

subject here. It has already been amply dealt with at the commencement of my reply: I will only add, when it is concluded from the hypothesis of a cubical arrangement of the particles, acting by forces which vary according to the Newtonian law, that the direction of one side of the cube is stable and of one unstable (Earnshaw on the Nature of Molecular Forces, Art. 15), ought we not to ask, Is it the hypothesis, or the reasoning based on it which is erroneous? Must it not of necessity be the latter?

We have now done with the objections to the statical possibility of the law. It remains to reply to the two objections to its dynamical applicability. It is fit that a matter so important as the rejection of a law which explains so many phænomena (see Gauss, in the last No. of the Scientific Memoirs), which has so strong an *à priori* probability, and which is the proved law of material action, should rest on none but the most unexceptionable evidence. Whatever may become of the question ultimately, I trust that by rigidly examining that evidence which has been afforded and showing its inadequacy, I shall be considered as actuated by no captious or unphilosophical spirit. My next communication will be a reply to M. Cauchy, whose arguments being based on a refined analysis, can scarcely be answered without the use of similar means.

[To be continued.]

XLVI. *Observations on the Formation of Compounds of Boron and Silicon with Nitrogen and certain Metals.* By W. H. BALMAIN, Esq., Lecturer on Chemistry in the Mechanics' Institution, Liverpool*.

CONSIDERING the strong affinity existing between hydrogen and nitrogen, and between carbon and nitrogen, together with the circumstances under which they will combine, and their chemical relations to boron and silicon, I was led to imagine that the two latter elements must have a very strong affinity for nitrogen, and concluded that they might be caused to combine with it by double decomposition; and, bearing in mind the strong affinities of ammonia and cyanogen, it appeared probable that the compounds, if obtained, would play an important part as chemical agents; and I had hopes that some of the bodies at present supposed to be elementary might prove to be compounds of nitrogen with these or other elements. Some experiments instituted to establish these points have been in a measure successful, but as they form only a small part of the great number which will at once

* Communicated by Dr. Kane.

suggest themselves to the mind of the chemist, and as my time is of necessity devoted to other objects and my means very limited, I beg leave to lay the few facts which I have been able to ascertain before the working chemists of the day through the medium of the Philosophical Magazine.

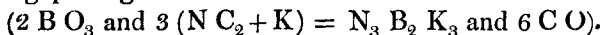
Silica and boracic acid undergo no change when heated in ammoniacal gas by means of the oxyhydrogen flame nearly to the point at which platina melts, but when heated to that temperature with cyanide of potassium instead of ammonia, apparent action ensues. Boracic acid and cyanide of potassium, in the proportion of two atoms of the former to three of the latter, were placed in a covered porcelain crucible, that inclosed in a larger Hessian crucible, and the space between being filled with small pieces of charcoal, the whole was heated to whiteness in a wind furnace. The result was a white porous substance, which was found not only at the bottom of the crucible, but also lining the sides and the top, having been carried there by spurious sublimation. The relative quantities given above were used in order that the carbon of the cyanide might be exactly in the right proportion for taking all the oxygen from the boracic acid and forming carbonic oxide only, and when by accident an excess of boracic acid or cyanide was employed it appeared to remain as an impurity in the white solid; but these points were not closely examined, because the white solid, which was homogeneous and evidently a distinct and stable compound, was a more interesting object of study. The following is the best process for preparing it:—Take seven parts of finely powdered anhydrous boracic acid and twenty parts of cyanide of potassium free from water, and as far as possible from cyanide of potass and iron; and having lined a Hessian crucible with a paste of powdered charcoal and gum, and heated it until all water has passed away, place the mixture in the crucible, cover it by inverting and luting a smaller crucible over it, and heat it to whiteness for an hour: it is advisable to use a crucible as a cover, that there may be sufficient room for spurious sublimation, and the vent-hole should be bored in the bottom of this crucible and not in the luting at the side; and further, to avoid the penetration of oxygen to the materials, it is well to line the upper crucible in like manner with the lower. The result found in both crucibles, when washed and dried, will be the white solid in a state of purity. It is a light porous solid which readily falls to powder, and when compressed, presents that peculiar surface which is observable in some of the precipitated cyanurets, and in a slight degree in chloride of silver, and in some iodides, &c.; it is infusible, insoluble, even when heated, in water, in solution of potass, hydrochloric acid, sul-

phuric acid (strong and diluted), nitric acid, and solution of chlorine; it is not altered upon exposure to air, nor does it affect the most delicate turmeric paper when left upon it in a moist state. Passing over for the present the remarkable stability of this compound, these characters are important as proving the absence of boracic acid and cyanide of potassium (with some results it was found necessary to wash away the excess of cyanide of potassium; but this does not interfere with the nature of the white solid, and was not necessary when the boracic acid and cyanide of potassium were quite pure and free from water, and their proportions very carefully adjusted). Heated with hydrate of potass or soda it yields ammonia abundantly; in the deoxidizing flame of the blow-pipe it is not altered, nor does it communicate any colour to the flame, but in the oxidizing flame it gives a strong green colour, and gradually fuses, yielding a perfect bead, which is transparent, hot and cold, and when placed with a drop of water upon test papers, turned tumeric brown, and red litmus blue. When the outside flame impinges upon a large surface of the substance in powder, as when a glass tube soiled with it is held at the extreme point of the flame, it presents a beautiful green phosphorescence, owing no doubt to the gradual formation of boracic acid at the surface, and if it be removed to the inner flame, the centre will incandesce, while the outer edges, where it meets with the oxygen of the air, will still yield the elegant green. When thrown upon fused chlorate of potass it deflagrates with a soft green light, and it will also deflagrate with nitrate of potass. It is not altered by being gently heated with potassium or sodium, nor when heated before the blowpipe on charcoal, with lead, zinc, &c. Chlorine has no action upon it at a low red heat, and iodine, sulphur and corrosive sublimate may be sublimed from it without decomposing it. It is not decomposed by hydrogen at a red heat, but below that temperature is decomposed with the evolution of ammonia by the vapour of water, or by any substance which will yield water, as hydrate of potass, hydrate of lime, common clay, hydrated phosphoric acid, and the rhombic phosphate. It is not decomposed by hydrochloric acid at a low red heat, and I think it is not altered by hydrofluoric acid, for a small portion of it was mixed with a large quantity of fluorspar, with more than sufficient sulphuric acid to make it all into hydrofluoric acid, and heated as long as fumes passed off, when, after the sulphate of lime had been washed away with dilute nitric acid, it still yielded ammonia with hydrate of lime.

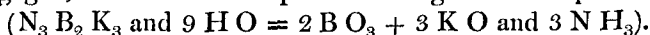
From some of these facts it appears that the compound contains boron, nitrogen, and potassium, and I suppose that the

nitrogen and boron are united, and that the compound so formed is combined by a very strong affinity with potassium.

My inability to obtain a better balance than such as I could construct myself of wood and paper, or suitable apparatus for an analysis, prevents me from speaking at all positively as to the proportion of the elements; but some analyses and decompositions seem to point out the proportion $K_3 N_3 B_2$ as the correct one, from which it would appear that during its preparation there is no loss either of potassium or of nitrogen; nothing passing off but carbonic oxide:



This theory very nearly agrees with several estimations of the quantity of ammonia and boracic acid found when the compound is decomposed by the hydrates of lime and potass, and is corroborated by there being no gas but ammonia disengaged, and no boron deposited during the decomposition:



However, it may be that there are only two atoms of potassium, since the compound can only be obtained at such a temperature as would volatilize potassium; from which it would appear that potassium was set free during its formation; and moreover, during the decomposition by hydrate of potass or lime, a new compound is formed which may possibly contain the original compound with oxygen, being somewhat analogous to cyanate of potass, in which case the oxygen, set free from the hydrogen which has to form ammonia, might be theoretically disposed of without the supposition that there are three atoms of potassium ($N_3 B_2 K_3$ and $9 H O = 2 B O_3 + 2 K O$ and $3 N H_3$ and O , which would go to undecomposed substance); but at the same time, this new compound may contain oxygen and have derived it, not from the decomposed water, but from the air in the vessel. It is formed when the "boronitruret of potassium" is fused with potass, and an excess of acid added to the solution of the result; at first it appears as a milkiness in the liquid, but by continued ebullition, collects into a distinct precipitate, which when dry is a remarkably coherent thready solid.

When heated before the blowpipe it gives a strong green flame without melting; it yields ammonia abundantly with hydrate of lime and carbonate of potass (a mixture which I used instead of hydrate of potass), and in other respects behaves like the "boronitruret of potassium," excepting that it yields no phosphorescence, and when slowly oxidized forms a very fusible bead, which during its oxidation throws out small vesicles owing to the escape of gas. The substance operated

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upon was obtained chiefly from an incomplete analysis of the "boronitruret of potassium," by heating it with hydrate of lime; the result being diffused through water, a stream of carbonic acid passed through it, and the whole boiled, borate of potass was in solution and carbonate of lime precipitated, which, being acted upon by muriatic acid, yielded an imperfectly transparent liquid, and from this the thready substance was deposited on long-continued ebullition.

All attempts to decompose the "boronitruret of potassium," so as to isolate the theoretical "boride of nitrogen," have hitherto been unsuccessful; each experiment adding its testimony to the remarkable stability of the compound. It cannot be done by means of oxidizing agents, for both the potassium and the boron take oxygen at the same time, and either boracic acid and potass are formed, or else the thready substance alluded to above, as appeared to be the case when peroxide of manganese with boracic or sulphuric acid was used as the oxidizing agent, since, after diluting and acting upon the residue with a solution of oxalic and sulphuric acids to remove boracic acid and any remaining peroxide of manganese, a white solid was left which had the same appearance and, before the blowpipe, the same characters as that substance.

Finding that cyanogen passed over a mixture of boracic acid and charcoal heated to redness gave me no result, I endeavoured, as a last resource, to obtain compounds of "boride of nitrogen" with the common metals by heating their cyanides with boracic acid, fully expecting that these cyanides would decompose at too low a temperature for the deoxidation of the boron to take place, and I was agreeably surprised when upon trial it appeared that the cyanide of copper heated with boracic acid gave a result, which, after being washed, yielded ammonia when heated with a mixture of hydrate of lime and carbonate of potass; and cyanide of lead, a result which not only yielded ammonia, but produced a phosphorescence before the blowpipe which differed from that of the "boronitruret of potassium" only in its colour, which was more yellow and less green.

Both of these results were so impure, owing to the presence of oxides in the cyanides, that their characters could not be taken as those of the compounds of the metals with "boride of nitrogen," and they were only valuable as proving the possibility of making those compounds by such a process. The copper result gave a very fine green flame before the blowpipe, but would not phosphoresce; and after the metallic copper had been removed by nitric acid a substance remained which appeared more like the "thready compound" supposed

to contain oxygen, than the "boronitruret of potassium." Cyanide of mercury heated with boracic acid gave cyanogen abundantly, which burned with a tinge of green in its flame; and at the same time a small quantity of white crystalline solid sublimed, which may prove to be a compound of mercury with the "boride of nitrogen," and being such, if it could be obtained in larger quantity, might probably be a means of isolating the much-wished for "boride of nitrogen." It was soluble in water, giving it a bitter taste; and the solution gave no precipitate with a salt of iron, but an abundant white with protochloride of tin: with iodide of potassium none, with acetate of lead none, with nitrate of silver a slight precipitate, which was insoluble in excess of acid. It was likewise soluble in alcohol, but the solution did not burn with a green flame. Boiled with a solution of carbonate of potass it yielded ammonia, and it communicated a green colour to flame, passing off rapidly in vapour, and giving a greenish blue colour to the flame in its immediate neighbourhood.

A mixture of one part of anhydrous boracic acid with two and a half parts of cyanide of zinc, heated to whiteness in a lined crucible (covered and well luted), yielded a white solid similar in appearance to that obtained by heating a mixture of boracic acid and cyanide of potassium. It gave ammonia abundantly when heated with a mixture of hydrate of lime and carbonate of potass, and was insoluble (with and without heat) in water, sulphuric acid, hydrochloric acid, nitric acid, solution of chlorine, solution of potass and ammonia. It is not decomposed by chlorine at a *full red heat*, nor by corrosive sublimate, nor by potassium or sodium. Before the blowpipe it is infusible, but in the oxidizing flame communicates a green colour, and when at the outer edge emits a very brilliant bluish phosphorescence, which appearance it also produces when simply dropped into the flame of a spirit-lamp. Thrown on fused chlorate of potass it deflagrates with a faint blue light. These characters are exactly such as we should expect to find in a compound of zinc with "boride of nitrogen" analogous to the compound of potassium. It appeared to be in a state of purity, and is more readily obtained than the potassium compound, since the preparation of a pure cyanide of zinc is accomplished with greater facility than that of cyanide of potassium. Besides its interest in being distinctly a second compound of the kind, and the remarkable beauty of its phosphorescence before the blowpipe, it is of importance as affording a means of preparing the analogous compound of other metals by heating it with their chlorides. Heated to whiteness in a lined crucible in the proportion of one atom of itself (taking

its composition to be $Zn_2 N_3 B_2$) to two atoms of the chloride, it yielded, with chloride of lead, a white solid which gave ammonia abundantly when heated with a mixture of hydrate of lime and carbonate of potass, and phosphoresced with a yellowish green light at the point of the blowpipe flame; water boiled with it afterwards gave no precipitate with nitrate of silver, and when it was heated before the blowpipe with soda upon charcoal, it gave a distinct button of lead and only a minute trace of zinc; with chloride of copper, a result similar to that obtained by heating together cyanide of copper and boracic acid.

With chloride of silver, a result which resembled the lead compound, and phosphoresced brilliantly with a yellowish-green light. It was not decomposed by hydrochloric acid, nor by chlorine at a low red heat, nor by corrosive sublimate, and indeed appeared under all circumstances as stable as the rest, remaining unaltered even when heated in a tube with sodium and potassium. With the chlorides of sodium, barium, strontium, calcium and manganese, results which appeared to be "boronitrurets" of those metals; but in these cases the experiments were made with small quantities, solely with a hope of finding a soluble compound; and as not one of them would yield ammonia when boiled in water with hydrate of lime and carbonate of potass, and as water after ebullition in contact with them gave no precipitate with solutions of the oxides of lead, silver, copper, iron, &c., I concluded that I had not been successful in my search.

Six parts of silica heated to whiteness with thirteen parts of cyanide of potassium gave a brittle porous vitreous solid, which, after being well washed, yielded ammonia abundantly when heated with hydrate of lime and carbonate of potass. Heated with fused potass it yielded ammonia abundantly. After ebullition with sulphuric acid it still yielded ammonia when heated with hydrate of lime and carbonate of potass. In the deoxidizing flame it fused tranquilly, and in the oxidizing with escape of gas. With carbonate of soda it gave a red bead in the deoxidizing flame, the colour of which disappeared in the oxidizing flame, and could not be recovered. After being heated with nitrate of ammonia and well washed, it yielded ammonia with hydrate of lime and carbonate of potass, more abundantly than before. From this it appears that a compound of silicon and nitrogen with potassium analogous to the boron compound had been formed, and that it is nearly as stable as that substance; but as I had no means of separating the compound from impurity, nothing further can be said at present.

From the above results, and from a few doubtful experiments which have not been mentioned, I conclude that compounds of nitrogen with boron and silicon had been formed, and that their chemical relations are similar to those of cyanogen; and I have no doubt that analogous compounds of aluminium, glucinium, &c. may also be formed; moreover, I have hopes that the fundamental principles of the science of chemistry may be further elucidated by some of these compounds proving to be, if not some of our "elements," at least of a nature closely analogous. We are not to suppose that the affinity of nitrogen for the other elements is weak because it will not unite with them directly as by a process of combustion, especially as the compounds of nitrogen at present known are not formed directly, and in many the affinity has proved stronger than was at first supposed. This compound of boron and nitrogen resists all agents but oxygen, and analogous compounds with bases not so easily oxidized might appear to us elementary, and a glance over the relative constitution of our earth and atmosphere may in some measure justify us in expecting to find nitrogen abundantly in the mineral kingdom; and this point decided positively, may throw much light upon the connexion between organic and inorganic chemistry. My opinion is founded upon a careful review of many well-known facts, and is not solely dependent upon these recent experiments for its support, but, on the contrary, *they* have been instituted to discover evidence, and I hope that while my labours are still continued others will be induced to join in the same pursuit.

WILLIAM H. BALMAIN.

XLVII. *On the Optical Constants of Tourmaline, Diopase and Anatase.* By W. H. MILLER, M.A., F.R.S., Professor of Mineralogy in the University of Cambridge*.

THE values of the optical constants of Tourmaline were deduced from observations made with a prism cut out of a colourless crystal in the possession of Mr. Brooke, which, though not sufficiently perfect to show the dark lines in the spectrum, exhibits the bright line in the flame of alcohol very distinctly. For this light the index of refraction of the ordinary ray out of air into the crystal is 1.6366; in an extraordinary ray perpendicular to the axis of the rhombohedron the velocity of light in air divided by its velocity within the crystal is 1.6193. A slice of the same crystal bounded by planes perpendicular to the axis, 0.68 inch thick, being placed in a po-

* Communicated by the Author.