185·1	$20^\circ 9$	370·4mm	753·9mm	62·81
After absorption of					
$CO_2$ (dry) . . .	40·8	$20^\circ 8$	517·4 ,,	755·8 ,,	9·04

Hence it follows, that the proportion of carbonic acid to nitrogen = 6 : 1·009.

Per centage composition : (C = 75 ; H = 12·5).

\* In this and the following analysis, after the termination of the combustion, a stream of oxygen was led over the reduced copper; this gas was furnished by heating a small quantity of fused perchlorate of potash placed at the posterior end of the combustion tube and separated from the oxide of copper by about  $\frac{3}{4}$  of an inch of recently ignited asbestos. Perchlorate of potash answers the purpose better than the chlorate, since the evolution of gas from the former is more regular, and less rapid, on the first application of heat. The potash apparatus was also furnished with a small tube containing a stick of fused potash, to absorb the aqueous vapour imbibed by the bubbles of gas in their passage through the potash ley; both were weighed together. Lastly, the

	Calculated.	Experiment.	
C <sub>6</sub> . . .	65.5	65.6	65.6
H <sub>5</sub> . . .	9.1	9.3	9.2
N . . .	25.4	25.5	25.5
	100.0	100.4	100.3

The compound analyzed has, therefore, the composition of cyanide of ethyl; it is, however, far from participating in any of its qualities. It dissolves in all acids with ease, forming with them in some cases beautiful crystallizable salts, which are soluble in water and alcohol; from these it is precipitated unchanged by potash, ammonia, and the alkaline carbonates; in short, it is an organic base. We propose to call it kyanethine, on account of its derivation from cyanide of ethyl. The formula of cyanide of ethyl does not, however, express the atomic constitution of kyanethine, but must be trebled in order to do so, as is proved by the analyses of its salts. One atom of the base, therefore, consists of C<sub>18</sub> H<sub>15</sub> N<sub>3</sub>.

Kyanethine is, when pure, a white volatile substance, inodorous, and almost tasteless; it melts at about 190° C. (376° F.), and begins to boil at about 280° C. (536° F.), undergoing at the same time partial decomposition.

It is soluble in alcohol in almost all proportions; it is very slightly soluble in cold, but tolerably so in hot water; from the latter it separates, as was stated, by slow cooling in small, shining, crystalline scales. The solution in warm water shows a slight but distinct alkaline reaction. This base can be boiled with potash ley, without suffering the decomposition of cyanide of ethyl or undergoing any other change. When the ley containing it is evaporated to dryness, and the mass fused in a silver crucible, the greater part of the base sublimes without the separation of carbon.

Most of the salts of kyanethine have a bitter astringent taste, and are all soluble in alcohol and water.

Nitrate of kyanethine, C<sub>18</sub> H<sub>15</sub> N<sub>3</sub> + HO NO<sub>5</sub>, prepared by digest-

potash apparatus was detached from the chloride of calcium tube, and the oxygen which might possibly be still retained in the former, was displaced by atmospheric air.

Many compounds, rich in carbon, are not perfectly burnt by oxide of copper without the assistance of oxygen. Benzole, naphthaline, and similar volatile bodies give on an average  $\frac{1}{2}$  per cent. carbon too little; but by the simultaneous use of oxygen, an extreme degree of accuracy is attained. The loss appears to be occasioned by the formation of a carburet of copper.

ing the base in dilute nitric acid, crystallizes by spontaneous evaporation in large colourless prisms; after re-crystallization it exhibits a perfectly neutral reaction. The analysis of this salt dried at 100° C. gave the following numbers :

·401 grms. gave ·699 grms. carbonic acid and ·256 grms. water.

Two determinations of nitrogen, according to Bunsen's method, yielded the following results :

## I.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Volume of mixed gases					
CO <sub>2</sub> + N (moist) . . .	132·0	21°·2	134·6mm	746·9mm	72·74
After absorption of					
CO <sub>2</sub> (dry) . . .	28·2	21°·2	236·8 ,,	746·9 ,,	13·30

## II.

Volume of mixed gases					
(moist) . . . . .	134·7	18°·4	130·0 ,,	745·3 ,,	75·76
After absorption of					
CO <sub>2</sub> (dry) . . . . .	28·5	17°·9	235·0 ,,	750·9 ,,	13·80

Hence the proportion of carbonic acid to nitrogen :

I. 4·5 : 1·007

II. 4·5 : 1·002

Composition in 100 parts :

	Calculated.	Experiment.
C <sub>18</sub> . . . . .	47·4	47·5
H <sub>16</sub> . . . . .	7·0	7·0
N <sub>4</sub> . . . . .	24·5	24·6
O <sub>6</sub> . . . . .	21·1	
	100·0	

Sulphate and chloride of kyanethine are very soluble in water, and uncrystallizable. The acetate loses acetic acid by evaporation even in vacuo, and is changed into an insoluble basic compound. The oxalate, obtained by neutralizing oxalic acid with an excess of the base, gives large well-formed prismatic crystals, by spontaneous evaporation of the filtered liquor. The chlorocarbohyposulphate of kyanethine also shows a strong disposition to crystallize.

Like ammonia and the organic bases, chloride of kyanethine forms with chloride of platinum a double salt, of remarkable beauty, which separates in the form of a yellowish red crystalline precipitate when concentrated solutions of both salts are mixed. It is soluble in alcohol as well as in a mixture of alcohol and ether; in water it is difficultly soluble, and crystallizes by the slow evaporation of its watery solution in large ruby-red octohedrons. The alcoholic solution undergoes decomposition by boiling, and ammonio-chloride of platinum is subsequently formed.

The above precipitate, washed several times with water, pressed between blotting-paper, and dried at 100° C., gave on analysis the following numbers :

0.797 grm. moistened with alcohol, inflamed and afterwards strongly ignited, left 0.209 grm. platinum.

0.427 grm. gave 0.456 grm. carbonic acid and 0.169 grm. water.

Composition :  $\text{Pt Cl}_2 + \text{C}_{18} \text{H}_{15} \text{N}_3, \text{H Cl}$ .

	Calculated.	Found.
$\text{C}_{18}$ . . .	29.1	29.1
$\text{H}_{16}$ . . .	4.3	4.4
$\text{N}_3$ . . .	11.4	
$\text{Cl}_3$ . . .	28.7	
Pt . . .	26.5	26.2
	100.0	

We have in vain endeavoured to discover the conditions which determine this remarkable transformation of the elements of cyanide of ethyl into kyanethine. All attempts to form this substance by other methods than the one already mentioned, have proved fruitless. Even when we altered the process only so far that, instead of allowing the cyanide of ethyl to fall in drops upon the potassium, the latter was thrown into that liquid, methyl gas was, it is true, formed, but scarcely a particle of this base. Cyanide of ethyl underwent just as little change when it was heated to 240° C. (464° F.) in a hermetically sealed glass tube, either alone or in conjunction with anhydrous cyanide of potassium. Lastly, the quantity of the base obtained by the above method was very small ; it amounted to only a trifling per centage of the cyanide of ethyl used.

It is difficult to form an opinion regarding the rational composition of kyanethine. But we may assume the hypothesis which has already been applied to aniline, and to which we have nothing to add,

viz., that it is like this substance, a conjugate amide, in which 2 eqs. of hydrogen are replaced by 2 eqs. of cyanogen  $C_{14} \left( \begin{smallmatrix} H_{13} \\ Cy_2 \end{smallmatrix} \right) + NH_2$ . The truth or fallacy of this view must be decided by further researches.

The above investigation was conducted in the laboratory of Prof. Bunsen, the use of which he, in the most friendly manner placed at our disposal during our stay in Marburg. We gladly avail ourselves of the present opportunity of expressing our warmest thanks for his uniform kindness towards us.