

W = total moles of fixed liquid in the GLPC column
 y = mole fraction in the vapor phase
 Z = compressibility factor of methane
 Z_o = compressibility factor of elution gas corresponding to P_o, T_o
 Z_M = compressibility of elution gas

Superscripts

* = property of tracer component

Subscripts

i, j, k = component identification
 1, 2 = methane and solvent, respectively, in methane binaries
 1, 2, 3, T = methane, ethane, propane, and tritium, respectively

LITERATURE CITED

- (1) Akers, W.W., Burns, J.F., Fairchild, W.R., *Ind. Eng. Chem.* **46**, 2531 (1954).
- (2) Bloomer, E.H., Gami, D.C., Parent, J.D., *Inst. Gas Technol. Res. Bull.* **22**, (1953).
- (3) Chang, H.L., Rice University, Houston, Tex., private communications, 1966.
- (4) Chang, H.L., Hurt, L.J., Kobayashi, Riki, *A.I.Ch.E.J.* **12**, 1212 (1966).
- (5) Chao, K.C., Seader, J.D., *Ibid.*, **7**, 598 (1961).
- (6) Fenske, M.R., Braun, W.G., Holmes, A.S., "Bibliography of Vapor-Liquid Equilibrium Data for Hydrocarbon Systems," No. 1, 1963, American Petroleum Institute, New York, 1963.
- (7) Flynn, T.M., *Natl. Bur. Std. Tech. Note* No. 56 (1960).
- (8) Hurt, L.J., Ph.D. thesis, Rice University, July 1962.
- (9) Katz, D.L., Rzasas, M.J., "Bibliography for Physical Behavior of Hydrocarbons Under Pressure," J.W. Edwards, Inc., Ann Arbor, Mich., 1946.
- (10) Kohn, J.P., *A.I.Ch.E.J.* **7**, 514 (1961).
- (11) Kohn, J.P., Bradish, W.F., *J. CHEM. ENG. DATA* **9**, 5 (1964).
- (12) Koonce, K.T., Ph.D. thesis, Rice University, November 1963.
- (13) Koonce, K.T., Deans, H.A., Kobayashi, Riki, *A.I.Ch.E. J.* **11**, 259 (1965).
- (14) Koonce, K.T., Kobayashi, Riki, *J. CHEM. ENG. DATA* **9**, 490 (1964).
- (15) *Ibid.*, p. 494.
- (16) Muckleroy, J.A., "Bibliography on Hydrocarbons, 1946-1960," Natural Gas Processors Association, Tulsa, Okla., 1962.
- (17) Price, A.R., Kobayashi, Riki, *J. CHEM. ENG. DATA* **4**, 40 (1959).
- (18) Reamer, H.H., Sage, B.H., Lacey, W.N., *CHEM. ENG. DATA SER.* **1**, 29 (1956).
- (19) Roberts, L.R., Wang, R.H., Azarnoosh, A., McKetta, J.J., *J. CHEM. ENG. DATA* **7**, 484 (1962).
- (20) Sage, B.H., Lacey, W.N., "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," Am. Petroleum Inst., New York, 1950.
- (21) Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **30**, 1296 (1938).
- (22) Shim, J., Kohn, J.P., *J. CHEM. ENG. DATA* **7**, 3 (1962).
- (23) Shipman, L.M., Kohn, J.P., *Ibid.*, **11**, 176 (1966).
- (24) Stalkup, F.I., Ph.D. thesis, Rice University, August 1961.
- (25) Stalkup, F.I., Deans, H.A., *A.I.Ch.E.J.* **9**, 118 (1963).
- (26) Stalkup, F.I., Kobayashi, Riki, *Ibid.*, **9**, 121 (1963).
- (27) Van Horn, L.D., Ph.D. thesis, Rice University, March 1966.
- (28) Van Horn, L.D., Kobayashi, Riki, *A.I.Ch.E.J.*, to be published.

RECEIVED for review May 13, 1966. Accepted April 4, 1967.

Solubility Isotherms in the System Sodium Oxide-Boric Oxide-Water

Revised Solubility-Temperature Curves of Boric Acid, Borax, Sodium Pentaborate, and Sodium Metaborate

NELSON P. NIES and RICHARD W. HULBERT
 U. S. Borax Research Corp., Anaheim, Calif. 92803

Isotherms at 0°, 5°, 10°, 20°, 30°, 40°, 50°, 60°, 75°, and 94° C. have been determined in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ in the range of $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio from 0 to 1.2. The compounds found were those with $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ molar proportions 0:1:3, 1:1:1, 1:1:4, 1:1:8, 1:2:4, 1:2:5, 1:2:10, 1:5:2, 1:5:4, 1:5:10, 2:5:5, 2:5:1:7, and 2:9:11. Revised solubility-temperature curves are given for boric acid, borax, sodium pentaborate, and sodium metaborate.

EARLY WORK on the solubility isotherms in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$, by Dukelski (7) at 30°, and by Sborgi *et al.* (16) at 0°, 20°, 35°, 45°, 60°, and 90° C., gives the approximate locations of the isotherms, but is limited and partly inaccurate. Isotherms at 35° and 50° in the region of $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio from 0 to 0.5 were determined by Suhr (17), and agree well with the present work. Recently, Bouaziz and Milman have published diagrams showing the 100° isotherm (5) and portions of the 46°,

56°, and 80° isotherms (11). Their results differ from the present work in some respects.

In the present investigation, the 0°, 5°, 10°, 20°, 30°, 40°, 50°, 60°, 75°, and 94° C. isotherms were determined, including curves for several compounds which were unknown to the early investigators. Except for a few determinations at 40°, 60°, and 98.6° C., this work was limited to the region having $\text{Na}_2/\text{B}_2\text{O}_3$ mole ratios less than 1.2, which is of more practical interest than the very alkaline

region. Also, sufficient experimental work was done on the solubility-temperature curves of borax, boric acid, sodium pentaborate, and sodium metaborate to clear up discrepancies in the literature.

EXPERIMENTAL

Special quality borax and boric acid (United States Borax & Chemical Corp., typical analysis 0.2 to 6 p.p.m. of Cl, SO₄, PO₄, Fe, Ca, and heavy metals as Pb), photographic grade sodium metaborate tetrahydrate and dihydrate (United States Borax & Chemical Corp., typical analysis 60 p.p.m. of SO₄ and less than 10 p.p.m. of Fe and Cl), and reagent grade 50% liquid caustic soda (Mallinckrodt, maximum Na₂CO₃ content, 0.1%) were used as starting materials. The distilled water used for the determination of the solubility of borax in water was freshly boiled to eliminate CO₂, which causes high solubility values at the lower concentrations. Suitable mixtures were agitated in 250-ml. screw-capped bottles in a water, brine, or oil bath controlled to within 0.1° C. Both a modified American Instrument Co. shaking bath and a bath provided with a rotating bottle holder were used. Equilibrium was usually approached from below. Polypropylene bottles were used where the Na₂O/B₂O₃ mole ratio was greater than about 0.45, in order to avoid attack on the glass by alkaline solutions. "No Solvit" glass bottles were used for mole ratios less than 0.45. After the mixture reached equilibrium, a sample of the liquor was removed, usually by immersing the lower part of an 8- to 10-mm. I.D. glass tube, having the lower end covered with filter paper, in the solution for a few minutes and then quickly pouring the filtered liquor from the tube into a weighing bottle. When a large or viscous sample was needed, the sample was removed by applying pressure with a squeeze bulb to force the liquid through a cotton plug into a weighing bottle. Na₂O and B₂O₃ were determined by titration with 0.5N HCl using methyl red, followed by titration to phenolphthalein with 0.5N sodium hydroxide, which had been standardized against recrystallized dry boric acid. Most of the solutions were made up to contain a little less than the equilibrium concentration and then seeded at the operating temperature with a large excess of the solid phase or phases desired. The solubility values for the stable points (Table I) are the average of three or more samples taken during a period of usually one to several days after the composition showed no progressive change. The solubility values at the metastable points in Table I were usually determined with agitation for several hours, but at a few points it was necessary to use a very short agitation time. For example, in determining the point saturated with boric acid and borax at 30° (Na₂O/B₂O₃ mole ratio 0.249), 104.6 grams of borax and 81.2 grams of boric acid were added to 94 grams of water at room temperature, giving an over-all composition of 30% B₂O₃. After being agitated in the constant temperature bath for 20 minutes, the liquor contained 23.2% B₂O₃. A liquor sample taken after 40 minutes gave only 18.8% B₂O₃ because of crystallization of sodium pentaborate. The 20-minute value was therefore taken as the approximate metastable isothermal invariant point. In some cases, evaporation by boiling was necessary, using a nickel beaker in case of alkaline solutions, to obtain the desired composition. In case of any doubt as to the identity of the solid phases, they were identified by means of their x-ray diffraction patterns.

The boiling point of solutions saturated with sodium metaborate hemihydrate was determined in a 1000-ml. nickel beaker provided with a rubber cover, stirrer, thermometer, and reflux condenser.

The results of the solubility experiments, including a few values taken from the literature, are given in Figures 1 to 4. Selected results, in order of increasing Na₂O/B₂O₃

Table I. Solubility Data in the System Na₂O-B₂O₃-H₂O

Na ₂ O, Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases
Temperature, 0° C.			
0:1:3		= H ₃ BO ₃	
1:1:1		= Na ₂ O·B ₂ O ₃ ·H ₂ O or NaBO ₂ ·0.5H ₂ O	
1:1:4		= Na ₂ O·B ₂ O ₃ ·4H ₂ O or NaBO ₂ ·2H ₂ O	
1:1:8		= Na ₂ O·B ₂ O ₃ ·8H ₂ O or NaBO ₂ ·4H ₂ O	
1:2:4		= Na ₂ O·2B ₂ O ₃ ·4H ₂ O	
1:2:5		= Na ₂ O·2B ₂ O ₃ ·5H ₂ O	
1:2:10		= Na ₂ O·2B ₂ O ₃ ·10H ₂ O	
1:5:10		= Na ₂ O·5B ₂ O ₃ ·10H ₂ O or NaB ₅ O ₈ ·5H ₂ O	
2:5:5		= 2Na ₂ O·5B ₂ O ₃ ·5H ₂ O	
2:5:1:7		= 2Na ₂ O·5.1B ₂ O ₃ ·7H ₂ O	
2:9:11		= 2Na ₂ O·9B ₂ O ₃ ·11H ₂ O	
(m)		= Metastable	
0	1.42	0	0:1:3
0.18	2.18	0.095	0:1:3
0.70	4.23	0.186	0:1:3
0.82	4.79	0.192	1:5:10(m)
0.81	4.66	0.196	0:1:3 & 1:2:10
0.88	4.93	0.201	1:5:10(m)
0.90	4.94	0.205	1:5:10(m)
0.53	2.85	0.208	1:2:10
0.31	1.14	0.306	1:2:10
0.324	0.727	0.500	1:2:10
1.401	1.607	0.980	1:2:10
4.67	5.27	0.997	1:2:10
6.80	7.63	1.002	1:2:10 & 1:1:8
7.14	6.67	1.203	1:1:8
Temperature, 5° C.			
0	1.677	0	0:1:3
0.195	2.47	0.089	0:1:3
0.763	4.81	0.179	0:1:3
0.99	5.68	0.197	0:1:3 & 1:5:10
1.02	5.73	0.200	1:5:10
1.15	6.28	0.206	0:1:3 & 1:2:10(m)
1.09	5.90	0.207	1:2:10 & 1:5:10;
0.88	4.70	0.210	1:2:10
0.715	3.71	0.217	1:2:10
0.48	2.14	0.251	1:2:10
0.382	1.137	0.380	1:2:10
0.402	0.902	0.501	1:2:10
0.556	0.821	0.762	1:2:10
5.43	6.13	0.996	1:2:10
7.35	8.29	1.00	1:2:10 & 1:1:8
7.69	7.24	1.19	1:1:8
Temperature, 10° C.			
0	1.967	0	0:1:3
0.27	3.11	0.096	0:1:3
0.73	4.97	0.164	0:1:3
1.13	6.57	0.193	0:1:3 & 1:5:10
1.21	6.74	0.201	1:5:10
1.65	8.62	0.215	0:1:3 & 1:2:10(m)
1.36	7.04	0.217	1:5:10 & 1:2:10
1.21	6.2	0.220	1:2:10
0.90	4.4	0.229	1:2:10
0.70	3.2	0.246	1:2:10
0.56	2.25	0.279	1:2:10
0.502	1.78	0.317	1:2:10
0.499	1.125	0.500	1:2:10
0.555	1.02	0.612	1:2:10
0.632	1.00	0.710	1:2:10
0.997	1.26	0.888	1:2:10
2.23	2.595	0.975	1:2:10
5.38	6.10	0.991	1:2:10
8.03	9.05	0.996	1:2:10 & 1:1:8
8.13	8.24	1.110	1:1:8
8.36	7.72	1.218	1:1:8
Temperature, 20° C.			
0	2.66	0	0:1:3
0.373	4.29	0.098	0:1:3
0.97	6.80	0.160	0:1:3
1.43	8.68	0.1855	0:1:3 & 1:5:10
1.59	8.96	0.200	1:5:10
1.87	9.56	0.220	1:5:10
3.45	16.41	0.236	0:1:3 & 1:2:10(m) ^a
2.19	10.35	0.238	1:5:10 & 1:2:10

(Continued on page 305)

Table I. Solubility Data in the System Na₂O–B₂O₃–H₂O (Continued)

Na ₂ O Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases	Na ₂ O, Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases
Temperature, 20° C.				Temperature, 50° C.			
1.40	6.3	0.25	1:2:10	19.62	26.90	0.820	1:2:5 & 1:1:4(m)
1.05	4.4	0.268	1:2:10	6.36	8.70	0.821	1:2:10
0.783	2.5	0.352	1:2:10	16.94	22.81	0.835	1:2:5
0.765	1.72	0.500	1:2:10	13.27	17.83	0.837	1:2:5
0.994	1.53	0.279	1:2:10	8.51	11.35	0.842	1:2:10
1.77	2.18	0.911	1:2:10	17.67	22.25	0.893	1:1:8
6.27	7.18	0.981	1:2:10	16.17	18.25	0.996	1:1:8
9.53	10.88	0.984	1:2:10 & 1:1:8	16.02	17.90	1.006	1:1:8
9.54	9.63	1.114	1:1:8	16.12	16.74	1.082	1:1:8
9.74	9.14	1.198	1:1:8	16.56	15.95	1.167	1:1:8
Temperature, 30° C.				Temperature, 60° C.			
0.517	5.83	0.100	0:1:3	0	7.22	0.000	0:1:3
1.237	8.8	0.158	0:1:3	1.04	11.9	0.098	0:1:3
1.83	11.22	0.183	0:1:3 & 1:5:10	2.08	16.5	0.142	0:1:3;
2.12	11.75	0.203	1:5:10	3.36	21.77	0.174	0:1:3 & 1:5:10
2.91	13.6	0.240	1:5:10	3.58	22.60	0.178	0:1:3 & 2:9:11(m)
5.14	23.16	0.249	0:1:3 & 1:2:10(m) ^a	3.97	22.62	0.198	1:5:10 & 2:9:11
3.46	15.08	0.258	1:5:10 & 1:2:10	4.30	23.68	0.204	1:5:4(m) ^a
2.33	9.7	0.270	1:2:10	4.13	22.74	0.204	2:9:11
1.59	6.04	0.296	1:2:10	4.21	23.10	0.205	1:5:10(m)
1.27	3.94	0.362	1:2:10	5.61	26.13	0.241	1:5:10 & 2:5:1:7(m)
1.17	2.63	0.499	1:2:10	5.40	24.83	0.245	2:9:11 & 2:5:1:7
1.36	2.32	0.661	1:2:10	7.09	29.90	0.266	1:5:10(m)
1.97	2.66	0.831	1:2:10	4.36	17.80	0.275	2:5:1:7
3.24	3.95	0.921	1:2:10	10.25	37.92	0.304	1:5:10 & 1:2:4(m)
4.63	5.49	0.949	1:2:10	9.18	33.29	0.310	1:2:4 & 2:9:11(m)
11.48	13.46	0.959	1:2:10 & 1:1:8	10.98	39.57	0.312	1:5:10 & 1:2:5(m)
8.20	9.59	0.961	1:2:10	11.85	41.84	0.318	1:5:10 & 1:2:10(m)
11.07	12.37	1.006	1:1:8	9.52	33.51	0.319	1:2:5(m)
11.18	11.42	1.100	1:1:8	7.55	26.00	0.326	1:2:4(m)
11.47	10.70	1.205	1:1:8	7.88	26.31	0.337	1:2:5(m)
Temperature, 40° C.				Temperature, 60° C.			
0.68	7.6	0.101	0:1:3	8.11	26.48	0.344	1:2:10(m) ^a
1.48	11.1	0.150	0:1:3	6.71	21.01	0.359	1:2:5(m) ^a
2.26	14.25	0.178	0:1:3 & 1:5:10	6.96	21.63	0.361	1:2:10(m) ^a
2.76	15.1	0.205	1:5:10	3.94	11.83	0.375	2:5:1:7
3.57	17.0	0.236	1:5:10	5.40	16.07	0.378	1:2:4(m)
4.29	18.86	0.255	1:5:10 & 2:5:1:7	5.52	15.72	0.395	1:2:10
5.51	22.17	0.280	1:5:10 & 1:2:10(m)	6.14	18.25	0.378	1:2:10(m) ^a
3.78	15.77	0.270	2:5:1:7	6.09	18.02	0.380	1:2:5(m) ^a
4.70	18.6	0.284	1:2:10(m)	5.59	15.83	0.397	1:2:5(m)
3.39	12.92	0.295	1:2:10 & 2:5:1:7	4.63	11.58	0.450	1:2:4 & 2:5:1:7
2.74	9.9	0.311	1:2:10	5.01	12.45	0.452	1:2:10(m)
2.31	7.7	0.337	1:2:10	5.11	12.71	0.452	1:2:5(m)
1.893	5.32	0.399	1:2:10	4.95	11.89	0.468	1:2:10 & 2:5:1:7(m)
1.82	4.10	0.499	1:2:10	5.03	11.32	0.499	1:2:5(m)
2.00	3.67	0.613	1:2:10	4.52	10.23	0.497	1:2:4
2.71	3.95	0.772	1:2:10	4.94	11.14	0.498	1:2:10(m)
4.68	5.93	0.884	1:2:10	5.28	10.02	0.592	1:2:10(m)
14.48	18.33	0.888	1:2:10 & 1:1:8	5.40	10.22	0.594	1:2:5(m)
12.72	15.88	0.900	1:2:10	4.96	9.29	0.601	1:2:4
9.83	12.03	0.917	1:2:10	5.70	10.30	0.621	1:2:5(m) ^b
13.14	14.78	1.000	1:1:8	5.72	10.23	0.629	1:2:10(m) ^a
13.27	13.71	1.088	1:1:8	5.89	10.36	0.639	1:2:5(m) ^a
13.60	12.72	1.202	1:1:8	6.05	10.57	0.643	1:2:10(m) ^a
42.17	4.46	10.63	1:1:1 ^b	6.69	10.94	0.688	1:2:5(m) ^b
Temperature, 50° C.				Temperature, 67° C.			
0	5.78	0	0:1:3	6.27	9.98	0.706	1:2:4
0.912	9.93	0.103	0:1:3	7.77	12.27	0.712	1:2:10(m) ^a
2.76	17.74	0.175	0:1:3 & 1:5:10	8.47	12.73	0.748	1:2:5(m)
3.44	20.49	0.189	0:1:3 & 2:9:11(m) ^a	8.22	11.94	0.773	1:2:4
3.33	18.53	0.202	1:5:10	21.56	31.42	0.771	1:2:5 & 1:1:4(m)
4.20	21.48	0.220	2:9:11(m) ^a	12.00	16.92	0.797	1:2:5(m)
4.34	20.9	0.233	1:5:10	18.83	26.45	0.800	1:2:5(m)
4.98	22.73	0.246	2:5:1:7 & 2:9:11(m)	15.65	21.83	0.806	1:2:5(m)
4.88	22.13	0.247	1:5:10 & 2:5:1:7	20.66	28.58	0.813	1:2:4 & 1:1:4
5.63	24.27	0.260	2:9:11 & 1:5:10(m)	13.43	18.20	0.829	1:2:4
3.77	14.84	0.286	2:5:1:7	16.66	22.52	0.831	1:2:4
8.64	32.09	0.303	1:5:10 & 1:2:10(m)	19.46	24.64	0.888	1:1:4
8.23	30.52	0.303	2:9:11 & 1:2:10(m)	18.14	20.55	0.992	1:1:4
6.89	25.3	0.306	1:2:10(m)	18.03	18.48	1.096	1:1:4
4.63	15.9	0.327	1:2:10(m)	18.39	16.53	1.250	1:1:4
3.48	10.75	0.364	1:2:10 & 2:5:1:7	19.45	13.14	1.664	1:1:4
3.19	9.06	0.396	1:2:10	21.77	9.52	2.57	1:1:4
2.91	6.56	0.499	1:2:10	28.49	6.31	5.07	1:1:4
3.16	5.88	0.605	1:2:10	18.81	21.13	1.001	1:1:4
3.99	6.24	0.719	1:2:10	18.84	21.35	0.992	1:1:4
17.13	23.99	0.803	1:2:10(m) ^a				
19.34	26.50	0.820	1:2:5 & 1:1:8				

(Continued on page 306)

Table I. Solubility Data in the System Na₂O-B₂O₃-H₂O (Continued)

Na ₂ O, Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases	Na ₂ O, Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases
Temperature, 75° C.				Temperature, 94° C.			
1.53	16.45	0.105	0:1:3	7.45	17.72	0.472	2:5:1:7(m)
3.92	26.48	0.167	0:1:3 & 2:9:11	7.55	17.10	0.496	2:5:5 & 1:2:4
4.41	28.34	0.173	0:1:3 & 1:5:10(m) ^b	9.34	21.04	0.499	1:2:5(m)
4.49	25.89	0.195	2:9:11	7.54	16.95	0.500	1:2:4
6.84	32.67	0.235	1:5:10 & 2:5:1:7(m) ^b	9.46	20.43	0.521	2:5:1:7 & 1:2:5(m)
6.10	28.09	0.244	2:9:11 & 2:5:1:7 ^a	7.66	16.48	0.522	1:2:4
7.86	35.15	0.251	1:5:10 & 2:5:5(m)	9.78	20.11	0.547	2:5:5 & 1:2:5(m)
6.98	29.96	0.262	2:9:11 & 2:5:5(m)	8.30	15.86	0.588	1:2:4
4.69	17.15	0.300	2:5:1:7	10.50	19.71	0.599	1:2:5(m)
12.74	46.9	0.305	1:5:10 & 1:2:4(m)	9.58	16.50	0.653	1:2:4
14.13	50.36	0.315	1:5:10 & 1:2:5(m)	12.80	21.84	0.658	1:2:5(m)
10.59	37.77	0.316	2:9:11 & 1:2:4(m)	24.03	40.16	0.673	1:2:5(m)
5.40	19.16	0.317	2:5:5(m)	10.30	17.20	0.673	1:2:4
11.54	39.73	0.326	2:9:11 & 1:2:5(m)	15.54	25.58	0.683	1:2:5(m)
9.23	29.78	0.348	1:2:5(m)	20.22	32.81	0.693	1:2:5(m)
4.58	14.29	0.360	2:5:1:7	25.81	41.55	0.698	1:2:4
5.30	16.26	0.367	2:5:5(m)	12.47	19.97	0.702	1:2:4
6.58	19.40	0.381	1:2:4(m)	16.32	25.10	0.731	1:2:4
7.41	21.27	0.391	1:2:5(m)	27.56	39.60	0.782	1:1:4
4.84	13.48	0.403	2:5:1:7	24.86	32.11	0.870	1:1:4
5.85	15.42	0.427	2:5:5 & 1:2:4(m)	23.19	26.33	0.990	1:1:4
5.66	13.84	0.460	2:5:1:7 & 1:2:4	23.03	24.20	1.070	1:1:4
6.53	15.72	0.466	2:5:5 & 1:2:5(m)	Temperature, 98° C.			
6.52	14.75	0.497	2:5:1:7 & 1:2:5(m)	7.56	42.33	0.201	1:5:10(m)
5.63	12.67	0.499	1:2:4	8.10	18.24	0.499	1:2:4(m)
7.15	13.41	0.600	1:2:5(m)	10.14	22.76	0.500	1:2:5(m)
6.27	11.69	0.602	1:2:4	7.76	17.46	0.499	2:5:5
9.40	15.24	0.693	1:2:5(m)	Temperature, 98.6° C.			
7.91	12.78	0.699	1:2:4	27.06	19.23	1.58	1:1:1 ^b
25.53	40.92	0.701	1:2:5 & 1:1:4(m)	27.55	17.55	1.76	1:1:1 ^b
22.40	34.48	0.730	1:2:5(m)	28.77	14.20	2.28	1:1:1 ^b
24.41	36.75	0.748	1:2:4 & 1:1:4	29.42	12.70	2.60	1:1:1 ^b
19.55	29.2	0.753	1:2:5(m)	30.05	11.73	2.88	1:1:1 ^b
14.53	21.64	0.755	1:2:5(m)	39.60	5.24	8.49	1:1:1 ^b
11.39	16.71	0.766	1:2:4	Temperature, 104° C.			
18.72	26.73	0.787	1:2:4	26.11	29.62	0.991	1:1:4
15.44	21.93	0.791	1:2:4	25.92	29.10	1.001	1:1:4
22.96	32.22	0.801	1:1:4	26.02	29.20	1.002	1:1:4 ^b
21.00	26.42	0.894	1:1:4	Temperature, 106° C.			
19.91	22.53	0.993	1:1:4	26.34	30.04	0.986	1:1:1
19.82	22.16	1.006	1:1:4	26.88	30.57	0.988	1:1:4(m)
19.70	20.55	1.078	1:1:4	26.28	29.84	0.990	1:1:1
Temperature, 85° C.				26.86	30.43	0.992	1:1:4(m)
21.41	24.29	0.991	1:1:4	26.87	30.19	1.000	1:1:4(m)
21.37	23.93	1.004	1:1:4	26.34	29.62	1.000	1:1:1
Temperature, 94° C.				26.80	29.98	1.004	1:1:4(m)
2.40	23.04	0.117	0:1:3 ^b	26.08	29.98	1.012	1:1:1
4.48	31.92	0.158	0:1:3 & 2:9:11	Temperature, 107° C.			
6.10	38.59	0.178	0:1:3 & 1:5:10(m)	8.53	47.89	0.200	1:5:10(m) ^a
5.10	30.94	0.185	2:9:11	Temperature, 112° C.			
7.11	39.80	0.201	1:5:10(m)	26.26	29.99	0.984	1:1:1
5.96	31.06	0.216	2:9:11	26.28	29.48	0.999	1:1:1
8.90	43.00	0.233	1:5:10 & 2:5:1:7(m)	Temperature, 119.8° C.			
9.60	44.52	0.242	1:5:10 & 2:5:5(m)	26.19	29.93	0.984	1:1:1
7.07	32.78	0.243	2:9:11 & 2:5:1:7	26.10	29.88	0.986	1:1:1
7.50	33.56	0.251	2:9:11 & 2:5:5(m)	26.12	29.20	1.002	1:1:1
6.22	25.40	0.275	2:5:5(m)	Temperature, 120.2° C. (Boiling Point)			
5.85	23.94	0.275	2:5:1:7	26.31	29.54	1.001	1:1:1
5.36	18.60	0.324	2:5:5	26.35	29.56	1.002	1:1:1
5.48	18.96	0.325	2:5:1:7(m)				
5.75	16.22	0.398	2:5:5				
5.95	16.71	0.400	2:5:1:7(m)				
9.42	23.63	0.448	1:2:5(m)				
7.67	19.16	0.450	1:2:4(m)				
6.27	16.20	0.456	2:5:5				

^a Agitation limited to 1 hr. or less to avoid formation of stable phase. ^b Identity of solid phase confirmed by x-ray.

ratio are also given in Table I. The rest of the experimental data are on file with ADI.

X-ray powder patterns were obtained with a Norelco diffractometer. Because of lack of space, the patterns for the 2:5:5 compound (Auger's borate or synthetic nasinite), 2:5:1:7 (Suhr's borate or synthetic ezcurrite), 2:9:11 (sodium 2 to 9 borate), 1:1:1 (sodium metaborate hemihydrate), 1:5:4 (sodium pentaborate dihydrate), and 1:5:2 (sodium pentaborate monohydrate) are not given here but have

been submitted to the A.S.T.M. Powder Diffraction File.

Preparation and Composition of Suhr's Borate. Suhr's borate was prepared by dissolving borax and boric acid in water in the amounts shown in experiment 1, Table II, and stirring in a closed flask at about 90° C. for 2 days. During this period, Suhr's borate crystallized. A 25-ml. portion of the slurry was poured rapidly with stirring into about 300 ml. of water at room temperature, immediately filtered on a Büchner filter, and washed quickly with water, then with

Table II. Changes in Solution Composition on Crystallization of Suhr's Borate at 90° C.

	Experiment No.			
	1	2	3	4
Borax, g.	600	600	600	562
Boric acid, g.	108.8	85.4	103	65
Water, g.	450	450	350	400
Days agitated at 90° C. for crystallization	2	3	1	3
Mole ratio Na ₂ O-B ₂ O ₃ in solution				
Before crystallization	0.390	0.411	0.395	0.420
After crystallization	0.388	0.414	0.399	0.440

acetone, and dried in air at room temperature. As the mother liquor was somewhat viscous, it could not be completely removed from the crystals unless diluted in this way before filtration. Analysis of the crystals from experiment 4, Table II, gave the following results:

	Na ₂ O, %	B ₂ O ₃ , %	H ₂ O By Differ- ence, %	Mole Ratio Na ₂ O/ B ₂ O ₃
Found	20.48	58.74	20.78	0.392
Calcd. for 2Na ₂ O·5B ₂ O ₃ ·7H ₂ O	20.72	58.20	21.08	0.4
Calcd. for 3Na ₂ O·8B ₂ O ₃ ·10H ₂ O	20.14	60.35	19.51	0.375

Since the Na₂O/B₂O₃ mole ratio was appreciably different from 0.4, several experiments were done to show whether the crystals might have the 0.4 mole ratio when formed, and change to 0.392 during filtration and washing. In these experiments, the Na₂O/B₂O₃ ratio in the liquor was determined before and after crystallization. The results are summarized in Table II.

Preparation and Composition of Auger's Borate. To prepare Auger's borate, 150 grams of borax and 24.4 grams of boric acid were dissolved in 50 grams of water by heating, to give a solution of Na₂O/B₂O₃ mole ratio 0.4. This solution was placed in a sealed bottle at 120° C. for several days. A 25-gram portion of the polycrystalline mass, produced in this bottle, was ground and added as seed to a solution of 178.5 grams of borax, 29.0 grams of boric acid, and 72.6 grams of water at 94° C., which was rotated in a thermostat at 94° for 10 days (Table I, mole ratio 0.398). A small sample of the crystals was filtered with suction, washed quickly with water and then with acetone (sample 1). Sample 2 was prepared by dissolving 2945 grams of borax and 472 grams of boric acid in 1422 grams of water at 97°, seeding with Auger's borate, stirring for 24 hours at 97° C., filtering with suction, washing quickly with cold water, then with acetone, and drying in air at room temperature. Analyses were as follows:

Sample No.	Na ₂ O, %	B ₂ O ₃ , %	H ₂ O by Differ- ence, %	Mole Ratio Na ₂ O/ B ₂ O ₃	Mole Ratio H ₂ O/ 5B ₂ O ₃
1	22.03	61.79	16.18	0.4004	5.06
2	21.85	61.50	16.65	0.3993	5.23
Calcd. for 2:5:5	22.05	61.93	16.02	0.4	5

A portion of sample 2 was washed with hot water and then with acetone. The resulting material contained 10.8 moles of H₂O per 5 moles of B₂O₃, and its x-ray pattern showed the presence of borax as well as Auger's borate.

The specific gravity of a sample having a composition near that of sample 1 was 2.135 at 21° C.

Preparation and Composition of Sodium (2 to 9) Borate Undecahydrate. Sodium (2 to 9) borate, 2Na₂O·9B₂O₃·11H₂O, crystallized slowly when a mixture of 150 grams of sodium pentaborate and 50 ml. of water was agitated at 94° C. After 1 day of agitation the Na₂O/B₂O₃ mole ratio in solution changed from the original 0.2 to 0.1986. After 8 days of agitation, the mole ratio had changed to 0.170, and the B₂O₃ content had decreased from the original 39.4 to 31.0%. After 20 days of agitation, the composition of the solution had not changed further appreciably. The solid phase was filtered, quickly washed with cold water, then with acetone, and dried in air at room temperature. Analysis gave 13.02% Na₂O, 65.85% B₂O₃, and 21.15% H₂O by difference, corresponding to 2Na₂O·9.01B₂O₃·11.17H₂O. The calculated values for 2Na₂O·9B₂O₃·11H₂O are 13.06% Na₂O and 66.0% B₂O₃.

When a mixture of 220 grams of NaB₅O₈·5H₂O was agitated with 50 ml. of water at 107° C. (Table I), the solution after 1 hour contained 47.9% B₂O₃ with a Na₂O/B₂O₃ mole ratio of 0.200. After 2 hours the B₂O₃ concentration had decreased to 44.9% and the mole ratio was 0.195. The crystals were identified as the 2:9:11 compound by their x-ray pattern. The crystals are prisms, usually less than 0.2 or 0.3 mm. in length. The x-ray pattern has been submitted to the ASTM Powder Diffraction File.

The specific gravity, measured pycnometrically at 21°, was 1.903.

RESULTS AND DISCUSSION

Boric Acid, H₃BO₃ (sassolite). REGION OF STABILITY. Figures 1 and 2 show that boric acid is the stable phase in contact with solutions having Na₂O/B₂O₃ mole ratios below values varying from 0.197 at 0° to 0.168 at 94° C.

SOLUBILITY. Because of discrepancies in the literature, the solubility of boric acid was redetermined at 0°, 5°, 10°, 20°, 30°, 40°, 50°, and 90° C. The results fall on a smooth curve which agrees well with some published values (8) but only partially with others (2, 13). The values given in Table III and Figure 3 are regarded as the best values.

Sodium Pentaborate Pentahydrate, NaB₅O₈·5H₂O (sborgitite). REGION OF STABILITY. Sodium pentaborate is stable in contact with its own solutions between 2° and 59.5°. Below 2°, its own saturated solutions are metastable with respect to borax (Figure 1), and above 59.5° they are metastable with respect to sodium (2 to 9) borate, 2Na₂O·9B₂O₃·11H₂O (Figure 3).

SOLUBILITY. The present results for the solubility of sodium pentaborate at 20° and 107° (Table I) and the values read from the isotherms of Figures 1 and 2 at 30°, 50°, and 60° agree well with the results of Blasdale and Slansky (2), but the values at 0°, 5°, 10°, 94°, and 98° C. do not. Most of the present values are lower than those

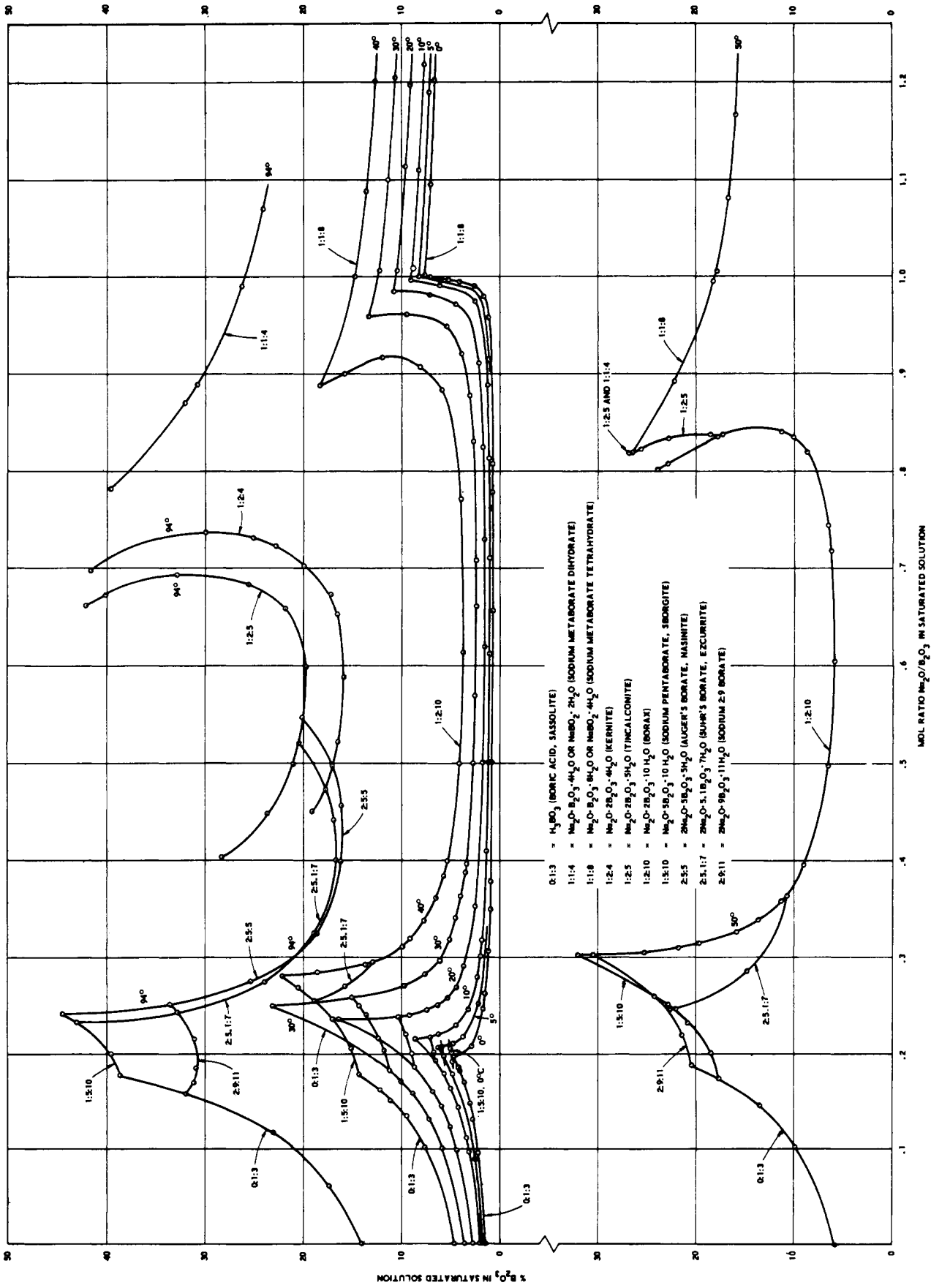


Figure 1. Solubility isotherms in the system $Na_2O-B_2O_3-H_2O$ at 0°, 5°, 10°, 20°, 30°, 40°, 50°, and 94°C.

Table III. Revised Solubility Data for Boric Acid, Borax, ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), Kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), Sodium Pentaborate ($\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$), and Sodium Metaborate ($\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$)
Expressed in grams per 100 grams of saturated solution

Temperature, °C.	Boric Acid, G. H_3BO_3	Borax, G. $\text{Na}_2\text{B}_4\text{O}_7$	Kernite, G. $\text{Na}_2\text{B}_4\text{O}_7$	Sodium Pentaborate, G. $\text{NaB}_5\text{O}_{10}$	Sodium Metaborate, G. NaBO_2
-5.77 ^c					13.1
-1.7 ^c				5.5	
-0.76 ^c	2.466				
-0.42 ^c		1.03			
0	2.52	1.05		5.77	14.5
5	2.98	1.30		6.75	15.7
10	3.49	1.63		7.90	17.0
15	4.08	2.00		9.30	18.5
20	4.72	2.48		10.55	20.0
25	5.46	3.06		12.20 ^d	21.6
30	6.23	3.80		13.72	23.6
35	7.12	4.76		15.60 ^d	25.6
40	8.08	5.92		17.50	27.9
45	9.12	7.50		19.63 ^d	30.8
50	10.27	9.45		21.72	34.1
53.6					36.9 ^e
55	11.55	12.25		24.30 ^d	37.2 ^f
58.0			14.20 ^g		
60	12.97	16.00	14.67	26.88	38.3 ^f
60.8		16.65 ^g			
60		16.35 ^g			
65	14.42	17.88 ^g	15.81	29.35 ^d	39.5 ^f
70	15.75	19.49 ^g	17.02	32.25 ^d	40.9 ^f
75	17.41	21.20 ^g	18.31	34.98 ^d	42.2 ^f
80	19.10	23.38 ^g	19.72	38.1	43.7 ^f
85	21.01	25.60 ^g	21.28	41.1	45.4 ^f
90	23.27	28.06 ^g	22.96	44.3	47.4 ^f
95	25.22	31.10 ^g	24.95	47.6	49.6 ^f
100	27.53	34.63 ^g	27.23	51.0	52.4 ^f
102.8 ^b		36.73 ^g			
103.3 ^b	29.27				
105				54.7	56.0 ^g
107				56.3	
110					55.8 ^g
115					55.5 ^g
120.2 ^b					55.3 ^g

^a Transition points. ^b Boiling points. ^c Cryohydric points, as determined by the intersection of our revised solubility curves with published composition-temperature curves for solutions in equilibrium with ice. Literature values (8-10, 15) are somewhat different for boric acid, sodium pentaborate, and borax. ^d Data from Blasdale and Slansky (2). ^e Solid phase $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$. ^f Solid phase $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$. ^g Solid phase $\text{NaBO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.

of Rollet and Peng (15). The values considered most reliable are given in Table III and used for the sodium pentaborate curve in Figure 3.

Sodium Pentaborate Dihydrate, $\text{NaB}_5\text{O}_{10} \cdot 2\text{H}_2\text{O}$. PREPARATION. When the dry granular pentahydrate, 4 to 6 cm. deep was heated in open beakers in an oven at 129° to 180° C. for one or two days, the material near the surface became largely amorphous and had the composition $\text{NaB}_5\text{O}_{10} \cdot 1.6$ to $1.9\text{H}_2\text{O}$, but the lower part had the composition $\text{NaB}_5\text{O}_{10} \cdot 2.05$ to $2.1\text{H}_2\text{O}$. As the lower part did not contain an appreciable amount of amorphous material, it is considered to be the 1:5:4 compound, $\text{NaB}_5\text{O}_{10} \cdot 2\text{H}_2\text{O}$. This material had an x-ray pattern similar to that of the compound regarded by Bouaziz (4) as the 1:5:2 compound, $\text{NaB}_5\text{O}_{10} \cdot \text{H}_2\text{O}$. The pattern was submitted to the ASTM Powder Diffraction File. The 1:5:4 compound was also obtained, as shown by its x-ray diffraction pattern, when the dry 1:5:10 compound was heated at 160° C. in a closed unstirred steel bottle for one to three

days, and the liquid was decanted off. The composition of the liquid was 12.26% Na_2O , 68.91% B_2O_3 , mole ratio $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 = 0.200$. The unchanged mole ratio indicated that the crystals were in fact a pentaborate. Heating the 1:5:10 compound in a sealed container at 134° or 148°, or heating for longer periods at 160° C. gave the 2:9:11 compound as well as 1:5:4. Three days' heating in a sealed container at 126° gave 2:9:11 but no 1:5:4. Apparently, the 1:5:4 compound is metastable in contact with its saturated solution at these temperatures.

SOLUBILITY. In an attempt to determine the solubility of the 1:5:4 compound, slightly unsaturated solutions of sodium pentaborate pentahydrate at 60°, 94°, 98°, and 107° C. were seeded with 12 to 18% of the 1:5:4 and in other experiments with the 1:5:10 compound. At 107° the concentration after agitation of 0.5 to 1 hour was 56.4% $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ when seeded with 1:5:10, and 55.6% when seeded with 1:5:4; at 98° in 40 minutes the concentrations were, respectively, 49.9 and 50.2%, indicating that the transition point 1:5:10 to 1:5:4 is between 98° and 107°, and probably about 102°, in contact with saturated solutions. At 94°, the concentrations reached in solutions seeded with 1:5:4 and 1:5:10 were about equal. This is attributed to rapid conversion of 1:5:4 to 1:5:10 at this temperature. At 60°, a solution seeded with 1:5:4 and sampled after agitation for 0.5 hour contained 23.7% B_2O_3 compared with 23.1% when seeded with 1:5:10 (Table I, mole ratio $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 = 0.204$).

Sodium Pentaborate Monohydrate, $\text{NaB}_5\text{O}_{10} \cdot \text{H}_2\text{O}$. When dry granular sodium pentaborate pentahydrate was heated for 24 hours at 240° C. in loosely covered or uncovered beakers, the compositions $\text{NaB}_5\text{O}_{10} \cdot 0.97\text{H}_2\text{O}$ and $\text{NaB}_5\text{O}_{10} \cdot 0.9\text{H}_2\text{O}$, respectively, were obtained. Both of these materials had the same x-ray diffraction pattern, which was different from that of the 1:5:4 compound. This new pattern, regarded as that of the 1:5:2 compound, has been submitted to the ASTM Powder Diffraction File. Using a graphical method (14) to identify the crystals, Rollet and Peng (15) believed that they had crystallized the 1:5:2 compound from hot saturated sodium pentaborate solutions. In the present authors' experiments (see Experimental section), the 2:9:11 compound crystallized from such solutions, rather than 1:5:2 compound.

Sodium (2 to 9) Borate Undecahydrate, $2\text{Na}_2\text{O} \cdot 9\text{B}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$. PREPARATION. In 1950, D.S. Taylor of the U. S. Borax research laboratories found that this new compound would crystallize from certain solutions containing borax, boric acid, and sodium chlorate. The authors have prepared it by agitating a slurry of $\text{NaB}_5\text{O}_{10} \cdot 5\text{H}_2\text{O}$ at 94° or at 107° C. (Experimental section). It crystallizes very slowly, and solutions supersaturated with it are easily formed.

SOLUBILITY. The solubility of sodium 2 to 9 borate in sodium pentaborate solutions, taken from the isotherms of Figures 1 and 2, is included in Figure 3. Interpolation between the isotherms indicates that sodium 2 to 9 borate is stable in contact with its own solution above 57° C.; its own saturated solution contains 23.4% B_2O_3 at 60°, 26.7% at 75°, and 31.2% at 94° C.

Sodium (2 to 5.1) Borate Heptahydrate $2\text{Na}_2\text{O} \cdot 5.1\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ (Suhr's Borate, ezcurrite). COMPOSITION. This compound was first prepared by Suhr (17). Both he and Cipriani (6) regarded the formula as $3\text{Na}_2\text{O} \cdot 8\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$. Cipriani's analysis gave a $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio of 0.378. Muessig and Allen (12) assigned the formula $2\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ to the naturally occurring mineral on the basis of two analyses which gave $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratios 0.395 and 0.386. The present authors' analyses of the synthetic compound (see Experimental section) correspond to the formula $2\text{Na}_2\text{O} \cdot 5.1\text{B}_2\text{O}_3 \cdot 6.98\text{H}_2\text{O}$, which has a $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio of 0.392 rather than the 0.375 of the 3:8:10 formula or the 0.400 of the 2:5:7 formula. Analyses of solutions before and after crystallization of Suhr's borate (Table II)

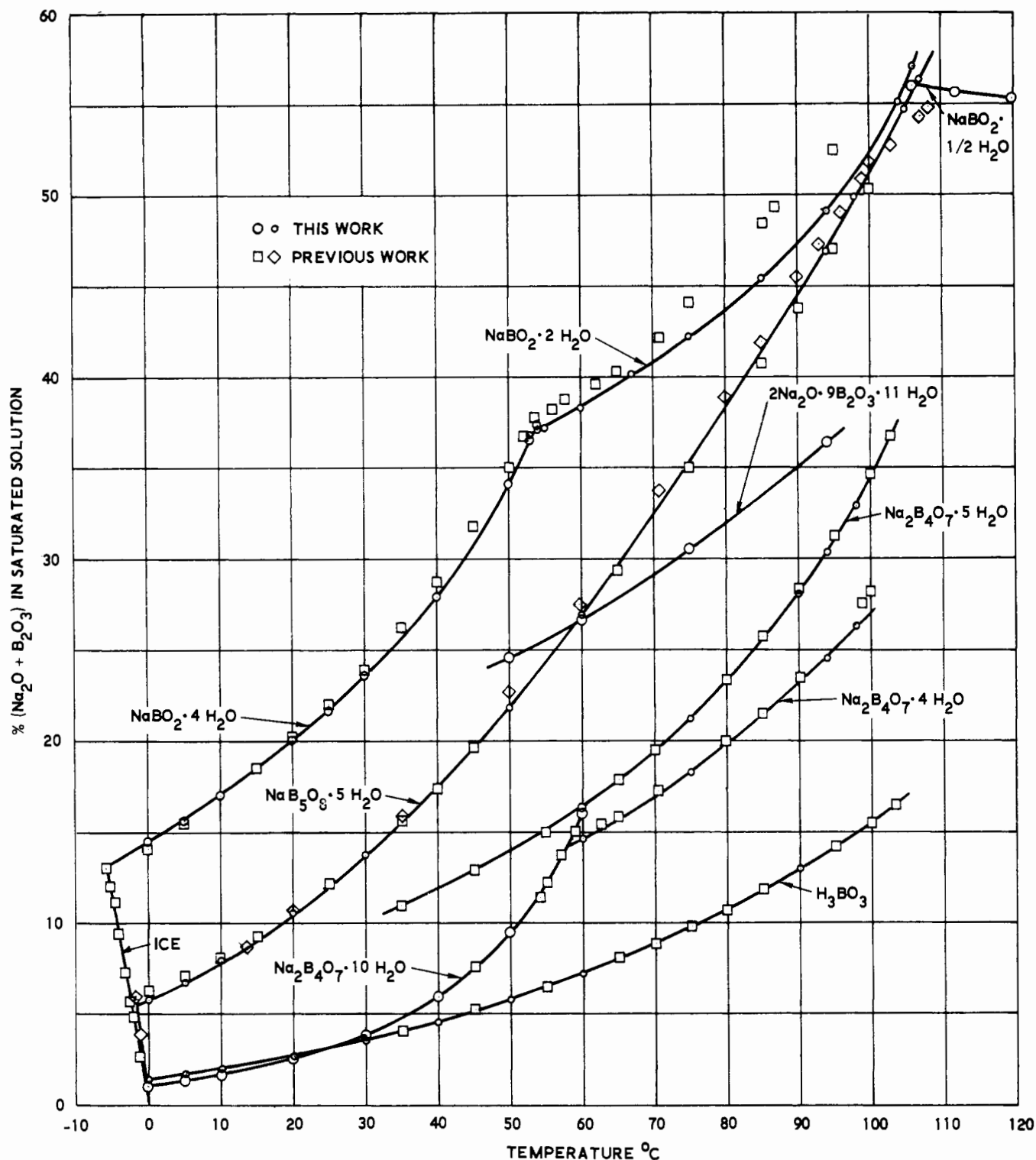


Figure 3. Solubility-temperature curves for boric acid, borax, sodium pentaborate, and sodium metaborate

confirm that the crystals, before separation from the mother liquor, have a mole ratio between 0.390 and 0.395. When Suhr's borate is crystallized from a solution having R ($= \text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio) originally 0.390, the value of R in the solution decreases. The value of R in the crystals therefore must be greater than 0.390. Similarly, when Suhr's borate is crystallized from a solution having R originally 0.395 or more, the value of R in the solution increases, indicating that the value of R in the crystals must be less than 0.395. The deficiency in Na_2O content of the crystals, compared with the composition of $2\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$,

therefore is believed to be real. The authors have no explanation for this deficiency at present. The composition is closer to the formula $2\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ than to the formula $3\text{Na}_2\text{O} \cdot 8\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$.

SOLUBILITY. Interpolation between the isotherms of Figures 1 and 2 indicates that the stability range of Suhr's borate in contact with its own solutions extends from about 53° to 90° , rather than from 57° to 135° , as stated by Milman and Bouaziz (11). Its own saturated solutions contain 11.5% B_2O_3 at 60° , 13.6% at 75° , and 16.9% (metastable) at 94°C . The elongated, sometimes lath-shaped, crystals

are usually 0.1-mm. long or less. Supersaturated solutions are readily formed. The x-ray diffraction powder pattern, similar to that of the naturally occurring mineral (12), has been submitted to the A.S.T.M. Powder Diffraction File.

Tetrasodium Decaborate Pentahydrate, $2\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Auger's Sodium Borate, nasinite). COMPOSITION. This compound was first prepared by Auger (1) and was found at Larderello and named nasinite by Cipriani (6). Synthetic nasinite was made in an autoclave at 100° to 200° C. by Cipriani and Vannuccini (6) whose analysis corresponded to the formula $2\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 6.98\text{H}_2\text{O}$. The present authors' analyses, however, indicate 5 moles of water, in agreement with Auger (see Experimental section). The x-ray pattern, which has been submitted to the A.S.T.M. Powder Diffraction File, agrees with that of Cipriani and Vannuccini except that their pattern contains some additional peaks. Some of these peaks apparently are due to borax. The somewhat elongated crystals are usually 0.2 mm. or less in length, and tend to form aggregates.

SOLUBILITY. Interpolation between the isotherms of Figures 1 and 2 indicates that in contact with its own saturated solution ($\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio = 0.4) Auger's borate is stable above 90°, rather than above 135° as stated by Milman and Bouaziz (11). The solubility of Auger's borate changes very little with temperature. Its own saturated solutions contain 15.6% B_2O_3 at 75° and 16.2% at 94° C. Auger's borate crystallizes more slowly than Suhr's borate. This slowness may explain Auger's observation that borax pentahydrate crystallized from a solution having a $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio of 0.4 even though the solution was seeded with a few crystals of Auger's borate.

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; Borax Pentahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$; and Kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$. REGION OF STABILITY. At 0°, borax decahydrate is stable in contact with solutions over the wide range in $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio from 0.196 to 1.00. The decahydrate is practically insoluble in saturated sodium metaborate solutions at 0° C. The decahydrate-pentahydrate transition temperature, 60.8° in contact with pure borax solutions (2), is lower in the more concentrated solutions which occur at both higher and lower $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratios. At temperatures near 60° there are then two separate ranges of composition in which decahydrate solutions are metastable with respect to the pentahydrate. Solutions saturated with borax pentahydrate are supersaturated with respect to kernite, and at temperatures near and above 94°, if their $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio is near or below 0.5, they are supersaturated also with respect to Suhr's and Auger's borates. Borax solutions saturated with kernite above 95° C. are metastable with respect to Auger's borate.

At 94°, the composition of solutions saturated with sodium metaborate dihydrate and either borax pentahydrate or kernite, could not be determined because of the high viscosity. The most concentrated solution saturated with borax pentahydrate that could be filtered at this temperature contained 24.78% Na_2O and 42.09% B_2O_3 (mole ratio 0.662). The most concentrated solution saturated with kernite that could be filtered at 94° C. contained 25.81% Na_2O and 41.55% B_2O_3 (mole ratio 0.698).

SOLUBILITY. Because of discrepancies in the literature, the solubility of borax decahydrate was determined at -0.37°, 0°, 5°, 10°, 20°, 30°, 40°, 50°, and 60°, and the pentahydrate and kernite at 60°, 75°, 90°, 94°, and 98° C. In these experiments, when a large excess of solid phase was added, the $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratio in solution was generally a little less than the stoichiometric value of 0.5. Using the slope of the isotherms, a small correction was made to correct the solubility to its value at the 0.5 mole ratio. A smooth curve was drawn through the points considered most reliable, using these corrected values and the results of Menzel (9) and Blasdale and Slansky (2). The values considered to be the best were read from the curve and

are given in Table III and Figure 3.

Sodium Metaborate Tetrahydrate $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$; Dihydrate, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$; and Hemihydrate, $\text{NaBO}_2 \cdot 0.5\text{H}_2\text{O}$. ISOTHERMAL INVARIANT POINTS. At 0° C., the sodium metaborate-borax isothermal invariant point is very near the $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio 1, but this high solubility point occurs in less alkaline solutions as the temperature is increased. At 75° C., the solution saturated with borax pentahydrate and sodium metaborate dihydrate has a $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio 0.701 and contains 40.92% B_2O_3 . At 94°, the composition at this point could not be determined because of the high viscosity. The most concentrated solution saturated with sodium metaborate dihydrate that could be filtered at this temperature contained 27.56% Na_2O and 39.60% B_2O_3 (mole ratio $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ 0.782).

SOLUBILITY. The 94° isotherm of Figure 1 indicated that the solubility of sodium metaborate was appreciably less than the published value (2) at this temperature. The solubility of sodium metaborate was therefore determined at temperatures from 0° C. to the boiling point. In these experiments, when a large excess of sodium metaborate was used, the $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratio was usually a little less than the stoichiometric value 1. Determinations were therefore made in which a little 50% sodium hydroxide solution was added to bring the mole ratio up to 1 or above (Table I). Interpolation was then made to the stoichiometric ratio 1. These values were plotted in Figure 3, together with previous data from the literature (2, 3, 10, 16, 18). The results fall on a smooth curve which, however, was usually appreciably lower than previous values. The data believed best, read from the curve, are given in Table III.

Some of the published data for sodium metaborate may have been affected by the dissolving of silica from glass bottles or by the presence of carbon dioxide in the solutions. An experiment at 55° C. indicated that a change in the CO_2 content from 0.06% to 1.18% changed the solubility of sodium metaborate from 37.2 to 40.1% NaBO_2 . In another experiment, at 94° C., addition of 3% SiO_2 (as $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} + 2\text{H}_3\text{BO}_3$) changed the solubility of sodium metaborate from 26.47 to 27.78% B_2O_3 . The polypropylene bottles used in the sodium metaborate work turned yellow and made the solutions slightly yellowish. One of the solubilities was therefore redetermined, using a nickel bottle. The solution contained 0.08% CO_2 as calculated from the CO_2 content of the starting materials. The result agreed with the polypropylene bottle experiments. The authors' solutions probably contained less than 0.1% CO_2 . The present results then should be accurate to within about 0.7% of the amount present.

REGIONS OF STABILITY. The solubility curve for sodium metaborate in water (Figure 3) indicates that the 1:1:4 compound $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ is the stable phase in contact with its solutions at temperatures from 53.6° to 105° and that the 1:1:1 compound $\text{NaBO}_2 \cdot 0.5\text{H}_2\text{O}$ is the stable phase from 105° to the boiling point. This conclusion does not agree with the statement of Bouaziz (3) that the 1:1:2 compound $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ is the stable phase from 105° to 155°. Bouaziz and Milman (5) also reported the 1:1:2 compound to be stable at 100° between $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratios 1.176 and 3.21. Therefore, several points at 98.6° between $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratios 1.58 and 8.49 were determined, without seeding (Table I). X-ray powder patterns indicated that the 1:1:1 compound $\text{NaBO}_2 \cdot 0.5\text{H}_2\text{O}$ was obtained in all these experiments. The present authors therefore regard the existence of the 1:1:2 compound, $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ or $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, as unproved. The early work of Sborgi (16) and Menzel's isothermal dehydration of the tetrahydrate (10) did not indicate the existence of a crystalline 1:1:2 compound.

Centrifugation of hot slurries of the 1:1:1 compound gave solids having the composition $\text{NaBO}_2 \cdot 0.52\text{H}_2\text{O}$ to

$\text{NaBO}_2 \cdot 0.9\text{H}_2\text{O}$, which had an x-ray pattern of the 1:1:1 compound containing a little 1:1:4. The elongated crystals were usually less than 0.05 mm. in length. The x-ray pattern of a sample having the composition $\text{NaBO}_2 \cdot 0.42\text{H}_2\text{O}$ after heating at 105° for 3 days in an oven was submitted to the A.S.T.M. Powder Data File.

LITERATURE CITED

- (1) Auger, V., *Compt. Rend.* **180**, 1602 (1925).
- (2) Blasdale, W.C., Slansky, C.M., *J. Am. Chem. Soc.* **61**, 917 (1939).
- (3) Bouaziz, R., *Ann. Chim.* **1961**, p. 345.
- (4) Bouaziz, R., *Bull. Soc. Chim. France* **1962**, p. 1451.
- (5) Bouaziz, R., Milman, T., *Compt. Rend.* **257**, 151 (1963).
- (6) Cipriani, C., Vannuccini, P., *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.* (8) **30**, 74 (1961); Cipriani, C., *Ibid.*, p. 235.
- (7) Dukelski, M., *Z. anorg. Chem.* **50**, 38 (1906).
- (8) Menzel, H., *Z. Anorg. Allgem. Chem.* **164**, 1, 38 (1927).
- (9) Menzel, H., Schulz, H., *Ibid.*, **245**, 157 (1940).
- (10) *Ibid.*, **251**, 167 (1943).
- (11) Milman, T., Bouaziz, R., *Bull. Soc. Chim. France* **1965**, p. 7.
- (12) Muessig, S., Allen, R.D., *Econ. Geol.* **52**, 426 (1957).
- (13) Nasini, R., Ageno, I., *Z. Phys. Chem.* **69**, 482 (1910); *Gazz. Chim. Ital.* **41**, I, 131 (1911).
- (14) Peng, C.-M., *Bull. Soc. Chim. France* (5) **2**, 985 (1935).
- (15) Rollet, A.P., Peng, C.-M., *Ibid.*, (5) **2**, 982 (1935).
- (16) Sborgi, U., *Gazz. Chim. Ital.* **62**, 3 (1932); Sborgi, U., Amelloti, L., *Ibid.*, **60**, 468 (1930); Sborgi, U., Mecacci, F., *Atti. Accad. Lincei, Rend., Classe Sci. Fis. Mat. Nat.* **25**, II, 327, 455 (1916); Sborgi, U., Lopez, B., *Atti Soc. Toscana Sci. Nat. Pisa* **35**, 46 (1926).
- (17) Suhr, H.B. (to American Potash & Chemical Corp.), U. S. Patent **2,096,266** (October 19, 1937).
- (18) Teeple, J.E., "Industrial Development of Searles Lake Brines," pp. 120-2, Chemical Catalog Co., New York, 1929.

RECEIVED for review June 20, 1966. Accepted May 1, 1967. Material supplementary to this article has been deposited as Document number 9460 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints, or \$1.75 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Low Pressure Vapor-Liquid Isotherms in the Methane-3-Methylpentane Binary System

JAMES P. KOHN and J. H. S. HAGGIN¹

Department of Chemical Engineering and Radiation Laboratory, University of Notre Dame, Notre Dame, Ind. 46556

Vapor and liquid compositions and molar volumes are reported at temperatures of 25° , 50° , 75° , and 100°C . and at pressures up to 30 atm. The data indicate that Henry's law expressed as fugacity of methane vs. mole fraction dissolved methane holds closely over the pressure range covered in the study. The molar liquid volumes in every case were linear with mole fraction methane.

ACCURATE values of phase compositions and molar volumes are necessary for accurate calculations of molecular mass transport. This study was undertaken to provide information on the methane-3-methylpentane binary system for use in a study involving the experimental determination of the molecular diffusion coefficient of methane in dilute liquid solutions of 3-methylpentane.

Although methane-*n*-hexane binary phase behavior over extensive temperature and pressure ranges has been reported (9), no phase behavior information on the methane-3-methylpentane system has been reported previously. Methane behavior has been reported in several studies (1, 2, 5-7), and vapor pressure and liquid density information on 3-methylpentane has been reported by Rossini *et al.* (8).

¹ Present address: Industrial and Engineering Chemistry, American Chemical Society, Washington, D. C. 20036

EXPERIMENTAL

The equipment and the experimental techniques were the same as those used in other recent studies of binary hydrocarbon systems (3, 4, 9-11). In obtaining bubble point isotherms, the equilibrium cell pressure was observed directly on a dead weight gage rather than on a bourdon tube gage as was done in the previous studies. The dead weight gage was sensitive to ± 0.007 atm. and was accurate to ± 0.06 atm. Temperatures of the equilibrium cell were taken on a platinum resistance thermometer which was accurate within 0.02°C . of the International Platinum Scale. The equilibrium cells were borosilicate glass cylindrical tubes of 12-ml. internal volume. Each cell contained a steel ball which could be actuated by a magnet outside the cell to provide stirring. They were marked and calibrated to read volume accurate to at least ± 0.01 ml. The equilibrium cells were immersed in a 3.5-liter water bath confined in a cylindrical Dewar flask.