of escape being possible. The upward force must necessarily have been slight, as it was insufficient to raise the bar lying on surface and weighing about 5 lbs. This view the author finds borne out by the manager of the foundry where this experiment was made, as he states that he has noticed the same action at times, but only *where air was present*, such as when draughts of air played over the surface at casting. The presence of air or gas also accounts for movements which have at times been observed to take place in the hemispherical moulds used for casting balls, as the author has been informed by moulders accustomed to this work, that sufficient opening of the two halves of the mould is noticeable to show the hot solid metal within, but that this is due to air or gases entangled in the casting.

(10) From some experiments made by the author with other metals, it appears that when the solid pieces float that their bulk is also increased as in the case of cast iron. Thus, when a piece of gun metal was placed in a crucible of molten gun metal it sank, but shortly reappeared; on being taken out it was found that it had increased in length by $\frac{1}{50}$ th part, whilst the shrinkage allowed for such an alloy would be even rather less than that.

Phosphor bronze also floated in molten phosphor bronze after sinking, behaving like the cast iron and gun metal. Type metal gave doubtful results with light pieces, heavy pieces going to the bottom of ladle and remaining there till melted. Lead, when tried also with large pieces, sank to the bottom, where the piece could be felt remaining there till melted; and incidentally it may be mentioned that when very large pieces of cast iron are used these remain so long at bottom of ladle as to have their ends melted off before rising to surface.

5. On an Oxycyanide, and a New Oxide, of Bismuth. By M. M. Pattison Muir, M.A., Fellow, and Prælector in Chemistry, of Gonville and Caius College, Cambridge.

1. Boedeker (*Annalen*, 123, 61), by the action of potassium cyanide on bismuth nitrate, obtained a reddish-brown salt, to which he assigned the formula $\text{Bi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. In an examination of the oxides

of bismuth in conjunction with Hoffmeister and Robbs (*Chem. Soc. Jour.*, 1881; *Proc.*, p. 21), I had occasion to prepare Boedeker's salt; a slight study of its properties proved it to be a compound of no little interest. When a concentrated aqueous solution of potassium cyanide is added to a solution of metallic bismuth in excess of nitric acid, and the mixture is boiled, a brownish-red solid and a more or less dark red liquid are obtained, and quantities of hydrocyanic acid are evolved. When the excess of nitric acid is nearly neutralised by potash before addition of potassium cyanide, the colour of the solid is a much lighter brown, and the supernatant liquid is nearly or quite colourless. When a large excess of nitric acid is present, no solid, but only a red liquid, is produced. After very many trials, this method of preparation was abandoned, and potassium cyanide solution was added to a solution of crystallised bismuth nitrate, in the minimum quantity of dilute nitric acid: much more constant results were thus obtained. Various preparations of the puce-coloured salt were made, using varying quantities of bismuth nitrate and potassium cyanide; in each case the puce-coloured precipitate was washed with boiling water until the washings were free from cyanogen and from potassium; in one or two instances the precipitate was also boiled with extremely dilute sulphuric acid (about 1:300), and again washed free from acid. The temperatures at which the various preparations were dried are noted in the following table.

Inasmuch as Boedeker states that he failed to obtain evidence of cyanogen in the new salt described by him, and as an examination for cyanogen by the ordinary tests confirmed this result, I was convinced that the salt must be an oxide of bismuth.

Bismuth was determined by heating over a Bunsen lamp, whereby the salt was decomposed with production of bismuthous oxide; the loss of weight (of the dehydrated salt) gave, as I supposed, the amount of oxygen in excess of that required to form Bi_2O_3 . Water was determined by heating in a current of dry air, and determining the increase of weight of a calcium chloride tube attached to the apparatus in which the salt was heated.

2. The following table contains the analytical results obtained:—

No.	Mode of Preparation.	Temp. at which Salt was Dried.	Percentages of Bismuth Found.	Mean Percentage of Bismuth.	Mean Percentage of Loss on Ignition, regarded as Oxygen.
I.	By addition of KCN to Bi in excess of HNO ₃ ,* . . . }	150°	78·53; 82·21	80·37	19·63
II.	By addition of KCN to Bi ₃ NO ₃ in nitric acid (exact proportions not noted), . . . }	150°	79·33; 80·29	79·81	20·19
III.	Do. do.† KCN : Bi ₃ NO ₃ = 1:1, . . . }	150°	81·04	81·04	18·96
IV.	Do. do. KCN : Bi ₃ NO ₃ = 3:1, . . . }	150°	{ 79·93; 79·88; 78·97; 80·49. }	79·82	20·18
V.	Do. do. KCN : Bi ₃ NO ₃ = 3·5 : 1, . . . }	100°	{ 78·07; 78·09; 78·62; 78·86; water in this salt=1·5 per cent. }	79·72‡	20·28
VI.	Same salt as No. V. } dried at . . . }	150°	79·08; 79·31	79·19	20·81
VII.	Do. do. KCN : Bi ₃ NO ₃ = 2·5 : 1, . . . }	100°	{ 75·07; 75·69; 75·85; water in this salt = 2·1 per cent. }	77·15‡	22·85
VIII.	Do. do. KCN : Bi ₃ NO ₃ = 2·5 : 1, . . . }	150°	{ 76·39; 76·69; 77·31; 77·80; 77·83 }	77·20	22·80
IX.	Addition of KCN (excess) to Bi ₂ O ₃ in slight excess of HCl, . . . }	150°	79·45	79·45	20·55

	Mean of Means.	Calculated for Bi ₂ O ₇ .
Bismuth	= 78·86	78·95
Oxygen	= 21·38	21·05
Oxygen in excess over Bi ₂ O ₃ =	12·40	12·03
Bi ₂ O ₃ : excess of O . .	= 117·16·2	117·16

3. These results seemed altogether to confirm the view that the salt to which Boedeker had given the formula Bi₂O₅.2H₂O contained,

* Many other preparations made by this method were analysed, but the results varied considerably ; the above is given only as a specimen.
† This salt was considerably lighter in colour than the others.
‡ Calculated on the *dry* salt.

when dried at 150°, bismuth and oxygen only, and these in the atomic proportion Bi_2O_7 .

But I subsequently found that the supposed oxide, when heated in a closed tube, evolved a little ammonia. I also proved the presence of nitrogen by the sodium test. Determinations were therefore made of nitrogen and of carbon, the former by burning with soda lime, the latter by burning with copper oxide.

1. 0.7075 grm. gave 0.0285 grm. N. = 4.03 per cent. = 7.49 per cent. cyanogen.
2. 0.867 „ „ 0.0365 „ N. = 4.20 „ = 7.80 „ „
3. 1.113 „ „ 0.046 „ N. = 4.14 „ = 7.69 „ „
4. 0.8275 „ „ 0.1275 „ CO_2 = 0.0348 grm. C = 0.0754 grm. CN = 9.10 per cent. cyanogen.
5. 1.2435 „ „ 0.145 „ CO_2 = 0.040 „ C = 0.0866 „ CN = 7.00 „ „

Determinations of water made simultaneously with those of carbon gave 4.60 and 4.75 per cent.

Hence mean percentage of cyanogen = 7.81

Do. do. of water = 4.67

The preparation used in these analyses contained 77.25 per cent. bismuth. The mean percentage of bismuth, calculated from analyses of those preparations which were dried at 120° and contained a little water, is 76.80 per cent.; taking this number and 4.67 as representing the amount of water in the salt, and determining oxygen by difference, the results agree very well with the complex formula $4\text{Bi}(\text{CN})_3 \cdot 5\text{Bi}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$. The analytical numbers agree fairly well with the formula $2\text{Bi}(\text{CN})_5 \cdot 5\text{Bi}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, which requires bismuth 75.40, cyanogen 7.78, oxygen 11.98, and water 4.85 per cent.

	Found.	Calculated for $4\text{Bi}(\text{CN})_3 \cdot 5\text{Bi}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$.
Bismuth, . . .	76.80	76.72
Cyanogen, . . .	7.81	8.15
Oxygen (by difference),	10.72	10.44
Water, . . .	4.67	4.69
	<hr/> 100.00	<hr/> 100.00

Calculating all the results on the dry salt, numbers are obtained which agree better with the formula $\text{Bi}_7(\text{CN})_6\text{O}_{15}$ than with any other.

	Found.	Calculated.
Bismuth, . . .	78.86	78.78
Cyanogen, . . .	8.14	8.37
Oxygen (by difference),	13.00	12.85
	<hr/> 100.00	<hr/> 100.00

The numbers agree also very well with the formula $2\text{Bi}(\text{CN})_5 \cdot 5\text{Bi}_2\text{O}_3$, which requires bismuth 79.24, cyanogen 8.18, and oxygen 12.58 per cent. Various other formulæ may be found, agreeing more or less closely with the analytical results, but in each the atomic proportion of oxygen to bismuth, in excess of that required to form $\text{Bi}(\text{CN})_3$ or $\text{Bi}(\text{CN})_5$, must be expressed by a formula Bi_2O_x where x is not less than 5; in other words the action of potassium cyanide has been an oxidising action, while at the same time producing a cyanogen compound.

4. Unless a considerable excess of potassium cyanide is added, but little of the new salt is produced. If the liquid be so nearly neutral before adding cyanide that one drop of moderately strong potash solution produces a permanent precipitate, the precipitate produced by the cyanide consists of nearly pure Bi_2O_3 , with small quantities of the new salt. If there be rather more free nitric acid than this, the precipitate produced by the cyanide is rich in an oxide of bismuth to be described in the sequel, viz., Bi_4O_7 (see par. 5).

In one instance one part of potassium cyanide was added to one part of bismuth nitrate, dissolved in the minimum quantity of dilute nitric acid, a portion of the liquid was boiled for three or four minutes, and another portion for twenty-five minutes. The precipitate produced in the latter liquid was darker in colour than that in the former, and contained rather less bismuth; the lighter coloured salt contained 81.59 per cent. bismuth, the darker salt gave bismuth = 80.89 per cent.

When from 2 to 2.5 parts potassium cyanide are used for each part bismuth nitrate in solution, and the liquid is boiled, the precipitate very quickly becomes of a uniform puce-red colour, while the supernatant liquid is reddish-brown. The best results are, I think, obtained with this proportion between cyanide and bismuth nitrate.

When the cyanide solution is added to a cold solution of bismuth nitrate, an almost colourless salt is thrown down, which becomes puce-red on boiling; this colourless salt is perfectly free from cyanogen, and appears to be bismuthous oxide. If, however, anhydrous bismuthous oxide be boiled with potassium cyanide solution,* no change occurs, nor does addition of potash induce any

* This has been confirmed by repeated trials, and by analysis.

reaction. Although the liquid, after addition of the cyanide, is markedly alkaline, nevertheless the presence of free acid in the bismuth solution is necessary; that this acid need not be nitric acid was shown by adding potassium cyanide to solution of bismuthous oxide in slight excess of hydrochloric and sulphuric acids respectively; in each case the puce-red salt was obtained on boiling.

It is, I think, evident, that to ensure production of the new salt, rapid chemical change—partly oxidation, partly formation of bismuth cyanide—must occur; neither bismuthous oxide nor any other salt must be allowed to get permanently produced, the whole system must not settle down into stable equilibrium until it is forced to assume that configuration of which the complex oxy-cyanide is a component part.

5. *Bismuth Oxycyanide*—probably $2\text{Bi}(\text{CN})_5 \cdot 5\text{Bi}_2\text{O}_3$ —when dried at 140° – 150° is a reddish-brown solid, somewhat similar in appearance to lead dioxide, but showing a more decided puce colour than that salt. It begins to undergo change at about 200° , but the loss of weight at that temperature is small; about half a gram of the salt lost 3.50 per cent. at 210° , and 7.50 per cent. at 350° (the oxycyanide in changing to Bi_2O_3 loses about 12 per cent.). When a large quantity of the salt is heated in a crucible, a considerable amount of metallic bismuth is produced; but when quantities of from 0.5 to 1.0 grams are so heated the residue consists only of bismuthous oxide.

The oxycyanide scarcely takes up water when exposed to ordinary or to moist air; thus about half a gram increased only 1.80 per cent. in weight after 144 hours' exposure over water. It does not suffer change when covered with water and exposed to the action of sunshine.

Bismuth oxycyanide is dissolved by hot concentrated nitric or sulphuric acid, with production of dark-red liquids, from which water causes precipitation of red substances containing bismuth, and soluble in hot potash solution. Hydrochloric acid dissolves the oxycyanide more slowly, a portion remaining undissolved even after continued action. When heated with a *slight* excess of potash these liquids yield reddish precipitates, which are mostly soluble in hot concentrated potash solution, and when any of these deep red acid solutions is boiled it is *very slowly* decomposed with ultimate

production of bismuthous nitrate, sulphate, or chloride. When sulphuric acid is employed as solvent, the salt which separates after concentration is probably $\text{BiHSO}_4 \cdot 3\text{H}_2\text{O}$ (47·9 per cent. bismuth was obtained instead of 45·95 per cent. required by this formula). The specific gravity of bismuth oxycyanide at 20° is 4·64 referred to water at the same temperature (mean of 4·67 and 4·61; weighings done in benzene, specific gravity at $20^\circ = 0\cdot8804$).

6. Bismuth oxycyanide is readily acted on by hot, and more slowly by cold, concentrated aqueous potash, with production of a very deep red liquid. So far as I have examined this action, about 75 per cent. of the oxycyanide is invariably converted into the oxide Bi_2O_3 , while 25 per cent. goes into solution. This change appears to be independent of the quantity of potash, provided there be excess, and of the time of action of the hot liquid on the oxycyanide.

When the strongly alkaline red liquid is neutralised, preferably by hydrochloric acid, a reddish-brown flocculent precipitate is formed, which, after washing with hot water, contains the whole of the bismuth originally in solution, but is free from potassium. When the precipitate has been dried at 100° , it appears as a nearly black hard crystalline substance resembling magnetic oxide of iron, and is now only dissolved by long-continued boiling in strong acids, with formation of deep red liquids, which are scarcely decomposed except by evaporation to dryness. This salt is strongly decomposed when heated to redness in air, with production of bismuthous oxide; heated in a limited supply of air a portion remains as metallic bismuth; the salt contains a considerable quantity of water; it is unchanged, otherwise than that it loses water, at 300° . It may be readily dissolved and decomposed by treatment with bromine and aqueous potash.

I have made many analyses of this peculiar substance, but the results show great variations; inasmuch, however, as the preparation of this substance in quantity involves the use of much potassium cyanide, which is an extremely disagreeable reagent to work with, especially when added to hot acid liquids, and the expenditure of a great deal of time, I think it may be well to put on record a synopsis of the results obtained.

No.	Preparation.	Temp. at which Dried.	Percentage of Bismuth.		Total Loss when Heated over Blowpipe. Per cent.	Percentage of Water; determined by Heating in Dry Air with CaCl_2 Tube attached.
			By Preci- pitation as Carbonate.	By Ignition in Air, and weighing Residue as Oxide.		
I.	Made in earlier part of investigation, . . }	150°	23·7; 21·0	24·0	73·4	...
II.	Made at later part of investigation, . . }	300°	25·5; 27·5	...	...	...
III.	Made from same oxy- cyanide as No. II., }	300°	...	{ 7·08; 6·70; 7·17; 7·77 }	{ 92·1; 91·4; 92·0; 91·8 }	{ 18·75; 28·28; 26·10; 31·0; 20·0 }
IV.	Made from same oxy- cyanide as No. II., }	300°	...	...	...	16·9
V.	Made from another preparation of oxy- cyanide, . . . }	300°	...	6·7	...	17·5
VI.	From another prepara- tion of oxycyanide, }	250°	{ Burned with soda lime, gave 36·34 per cent. N. = 67·47 per cent. CN.			
VII.	From another prepara- tion of oxycyanide, }	250°	{ Burned with soda lime, gave 36·32 per cent. N. = 67·45 per cent. CN. Burned with CuO, gave 15·80 per cent. C. = 34·23 per cent. CN.			

From the three last determinations I conclude that the salt probably contains a considerable quantity of nitrogen, in addition to a large percentage of cyanogen. The variations in the quantities of bismuth found are remarkable; to attempt the construction of a formula from these results would be useless.

7. It has been already stated, that under certain conditions (see par. 4) the precipitate formed by the action of aqueous potassium cyanide on bismuth nitrate contains considerable quantities of the oxide Bi_4O_7 ; also that the same oxide is produced by the action of hot concentrated aqueous potash on bismuth oxycyanide; the formation of this oxide in the first of these reactions is almost certainly to be traced to a secondary change proceeding after the production of the oxycyanide.

Various preparations of the new oxide were made; when thoroughly washed with hot water the salt contains no potassium, it is very difficult to remove every trace of cyanogen; after the analyses detailed in the following table had been made, it was

found that the various preparations when mixed contained about 0·25 per cent. cyanogen (mean of three determinations—two of nitrogen, and one of carbon). The salt after drying at 100° is anhydrous. The analytical results are collected in the following table:—

No.	Mode of Preparation.	Temp. at which Salt was Dried.	Percentage of Bismuth Found.	Mean Per- cent- age of Bis- muth.	Mean Per- cent- age of Oxy- gen.	Mean Percentage of Oxygen in excess of that to form Bi_2O_3 .	Propor- tion of Bi_2O_3 : excess of O.
I.	Addition of KCN to Bi in HNO_3 , and boiling precipitate in concentrated KOH, . . . }	100°	88·59; 89·05	88·82	11·16	0·91	117; 1·1
II.	Similar to No. I., but precipitate by KCN boiled with very dilute H_2SO_4 before treatment with KOH, . . . }	100°	88·34; 88·73	88·53	11·47	1·22	117; 1·5
III.	KCN to Bi_3NO_3 in di- lute HNO_3 , and sub- sequent boiling pre- cipitate with KOH }	100°	88·43	88·43	11·57	1·32	117; 1·6
IV.	Nos. I., II., and III. mixed, again boiled with KOH, &c., . }	160°	{88·59; 88·72; 88·81; 88·90;}	88·75	11·25	1·00	117; 1·3

Mean of Means.				Calculated for Bi_4O_7 .	
Bismuth	.	.	=	88·64	88·24
Oxygen	.	.	=	11·36	11·76
Oxygen in excess over Bi_2O_3	=			1·11	1·65
Bi_2O_3 : excess of O	.	.	=	117; 1·4	117; 1·9

The best method of preparing this salt is to boil a solution of bismuth nitrate in the minimum quantity of dilute nitric acid, with three or four times its weight of potassium cyanide dissolved in a little water, to add a considerable excess of potash, and to continue boiling for some time; to pour off the red liquid and boil again with potash as long as the liquid becomes coloured, to wash with hot water till the washings are quite free from alkali, and to dry at about 150°.

This salt is quite unacted on by hot potash.

8. *Bismutho-hypobismuthic oxide* (I think the oxide Bi_4O_7 may be thus named) is a heavy dark grey crystalline salt; the specific gravity varies, according to the method of preparation, from 7·8 to 8·5 (at 20° referred to water at the same temperature, weighings made in benzene), which is higher than that of any other oxide of bismuth. This oxide suffers no loss of weight at 300°; it gives off oxygen at a red heat with production of Bi_2O_3 . It undergoes no change either in ordinary or in moist air, nor is it affected when covered with water and exposed to direct sunlight for some days. Strong hot nitric acid readily dissolves this oxide with formation of a purple-red liquid, which is *slowly* decomposed on evaporation. A solution of the salt in strong hydrochloric acid, which solution is also red-coloured, is more quickly decolorised on boiling; hot concentrated sulphuric acid partly dissolves this oxide, forming a brown-red liquid, and partly converts it into an almost colourless salt, which, after being washed free from acid, appeared to be $(\text{BiO})_2\text{SO}_4\cdot\text{H}_2\text{O}$ (Bi found = 75·0 per cent.; calculated = 74·21 per cent.). The sulphuric acid solution, on evaporation, yielded colourless crystals which, after drying on a porous tile, contained about 56 per cent. of bismuth ($\text{Bi}_2\cdot 3\text{SO}_4$ requires 59·32 per cent.). I think it very probable that the green oxide of bismuth described by Arppe, (*Pogg.* 64, 237) as produced by the action of boiling nitric acid on (so-called) bismuthic acid, consisted of Bi_4O_7 containing a little undecomposed Bi_2O_5 .

6. Mathematical Note. By Mr. T. B. Sprague.

7. On the manner in which Silicon, Phosphorus, Manganese, and other elements exert their influence upon Steel.
By R. Sydney Marsden, D.Sc., F.R.S.E., F.C.S., &c.

(*Abstract*).

This paper is a continuation of the author's previous paper on "The state of carbon in iron and steel, a new hypothesis of the hardening of steel" (read on the 19th December 1881, see p. 368), and is an attempt to give an explanation in accordance with the