

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XIII.—*On Aluminum Nitride, and the Action of Metallic Aluminum upon Sodium Carbonate at High Temperatures.*

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WISHING to try whether aluminum can be made to take up carbon as iron does in the production of steel, I proposed to myself to heat very strongly a mixture of metallic aluminum (in excess) and an alkaline carbonate; it having been stated\* that from these materials free carbon and an alkaline aluminate are produced. The result was negative so far as the formation of any well defined aluminum carbide was concerned, very little carbon apparently being taken up by the surplus metal, and that little mostly, if not altogether, in a state of mere admixture, and producing no marked effect on the physical properties of the metal. Incidentally, however, certain other results were obtained which are worth recording.

In the first place, although the reaction seems to begin as above stated, it goes further, and at a very high temperature the sodium is completely reduced, and volatilised so completely that the residue from the interior of the crucible, if examined with due care to avoid dust, handling, &c., actually fails to afford more than the faintest spectroscopic indication of the presence of the alkaline metal. At first the arrangement used was that of weighed pieces of aluminum ingot, of 10 or 15 grams each, imbedded in dry sodium carbonate, or aluminum filings mixed with the carbonate, contained in a crucible of Bunsen's hard carbon with a cover of the same, the whole placed in an outer plumbago crucible of good quality with plumbago cover, the inner crucible being enclosed on all sides by a thick layer of well-rammed lamp-black. A wind furnace of strong draught was used, with the hard carbon deposit from coal-gas retorts as the fuel. This material, whose employment was suggested by Violette,† when broken into pieces the size of a small egg, affords an extremely high temperature, the draught through grate and fuel

\* Ch. and A. Tissier, *Comptes rendus de l'Académie des Sciences*, 29 Déc., 1856, p. 1187, as quoted by Ed. Uhlenhuth, *Die Darstellung des Aluminiums*, u.s.w. (The abstract in the *Comptes rendus* does not give all the details quoted.)

† *Comptes rendus de l'Académie des Sciences*, 28 Oct., 1872, p. 1028. I obtained a supply of 3 or 4 tons of this retort carbon from the Richmond gas works.

remaining unimpeded by ash or clinker, since the amount of mineral matter\* present is very small and is separated during combustion in such a light, finely-divided state, that nearly all of it goes up the chimney. The fire was kept up for four or five hours with full intensity, and 24 hours afterwards the crucible on being taken out was too hot to be easily handled. The plumbago crucible was in great measure burned away and melted down upon the fire-brick used as a support, but was nowhere entirely pierced. The lamp-black was intact. The sodium disappearing from the residue, much of the aluminum was found oxidised, but as the reduction of the former metal might be attributed to the carbon of the crucible, while the oxidation of the latter might be due to carbon monoxide reaching it, the experiment was varied by enclosing the alkaline carbonate and aluminum in a *lime* crucible (with cover of the same), this being placed inside that of hard carbon, and the latter packed with lamp-black into a plumbago pot. The result was the same, the sodium disappearing completely, while an amount of aluminum somewhat more than equivalent to the oxygen of the carbonate used was found converted into alumina. The explanation of this excess, namely, the action of the metal upon carbon monoxide, was afterwards examined.

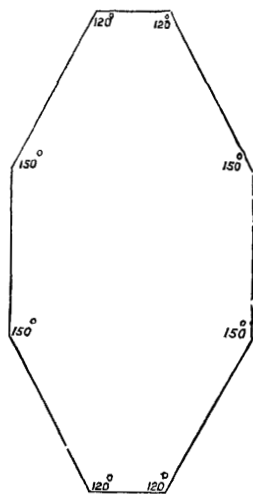
Beside a fused regulus of surplus metallic aluminum, the residue found in the crucible consisted in each case of a dark-grey, nearly black mass, sintered together and porous, the cavities of which were lined with lustrous little crystals of colourless alumina, hard enough to scratch topaz and chrysoberyl when rubbed on with the end of a rod of block tin.

These crystals were sometimes grouped, but for the most part independent hexagonal scales, occasionally thin enough to exhibit brilliant interference colours when examined with the microscope.

They were generally shortened in the direction of one lateral axis of the hexagonal prism, the two angles at whose extremities were replaced, thus giving the projection as figured; but several modifications were observed. A few thicker crystals were met with, showing lateral faces, both rhombohedral and prismatic.

The largest scales measured  $\cdot 510$  milli-

\* The amount of ash and its composition have been examined by one of the students in the University of Virginia Laboratory, and the results will soon be published.



metre across on the major diameter, but most of them did not exceed  $\cdot 025$  mm.

Carbon was found in the residue in three different forms—viz. :

1. Much the larger part was black, opaque, pulverulent, altogether amorphous, and without lustre. Particles of this were sometimes caught in the little alumina crystals, and more or less symmetrically distributed in them.

2. In cavities of the crucible residue a few delicate locks of fine threads were found, appearing under the microscope as long, slender filaments with even surface, black, opaque, and lustrous, often singularly contorted. Some of these were as much as 6 or 7 mm. long, with a diameter of about  $\cdot 013$  mm. They burned completely away in oxygen, producing  $\text{CO}_2$ .

3. Other threads were occasionally found of less length and double or treble diameter, having the same general appearance under the microscope, except that the surface was mammillated, forming a succession of little knobs or protuberances. These often penetrated the crystalline scales of alumina at right angles to the principal surface, several of the little crystals occurring spitted upon the same carbon thread. The carbon left a scarcely visible trace of ash on combustion in oxygen.

These capillary forms of carbon are probably identical with those observed by Gay-Lussac\* as deposited in porcelain furnaces with bad draught, and by Colquhoun and Braylay\* as produced in the manufacture of steel by cementation in an atmosphere of coal-gas.

To determine whether carbon monoxide is decomposed by aluminum at high temperatures, a lump of the metal was exposed to the full heat of the furnace for several hours, in one instance in an otherwise empty hard carbon crucible, in a second experiment imbedded in loose, porous lime filling a similar crucible; in both cases lamp-black well rammed on the outside to a thickness of three-quarters of an inch ensured any carbon dioxide of the furnace atmosphere being reduced to monoxide in passing through. The aluminum was found covered with a hard, mammillated crust of carbon, like that from gas-retorts,  $\cdot 2$  to  $\cdot 3$  mm. thick, not easily detachable, and fully as difficult to burn in oxygen as diamond. The amount of carbon thus deposited was determined, and found to be far less than that obtained under the same conditions—quantity of materials, surface exposed, temperature, time, &c.—save that the metal was surrounded by sodium carbonate; leaving no doubt of the reduction of the latter by aluminum.

On the outside surface of the aluminum regulus obtained in all the above experiments, and projecting from the surface of cavities therein,

\* Gmelin's *Handbook of Chemistry* (Cav. Soc. transl.), vol. ii, p. 84, quoting *Ann. Chim. Phys.*, vol. iv, p. 67, and *Ann. Phil.*, vol. xxviii, 1 and 192, &c.

some little crystalline particles of yellow colour were seen, and these were brought to light in large number, along with little yellow amorphous crusts, on dissolving the metal in well diluted hydrochloric acid. On examination, this yellow substance turned out to be aluminum nitride, a compound which has not, I believe, hitherto been produced and described. As most of it was found after solution of the metal mixed with a much larger quantity of alumina and carbon, it proved to be a matter of great difficulty to obtain enough of it in a reasonably pure state for analysis.

The nitride is of pale-yellow colour when amorphous, bright honey-yellow and translucent when crystallised. The crystals, though beautifully sharp and lustrous, were very minute—the largest not more than .2 mm. in diameter—and so grouped together as to make it almost impossible to get such projections under the microscope as would permit plane angles to be measured. The general aspect was that of short rhombic prisms with dihedral summits, the end faces inclined on the lateral edges at angles not far from  $120^{\circ}$ .

The little particles were brittle, and not hard enough to scratch glass. Enough could not be collected free from foreign matter to determine the specific gravity. On exposure to damp air at common temperatures, the crystalline nitride gradually becomes sulphur-yellow and opaque, and in the course of a week or two crumbles down into white, pulverulent alumina, giving off ammonia. The amorphous nitride undergoes the same change, but in less time. Water, hot or cold, seems to have no immediate effect. Acids and caustic alkalis in solution attack it, rapidly if concentrated, slowly if dilute—an ammonium salt or free ammonia being produced, and the aluminum dissolved at the same time. When it is fused with potassium or sodium hydrate, ammonia is readily given off, and an alkaline aluminate formed. Heated alone in the air, the nitride slowly changes to dingy-grey, and is converted into alumina, but after two hours' roasting at a red-heat the residue still gave off ammonia on fusion with caustic alkali. Treatment with chlorine-gas, and with sodium thiosulphate, both failed to give any evidence of the presence of a cyanide.

Selecting the cleanest portions of aluminum regulus, dissolving out most of the metal with very dilute hydrochloric acid, but stopping the action before the steady evolution of hydrogen had ceased, and then carefully picking out under a lens the little crystalline grains of nitride, I succeeded with much trouble in collecting but .0374 gram (quickly dried at  $120^{\circ}\text{C.}$ ) in a state of nearly perfect purity. This small quantity was fused at a gentle heat with sodium hydrate in a little silver crucible placed in a tube of hard glass; the ammonia formed was swept out by a current of pure hydrogen, collected in hydrochloric acid, and determined as chloroplatinate. The contents of the crucible,

dissolved out with hydrochloric acid, left a minute residue of hard crystalline alumina, and from the solution the aluminum of the nitride was determined.

The results were—

		Per cent.
Aluminum .....	·0243	65·0
Nitrogen .....	·0115	30·7
Alumina (cryst.) .....	·0008	2·1
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	·0366	97·8

2·132 grams of the *crude* residue from action of dilute hydrochloric acid on the aluminum regulus, taken in fine powder, was boiled with moderately strong solution of sodium hydrate, the ammonia given off collected, the solution cooled, diluted, and filtered, the filtrate acidified and evaporated to dryness to remove a little silica,\* and on re-solution the aluminum (assumed as that of the nitride) determined.

The portion undissolved by sodium hydrate was dried at 120° C., weighed, and strongly heated in oxygen to burn off carbon; it left nothing but crystalline alumina with a little ferric and cupric oxides\* and traces of combined silica.\*

The results were—

		Per cent.
Aluminum (dissolved) .....	·239	11·21
Nitrogen .....	·111	5·21
Dissolved silica .....	·018	·85
Crystalline alumina .....	1·504	70·54
Carbon .....	·249	11·68
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	2·121	99·49

From the above figures we may fairly deduce the formula  $\text{Al}_2\text{N}_2$ , since, throwing out all mechanically mixed substances and loss, and looking only to the ratio between aluminum (of the nitride) and nitrogen, we have—

	Found.		Calculated.
	No. 1.	No. 2.	
Aluminum .....	67·9	68·27	66·18
Nitrogen .....	32·1	31·73	33·82
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	100·0	100·00	100·00

An excess of aluminum was to be expected, as some crystalline alumina must have been taken up by the sodium hydrate.

The quantity of the nitride formed in each experiment was small,

\* Impurities of the original ingot of metallic aluminum.

but varied a good deal, apparently in consequence of the temperature required being very high, and more or less early closing the pores of the plumbago crucible by partial fusion, so that nitrogen from the furnace atmosphere no longer passed through. When aluminum alone was heated, no sodium carbonate being used, but very few yellow specks of nitride were visible, yet on exposure to moist air in a closed bottle the whole surface in time became covered with a white powder of alumina, and a piece of reddened litmus paper suspended to the stopper became blue.

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