123. The System Sodium Carbonate–Sodium Borate–Water at 35°.

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This ternary system has been studied at 35° in order to find out if compound formation occurred between the carbonate and the borate. No compounds were observed in contact with solutions containing less than 20% of the carbonate, and beyond this point the system became quaternary with the formation of a solid containing sodium hydrogen carbonate, *i.e.*, sesquicarbonate (Na₂CO₃,NaHCO₃,2H₂O).

THE system under consideration is in effect only a part of the quaternary system $Na_2O-B_2O_3-CO_2-H_2O$. It is also contained in the more restricted system $Na_2CO_3-Na_4CO_3-Na_2B_4O_7-Na_2B_2O_4-H_2O$ which was studied as a reciprocal salt pair by Teeple ("The Industrial Development of Searles Lake Brines," 1929, pp. 124—125), who, however, did not examine the section represented by the system under discussion. In dealing with our ternary system a careful watch was kept for any departure from ternary phenomena. This involved a systematic check on the relationship between sodium oxide and carbon dioxide plus boric oxide in the system phases. It was found that the solubility of hydrated borax could be followed in sodium carbonate solutions of increasing concentration up to about 20% by weight. Beyond this point the system lost its ternary character since sodium sesquicarbonate appeared as a solid phase. A few determinations were then made for quaternary solutions in equilibrium with sesquicarbonate and borax; the complete system $Na_2O-B_2O_3-CO_2-H_2O$ was not dealt with.

The limit of ternary phenomena and the composition of the two isothermal invariant solutions obtained in the four-component system are in substantial agreement with Teeple's results.

EXPERIMENTAL.

The analyses included determination of sodium oxide by titration with standard acid (methyl-orange), followed by addition of glycerol and titration of the boric acid (phenolphthalein). The carbonate was determined gravimetrically by liberating carbon dioxide with acid and weighing it after absorption in potassium hydroxide solution.

Each solubility mixture was placed in a glass bottle fitted with a rubber stopper carrying a glass stirrer which was rotated at about 300 r.p.m. The stirring time for the different mixtures varied from 3 to 11 days, after which agitation was stopped and the bottle contents allowed to settle. Samples of equilibrium solution were withdrawn by a dry warm pipette, then weighed and analysed. The solid phases were filtered off and eventually dissolved and analysed. The identity of each solid phase was determined graphically by plotting the composition of each solution with that of the unwashed solid ("rest").

Two tables of solubilities are given : the ternary system $Na_2CO_3-Na_2B_4O_7-H_2O$ as far as it can be followed at 35° and points on the quaternary system. In the first table the "rest" compositions have been included with the solution data, but in the second, "rests," though analysed have been omitted, solution composition being expressed both as weight percentages and also per 100 parts by weight of $Na_2O + B_2O_3 + CO_2$.

Ternary system Na₂CO₃-Na₂B₄O₇-H₂O at 35°.

(Solid phase = $Na_2B_4O_7$, $10H_2O_2$)

| | | Solution. | | " Rest." G. per 100 g. | | | |
|-----------------|-----------------------------------|---|------------------|---------------------------|----------------|---------------|--|
| | | G. per 100 g. | | | | | |
| d_{15}^{35} . | Na ₂ CO ₃ . | Na ₂ B ₄ O ₇ . | H_2O_{\bullet} | Na₂CO₃. | $Na_2B_4O_7$. | H_2O . | |
| | | 4.8 * | 95·2 * | | | | |
| 1.036 | | $4 \cdot 84$ | 95.16 | | | | |
| 1.058 | 3.27 | 3.33 | 93.40 | 0.56 | 45.22 | 54.22 | |
| 1.090 | 6.41 | 3.41 | 90.18 | 1.39 | 43.38 | 55.23 | |
| 1.134 | 10.47 | $3 \cdot 40$ | 86.13 | 1.49 | 46.89 | 51.62 | |
| 1.172 | 14.02 | 3.19 | 82.79 | 2.12 | 46.21 | 51.67 | |
| 1.210 | 17.32 | 3.30 | 79.38 | 4.56 | 40.29 | $55 \cdot 15$ | |
| 1.243 | 20.46 | 3.28 | 76.26 | 4.34 | 43.12 | 52.54 | |

* From Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd edtn., Vol. I, p. 1149.

Quaternary system Na₂O-B₂O₃-CO₂-H₂O at 35°.

Composition of solution.

| | | | G. per 100 g. | | Per 100 parts (by wt.) of $Na_2O + B_2O_3 + CO_2$. | | | | |
|-------------------|-----------------|----------|---------------|-------------------|---|--------------|----------------|-------------------|---------------|
| Solid phases.* | d_{15}^{35} . | $Na_2O.$ | B_2O_3 . | CO ₂ . | H ₂ O. | $Na_2O.$ | В 2 О3. | CO ₂ . | $H_2O.$ |
| 7 + S† | | 19.2 | | 13.8 | 67.0 | 58.2 | | 41.8 | $203 \cdot 0$ |
| S + H + | | 11.9 | | 9.6 | 78.5 | 55.3 | | 44.7 | $365 \cdot 0$ |
| S | 1.304 | 16.14 | 2.52 | 10.46 | 70.88 | $55 \cdot 4$ | 8.7 | 35.9 | $243 \cdot 4$ |
| S | 1.348 | 17.94 | 3.27 | 11.15 | 67.64 | 55.4 | 10.1 | 34.5 | 209.0 |
| S | 1.360 | 18.95 | 2.88 | 11.90 | 66.27 | 56.2 | 8.5 | 35.3 | 196.4 |
| S + B | 1.306 | 16.13 | 2.49 | 10.55 | 70.83 | 55.3 | 8.5 | $36 \cdot 2$ | $242 \cdot 8$ |
| S + B | 1.343 | 17.78 | 3.27 | 11.01 | 67.94 | 55.5 | 10.2 | 34.3 | 211.9 |
| $M + B + S \dots$ | 1.379 | 19.25 | 4.35 | 11.31 | 65.09 | $55 \cdot 1$ | 12.5 | $32 \cdot 4$ | 186.5 |
| $H + B + S \dots$ | 1.232 | 12.41 | 1.99 | 9.26 | 76.34 | $52 \cdot 5$ | 8.4 | 39.1 | 322.7 |

* M = Na₂CO₃,H₂O; S = Na₂CO₃,NaHCO₃,2H₂O; H = NaHCO₃; B = Na₂B₄O₇,10H₂O; 7 = Na₂CO₃,7H₂O. † From Freeth, *Phil. Trans.*, 1922, A, **223**, 65.



Figs, 1 and 2 correspond to the ternary and the quaternary data, respectively. Fig. 1 is an incomplete triangular representation, whereas Fig. 2, also incomplete, shows the positions of the ternary points, etc., in relation to the sesquicarbonate field of the system $Na_2O-B_2O_3-CO_2-H_2O$ and of the more restricted system

Na₂CO₃-NaHCO₃-Na₂B₄O₇-Na₂B₂O₄-H₂O

studied by Teeple. K K



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