that the products are $RSO_4 \cdot TiOSO_4$ where R = a bivalent metal ion.

The data obtained for the compounds $MgSO_4 \cdot TiO_2SO_4$ and $MgSO_4 \cdot TiOSO_4$ are given in Tables I and II for illustration.

TABLE I

| Magnesium carbonate, g. | Total loss on heating, % | Loss due to available oxygen, % | Loss calculated due to water, % | Available oxygen in the oily liquid minus water, % | Available oxygen calculated for $MgSO_4 \cdot TiO_2SO_4$, % |
|---|---|---|---|---|---|
| 0.2 | 55.38 | 2.38 | 53.0 | 5.1 | 5.4 |
| .3 | 56.26 | 2.46 | 53.8 | 5.3 | 5.4 |
| .4 | 55.35 | 2.45 | 52.9 | 5.2 | 5.4 |

The above data as well as the data of earlier publications indicate that three series of compounds appear to exist: (1) $RSO_4 \cdot Ti(SO_4)_2$; (2) $RSO_4 \cdot TiO_2SO_4$ and (3) $RSO_4 \cdot TiOSO_4$ in which R = a bivalent metal. It is suggested that in any continuation of this work efforts may be made to find conditions under which $Ti(SO_4)_2$ and the peroxide compound $TiO_2SO_4$ can be isolated; $TiOSO_4$ is already known.

TABLE II

$MgSO_4 \cdot TiOSO_4$ requires 17.08% Ti, 8.68% Mg, 68.52% $SO_4$.

| Magnesium carbonate, g. | Wt. of oily liquid, g. | Wt. of residue after heating the oily liquid, g. | Mg, % | Ti, % | $SO_4$, % |
|---|---|---|---|---|---|
| 0.2 | 0.278 | 0.124 | 8.5 | 16.5 | 69.2 |
| .3 | .290 | .127 | 8.2 | 16.8 | 68.9 |
| .4 | .260 | .116 | 8.7 | 16.2 | 69.2 |

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE ROYAL INSTITUTE OF SCIENCE]

# H-Ion Concentration of Aqueous Solutions Containing Boric Acid and Hydroxylic Substances

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Levulose has been found to be more effective in increasing the acidity of boric acid in concentrated solutions than either mannitol or sorbitol. The *p*H values obtained in this investigation in the case of levulose are in good agreement with those of Böeseken, Vermaas and Kuchlin but differ from those obtained by Krantz, Beck and Carr. By use of an expression derived by Böeseken, Vermaas and Kuchlin the values of "$n$" (the number of molecules of a polyhydric substance in combination with one mole of boric acid) have been calculated.

In this paper the H-ion concentration of solutions containing varying proportions of boric acid and hydroxylic substances, *viz.*, (1) mannitol, (2) sorbitol, (3) levulose, (4) glucose, (5) galactose and (6) mannose is reported. It was determined by the quinhydrone method using an electrode vessel of the Morton type and saturated KCl as the bridge liquid. An amplifying unit was used to measure the e.m.f. The apparatus was standardized with $M/20$ potassium hydrogen phthalate. From the observed e.m.f. the *p*H was obtained from the expression $pH = (0.455 - E)/0.06$.

The results obtained are given in the Table I in which the following symbols have been used: $R$ = ratio boric acid:hydroxylic substance; $C$ = molar concentration of boric acid in the solution.

TABLE I

BORIC ACID:MANNITOL

| $R$ / $C$ | 1:3 *p*H | 1:2 *p*H | 2:3 *p*H | 1:1 *p*H | 2:1 *p*H | 3:1 *p*H |
|---|---|---|---|---|---|---|
| 0.200 | 2.683 | 2.899 | 3.083 | 3.207 | 3.525 | 3.692 |
| .125 | 2.961 | 3.207 | 3.35 | 3.508 | 3.832 | 4.007 |
| .100 | 3.099 | 3.341 | 3.482 | 3.642 | 3.975 | 4.159 |
| .050 | 3.541 | 3.799 | 3.95 | 4.1 | 4.466 | 4.658 |
| .025 | 3.999 | 4.287 | 4.424 | 4.633 | 4.923 | 5.116 |
| .005 | 5.041 | 5.258 | 5.428 | 5.474 | 5.492 | 5.692 |

B. Boric acid:sorbitol

| | | | | | | |
|---|---|---|---|---|---|---|
| 0.200 | 2.906 | 3.042 | 3.108 | 3.445 | 3.517 | 3.642 |
| .125 | 3.188 | 3.323 | 3.375 | 3.692 | 3.816 | 3.916 |
| .100 | 3.325 | 3.475 | 3.523 | 3.850 | 4.058 | 4.142 |
| .050 | 3.808 | 3.907 | 3.941 | 4.142 | ... | 4.508 |
| .025 | 4.249 | 4.333 | 4.441 | 4.474 | 4.681 | 4.775 |

C. Boric acid:levulose

| | | | | | | |
|---|---|---|---|---|---|---|
| 0.200 | 2.678 | 2.774 | | 3.180 | 3.458 | 3.591 |
| .125 | 3.011 | 3.191 | | 3.466 | 3.716 | 3.991 |
| .100 | 3.191 | 3.375 | | 3.624 | 3.978 | 4.092 |
| .050 | 3.709 | 3.824 | | 4.007 | 4.271 | ... |
| .025 | 4.058 | 4.241 | | 4.325 | ... | 4.704 |
| .005 | 4.708 | 4.725 | | 4.808 | 4.907 | 5.058 |

D. Boric acid: glucose

| | | | | | | |
|---|---|---|---|---|---|---|
| 0.200 | 3.816 | 3.958 | 4.108 | 4.192 | 4.441 | 4.591 |
| .125 | 4.142 | 4.175 | 4.391 | 4.508 | 4.742 | 4.825 |
| .100 | 4.308 | 4.341 | 4.474 | 4.591 | 4.808 | 4.841 |
| .050 | 4.633 | 4.541 | 4.874 | 4.708 | 4.857 | 4.891 |
| .025 | 4.775 | 4.625 | 4.391 | 4.991 | 4.991 | 4.941 |
| .005 | 4.991 | 4.742 | 5.041 | 5.041 | 5.024 | 5.024 |

E. Boric acid:galactose

| | | | | | | |
|---|---|---|---|---|---|---|
| 0.200 | 3.824 | 3.999 | 4.133 | 4.275 | 4.241 | 4.475 |
| .125 | 4.100 | 4.241 | 4.441 | 4.525 | 4.591 | 4.633 |
| .100 | 4.258 | 4.357 | 4.483 | 4.575 | 4.792 | 4.808 |
| .05 | 4.575 | 4.591 | 4.708 | ... | 4.857 | 4.891 |
| .025 | 4.691 | 4.766 | ... | 4.891 | 4.907 | 4.923 |

F. Boric acid:mannose

| | | | | | | |
|---|---|---|---|---|---|---|
| 0.200 | 3.741 | 3.891 | 3.991 | 4.168 | 4.291 | 4.451 |
| .100 | 4.058 | 4.072 | 4.325 | 4.408 | 4.608 | 4.608 |
| .050 | 4.180 | 4.325 | 4.474 | 4.523 | 4.725 | 4.742 |
| .025 | 4.461 | 4.505 | 4.605 | 4.708 | 4.934 | 4.907 |
| .005 | 4.651 | 4.951 | 4.920 | ... | 5.308 | 5.208 |

**Discussion.**—When the *p*H values are plotted against dilution, curves are obtained which show that the *p*H of all the mixtures increases with dilution. These curves are nearly all of the same type except in the case of galactose and glucose which exhibit a linear relationship between $p$H and concentration.

The general nature of these curves is the same as observed by Krantz, Beck and Carr[1] for erythritan–boric acid mixtures and by Tang[2] and Sung for glucose–boric acid mixtures. It is also noticed that the change in $p$H with dilution in concentrated solutions containing mannose is not so rapid as in the case of the other substances.

On a comparison of the data for the polyalcohols and sugars it is observed that the effect of levulose in concentrated solutions in increasing the acidity of boric acid is greater than that of mannitol and of both these substances greater than that of sorbitol. Again mannose is more effective in this respect than galactose.

The remarkable effect of levulose in increasing the acidity of boric acid has also been observed by Thomas[3] and Kalman and by Krantz, Beck and Carr[1] who found that an aldehydic or ketonic group in the molecule augments the dissociation of boric acid in a very striking manner.

The observed increase in $p$H on dilution can be attributed to an increase in the dissociation of the complex acid formed in solution. The complexes formed by polyhydric substances in concentrated solutions undergo hydrolysis on dilution. Since boric acid in the free condition would contribute only in a small measure toward the acidity of the solution, an increase in $p$H is observed.

When the curves of $p$H against the ratio boric acid:hydroxylic substance were plotted it was observed that at all dilutions there was at first a slow decrease in $p$H with a relative increase in the amount of the hydroxylic substance added until the ratio 1:1 was reached, after which there was a rapid fall.

It would not be justifiable to conclude that an equimolecular compound is formed in the case of all the hydroxylic substances examined, but it is fair to assume that in all probability a compound is formed after this ratio of boric acid:hydroxylic substance is reached.

Böeseken,[4] Vermaas and Küchlin have obtained the values of "$n$" representing moles of a polyalcohol which combine with one mole of boric acid on certain assumptions. The values of Böeseken as well as of Krantz, Beck and Carr[1] for 0.1 $M$ solution of $H_3PO_3$ in the case of levulose are given in Table II along with those obtained by the authors.

Krantz, Beck and Carr[1] stated that they were unable to account for the observed difference between their values and those of Böeseken but that their value for the ratio 4:1 is in agreement with that of Mellon and Morris.[5]

The $p$H values obtained by the authors are in good agreement with those of Böeseken[4] and it appears that the values given by Krantz,[1] Beck and Carr are probably in error.

(1) J. C. Krantz, Jr., F. F. Beck and C. J. Carr, *J. Phys. Chem.*, **41**, 1087 (1937).
(2) P. S. Tang and P. N. Sung, *Nature*, **275** (1936).
(3) P. Thomas and C. Kalman, *Compt. rend.*, **196**, 1672 (1933).
(4) J. Böeseken, N. Vermaas and A. Th. Küchlin, *Rec. trav. chim.*, **49**, 711 (1930).
(5) M. G. Mellon and V. N. Morris, *J. Ind. Eng. Chem.*, **16**, 123 (1924).

Table II

| Ratio polyol: boric acid | $p$H Authors | $p$H Böeseken | $p$H Krantz, Beck and Carr | $a$ | $n$ Böeseken | $n$ Krantz, Beck and Carr | Authors $a$ | Authors $n$ |
|---|---|---|---|---|---|---|---|---|
| 4:1 | .. | 3.01 | 2.86 | $\frac{4:1}{3:1}$ | 2.3 | 1.4 | ... | .. |
| 3:1 | 3.15 | 3.15 | 2.95 | $\frac{3:1}{0.5:1}$ | 2.0 | 1.3 | $\frac{3:1}{1:1}$ | 1.98 |
| 2:1 | 3.32 | .. | .. | ... | ... | ... | $\frac{3:1}{2:1}$ | 1.93 |
| 1:1 | 3.62 | 3.60 | 3.27 | $\frac{4:1}{0.5:1}$ | 2.1 | 1.4 | $\frac{2:1}{1:1}$ | 1.99 |
| 0.5:1 | 3.95 | 3.94 | 3.47 | $\frac{4:1}{1:1}$ | 2.0 | 1.4 | $\frac{3:1}{0.5:1}$ | 2.06 |

$^a$ Ratio of quantities of the polyalcohol in the two solutions.

Similar attempts were made to calculate the values of "$n$" from the data obtained in this investigation for mannitol, sorbitol, glucose, galactose and mannose in 0.1 $M$ boric acid and the results obtained are given in Tables III and IV.

Table III

| Ratio polyol:boric acid | $a$ | Mannitol $p$H | Mannitol $n$ | Mannose $p$H | Mannose $n$ |
|---|---|---|---|---|---|
| 3:1 | $\frac{3:1}{1:1}$ | 3.10 | 2.26 | 4.06 | 1.47 |
| 2:1 | $\frac{2:1}{0.5:1}$ | 3.30 | 2.26 | 4.08 | 1.69 |
| 1:1 | $\frac{1:1}{0.5:1}$ | 3.64 | 2.26 | 4.41 | 1.20 |
| 0.5:1 | $\frac{3:1}{0.5:1}$ | 3.98 | 2.26 | 4.59 | 1.36 |

Table IV

| Ratio polyol: boric acid | $a$ | Sorbitol $p$H | Sorbitol $n$ | $a$ | Glucose $p$H | Glucose $n$ | Galactose $p$H | Galactose $n$ |
|---|---|---|---|---|---|---|---|---|
| 3:1 | $\frac{3:1}{1:1}$ | 3.32 | 2.14 | $\frac{3:1}{1:1}$ | 4.22 | 1.47 | 4.31 | 1.30 |
| 2:1 | $\frac{2:1}{1:1}$ | 3.50 | 2.19 | $\frac{2:1}{0.5:1}$ | 4.32 | 1.56 | 4.38 | 1.33 |
| 1:1 | $\frac{3:1}{2:1}$ | 3.83 | 2.05 | $\frac{2:1}{1:1}$ | 4.57 | 1.66 | 4.62 | 1.59 |
| 0.5:1 | ... | .. | .. | $\frac{3:1}{0.5:1}$ | 4.79 | 1.47 | 4.78 | 1.21 |

It will be seen from the above that the values of $n$ for glucose, galactose and mannose are not integral and although in the case of glucose they are nearly constant (mean value of $n$ = 1.54) those for galactose and mannose show a variation. It is likely that in the case of these substances the assumptions made by Böeseken, Vermaas and Kuchlin are not valid or as suggested by Krantz, Beck and Carr[1] the solutions contain more than one complex. In the case of mannitol and sorbitol, however, the values of $n$ are constant and equal to 2.26 and 2.13, respectively. The value for mannitol obtained in this investigation is in fair agreement with the value 2.0 calculated by Böeseken[4] and co-workers from the data of Van Liempt.

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