Immiscibility Diagrams of Molten Sodium Chloride–Sodium Polyborates at 810° and 980° C.

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Immiscibility isotherms at 810° and 980° C. were obtained for the boron oxide–sodium metaborate–sodium chloride system. Mixtures of the components were equilibrated in graphite crucibles, which were vacuum-sealed in silica-glass cartridges. For the mixtures with an $NaBO_2$:B_2O_3 ratio greater than 2:3, the two isotherms are nearly similar in shape but differ in the inclines of their tie lines. In the boron oxide–rich phase, the components appear to form mixed compounds.

EXCEPT FOR THE FLUORIDES, the mixtures of alkali and alkaline earth metal halides with their respective polyborates form two phases in the molten state. This property was originally reported by Stalhane (*5*, *6*), who presented fragmentary immiscibility diagrams at 850° C. for the systems sodium chloride–sodium polyborate and potassium chloride–potassium polyborate, and at 830° C. for the corresponding bromide systems.

In the above systems, the phase with alkali chloride as a major component forms the upper layer. The reverse holds with alkali bromides.

Unfortunately, Stalhane fused his salts in open platinum crucibles, which method is open to question for several reasons—the method is conducive to undesirable volatilization of the halides during equilibration, and exposure of the melts to the atmosphere liberates free halogens by the reaction

$$4NaCl + O_2(\text{atmospheric}) + 2B_2O_3 = 2Cl_2\uparrow + 4NaBO_2 \qquad (1)$$

which may account for the observed corrosion of the platinum crucible, and the technique of sampling of the phases could not be applied for the melts with compositions approaching the plait points.

The immiscibilities of binary systems MCl-B_2O_3 and $MeCl_2$-B_2O_3 (M and Me stand for the alkali and alkaline earth metals, respectively) were investigated by Kotlova, Ol'shanskiĭ, and Tsvetkov (*2*), at temperatures between 750° and 1000° C. These workers used clinched molybdenum crucibles bathed in hydrogen atmosphere. Although this precaution prevented reaction (*1*), it did not hinder halide volatilization and crucible corrosion by the melts.

Finally, Rowell reported a partial immiscibility isotherm for the sodium chloride–sodium polyborate systems at 830° C. (*4*). Rowell used essentially Stalhane's technique, as he was interested in the distribution of various solutes between the two liquid phases. Since these distributions vary with the compositions of the phases, Rowell presented his phase diagram for their documentation.

In the present study, complete immiscibility diagrams of the sodium chloride–sodium polyborate system were obtained. The technique used eliminates atmospheric effects, evaporation, and perturbations involved in sampling. Moreover, it is particularly suitable for studies extended to temperatures considerably higher than those employed by previous investigators.

EXPERIMENTAL

Preparation of Sodium Chloride–Polyborate Mixtures. The components of the mixtures used in the fusions were either sodium chloride, boron oxide, and disodium tetraborate, or sodium chloride, disodium tetraborate, and sodium metaborate. Boron oxide was Baker's C.P. grade, and the other components were analytical reagent grade (Baker's or Mallinckrodt's).

The components first were dried in partially covered borosilicate test tubes at 300° C. As they caked, they were reground periodically and further heated until caking ceased. Then they were mixed in such proportions that the composition of the mixture would be near the mid-point of a tie line, and fused in capsule-type graphite crucibles (Figure 1).

The crucibles were made of UF-4S grade graphite by the United Carbon Products Co., Bay City, Mich. Each crucible had two parts, which were fitted together by means of a tapered joint to form the capsule.

Fusion Cartridges. The crucible, filled with a sodium chloride–polyborate mixture, was placed between two graphite spacers in a silica-glass test tube, and a silica-glass cup with an attached 8-mm. O.D. tube was sealed to the open end of the tube. To prevent breakage of the tube during agitation of the melt (described later), the crucible was held tightly between the graphite spacers. During the sealing, dry argon was blown gently through a narrow silica-glass tube inserted into the 8-mm. tube to avoid burning the graphite and to circumvent condensation of moisture (from the torch flame) in the test tube. The tube with the enclosed graphite crucible then was kept at 300° C. under high vacuum. The line leading to the pump was provided with a long glass tube containing KOH pellets to trap any evolving hydrogen chloride or chlorine. Finally, to ensure complete elimination of these gases, each tube was heated under vacuum for 3 to 4 hours at about 900° C., and then sealed.

Fusions. In the fusion cartridges, the mixtures were equilibrated for 24 hours in the Lindberg (Chicago, Ill.) CR-5-type furnace at either 810° or 980° C. The 810° C. temperature was selected because sodium chloride melts at 801° C. The 980° C. was the maximum temperature allowed for the continuous operation of the furnace. At the maximum, three cartridges were heated in the furnace, where they

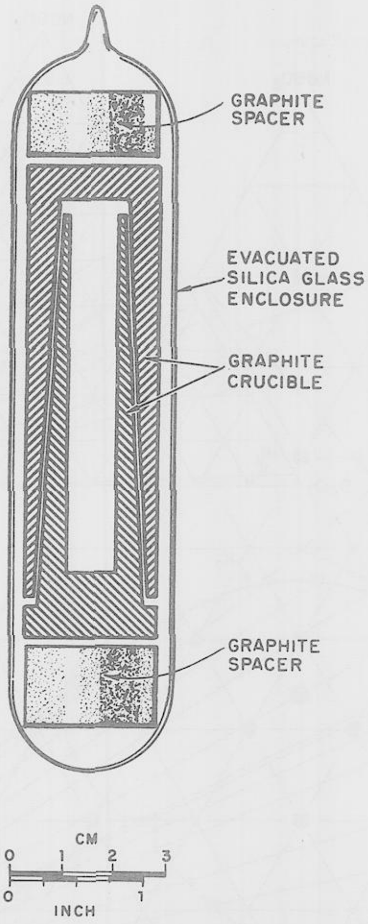


Figure 1. Fusion cartridge

were kept upright in the wells of a ceramic block. For equilibrations of the melts, the cartridges were withdrawn from the furnace at 20- to 30-minute intervals during the initial 8 hours, and briefly but vigorously agitated by means of a device described below. Then they were left undisturbed in the furnace for about 16 hours more.

Agitating Device. The agitating device (Figure 2) consisted of two fire bricks enclosed, one above the other, in a two-piece metal box, permanently hinged on one side and lockable by a hinge pin on the other. A handle that passed through a sleeve bearing mounted in a heavy metal shield was attached perpendicularly to the center of the box. The cartridges were placed in the wells drilled in the lower brick. The upper brick was hollowed out to accommodate the portions of the cartridges protruding from the wells. When the cartridges were placed in the device, the box rested on a platform. Then it was locked, shifted away from the platform, and rocked vigorously.

Recovery and Analysis of Melts. After the melt was equilibrated, the cartridge was air-quenched in wire gauze tube. It took about 0.8 minute for the temperature to drop from 980° to 810° C., or from 810° to 680° C. The graphite crucible recovered from the capsule was opened with a hacksaw blade, and representative samples of the two solidified phases, weighing between 0.5 and 1.5 grams, were dissolved in warm or gently boiling water in 250-ml. volumetric flasks. The solutions, when cooled to room temperature, were brought to adequate volume, permitting 25-ml. aliquots (measured with the same pipet) to be analyzed in duplicate for each component. Since the solutions—except those containing B_2O_3 and NaCl only—were alkaline, the analyses were done on the same day.

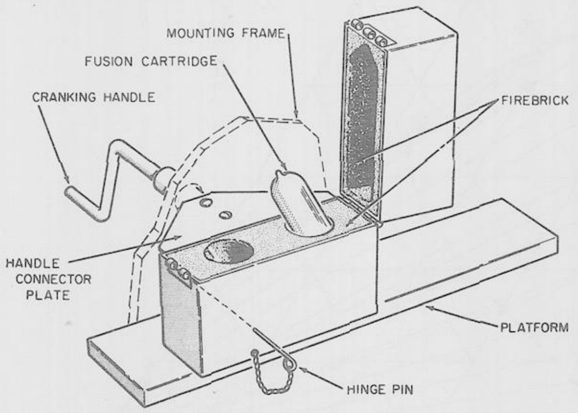


Figure 2. Device for agitating melts in fusion cartridges

Table I. Equilibrium Composition of Conjugate B_2O_3 and NaCl Phases (Mole %) for NaCl–B_2O_3–$NaBO_2$ System.

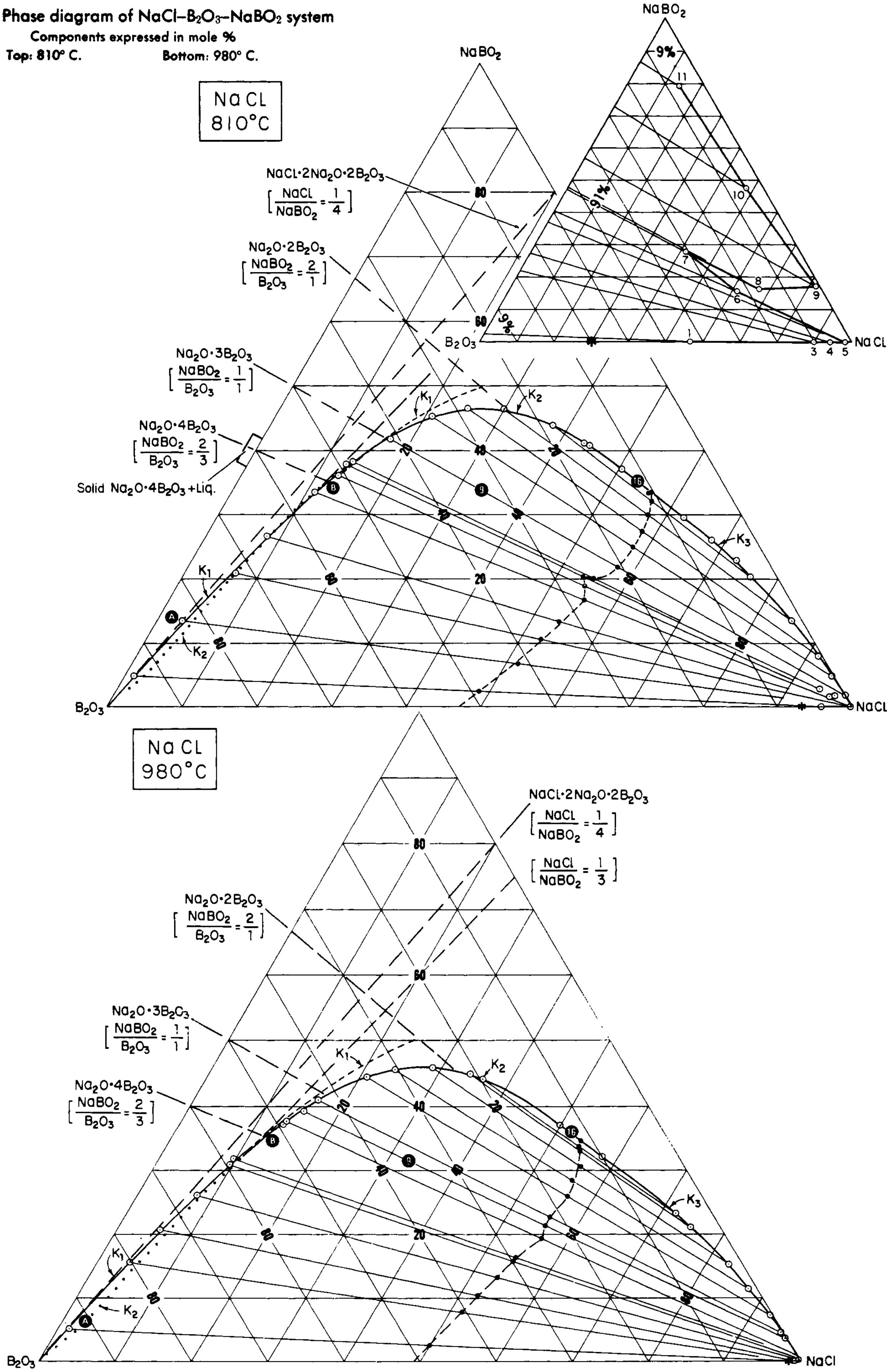
	B_2O_3 Phase			NaCl Phase		
Run No.	NaCl	$NaBO_2$	B_2O_3	NaCl	$NaBO_2$	B_2O_3
810° C.						
B_2O_3–NaCl Mixture[a]	...	...	100.00	93.00	...	7.00
1	1.16	4.86	93.98	95.65	0.04	4.31
2	3.26	13.54	83.20	...	...	...
3	6.77	20.88	72.35	98.98	0.00	1.02
4	8.04	26.67	65.29	99.41	0.00	0.59
5	11.01	33.50	55.49	99.80	0.00	0.20
$NaBO_2:B_2O_3 = 2:3$						
6	12.79	36.20	51.01	96.15	1.57	2.28
7[b]	13.10	37.89	49.01	94.16	2.78	3.06
8	13.71	38.28	48.01	96.69	1.63	1.68
$NaBO_2:B_2O_3 = 1:1$						
9	16.99	41.76	41.25	98.18	1.71	0.11
10	20.76	45.25	33.99	94.77	4.78	0.45
11	24.79	46.50	28.71	91.41	7.92	0.67
12	29.87	46.41	23.72	85.04	13.38	1.58
$NaBO_2:B_2O_3 = 2:1$						
13	37.63	43.76	18.61	75.96	20.24	3.80
14	43.22	40.95	15.83	72.83	22.82	4.35
15	44.25	40.54	15.21	67.86	26.00	6.14
16	50.38	36.88	12.74	62.58	29.35	8.07
Plait point[a]	56.20	33.30	10.50	56.20	33.30	10.50
980° C.						
B_2O_3–NaCl Mixture[a]	...	...	100.00	98.40	...	1.60
1	1.54	4.99	93.47	98.44	0.00	1.56
2	4.07	15.65	80.28	98.65	0.00	1.35
3	5.53	20.74	73.73	99.23	0.00	0.77
4	7.67	26.18	66.15	99.56	0.32	0.12
5	9.61	30.90	59.49	98.99	0.70	0.31
6	9.57	31.88	58.55	99.02	0.86	0.12
$NaBO_2:B_2O_3 = 2:3$						
7	13.49	37.16	49.35	...	...	...
8	13.51	37.60	48.89	...	...	...
9	15.22	39.24	45.54	96.27	3.54	0.19
10	15.96	41.02	43.02	95.27	4.40	0.33
$NaBO_2:B_2O_3 = 1:1$						
11	20.62	44.50	34.88	92.23	7.32	0.45
12	23.87	45.54	30.59	87.50	11.43	1.07
13	28.68	45.92	25.40	82.80	15.40	1.80
$NaBO_2:B_2O_3 = 2:1$						
14	34.07	44.93	21.00	74.93	21.06	4.01
15	36.19	44.23	19.58	71.83	23.20	4.97
16	49.90	37.06	13.04	57.96	32.12	9.92
Plait point[a]	53.50	34.70	11.80	53.50	34.70	11.80

[a] Data estimated from conjugation curve. [b] Data from two runs with analytically identical results.

Figure 3. Phase diagram of NaCl–B_2O_3–$NaBO_2$ system

Components expressed in mole %

Top: 810° C. Bottom: 980° C.



The analytical methods were: for boron oxide—acid-base titration, in presence of mannitol (*7*); for sodium metaborate—acid-base titration, in presence of methyl orange; and for sodium chloride—Volhard titration. The analytical reproducibility, with respect to the minimum and maximum combined volumes of $0.1N$ reagents used, was better than 0.1% in the case of larger sample weights and 0.2% in the case of smaller samples. The solutions used in titrations were $0.1N$ hydrochloric acid standardized against three weighed quantities of HgO (*1*), carbonate-free $0.1N$ sodium hydroxide standardized against three weighed quantities of potassium hydrogen phthalate (*8*), and $0.1N$ silver nitrate solution standardized against $0.1N$ KCNS, which in turn was standardized with respect to $0.1N$ mercuric nitrate (*9*). The correspondence between the prepared standard solutions was further checked by titrations of hydrochloric acid with sodium hydroxide and silver nitrate solutions.

The analytical data given in mole per cent B_2O_3, $NaBO_2$, and NaCl are presented in Table I. The phase diagrams constructed from the data are depicted in Figure 3. In addition, Figure 4 shows the log-log plots of the ratios of $NaBO_2$ to the major components (boron oxide and sodium chloride) in the respective conjugate phases. The first and last points of these plots are marked by numbers 9 and 16, respectively. The corresponding tie lines in the diagrams are similarly numbered to show the range of runs to which the log-log plots apply.

RESULTS

The phase diagrams (Figure 3) show that, for mixtures with a $NaBO_2$:B_2O_3 ratio larger than 2:3, the temperature has rather small effect on the shapes of the isotherms. This small effect was also observed by Stalhane (*5*), who made several equilibrations in the temperature range between 810° and 890° C.

With binary B_2O_3–NaCl mixtures, B_2O_3 dissolves partially in sodium chloride. This solubility decreases with the temperature increase. When sodium metaborate is added gradually to the mixture, the solubility of B_2O_3 in sodium chloride phase decreases and becomes virtually nil when the 2:3 ratio of $NaBO_2$ to B_2O_3 in the boron oxide phase is reached. The molar ratios of $NaBO_2$ to B_2O_3 equal to 2:3, 1:1, and 2:1 in the boron oxide phases are appropriately indicated in the diagrams and the table.

However, the solubility of B_2O_3 returns as soon as the ratio of $NaBO_2$ to B_2O_3 in the boron oxide phase becomes greater than 2:3, and it is accompanied by marked dissolution of $NaBO_2$. At the same time, the solubility of sodium chloride in the boron oxide phase increases in a manner practically independent of temperature. In this region the two isotherms differ in the respect that at 810° C., the solution of B_2O_3 in the sodium chloride at first considerably increases and then diminishes, as seen in the insert to Figure 3, top.

Significantly, the disappearance and reappearance of the solubility of B_2O_3 in the sodium chloride phase coincide with the stoichiometric $NaBO_2$-to-B_2O_3 ratio equivalent to that of disodium octaborate, $Na_2O \cdot 4B_2O_3$ (m.p. 816° C.), the existence of which was established by Morey and Merwin (*3*). At 810° C., solid disodium octaborate separates from binary mixtures of $NaBO_2$ and B_2O_3 in the range of 62.62 to 58.23 mole % B_2O_3. This range is indicated in Figure 3, top, by the notation "solid $Na_2O \cdot 4B_2O_3$ + liq." The composition curves of the boron oxide phase at the point corresponding to the disodium octaborate (*B*) are slightly indented.

The phase diagrams contain the conjugation curves (the lines crossing the mid-points of the tie lines) extrapolated both to the B_2O_3–NaCl base lines and to the immiscibility curves. From these extrapolations, estimates have been made of the saturation solubilities of B_2O_3 in pure sodium

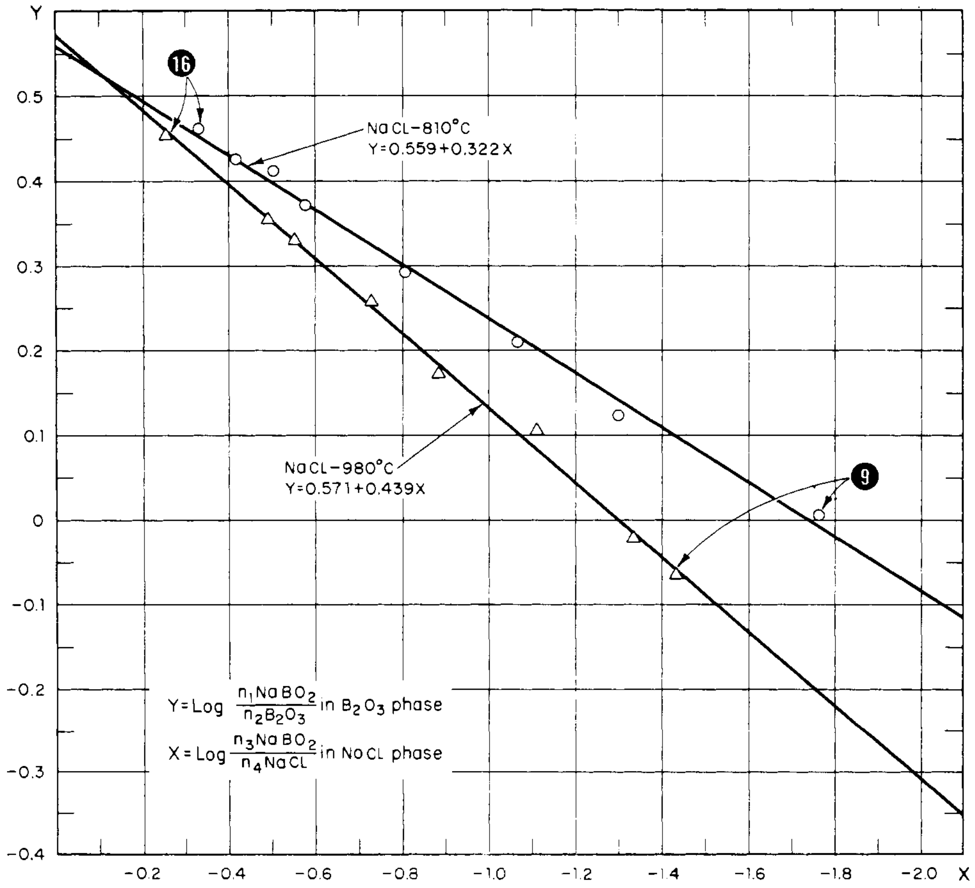


Figure 4. Log-log plots of distribution of $NaBO_2$ between B_2O_3 and NaCl in conjugate phases at 810° and 980° C.

Table II. Apparent Stoichiometric Combinations of Sodium Chloride with Disodium Octaborate in Boron Oxide Phase of NaCl–B_2O_3–$NaBO_2$ System at 810° and 980° C.

Reference Points, Figure 3	$\frac{NaCl}{Na_2O \cdot 4B_2O_3}$	Remarks
B_2O_3 corner up to *A*	1:2	Mixtures of one combination of NaCl with $Na_2O \cdot 4B_2O_3$ and uncombined B_2O_3. (At 830° C., viscosity of melts decreases[a])
A to *B*	1:2 and 2:3	Mixtures of two combinations of NaCl with $Na_2O \cdot 4B_2O_3$ and uncombined B_2O_3. (At 830° C., viscosity of melts increases[a])
B	2:3	Uncombined B_2O_3 absent. (At 830° C., viscosity past point B decreases[a])

[a] Viscosity observations by M.H. Rowell (of this laboratory).

chloride (indicated by asterisks) and estimates of the plait point compositions of the mixtures. The respective data, incorporated in the table, indicate that the solubility of B_2O_3 in sodium chloride diminishes with increasing temperature; therefore, it is exothermic. On the other hand, the compositions of the systems at the plait points do not differ appreciably at the two temperatures used.

The log-log regression lines of the molar distribution of $NaBO_2$ between the major components of the conjugate phases (Figure 4) show that more $NaBO_2$ is available for extraction by the sodium chloride phase at 980° C. than at 810° C. This may suggest that the stabilities of disodium octaborate and disodium tetraborate, regarded as present in the systems (3), are temperature-dependent according to the equations:

$$Na_2O \cdot 4B_2O_3 \underset{T_1}{\overset{T_2}{\rightleftharpoons}} Na_2O \cdot 2B_2O_3 + 2B_2O_3 \qquad (2)$$

and

$$Na_2O \cdot 2B_2O_3 \underset{T_1}{\overset{T_2}{\rightleftharpoons}} 2NaBO_2 + B_2O_3 \qquad (3)$$

where T_1 refers to the lower and T_2 to the higher temperature.

Stoichiometric Relationships. The phase diagrams suggest that, in the composition range between the B_2O_3 corner and point *B*, two types of stoichiometric combination between NaCl and $Na_2O \cdot 4B_2O_3$ in the boron oxide phase may be formed. These stoichiometric combinations are indicated in Table II.

Empirical Equations. Neglecting the deformity at the NaCl corner at 810° C., the phase diagrams can be constructed by using the following three quantitative expressions

$$K_1 = \frac{[NaCl]}{[NaBO_2]} \cdot [B_2O_3]^{1/2} = 2.519 \text{ (mole \%)}^{1/2} \text{ at } 810° \text{ C., and}$$
$$= 2.462 \text{ (mole \%)}^{1/2} \text{ at } 980° \text{ C.}$$

for the segments of the immiscibility curve from the B_2O_3 corner to the point of the $2NaBO_2{:}3B_2O_3$ ratio,

$$K_2 = \frac{[NaCl]}{[NaBO_2]^{1/2}} \cdot [B_2O_3] = 1.0580 \times 10^2 \text{ (mole \%)}^{3/2} \text{ at } 810° \text{ C., and}$$
$$= 1.0819 \times 10^2 \text{ (mole \%)}^{3/2} \text{ at } 980° \text{ C.}$$

for the following segments to the vicinity of the respective plait points, and

$$K_3 = \frac{[NaCl]^{1/2}}{[NaBO_2]^2} \cdot [B_2O_3] = 7.625 \times 10^{-2} \text{ (mole \%)}^{-1/2} \text{ at } 810° \text{ C., and}$$
$$= 7.572 \times 10^{-2} \text{ (mole \%)}^{-1/2} \text{ at } 980° \text{ C.}$$

from the respective plait points to the NaCl corners. The curves in Figure 3 were drawn according to the above relationships.

ACKNOWLEDGMENT

The illustrations were drawn by Ichiro Hayashi.

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(6) *Ibid.,* **36,** 404 (1930).
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(9) *Ibid.,* p. 266.

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CORRECTION

In the article "Equilibria in the Hydration of Propylene and of Butylenes" by C. S. Cope [J. CHEM. ENG. DATA **11**, 379 (1966)], the following corrections should be made:

Page 380, column 2, line 12: "of olefin" should read "of olefin and ether"

Page 380, Figure 1: "Ethylene Hydration (*1*)" should read "Ethylene Hydration (*6*)"

Page 381, Reaction 3: "$CH_3CH_2=CH_2$" should read "$CH_3CH_2CH=CH_2$"

Page 381, Table V, footnote *i*: "summed" should read "assumed".

CORRECTION

In the article "Equations of State for Propyne" by T. M. Stark and Joseph Joffe [J. CHEM. ENG. DATA **9**, 327 (1964)], the equation at the bottom of page 328 should be corrected to read:

$$\frac{P}{2.0482} = \frac{T}{V} + \frac{1.734T - 1554 - 1.949 \times 10^8/T^2}{V^2} + \frac{9.241T - 5294}{V^3} +$$
$$\frac{22{,}533}{V^6} + \frac{8.342 \times 10^8 (1 + 7.759/V^2)e^{-7.759/V^2}}{V^3T^2}$$

In the nomenclature on page 329, the units for the gas constant, *R*, should be changed from cc. atm./mole ° K. to cc. atm./gram ° K.