

NOTES ON THE OCCURRENCE AND ESTIMATION OF
NITROGEN IN MAGNESIUM.

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IT is well known that magnesium very readily forms a nitride, $Mg_3 N_2$, when heated in contact with nitrogen or ammonia. This is a greenish-yellow amorphous substance, which, when heated in dry Oxygen, is converted with incandescence into magnesia. Advantage is taken of this formation of nitride in the separation of argon from atmospheric air.

Deville and Caron, when preparing magnesium, observed that the distilled metal sometimes appeared covered with small, transparent needles, which decomposed in moist air with formation of ammonia and magnesia, and, therefore, contained a nitride of magnesium.

The following experimental work was undertaken by the author to ascertain whether nitrogen was occluded or combined with magnesium in the production of the commercial metal.

Mr. J. B. Kirkland, Demonstrator of Chemistry at the Melbourne University (Proceedings Australasian Association for the Advancement of Science, 1893), some years ago made some experiments in which magnesium was volatilised at a dull, red heat in a glass vessel of hydrogen. The glass in contact with the magnesium, and some distance away, was attacked owing to the more powerful affinity of magnesium for oxygen ; a brown film of silicon, reduced from the silica of the glass being left. This is due, in the author's opinion, to the volatilisation of the magnesium in hydrogen, but Mr. Kirkland considers that he offers a more plausible explanation in that the magnesium may form a volatile hydride readily decomposable.

Mr. Kirkland further noticed that if a coil of magnesium ribbon be taken and gently squeezed in a vice, or between the fingers, the metal emits a strong odour—reminding one of phosphine,—yet the metal, before pressure, has no smell. This suggested the possibility of phosphorus or, preferably, nitrogen being present in the magnesium.

PREPARATION OF COMMERCIAL MAGNESIUM.

Magnesium is prepared generally by fusing together the double chloride of potassium and magnesium, flour spar and metallic sodium, and purified by distillation out of contact with air—the air being replaced by hydrogen or coal gas. The impurities in the crude metal, according to Roscoe and Schorlemmer, are carbon silicon, and nitrogen.

The magnesium was fitted in a lathe, and some filings were turned. During the operation, a strong smell, resembling ammonia, was noticed. This pointed to the existence of nitrogen in the metal; for, if not present, the only way for the ammonia to form would be from the action of nitrogen of the air on aqueous vapour caused by heat from the friction of the tool on the magnesium. If this were the case, a faint smell of ammonia ought to be noticed when iron or steel is being turned.

To see whether any phosphorus was present in the metal, about five grains of the latter was dissolved in dilute hydrochloric acid, and tested for by means of nitric acid and ammonium molybdate. No yellow precipitate was seen on warming at 60° C. for an hour, nor on standing overnight. So it was concluded that no appreciable amount of phosphorus was present.

Some of the filings were then taken and about three grains were placed in a small flask, and covered with a strong solution of caustic potash. This was distilled into a small beaker containing two cubic centimetres of Nessler's solution in about 100 C.C. of water, care being taken that the solution did not boil furiously, so that the contents of the distilling flask did not reach the distillate, except as gas or steam.

A similar experiment was made on the same amount of caustic potash solution. The results were ÷ In the first experiment, after two minutes, a large, brown precipitate formed in the beaker. In the second, a faint yellow precipitate only formed. In both experiments, distilled water was used, and any dissolved gases were expelled by boiling.

Still the Nessler reagent showed that there was some nitrogen in the water, or in the caustic potash used. The precipitate from the distillation of the caustic potash with the magnesium was so excessive in comparison to the first, that it was concluded that nitrogen was present, either as nitride or occluded nitrogen. Care was taken that the apparatus was perfectly clean.

The Nessler reagent employed was similar to that used by Wanklyn in his Water Analysis.

METHODS PROPOSED FOR THE ESTIMATION OF THE NITROGEN.

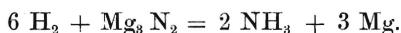
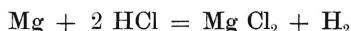
Since the precipitate obtained with the Nessler's solution was large, it was impossible to use the solution in the way it is used for water analysis, where free and albulinoid ammonia are estimated in exceedingly small quantities.

Three or four methods were proposed.

I propose to enumerate these, state results obtained, and criticise them :—

(1). Watt, in his dictionary, says that nitrogen present as magnesium nitride is converted into an ammonium salt on dissolving in dilute acids ; either hydrochloride acid or sulphuric acid.

In this method, magnesium was dissolved slowly in dilute acid, the hydrogen evolved converting all the nitrogen as nitride into ammonium chloride ; then it was distilled, after adding excess of caustic potash, the ammonia which is evolved passing through a Liebig condenser into standard acid. The latter being liberated with equivalent alkali solution, as in Kjeldahl's method for determining nitrogen in manures and in other compounds.



Normal solutions of sodium hydroxide and sulphuric acid were prepared.

1 C.c. of normal acid neutralised corresponds to .014 grammes of Nitrogen. Solid Mg. was placed in a flask, dilute acid poured in, and the hydrogen evolved was allowed to escape very slowly through an indiarubber valve.

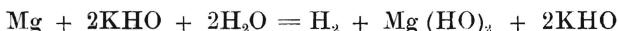
Weight Solid Magnesium.	Amount Acid Neutralised.	Corresponding Amount of Nitrogen.	Nitrogen Percentage.	Mean.
1.3166 grns. 0.7956 ,,	0.08 c.c. 0.06 ,,	.00112 grns. .00084 ,,	0.085 % 0.106 %	.096 % —

(2.) Magnesium filings were distilled with strong pure caustic potsah into standard acid. In turning the magnesium to prepare the filings, a faint smell of ammonia was noticed, as previously observed by others, and also a suspicion of phosphine.

In this process the flask was connected tightly to a Liebig condenser, with standard acid at the end, as in Kjeldahl's method.

The caustic potash was of strength 2.13 KHO : 1H₂O. this in the last two experiments was made more dilute, viz. : (1 KHO : 1 H₂O).

The magnesium decomposed the caustic potash with liberation of hydrogen, the latter combined with nitrogen to form ammonia.



RESULTS.

No.	Magnesium taken.	Amount Acid Neutralised.	Corresponding Weight of Nitrogen.	Nitrogen Percentage.	Remarks.
1	2.0027 grns.	{ KHO used too concentrated ; sudden evolution of gas.
2	1.1727 ,,	6.70 c.c.	0.0938 grns.	8.0 %	{ KHO used too concentrated ; sudden evolution of gas.
3	1.0000 ,,	0.41 c.c.	0.00574 ,,	0.574 %	Experiment successful.
4	1.0000 ,,	0.44 c.c.	0.00616 ,,	0.616 %	Do. do.

In connection with the first two experiments some curious phenomena were observed. On boiling the strong potash solution with the magnesium, the potash was decomposed with gradual liberation of hydrogen ; but as there was no boiling apparatus to cause steam to pass through, the solution became very concentrated and there was little steam coming off to collect the ammonia. On taking away the flame, the liquid began to solidify and there was a sudden interaction and a violent evolution of gas, accompanied by a slight incandescence in the flask. This final rush of gas spoilt the determination.

Some difficulties now presented themselves ; viz. :—If a weaker solution of potash were used, it would not be decomposed quickly enough by the magnesium, and further as distillation proceeds the solution will become concentrated, and an occurrence similar to the above will very probably happen. So in the next experiment—No. 2 ; a flask from which steam was passed through the potash solution (of the same strength) was connected. This was thought advisable as it would prevent bumping and concentration of the solution, and would help the evolution and condensation of the ammonia.

This experiment worked well till nearly all the magnesium has been transformed into magnesium hydroxide, when there was a sudden rush of gas as before ; and the solution spouted up into the tube connected with the inner tube of the Liebig condenser, and some potash was afterwards detected in the normal sulphuric acid.

In the third and fourth experiments potash solution (1 : 1) was used, and steam was passed through as in No. 2. The experiments lasted much longer than the two previous ones, but otherwise they were considered successful.

In connection with the incandescence seen in No. 1, I performed the following experiment :—Some magnesium filings were placed in a piece of hard combustion tubing in closed end and a piece of solid potash was placed above it, a gentle flame was allowed to play on the tube just below the potash, and this as it melted, ran on to the magnesium filings. The KHO was suddenly decomposed with incandescence. I have not been able to find any mention of this incandescence in any books available.

(3). Combustion method, or Dumas, absolute method for nitrogen. This is used for the estimation of nitrogen in steel.

In this method, magnesium filings and copper oxide are mixed and placed in a hard piece of combustion tubing, one end of which is closed and filled with dried acid sodium carbonate to drive out the air by the carbon dioxide formed from its decomposition. A delivery tube is fitted at the other end into a trough of mercury. The end of the delivery tube fits into the lower end of measuring tube filled with strong potash solution inverted over mercury.

The acid carbonate is heated gently to drive out all the air, and when the gas that comes over is seen to be absorbed by the KHO, the combustion is begun. Nitrogen is evolved, collected, and measured under normal conditions. This is in reality Dumas' method for nitrogen in organic substances.

RESULTS.

No.	Amount Filings Taken.	Volume Nitrōgen Measured.	Temperature.	Barometer Pressure.	Percentage Nitrogen.	Remarks.
1	1·6100 gns.	6·4	24·2° c.	755·6 min.	0·443 %	—
2	1·0000 ,,	3·77	21·0° c.	756· ,,	0·427 %	{ Co ₂ passed from a generator.

In the first method, it will be seen that the results are low, and this is explained, probably, by the fact, that is, the nitrogen present in the magnesium does not all form an ammonium salt when dissolved in dilute acids? If, as Watt says, nitrogen as nitride is converted into ammonia when dissolved in dilute acids, it may be inferred that the nitrogen is not present as nitride.

In the second and third methods, it was necessary to prepare filings from the metal, and as there was a great probability of the ammonia-like odour being derived from the metal; this may have constituted a loss.

The results obtained by the successful experiments in No. 2 method indicate (in the author's opinion) a fair estimate of the amount of nitrogen present. The results in No. 3 are lower, and this may be due to the fact that in combustion of the magnesium filings it was impossible to get rid of the last trace of nitrogen.