"Some Physical Characters of the Sodium Borates, with a New and Rapid Method for the Determination of Melting Points."

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Some time ago we published a note* containing some new observations on the solubility of metallic oxides in fused boric anhydride. Since its publication we have been further studying some of the points therein mentioned, but have been in part anticipated by W. Guertler,† who has examined many of the phenomena we remarked, in a more complete manner. As, however, our experiments do not cover exactly the same ground as his, we have arranged in the following paper the results relating to the sodium borates, which we believe are completely new, and, at the same time, present many interesting features towards the study of these complex bodies.

When a quantity of ordinary pure borax glass is heated for some hours at a temperature which gives it about the consistency of a thick syrup, it gradually changes to a mass of colourless crystals. The crystallisation begins at two or three points on the surface of the mass, generally around a particle of dirt, or minute fragment of imperfectly fused borax, and spreads in more or less spherulitic growths throughout the glassy portion. As the crystals grow, there appears to be a contraction of volume, since the glass around them appears as raised hummocks, and a subsequent investigation of the specific gravities of the crystals and glass showed that this was really the case.

The crystals do not seem to grow at a uniform rate. They start rapidly, but as development continues, they take longer and longer to form, so that many hours are occupied in changing from pure glass to a holocrystalline aggregate.

We have not been able to isolate any individual crystals, and so study their characters, but the whole crystalline mass appears to be composed of dense, matted clusters of very minute needles, which are doubly refracting, and have a pearly lustre. They are about as soluble in water as ordinary borax glass, are not hygroscopic, and melt at a higher temperature than the glass, into which they are reconverted on melting, and then cooling quickly.

We find, however, that it is not borax glass alone which exhibits this phenomenon of crystallisation on reheating, but that the glasses obtained by fusing mixtures of boric anhydride and sodium carbonate,

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* 'Journ. Chem. Soc. Proc.,' 1903, p. 221.

† 'Zeit. Anorg. Chem.,' vol. 40, 2, pp. 225 and 268; vol. 40, 3, p. 337.

in which the ratio of the boric anhydride to the sodium carbonate is not 2 : 1, also exhibit it in varying degree.

Thus, all mixtures in which the ratio varies from 6 : 1 to 8 : 5, give a glass when fused, and are all capable of being changed completely into crystals on reheating, exactly like borax. Mixtures in which the boric anhydride is present in greater proportion than 6 : 1, only change with difficulty on prolonged heating; and when they do, the crystals are always found to be mixed with more or less truly glassy material, till, when the ratio 40 : 1 is reached, it seems impossible to obtain crystals at all. So far as we can ascertain, a mixture of this composition is always a true glass in any circumstances.

Mixtures, on the other hand, in which the ratio of boric anhydride is less than 8 : 5, when fused, and allowed to cool, yield nearly opaque, white substances, which seem to be micro-crystalline. Nevertheless, these mixtures if heated to a high temperature, and then suddenly chilled by being poured into mercury, also yield glasses.

The glasses obtained by this sudden chilling seem to be very unstable, as on gently heating by means of a Bunsen flame, they change completely, and almost instantaneously, into crystals.

There seems then to be a gradual alteration in the rapidity and completeness with which this change occurs, and as it seemed probable that the crystallisation of some borate rich in sodium was the cause of it, we proceeded to determine what was the composition of the borate richest in sodium which could be obtained by fusing boric anhydride with sodium carbonate.

When boric anhydride is fused with sodium carbonate, carbon dioxide is evolved, and the product may be regarded as boric anhydride combined with sodium oxide (Na_2O). Thus, by heating boric anhydride with a large excess of sodium carbonate, and determining the amount of carbonate decomposed, the greatest proportion in which boric anhydride combines with sodium oxide can be ascertained, and ought to give the composition of the richest sodium borate obtainable by fusion.

We have performed this experiment several times, and have obtained the following results:—

(i) One part of B_2O_3 combines with 1·29 parts Na_2O
(ii) One " " 1·34 "
(iii) One " " 1·32 "

These results are probably a little too low, as the sodium carbonate loses some carbon dioxide merely on heating alone, but this amount is negligible, and does not in any way affect the conclusion that the product obtained in this way is not sodium metaborate ($NaBO_2$), in which the ratio of boric anhydride to sodium oxide is 1 : 1, and that sodium orthoborate (Na_3BO_3), in which the ratio is 1 : 3, cannot in any case be formed by fusion of boric anhydride and sodium carbonate.

The object of the research became thus threefold:—

(*a*) To determine what compounds are present in crystals obtained with various mixtures of boric anhydride and sodium carbonate;

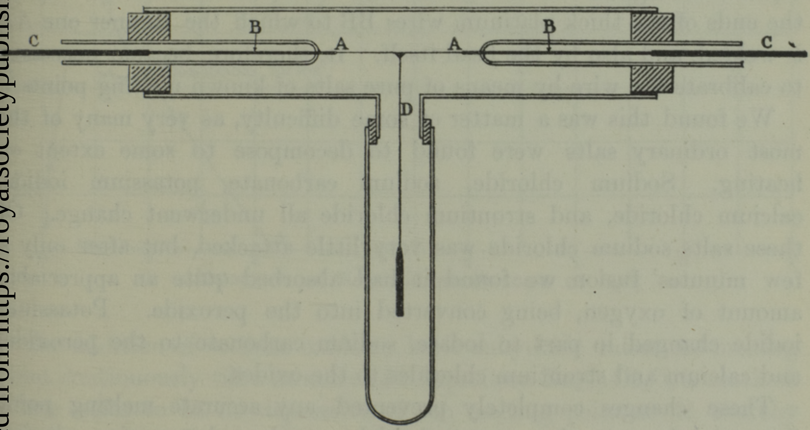
(*b*) What is the nature of the glass;

(*c*) What is the nature of the change from glass to crystals.

The most obvious method seemed to be to determine the melting points of crystals and glasses of varying composition, to see if compounds existed, and to compare and correlate the melting point curves obtained. To do this it was necessary to employ some new melting point method, as none is known by which the melting point of glasses can be determined at all accurately.

We devised an apparatus which is somewhat similar to the "meldometer" described by Joly,[*] and we found it to be both rapid and peculiarly suitable in the case of plastic substances, which have hitherto been supposed to possess no definite melting point.[†] Our apparatus is represented in fig. 1.

FIG. 1.



A uniform piece of platinum wire, AA, about 4 cms. long, was welded to two stouter pieces of the same metal, BB. These were sealed into two thin glass tubes, and were welded to two thick copper wires, CC, which conveyed the current. The whole was fixed by two rubber stoppers in a glass tube, with an opening at D.

A small bead of the material whose melting point was desired, was made on one end of a very thin platinum wire, to which a weight of about a gramme was attached.

A current of 4—6 ampères was passed through the wire AA so as to raise its temperature considerably above that at which the bead

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[*] 'Roy. Irish Acad.,' 1889.

[†] We use the words "melting point" to denote the sudden decrease in viscosity which occurs at a very well defined temperature in glasses.

melted. The bead was then inserted through the opening D, when on touching the wire it became fused. The current was switched off, and the bead, on solidifying, remained attached to the edge of the wire AA. Air currents were prevented by closing the opening D with a test-tube.

A slowly increasing current was then passed through the wire till the portion of the bead in contact with it melted, when the weight and bead fell into the test-tube. The moment this occurred, the voltage between the ends of the wire and the ampères passing through it were carefully noted. From the values obtained the resistance was calculated, and thence the temperature.

The weight hanging from the bead had no decided effect on the melting point. We found that with weights varrying from 0·2—5 grammes, the bead dropped off at practically identical temperatures. This temperature at which beads of various compounds drop off the wire is extremely well defined, even in the case of substances which become plastic on heating, like glass, so that provided no chemical change occurs during the heating, the method proved rapid and elegant. A certain amount of heat is conducted away by the ends of the thick platinum wires BB to which the thinner one AA is welded, and also by the bead itself. It, therefore, became necessary to calibrate the wire by means of pure salts of known melting points.

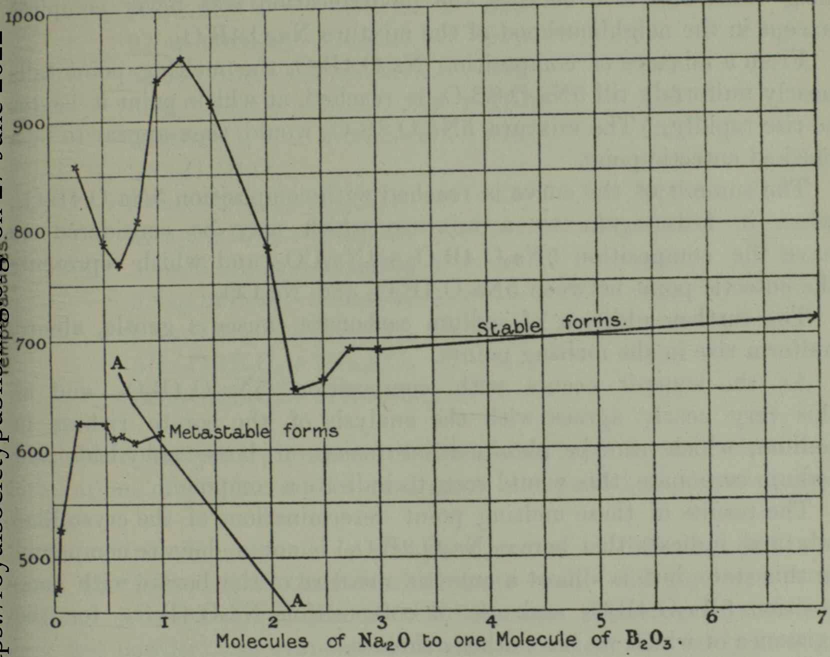
We found this was a matter of some difficulty, as very many of the most ordinary salts were found to decompose to some extent on heating. Sodium chloride, sodium carbonate, potassium iodide, calcium chloride, and strontium chloride all underwent change. Of these salts sodium chloride was very little attacked, but after only a few minutes' fusion we found it had absorbed quite an appreciable amount of oxygen, being converted into the peroxide. Potassium iodide changed in part to iodate, sodium carbonate to the peroxide, and calcium and strontium chlorides to the oxides.

These changes completely prevented any accurate melting point determinations, so after repeated trials we adopted potassium nitrate, lithium chloride, and potassium chloride as standards. It is true that potassium nitrate decomposes on heating, but as the nitrite (to which it changes) has almost the same melting point, the small amount of change was found to be immaterial. The chlorides we employed seemed to be, on the whole, very stable.

The melting points given in Carnelley's tables for these three standard substances were assumed as correct; they were used in fixing three points on the temperature-resistance curve.

Thus, any temperature between the melting points of potassium nitrate and potassium chloride could be obtained by interpolation from the measured resistance, and those above the melting point of potassium chloride by extrapolation. The results did not seem to contain an error larger than 1 per cent., so that we considered the method was satisfactory enough. The melting point curves for the glasses and crystals are represented on fig. 2. The curve for the glasses presents some features which are difficult to explain, since, so far as we are aware, no such curve has before been described.

FIG. 2.



The addition of sodium oxide to boric anhydride raises the melting point continuously till a mixture of composition $Na_2O.4B_2O_3$ is reached. There seems to be no depression of the melting point at all, thereby differing from the case of ordinary solution, and indicating the probability that there is no solid phase.

The curve then remains fairly level till a composition $Na_2O.2B_2O_3$ is reached, when it falls irregularly to $3Na_2O.4B_2O_3$.

The last point we could obtain on this curve was with composition $Na_2O.B_2O_3$, where the melting point practically coincided with the temperature of change from the glassy to the crystalline state of this mixture. Indeed it is a little above it, but it was possible by fairly rapid heating to melt the bead before the change had occurred.

At present we are unable to state exactly what the meaning of this melting point curve for the glasses may be. Glasses have hitherto been supposed to possess no sharp melting point, but this does not seem to be the case, as our results for each different temperature were remarkably close and well defined.

The melting point curve for the crystals is more easily explainable than that of the glass.

We were unable to obtain any point on it between pure boric anhydride and a mixture of composition $Na_2O.4B_2O_3$. This was because the crystallisation of the small mass of substance in the beads we employed for the melting point determinations took an extremely long time, and also because the devitrification was never complete except in the neighbourhood of the mixture $Na_2O.4B_2O_3$.

From a mixture of composition $Na_2O.4B_2O_3$ the melting point falls nearly uniformly till $5Na_2O.8B_2O_3$ is reached, at which point it begins to rise rapidly. The mixture $5Na_2O.8B_2O_3$ would then appear to be a marked eutectic point.

The summit of the curve is reached with composition $5Na_2O.4B_2O_3$, when it falls again to a mixture which may be considered to have the composition $5Na_2O.4B_2O_3 + 4Na_2CO_3$, and which represents the eutectic point between $5Na_2O.4B_2O_3$ and Na_2CO_3.

The further addition of sodium carbonate causes a gentle, almost uniform rise in the melting points.

As the summit occurs with composition $5Na_2O.4B_2O_3$, and as this very nearly agrees with the analysis of the borate richest in sodium, which can be obtained on fusion of boric anhydride and sodium carbonate, this would seem to indicate a compound.

The results of these melting point determinations of the crystalline mixtures indicate that borax ($Na_2O.2B_2O_3$) is not a definite compound in this state, but is almost a eutectic mixture of the borate with composition $5Na_2O.4B_2O_3$ and one of composition $Na_2O.4B_2O_3$, for the existence of which we have other evidence.

This melting point curve for the crystalline forms of these various mixtures cannot be regarded as truly representing either the *solidus* or *liquidus*. It seems probable that in this case they are situated close to each other, and that our melting points really represent temperatures close to the liquidus. The fact that a mass of crystals would apparently melt almost completely at an almost constant temperature certainly indicates that there cannot be any very great difference between the liquidus and solidus, and, as in the cases studied by Heycock and Neville, that the actually determined melting points lie probably very near to the liquidus.

The following table gives the melting points for the various glasses and crystals :—

	Melting point.	
Composition of mixture.	Glass.	Crystals.
B_2O_3	468°	—
$Na_2O.40B_2O_3$	470	—
$Na_2O.16B_2O_3$	528	—
$Na_2O.4B_2O_3$	628	858°
$Na_2O.2B_2O_3$	628	791
$9Na_2O.16B_2O_3$	613	—
$5Na_2O.8B_2O_3$	620	777
$3Na_2O.4B_2O_3$	610	815
$Na_2O.B_2O_3$	615	930
$5Na_2O.4B_2O_3$	—	960
$5Na_2O.4B_2O_3 + Na_2CO_3$	—	917
$5Na_2O.4B_2O_3 + 3Na_2CO_3$	—	783
$5Na_2O.4B_2O_3 + 4Na_2CO_3$	—	654
$5Na_2O.4B_2O_3 + 5Na_2CO_3$	—	664
$5Na_2O.4B_2O_3 + 6Na_2CO_3$	—	692
$5Na_2O.4B_2O_3 + 7Na_2CO_3$	—	685
$5Na_2O.4B_2O_3 + 27Na_2CO_3$	—	722

We have analysed a number of the glasses and crystals obtained with various mixtures, and obtained most unexpected and interesting results.

The analysis of a borate is always a matter of difficulty, but we found the following method worked quite well, and gave accurate results. A weighed quantity of the substance (glass or crystals in very fine powder) was evaporated to dryness twice with fairly strong hydrochloric acid. By this means all the sodium was converted into the chloride. The dry powder thus obtained was repeatedly treated with small quantities of methyl alcohol, and evaporated to dryness. By this means all traces of hydrochloric acid were removed, as well as the whole of the boracic acid, so that pure sodium chloride remained. This was dissolved in water and estimated by titration with N/10 silver nitrate solution, using potassium chromate as indicator.

The complete separation of the crystals from the glass was by no means an easy matter. We found that quite the easiest and most satisfactory method was to crush up the substance into coarse powder, and then to pick out with forceps the really glassy fragments and the crystalline masses. This was quite easy by using a lens.

Though the crystals and glass have different specific gravities, it was not found possible to obtain a real separation by means of a heavy liquid. This was because pieces of material which looked wholly crystalline often contained glass in the interior, so that they would float anywhere in the liquid.

We also tried extraction with hot methyl alcohol which is a solvent for boric anhydride, for, if the crystals had been due to a separation of a borate from its solution in boric anhydride, this should have left the compound pure. As a matter of fact we found that the methyl alcohol decomposed both the crystals and glass, giving methyl borate, boracic acid, and sodium methylate. Both glass and crystals were decomposed at the same rate.

Attempts to use water as a means of separation were also failures, since the solubility of both glass and crystals is about the same.

The results of our analyses are as follows:—

(i) *Mixture of Composition about* $Na_2O.2B_2O_3$.—This mixture crystallised completely in a few hours, giving a hard, white, completely crystalline mass. When about two-thirds had crystallised the glass and crystals were separated, and gave on analysis:—

Glass = 30·9 per cent. Na_2O; crystals = 31·0 per cent. Na_2O.

(ii) *Mixture of Composition about* $3Na_2O.8B_2O_3$.—This crystallised completely, and had the same characters as (i).

On analysis obtained:—

Glass = 25·86 per cent. Na_2O; crystals = 25·81 per cent. Na_2O.

(iii) *Mixture of Composition about* $Na_2O.4B_2O_3$.—This crystallised completely, and had the same characters as (i).

On analysis obtained:—

Glass = 18·70 per cent. Na_2O; crystals = 18·67 per cent. Na_2O.

(iv) *Mixture of Composition about* $Na_2O.6B_2O_3$.—This crystallised very nearly completely, but seemed to contain small translucent glass-like fragments.

On analysis obtained:—

Glass = 11·5 per cent. Na_2O; crystals = 13·7 per cent. Na_2O.

(v) *Mixture of Composition about* $Na_2O.8B_2O_3$.—This did not crystallise completely. After very prolonged heating it nearly all changed to a crystalline mass with an almost waxy lustre, but which was not really wholly crystalline. There was always in addition a portion of the mass which remained a glass.

On analysis obtained:—

Glass = 10·06 per cent. Na_2O; crystals = 11·90 per cent. Na_2O.

(vi) *Mixture of Composition about* $Na_2O.12B_2O_3$.—Only about half would crystallise, and this took a very long time.

On analysis obtained:—

Glass = 2·1 per cent. Na_2O; crystals = 12·2 per cent. Na_2O.

(vii) *Mixture of Composition about* $Na_2O.16B_2O_3$.—After heating this mixture for several days only a very small amount crystallised.

On analysis obtained:—

Glass = 4·18 per cent. Na_2O; crystals = 10·02 per cent. Na_2O.

(viii) *Mixture of Composition about* $Na_2O.40B_2O_3$.—This could not be crystallised at all.

From these numbers it appears that with mixtures between $Na_2O.4B_2O_3$ and $Na_2O.2B_2O_3$ the crystals and glass have absolutely identical composition, but with mixtures containing more boric anhydride than $Na_2O.4B_2O_3$, only a part (decreasing in quantity as the amount of boric anhydride present increases) crystallises, and this part has approximately the composition $Na_2O.6B_2O_3$.

As the crystals of the mixture of this composition contain more sodium than the glass, it seems probable that, could one obtain the crystals really pure and not entangling any glass, the composition might approach that of $Na_2O.4B_2O_3$.

The nearness in composition of the crystals obtained from mixtures varying from $Na_2O.16B_2O_3$ to $Na_2O.6B_2O_3$ makes it seem fairly certain that it is the same compound which separates out in all of them, and that the differences in the analyses are due to the crystals being mixed with more or less glass which it was impossible to remove. In experiment (vi) the crystals and glass were particularly well separated, and the result is shown by the great difference in their analyses.

It seemed so curious that with mixtures of composition $Na_2O.2B_2O_3$ to $Na_2O.4B_2O_3$ the glass and crystals should give similar analytical results, that we thought it worth while to try fractional crystallisation of the glasses, to see if we could detect any differences between the different crystalline portions.

The analyses of these various portions gave the following results:—

(i) *For a mixture of composition about* $Na_2O.2B_2O_3$—

		Per cent. Na_2O.
First portion	glass	= 29·7
	crystals	= 29·3
Second portion	glass	= 29·9
	crystals	= 29·2
Third portion	glass	= 30·3
	crystals	= 30·5
Fourth portion	glass	= 30·2
	crystals	= 30·1

(ii) *For a mixture of composition about* $Na_2O.4B_2O_3$—

		Per cent. Na_2O.
First portion	glass	= 18·7
	crystals	= 18·6
Second portion	glass	= 18·6
	crystals	= 18·4

We also fractionally crystallised borax itself five times, when the final crystalline portion was found to contain 30·8 per cent. Na_2O, theory for $Na_2B_4O_7$ requiring 30·7 per cent. Na_2O.

These differences are negligible, and the crystals that separate out from the glass have exactly the same composition from the beginning.

These results show at once that this crystallisation is not due to the separation of any single compound as we had previously supposed, but that it is more probably due to the formation of mixed crystals or a solid solution from a superfused liquid.

All the various crystalline fractions obtained from any one glass of composition $Na_2O.4B_2O_3$ to $Na_2O.2B_2O_3$ were found to melt at identical temperatures, as also did the residual glasses. Further, the crystalline portions when melted, gave glasses which had a melting point identical with that of the previous residual glass, and these residual glasses could, in their turn, be changed to crystals with similar melting points to those which had originally been separated.

This shows most conclusively the identity of the crystals and glass in chemical composition. We have also determined in the case of several mixtures the temperatures at which this crystallisation takes place. The curve indicating these temperatures is shown in fig. 2 by the line joining AA.

A bead of the glass was put on the platinum wire of our melting point apparatus, and the temperature raised extremely slowly, whilst the bead was watched with a lens. In the case of those mixtures which melted before the change occurred, no weight was attached to the bead. The crystallisation appeared to start at a fairly well defined temperature, and, if it was maintained, would gradually spread through the bead.

It is a little hard to say exactly what is the meaning of this curve AA, fig. 2, and all that seems certain is that it gives approximately the temperatures at which the rate of crystallisation assumes a sufficient velocity to visibly change the state of the substance.

From a consideration of the melting point curves, together with the analytical and other observations we have described, it is possible to form some idea as to the nature of these glasses and the crystals into which they are wholly or partially transformable.

The glass must be regarded as a superfused, and, therefore, metastable form of the crystals, behaving in several respects as if it were a liquid of enormous viscosity.

Now, on considering the behaviour of the glasses ranging in composition from pure boric anhydride to $Na_2O.6B_2O_3$, it will be noticed that the supposition of the existence of a borate of about the composition $Na_2O.5B_2O_3$, which is dissolved in boric anhydride, will explain the observed facts. A mixture of composition $Na_2O.40B_2O_3$ cannot be crystallised at all, and one of composition $Na_2O.16B_2O_3$ only partially rystallises, hence some point between these mixtures will give the maximum solubility of this borate in boric anhydride. On further increasing the amount of this borate present, the glass becomes a supersaturated and superfused liquid, the amount of crystallisation measuring the supersaturation.

Somewhere between $Na_2O.6B_2O_3$ and $Na_2O.4B_2O_3$ no free boric anhydride remains in the solution, and the whole mass will crystallise for the first time.

On further addition of sodium, another borate of composition near $Na_2O.4B_2O_3$ begins to be formed, and we have shown that in any mixture between these two compounds, both crystals and glass have identical compositions. We are here probably dealing with a case of solid solution, and the glass is merely its superfused form.

The character of the curve would indicate that there are two types of crystals, one rich in B_2O_3, the other rich in Na_2O, and the lowest point of the curve is the eutectic point formed by mixtures of these two.

That the crest of the curve does not occur with the composition $Na_2O.B_2O_3$ can be most conveniently explained by the fact that solid solutions cannot be treated as pure substances, and so a slight shifting of the maximum point is to be expected. The further depression of the melting point curve probably indicates the eutectic point between these crystals, rich in Na_2O, and sodium carbonate.

In conclusion we wish to express our thanks to Professor H. B. Dixon and Mr. D. L. Chapman, for the kindly interest they have taken in our work.