figure of 192.4, and by the ordinary process the figure found was 193.1. A sample of dragon's blood resin gave 124.9.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. XLV.]

## ON THE VOLATILITY OF BORAX.[1]

BY SIGMUND WALDBOTT, PH.D.

THE fact that borax is a volatile substance under ordinary laboratory conditions seems to have, hitherto, escaped notice. No reference is made to it in the literature of pure chemistry, and the following quotation from E. Cramer[2] would imply a general belief among technical chemists to the contrary:

"The boric acid must not be added in the form of vitreous boric acid, but in the form of sodium borate, whereby no volatilization will take place."

In the course of an investigation on the borates, carried on in connection with Prof. T. H. Norton, certain observations led to the suspicion that borax was not entirely unaffected by the heat of the ordinary blast-lamp.

A series of quantitative experiments was made, the results of which may be briefly summarized as follows:

If a small amount of pure borax, say four grams, be heated in a platinum crucible of fifty cc. contents, until the water of crystallization is quantitatively given off, and if the residue, borax glass, then be heated over a Bunsen burner for about ten minutes or longer, the weight will be found constant. If the crucible, half covered by the lid, be next heated over a gentle blast-flame, there will be noticed a very slight, yet distinctly perceptible loss in weight, increasing in proportion to the intensity of heat and the time of heating.

If now the uncovered crucible with its contents be subjected to an intense white heat, heavy vapors arise from the surface of the molten borax glass, and if heating is prolonged a very marked decrease in weight becomes evident.

The following experimental results are classified according to the general temperature maintained:

[1] Read before the Cincinnati Section, February 15, 1894.

[2] E. Cramer, *Thonindustrie-Zeitung*, *1892*, p. 155.

## A. VOLATILITY AT HIGHER TEMPERATURES.

The experiments recorded under this heading were all carried out at a white heat, as high a temperature as could be obtained by the ordinary laboratory blast-lamp. The borax used in these experiments, unless expressly stated otherwise, was purified by recrystallization and by drying for about twelve hours on unglazed porcelain.

### I.

1.2500 grams $Na_2B_4O_7+10H_2O$, when heated, lost 0.5968 gram $H_2O$=47.74 per cent. (Theoretical loss=47.12 per cent., drying on unglazed porcelain was omitted.)

0.6532 gram borax glass remained and was heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss. gram. | Total loss in per cent. |
|---|---|---|---|---|
| 5 | Crucible uncovered................ | 0.0055 | 0.0055 | 0.8 |
| 7 | " covered.................. | 0.0010 | 0.0065 | 1.0 |
| 10 | " uncovered............... | 0.0060 | 0.0125 | 2.0 |
| 7 | " half covered, chimney used | 0.0039 | 0.0164 | 2.5 |
| 10 | " uncovered............... | 0.0054 | 0.0218 | 3.3 |
| 5 | " " ............... | 0.0050 | 0.0268 | 4.1 |
| 2 | " " ............... | 0.0009 | 0.0277 | 4.2 |

0.6532 gram borax glass lost 4.2 per cent. in forty-six minutes.

### II.

7.9201 grams $Na_2B_4O_7+10H_2O$, when heated, lost 3.7356 grams H2O=47.17 per cent. (Theoretical loss=47.12 per cent.)

4.1845 grams borax glass remained and were heated as follows:

| Time of heating. minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---|---|---|---|---|
| 5 | Crucible open..................... | 0.0085 | 0.0085 | 0.23 |
| 10 | " half covered............. | 0.0040 | 0.0125 | 0.298 |
| 10 | " " " chimney used | 0.0045 | 0.0170 | 0.406 |
|  | Lid, covered with drops, was heated | 0.0023 | 0.0193 | 0.461 |
| 10 | Crucible open..................... | 0.0080 | 0.0273 | 0.652 |
| 10 | " " ..................... | 0.0076 | 0.0349 | 0.834 |

4.1845 grams borax glass lost 0.83 per cent. in forty-five minutes.

In comparing the results of these two experiments it will be seen that the absolute amount of borax evaporated in a given time is about the same in both cases, whether a large or a small quantity is used, indicating that the amount volatilized at a given high temperature depends chiefly on the surface of the fused mass.

In the following three experiments it was sought to determine in what form borax is volatile.

It is possible that either borax is volatile as such, or that it is dissociated at high temperatures, giving off $B_2O_3$ and leaving $Na_2O$ behind. An analysis of the residue after heating borax glass for a certain length of time would decide; for in case $B_2O_3$ is evolved the percentage of $Na_2O$ must be higher than if borax as such is volatilized. As the difference between the two values for $Na_2O$ under the latter supposition would increase rapidly with the loss in weight, samples of borax glass were heated long enough to bring about a loss of some twelve per cent.

## III.

1.5630 grams $Na_2B_4O_7+10H_2O$, lost on heating 0.7380 gram $H_2O$=47.21 per cent. (Theoretical loss=47.12 per cent.)

0.8250 gram borax glass remained and was heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---|---|---|---|---|
| 20 | Crucible partly covered | 0.0106 | 0.0106 | 1.3 |
| 20 | Crucible covered, small space allowed, fine drops on lid | 0.0020 | 0.0126 | 1.6 |
| | The lid alone was heated | 0.0060 | 0.0186 | 2.3 |
| 20 | Crucible uncovered | 0.0171 | 0.0357 | 4.4 |
| 60 | Crucible uncovered | 0.0365 | 0.0722 | 8.8 |
| 60 | Crucible uncovered, heat less intense | 0.0210 | 0.0932 | 11.34 |

0.8250 gram borax glass lost 11.34 per cent. in three hours.

The residue weighed 0.7318 gram, and was analyzed, yielding 0.2185 gram $Na_2O$ or 29.85 per cent.

| | Theory, if loss were $B_2O_3$. | Theory, if loss were $Na_2B_4O_7$. | Found. |
|---|---|---|---|
| $Na_2O$ | 34.62 per cent. | 30.69 per cent. | 29.85 per cent. |

## IV.

1.5691 grams $Na_2B_4O_7+10H_2O$, lost on heating 0.7387 gram $H_2O$=47.07 per cent. (Theoretical loss=47.12 per cent.)

0.8304 gram borax glass remained and was heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---|---|---|---|---|
| 30 | Crucible open | 0.0134 | 0.0134 | 1.6 |
| 90 | " " | 0.0565 | 0.0699 | 8.4 |
| 35 | " " | 0.0220 | 0.0919 | 11.07 |
| 20 | " " | 0.0121 | 0.1040 | 12.52 |

0.8304 gram borax glass lost 12.52 per cent. in about three hours.

The residue weighed 0.7264 gram, and yielded on analysis 0.21796 gram $Na_2O$.

| | Theory, if loss were $B_2O_3$. | Theory, if loss were $Na_2B_4O_7$. | Found. |
|---|---|---|---|
| $Na_2O$ ........ | 35.09 per cent. | 30.69 per cent. | 30.01 per cent. |

The low results obtained for $Na_2O$ in III and IV were found to be due to a slight loss liable to be incurred in the analytical process used (treatment with ammonium fluoride), which will be touched upon in a communication following this. This source of error was obviated in the following experiment:

### V.

0.9350 gram borax glass was heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---|---|---|---|---|
| 60 | Crucible uncovered .................. | 0.0387 | 0.0387 | 4.1 |
| 120 | " " .................. | 0.0914 | 0.1301 | 13.91 |

0.9350 gram borax glass lost 13.91 per cent. in three hours.

The residue weighed 0.8049 gram, and yielded on analysis 0.2439 gram $Na_2O$.

| | Theory, if loss were $B_2O_3$. | Theory, if loss were $Na_2B_4O_7$. | Found. |
|---|---|---|---|
| $Na_2O$ ........ | 35.65 per cent. | 30.69 per cent. | 30.31 per cent. |

These results show beyond doubt that borax is volatile as such, and are corroborated by the following observations:

A thin film of borax glass on the inside of a crucible can be entirely volatilized by persistent heating.

The drops which occasionally gather on the lid of the crucible in the experiments described, can also be driven off completely by continued heating.

SUMMARY OF THE RESULTS OF EXPERIMENTS A, I–V.

| Losses in per cent. at the end of | WEIGHTS OF BORAX GLASS. | | | | |
|---|---|---|---|---|---|
| | I, 0.6532 gram. | II, 4.1845 grams. | III, 0.8250 gram. | IV, 0.8304 gram. | V, 0.9350 gram. |
| 5 minutes ........... | 0.8 | 0.23 | ... | ... | ... |
| 12 " ........... | 1.0 | .... | ... | ... | ... |
| 15 " ........... | ... | 0.298 | ... | ... | ... |
| 20 " ........... | ... | .... | 1.3 | ... | ... |
| 22 " ........... | 2.0 | .... | ... | ... | ... |
| 25 " ........... | ... | 0.461 | ... | ... | ... |
| 29 " ........... | 2.5 | .... | ... | ... | ... |
| 30 " ........... | ... | .... | ... | 1.6 | ... |
| 35 " ........... | ... | 0.652 | ... | ... | ... |

| Losses in per cent at the end of | Weights of Borax Glass. I, 0.6532 gram. | II, 4.1845 grams. | III, 0.8250 gram. | IV, 0.8304 gram. | V, 0.9350 gram. |
|---|---|---|---|---|---|
| 39 '' | 3.3 | .... | ... | ... | ... |
| 40 '' | ... | .... | 2.3 | ... | ... |
| 44 '' | 4.1 | .... | ... | ... | ... |
| 45 '' | ... | 0.834 | ... | ... | ... |
| 46 '' | 4.2 | .... | ... | ... | ... |
| 60 '' | ... | .... | 4.4 | ... | 4.1 |
| 120 '' | ... | .... | 8.8 | 8.4 | ... |
| 155 '' | ... | .... | ... | 11.07 | ... |
| 175 '' | ... | .... | ... | 12.52 | ... |
| 180 '' | ... | .... | 11.34 | ... | 13.91 |

These values obtained for the volatility of borax at high temperatures suggested the study of the behavior of borax glass at a lower heat, with the following results:

## B. VOLATILITY AT LOWER TEMPERATURES.

### I.

4.0199 grams $Na_2B_4O_7+10H_2O$ were heated in a platinum crucible until the water was expelled and the weight was constant.

Water expelled=1.887 grams=46.96 per cent. (Theoretical loss=47.12 per cent.

2.1320 grams borax glass remained and were further heated as follows:

| Time of heating. minutes. | Mode of heating. | Loss each time. gram. | Total loss. gram. | Total loss in per cent. |
|---|---|---|---|---|
| 10 | Bunsen burner with chimney, full flame | 0.0000 | 0.0000 | 0.000 |
| 15 | Moderate blast-flame, crucible half covered | 0.0014 | 0.0014 | 0.065 |
| 15 | Moderate blast-flame, crucible half covered, drops noticed on lid | 0.0008 | 0.0024 | 0.112 |
| 20 | Moderate blast-flame, crucible half covered, drops noticed on lid | 0.0020 | 0.0044 | 0.206 |
| 5 | Strong blast-flame, crucible open | 0.0048 | 0.0092 | 0.431 |
| 10 | '' '' '' '' '' | 0.0073 | 0.0165 | 0.774 |
| 60 | Bunsen burner, full flame, crucible half covered | 0.0000 | 0.0165 | 0.774 |

### II.

2.4425 grams borax glass were heated for ten minutes over a strong blast-flame in order to insure perfect expulsion of water.

It weighed then 2.4327 grams and was further heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---|---|---|---|---|
| 30 | Bunsen burner, strong flame, crucible half covered | 0.0000 | 0.0000 | 0.000 |
| 15 | Gentle blast-flame, crucible half covered | 0.0015 | 0.0015 | 0.061 |
| 15 | Gentle blast-flame, crucible half covered | 0.0017 | 0.0032 | 0.131 |

### III.

0.6148 gram borax glass after being heated for a short time over a strong blast-flame, weighed 0.6126 gram and was further heated as follows:

| Time of heating, minutes. | Mode of heating. | Loss each time, gram. | Total loss, gram. | Total loss in per cent. |
|---|---|---|---|---|
| 15 | Stronger blast-flame, crucible half covered | 0.0034 | 0.0034 | 0.555 |
| 15 | Gentle blast-flame, crucible half covered | 0.0016 | 0.0050 | 0.816 |
| 15 | Gentle blast-flame, crucible half covered | 0.0018 | 0.0068 | 1.110 |

### SUMMARY OF THE RESULTS OF EXPERIMENTS B, I–III.

| Weight of borax glass. | Loss in per cent. at the end of | | | |
|---|---|---|---|---|
| | 15 minutes, per cent. | 30 minutes, per cent. | 45 minutes, per cent. | 50 minutes, per cent. |
| 2.1320 grams | 0.065 | 0.112 | .... | 0.206 |
| 2.4327 " | 0.061 | 0.131 | .... | .... |
| 0.6126 gram | 0.555 | 0.816 | 1.110 | .... |

The question here suggests itself how this behavior of borax might influence the accuracy of such determinations of boric acid as involve exposure of a borate to high temperatures, as for example in the determinations of boric acid by the methods of H. Rose and G. Schaffgotsch. (v. Fresenius Quant. Anal.)

As in these determinations borates of a higher basicity than borax are formed, the results just given, cannot be with certainty utilized, although the more basic borates are probably less volatile than borax. But even supposing these more basic borates to be as volatile as borax itself, a material error from this source can occur only, if there be but a small amount of the borate subjected to analysis, and if the expulsion of carbon dioxide be attempted at too high a temperature and maintained for an unduly long time.

To illustrate such an exceptional case let us refer for instance to the experiment under A I, where it is shown that 0.6532 gram borax glass lost in weight 0.0125 gram=two per cent., when exposed to a white heat for twenty-two minutes, while the crucible was uncovered for fifteen minutes.

If, therefore, 0.2805 gram boron trioxide be analyzed by the method of G. Schaffgotsch this amount would be equivalent to 0.6532 gram of the borate $B_4O_9Na_6$ formed in this process; this salt would lose in weight two per cent. in twenty-two minutes, if exposed to a white heat, if we assume that it be exactly as volatile as borax under the same conditions.

There would then remain 0.6401 gram of the borate, containing 0.2749 gram of $B_2O_3$, which implies a loss of $B_2O_3$ equal to 0.0056 gram or 1.99 per cent.

It is, however, evident from the above that a loss from volatilization of the borate will fall within the errors of manipulation, when in an analysis a normal amount of boric acid is taken, say not less than one gram and when the heating is maintained for about ten minutes at not too high a temperature. This is under the assumption that borates of a higher basicity than borax are volatile to the same extent as the latter. Whether this is the case or not I have not attempted to ascertain, but a preliminary experiment made with a borate of approximately the composition $B_4O_9Na_6$ shows that an increase of basicity in the molecule of borax does not guard the more basic borate from volatilization entirely, for I observed with this borate the same phenomena noticeable when heating borax; *viz.*, the evolution of heavy vapors from its surface, implying a loss in weight when subjected to a white heat. A statement contrary to this fact was made by G. Schaffgotsch[1] in claiming that the salt formed by the action of one and a half molecules of $Na_2CO_3$ on one molecule of $B_2O_3$ [$=B_4O_9Na_6$] is "gewichtsbeständig."

Prof. Karl Langenbeck, of Zanesville, Ohio, kindly consented to carry out some experiments on the volatilization of borax on a larger scale in kilns, making use of pyrometers. With the approval of Prof. Langenbeck, I herewith add his interesting

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[1] G. Schaffgotsch, *Pogg. Ann.*, 107, 427. Ueber die Bestimmung der Borsäure und über die Flüchtigkeit der Borsäure.

communications on the subject which are in perfect accord with the results obtained in the laboratory.

### I. JANUARY 30, 1894.

12.3036 grams of borax glass were placed in a small platinum dish and set in a fire-clay capsule four inches in diameter and four inches deep, and this placed next to the pyrometers of a kiln.

From incipient redness to the melting down of Seger's pyrometric cone No. 9, took about forty-eight hours when the firing was discontinued and the kiln allowed to cool, which in about twelve hours, was no longer red.

In other words the borax glass was at a red heat about sixty hours, and reached the temperature of the melting point of Seger's pyrometric cone No. 9, (=1410° C.). On removal from the kiln the inside of the clay capsule was heavily glazed and the borax glass in the platinum dish found to weigh 6.2776 grams, hence 6.0260 grams had been volatilized, or 48.98 per cent.

### II. FEBRUARY 6, 1894.

5.7698 grams $Na_2B_4O_7$ exposed to the heat of Seger's pyrometric cone No. 7 (1350° C.) lost 1.2926 grams or 22.40 per cent. This heat took ten hours less to reach and cooled about two hours more quickly, hence the specimen was about twelve hours less under a red heat.

9.2036 grams $Na_2B_4O_7$ exposed to the heat of the melting point of an alloy fifteen per cent. Ag, eighty-five per cent. Au (about 1050° C.) lost 0.7259 gram or 7.88 per cent.

To reach this heat from very low redness took about twenty hours, and the cooling to blackness six hours.

It looks very much as if it did not take so very much heat to begin the volatilization, and that the duration of fire rather than the temperature determines the amount of loss.

### III. FEBRUARY 13, 1894.

7.5803 grams borax glass were exposed in a platinum dish to a heat, which was just sufficient to melt silver (954° C.) and by careful regulation of the gas this temperature was held, within very narrow limits for three hours.

The furnace is an up and down draught made by Geith, of Coburg, Germany, from designs of Seger, and has a zone of at least seventy-five cubic inches that is perfectly uniform in heat. The dish of borax glass and the pyrometric trials were placed in the center of this zone.

The dish lost in three hours 0.1115 grams or 1.47 per cent.

SUMMARY OF THE RESULTS OBTAINED BY PROF. LANGENBECK.

| Amount of borax glass. grams. | Duration of heat. hours. | Maximum temperature. | Means of measuring the temperature. | Loss, grams. | Loss in per cent. |
|---|---|---|---|---|---|
| 2.3036 | 60 | 1410° C. | Seger's cone, No. 9. | 6.0260 | 48.98 |
| 5.7698 | 48 | 1350° C. | Seger's cone, No. 7. | 1.2926 | 22.40 |
| 9.2036 | 26 | 1050° C. | Alloy 15 % Ag 85 % Au. | 0.7259 | 7.88 |
| 7.5803 | 3 | 954° C. | Ag. | 0.1115 | 1.47 |

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. XLVI.]

# ON THE VOLATILITY OF SODIUM FLUORIDE.[1]

BY SIGMUND WALDBOTT, PH.D.

THE analyses mentioned in Experiments A III and A IV of the foregoing communication did not at first give perfectly satisfactory results. In the endeavor to ascertain the cause of the deficiency, the analytical method employed was subjected to a careful examination.

This method, as described by A. Reischle,[2] is based on the principle that boric acid can be easily driven off from a borate by mixing it with six times its weight of resublimed ammonium fluoride, and heating carefully until all the boron is volatilized as ammonium borofluoride.

The residue, consisting of the fluorides of the metals that were combined with boric acid, is then treated with sulphuric acid and evaporated to dryness. The sulphates are ignited and weighed, and the amount of boric acid, if desired, is calculated from the difference between the original weight and the weight of the oxides present in the sulphates.

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[1] Read before the Cincinnati Section, February 15, 1894.

[2] A. Reischle, *Ztschr. anorg. Chem.*, 4, 111-116. Abst. in *J. Chem. Soc.*, *1893*, (abstracts) p. 491.