stants were available. A smooth curve results but the physicochemical significance is not obvious.

CONCLUSIONS

Several nonprotogenic solvents for sucrose have been found.

The solubilities can be expressed by straight lines characterized by two parameters, one depending on the nature of solvent, the other on the nature of dissolved material. Even with the few results given it would appear that only the solubility of sucrose at one temperature and the dielectric constant of the solvent are required to predict the solubility at any other temperature.

Many further measurements are needed in order to determine the parameters more accurately and to find whether this rule can be applied to other substances than sucrose.

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LITERATURE CITED

(1) Bates, F. J., others, Natl. Bur. of Standards, Circ. C-440, p. 676, 1942.
(2) Berzelius, J. J., Ann. phys. 47, 321 (1839).
(3) Brown, F., Randle, D. G., Chemist Druggist 104, 81 (1926).
(4) Burne, B., Chem. News 110, 47 (1914).
(5) Cohen, E., Commelin, J. W., Z. physik Chem. 64, 45 (1908).
(6) Dehn, W. M., J. Am. Chem. Soc. 39, 1402 (1917).
(7) Dudley, J. R., others, Ibid., 75, 2986 (1951).
(8) Fey, M. F., Weil, I. M., Segur, J. B., Ind. Eng. Chem. 43, 1435 (1951).
(9) Fitzgerald, F. F., J. Phys. Chem. 16, 621 (1912).
(10) Graf, L., Angew. Chem. 14, 1077 (1901).
(11) Grossman, H., Bloch, F. L., Z. Ver deut. Zuckerind. 62, 57 (1912).
(12) Grut, E. W., Z. Zuckerind. Cechoslovak Rep. 61, 345 (1937).
(13) Gunning, J. W., Chem. Ztg. 15, 83 (1891).
(14) Heldermann, W. D., Z. physik. Chem. 130, 396 (1927).
(15) Helferich, B., Masamune, H., Ber. 64, B, 1257 (1931).
(16) Herz, W., Knoch, M., Z. anorg. Chem. 41, 315 (1904).
(17) Herzfeld, A., Z. Ver. deut. Zuckerind. 42, 181 (1892).
(18) Holty, J. G., J. Phys. Chem. 9, 776 (1905).
(19) Horsin-Deon, P., Fabr. Sucre, 2nd ed., Paris, 1900.
(20) Hruby, R., Kasjanov, V., Z. Zuckerind. Cechoslovak Rep. 63, 187 (1939); Internl. Sugar J. 42, 21 (1940).
(21) Hudson, C. S., Yanowski, E., J. Am. Chem. Soc. 39, 1038 (1917).
(22) Kaganow, I. N., Sakharnaya Prom. 23, 27 (1949).
(23) Kahlenberg, L., J. Phys. Chem. 10, 187 (1906).
(24) Karcz, M., Osterr, Ungar, Z. Zuckerind. 23, 21 (1889).
(25) Kitchen, L. J., Hanson, E. S., J. Am. Chem. Soc. 73, 1838 (1951).
(26) Kitchen, L. J., Pollard, C. B., Ibid., 69, 854 (1947).
(27) Koenig, A. E., J. Phys. Chem. 16, 461 (1912).
(28) Krug, W. H., MacElroy, K. P., J. Am. Chem. Soc. 6, 153 (1884).
(29) Kukharenko, I. A., Visnyk Tsukrovoi Prom.; Naukovi Zapiski Tsukrovoi Prom. (1921-25).
(30) Lindet, M. L., Compt. rend. 110, 795 (1890).
(31) Lippman, E. O. von, Chemie Zuckerarten, vol. II, p. 1197, Braunschweig, 1904.
(32) Lobry de Bruyn, C. A., Z. physik Chem. 10, 789 (1892).
(33) National Sugar Refining Co., private communication, March 1955.
(34) Orth, P., Bull. assoc. chim. 31, 94 (1913).
(35) Orth, P., Ibid., 54, 605 (1937).
(36) Pellet, H., Ibid., 15, 631 (1897).
(37) Pictet, A., Vogel, H., Helv. Chim. Acta. 11, 436 (1928).
(38) Plato, F., Domke, J., Harting, H., Z. Ver. deut. Zuckerind. 30, 1009 (1900).
(39) Power, F. B., Rogerson, H., J. Chem. Soc. (London) 101, 4 (1912).
(40) Reber, L. A., J. Am. Pharm. Assoc., Sci. Ed. 42, 192 (1953).
(41) Sandera, K., Mircev, A., Z. Zuckerind. Cechoslovak Rep. 50, 204 (1935).
(42) Scheibler, C., Ber. 5, 343 (1872).
(43) Ibid., 19, 2872 (1866).
(44) Schiff, N., Ann. 244, 20 (1888).
(45) Schrefeld, O., Z. Ver. deut. Zuckerind. 44, 970 (1894).
(46) Schukarew, A., Z. physik Chem. 71, 105 (1910).
(47) Scott-Macfie, J. W., Sucre belge 35, 283 (1906).
(48) Segur, J. B., Miner, C. S., J. Agr. Food Chem. 1, 567 (1953).
(49) Shah, S., Chakradeo, Y., Current Sci. (India) 4, 652 (1936).
(50) Sherry, R. H., J. Phys. Chem. 11, 559 (1907).
(51) Soc. Anon. des usines de Melle, French Patent 621075 (1927); German Patent 528564 (1926).
(52) Strohmer, F., Stiff, A., Osterr, Ungar, Z. Zuckerind. 24, 41 (1895).
(53) Urban, E., Centr. Zuckerind. 6, 637 (1898).
(54) Verhaar, G., Arch. Suikerindust. Ned. en Ned. Indie 1, 325 (1940-41).
(55) Ibid., p. 467 (1941).
(56) Vogel, H., Ber. 70, B, 1193 (1937).
(57) Vogel, H., George, A., "Tabellen der Zucker," p. 46-7, Berlin, 1931"
(58) Wilcox, G. N., J. Phys. Chem. 5, 596 (1901).
(59) Ibid., 6, 339 (1902).

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Carbon Dioxide Solubility in Water

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All available data on the solubility of carbon dioxide in water have been assembled and converted to a uniform basis. A chart has been prepared which smoothes the normal experimental deviations and thus permits a more accurate determination of solubility and changes in solubility of carbon dioxide in water as a function of temperature and pressure.

Solubilities are properties that are used constantly and therefore solubility data should be available in forms that are both convenient and uniform. Experimental results of any one investigator will not necessarily satisfy the needs of all users, and different investigators will not agree exactly in their results. Often data will be reported in different units or on different bases—e. g., the solubility of gases has been variously defined in coefficients or relationships carrying the names of the originators such as Bunsen, Henry, Kuenen, Ostwald, Raoult, and others. Though the data are sufficiently identified by the investigator to permit accurate interpretation, it is awkward to determine the difference between solubilities under any two conditions. In order to make information on the solubility of carbon dioxide in water more uniform, all the available data have been assembled and correlated on a single basis.

HISTORY

The solubility of carbon dioxide in water has been determined by many investigators (1-8, 11-19, 21, 24-35) and much of their data has been assembled by others (3, 9, 10, 20, 22, 23). The earliest work apparently

TABLE I. SOLUBILITY OF CARBON DIOXIDE

(Lb./100 lb. of water at 1 atm. and above)

Total Pressure, atm.	0° C.	5° C.	10° C.	12.4° C.	15° C.	18° C.(28, 30)	20° C.	25° C.	31.04° C.^{a}(28, 30)	35° C.(28, 30)	40° C.(28, 30)	50° C.(29)	60° C.(21)	75° C.(29)	100° C.	120° C.(19)
1^{b}	0.336(1)	0.280(1)	0.234(1)	0.218^{c}	0.200(1)	----	0.172(1)	0.149(1)	0.131^{d}	----	0.105(1)	0.087(1)	0.072(1)	----	----	----
	0.336^{c}	----	----	0.213(32)	0.201(24)	----	0.157^{e}(25)	0.148(18)	----	----	----	----	----	----	----	----
	0.353(32)	----	----	0.214^{g}	0.196(8)	----	0.152^{f}	0.149(16)	----	----	----	----	----	----	----	----
	0.353(8)	----	----	----	----	----	----	0.148(11)	----	----	----	----	----	----	----	----
	----	----	----	----	----	----	----	0.149(25)	----	----	----	----	----	----	----	----
5	1.698(32)	----	----	1.011(32)	0.901(8)	----	----	----	----	----	----	----	----	----	----	----
	1.710(8)	----	----	1.011^{d}	----	----	----	----	----	----	----	----	----	----	----	----
10	3.147(32)	----	----	1.894(32)	1.647(8)	----	----	----	----	----	----	----	----	----	----	----
	3.119(8)	----	----	1.894^{g}	----	----	----	----	----	----	----	----	----	----	----	----
15	4.283(8)	----	----	2.672^{g}	2.326(8)	----	----	----	----	----	----	----	----	----	----	----
20	5.231(32)	----	----	3.359(32)	2.986(8)	----	----	----	----	----	----	----	----	----	----	----
	5.208(8)	----	----	3.359^{g}	----	----	----	----	----	----	----	----	----	----	----	----
25	5.997(32)	----	----	3.987(32)	3.463(8)	3.830	3.151^{h}	----	2.784	2.542	2.281	1.906	----	1.339	1.054(29)	0.982
	5.979(8)	----	----	3.993^{g}	----	----	----	----	----	----	----	----	----	----	----	----
	5.989(35)	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
30	6.623(32)	----	----	4.564(32)	3.987(8)	----	3.516^{h}	----	----	1.994^{h}	----	----	----	----	----	----
	6.605(8)	----	----	4.564^{g}	----	----	----	----	----	2.229^{h}	----	----	----	----	----	----
35	7.210(32)	----	----	----	4.421(8)	----	----	----	----	----	----	----	----	----	----	----
38	7.434(32)	----	----	----	----	----	3.826^{h}	----	----	3.388^{h}	----	----	1.724	----	----	----
	----	----	----	----	----	----	----	----	----	2.511^{h}	----	----	1.552	----	----	----
40	----	----	----	----	4.798(8)	----	----	----	----	----	----	----	----	----	----	----
45	----	----	----	----	5.023(8)	----	----	----	----	----	----	----	----	----	----	----
50	----	----	----	6.977^{i}	5.312(8)	6.287	4.981^{h}	5.345(28, 30)	4.741	4.360	3.995	3.386	1.939	2.471	1.998(29)	1.865
	----	----	----	----	-----	----	----	----	----	3.212^{h}	----	----	2.173	----	----	----
	----	----	----	----	----	----	----	----	----	4.175^{h}	----	----	----	----	----	----
52	----	----	----	5.432(8)	----	----	5.275^{h}	----	----	----	----	----	----	----	----	----
58.1	----	----	----	----	----	----	----	----	----	3.879^{h}	----	----	2.291	----	1.301^{h}	----
	----	----	----	----	----	---	----	----	----	3.812^{h}	----	----	2.421	----	----	----
67.7	----	----	----	----	----	----	----	----	----	4.604^{h}	----	----	2.661	----	1.467^{h}	----
	----	----	----	----	----	----	----	----	----	4.679^{h}	----	----	2.766	----	0.929^{h}	----
75	----	----	----	7.132^{i}	----	6.645	----	6.119(28, 30)	5.757	5.465	5.067	4.423	3.591	3.345	2.805(29)	2.670
	----	----	----	----	----	----	----	----	----	5.565^{h}	----	----	3.127	----	1.603^{h}	----
	----	----	----	----	----	----	----	----	----	----	----	----	----	----	1.391^{h}	----
87.1	----	----	----	----	----	----	----	----	----	5.565^{h}	----	----	3.601	----	1.611^{h}	----
100	----	----	----	7.218^{i}	----	6.670	----	6.233(28, 30)	5.922	5.718	5.459	5.031	4.283	4.046	3.469(29)	3.376
125	----	----	----	----	----	----	----	----	----	----	5.636	5.255	5.070	----	3.946(19)	3.946
150	----	----	----	7.536^{i}	----	7.018	----	----	6.201	5.991	5.769	5.426	----	4.825	4.462(29)	4.338
200	----	----	----	7.807^{i}	----	7.296	----	----	6.435	6.248	6.034	5.720	----	5.233	5.043(29)	5.261
300	----	----	----	8.062^{i}	----	7.717	----	----	----	----	----	6.152	----	5.793	5.797(29)	5.889
400	----	----	----	----	----	----	----	7.581(28, 30)	7.220	7.014	6.845	6.535	----	6.258	6.358(29)	6.439
500	----	----	----	----	----	----	----	7.801(28, 30)	7.591	7.457	7.210	----	----	----	6.753(19)	6.894
600	----	----	----	----	----	----	----	----	----	----	----	7.210	----	----	7.145(19)	7.361
700	----	----	----	----	-----	----	----	----	----	----	----	7.526	----	7.379	7.557(29)	7.832

[a] Critical temperature of CO_2.
[b] Pressure of 1 atm. is CO_2 pressure only. Total pressure is given at all other values.
[c] Data at 0° C. and 12.4° C. are actually at 0.05° C. and 12.5° C. (9).
[d] Data at 31.04° C. are actually at 30° C. (1).
[e] t = 23° C.
[f] t = 24° C.
[g] Data at 12.4° C. are actually at 12.43° C. (31).
[h] Exact pressure at the nominal pressures of 25, 30, 38, 50, 52, 75, 100 and 125 atm. are respectively 24.2, 29.0, 38.7, 48.4, 53.2, 77.4, 96.8, and 116 atm. (21).
[i] Data at 12.4° C. are actually at 12.0° C. (28,30).

TABLE II. SOLUBILITY OF CARBON DIOXIDE

(Lb./100 lb. water at pressures below 1 atm.)

Press., mm. Hg	CO_2 Solubility
t = 0° C.(17)	
57.0	0.0202
160.0	0.0661
352.7	0.1412
530.2	0.2143
681.3	0.2929
853.0	0.3676
t = 10° C.(17)	
81.7	0.0240
206.1	0.0611
424.1	0.1297
644.8	0.1975
835.6	0.2475
t = 18° C.	
0.07(2)	0.000033
0.15(2)	0.000059
0.21(2)	0.000059
0.27(2)	0.000069
0.64(2)	0.000157
0.87(2)	0.000229
0.93(2)	0.000232
0.97(2)	0.000248
1.48(2)	0.000344
3.83(2)	0.000921
92.3(17)	0.0216
229.8(17)	0.0580
491.4(17)	0.1140
744.5(17)	0.1740
t = 25° C.(17)	
98.9	0.0200
253.2	0.0502
540.0	0.1025
822.2	0.1559

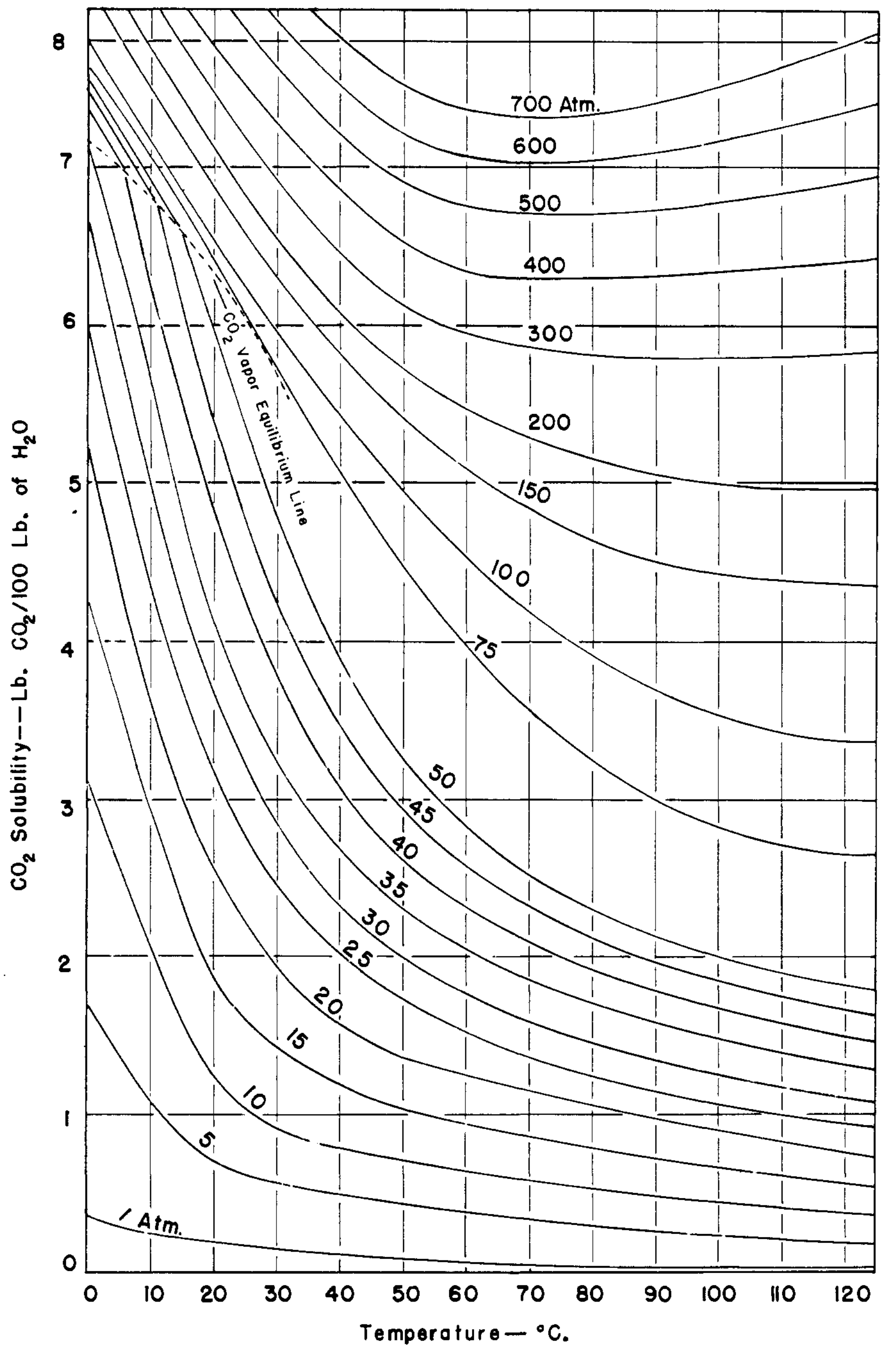

Figure 1. Effect of temperature and pressure upon the solubility of carbon dioxide in water

was done about 1882 by Wroblewski (31, 32) and about 1899 by Bohr (1). Considerable additional work has been done since 1930. Only Wiebe and his coworkers (28, 29, 30), Prutton and Savage (19), and Sander (21) collected data at pressures above 100 atmospheres. Buch (2) and Morgan and Maass (17) determined solubilities at pressures below one atmosphere.

DISCUSSION

All the available data were assembled and in order to minimize confusion about the basis for reporting, they were converted to weight units. The units used are pounds of carbon dioxide that would dissolve in 100 pounds of water. This is, of course, equivalent to grams of carbon dioxide soluble in 100 grams of water. The resulting values, with the original literature sources cited, are shown in Tables I and II. Table I shows values at one atmosphere pressure and above, while Table II applies principally to pressures below one atmosphere.

The data of Table I were plotted, and smoothed curves representing the best interpretation of these data are shown in Figure 1. Because of the deviation of the various values, any single curve plotted from the available data would result in confusion as to where the curve should be. Using data directly from such a curve would result in wide differences in values obtained, depending on whether interpolation was used or whether the data were plotted, and if so, where the resulting curve was drawn. However, when several curves are drawn and when cross plots are used, the deviations can be minimized, and a family of curves can be obtained that will provide more consistent information. Figure I is such a family of curves.

Figure 1 shows that at high pressures the solubility of carbon dioxide increases with an increase in temperature. This characteristic, encountered at high pressures, is not widely known because such conditions are uncommon and seldom met with in ordinary activity.

REFERENCES

(1) Bohr, C., Ann. Physik 68 (No. 3), 500 (1899).
(2) Buch, K., Soc. Sci. Fennica Commentationes Phys. Math. 2, (No. 16), 1 (1925).
(3) Chemical Engineers' Handbook (J. H. Perry, editor), 3rd ed., p. 674, McGraw-Hill, New York, 1936.
(4) Findlay, A., Creighton, H. J. M., J. Chem. Soc. (London) 97, 536 (1910).
(5) Findlay, A., Howell, O. R., Ibid., 107, 282 (1915).
(6) Findlay, A., Shen, B., Ibid., 101, 1459 (1912).
(7) Findlay, A., Williams, T., Ibid., 103, 636 (1913).
(8) Haehnel, O., Centr. Min. Geol. 25 (1920).
(9) Handbook of Chemistry and Physics (N. A. Lange, editor), 8th ed., pp. 1082-3, Handbook Publ. Sandusky, Ohio, 1952.
(10) International Critical Tables, vol. III, p. 260, McGraw-Hill, New York, 1928.
(11) Just, G., Z. Physik. Chem. 37, 342 (1901).
(12) Kiss, A., Lajtai, I., Thury, G., Z. Anorg. Chem., 233, 346 (1937).
(13) Koch, H. A., Jr., Stutzman, L. F., others, Chem. Eng. Progr. 45, 677 (1949).
(14) Kunerth, W., Phys. Rev. 19, 512 (1922).
(15) Manchot, W., Z. Anorg. Chem. 141, 38 (1924).
(16) Morgan, J. L. R., Pyne, H. R., J. Phys. Chem. 34, 2356 (1930).
(17) Morgan, O. M., Maass, O., Can. J. Research 5, 162 (1931).
(18) Orcutt, F. S., Seevers, M. H., J. Biol. Chem. 117, 501 (1936).
(19) Prutton, C. F., Savage, R. L., J. Am. Chem. Soc. 67, 1550 (1945).
(20) Quinn, E. L., Jones, C. L., "Carbon Dioxide," Reinhold, New York, 1936.
(21) Sander, W., Z. Physik. Chem. 78, 513 (1912).
(22) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., pp. 221-4, Van Nostrand, New York, 1940.
(23) Seidell, A., Linke, W. F., "Solubilities of Inorganic and Organic Compounds," 3rd ed. suppl., pp. 89-92, Van Nostrand, New York, 1952.
(24) Showalter, H. A., Ferguson, J. B., Can. J. Research (Sect. B), 14, 120 (1936).
(25) Van Slyke, D. C., J. Biol. Chem. 130, 545 (1939).
(26) Van Slyke, D. D., Sendroy, J., Jr., others, J. Biol. Chem. 78, 765 (1928).
(27) White, H. A., J. Chem. Met. Mining Soc., S. Africa 20, 1, 15, 97 (1919).
(28) Wiebe, R., Chem. Rev. 29, 475 (1941).
(29) Wiebe, R., Gaddy, V. L., J. Am. Chem. Soc. 61, 315 (1939).
(30) Ibid., 62, 815 (1940); 63, 475 (1949).
(31) Wroblewski, S., Ann. Phys. Chem. 18, 290 (1883).
(32) Wroblewski, S., Compt. Rend. 94, 1335 (1882).
(33) Zaalishvili, Sh. D., J. Phys. Chem. (U.S.S.R.) 14, 413 (1940).
(34) Zelv́enskii, Y. D., J. Applied Chem. (U.S.S.R.) 12, 1311 (1939).
(35) Zelv́enskii, Y. D., J. Chem. Ind. (U.S.S.R.) 14, 1250 (1937).

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Solubility of Some Mixtures of Alkali Borates

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Measurements were made of the solubility relationships of various combinations of sodium pentaborate and diborate, ammonium pentaborate, tetraborate and diborate, and potassium pentaborate and diborate, in water at 20° , 30° , and 40° C.

It was demonstrated that the solubility peaks in these mixed systems are controlled by pH. The narrow composition limits governing the solubility peak in the sodium oxide-boric system can be greatly widened by the addition of ammonium ion.

Boric acid and sodium borates have been used as timber preservatives since 1939 (2). Recent developments of the impregnation process (4) have required the formulation of aqueous solutions of maximum boric oxide solubility in the pH range 6 to 8. The present work takes the obvious approach of using mixtures of various alkali borates. Economic considerations limit interest in such systems to sodium oxide, potassium oxide, ammonium oxide, boric oxide, and water, and solubility relationships have now been established for the most concentrated boric oxide solutions in this restricted pH range.

The system sodium oxide-boric oxide-water has been investigated at 30° C. by Dukelski (3), at 0° C. by Rosenheim and Leyser (7), and over the range 0° to 90° C. by Sborgi (8). In addition, the solubilities of boric acid and the various sodium borates in water have been measured by Blasdale and Slansky (1). In Dukelski's paper the system potassium oxide-boric oxide-water at 30° C. is also described, and Sborgi and Ferri (9) have investigated the system ammonium oxide-boric oxide-water from 0° to 90° C. Apart from a few values for the solubility of sodium diborate with ammonium diborate given by Sborgi and Gallichi (10), no references have been found to work done on the mixed systems.

In the present work, solubility measurements were made by prolonged shaking of solid phases with water, employing those solid phases stable in equilibrium with the final solution. This has the advantage of ensuring that supersaturation cannot take place (provided the temperature is not at any stage allowed to rise above the final temperature), and it also enables equilibrium to be established relatively quickly. Any desired point on the solubility curve can be obtained by restricting the amount of one or more constituents, and thus the steep portions of the curve, where solubility relationships are changing rapidly with minor changes in composition, can be explored fully.

A constant-temperature room was used, controlled to ±0.2° C. While such a room is not as accurate as a water bath, it has considerable advantages when samples are withdrawn for filtration, or measurement of pH and density.

EXPERIMENTAL

In each solubility determination, 20 ml. of water was shaken with weighed amounts of the various desired solid phases stable in equilibrium with the final solution. Shaking was continued for approximately 4 days. The solutions were allowed to settle and then filtered rapidly through Whatman No. 41 paper. If the solutions were not quickly filtered and covered, the low humidity of the room caused evaporation and cooling. With the technique described, no lowering of temperature was observed. Immediately after filtration the room temperature was raised about 1° C. to avoid any possible crystallization. A 10-ml. sample was withdrawn in a calibrated pipet and weighed in a dry 100-ml. flask, which was afterwards made up to volume, thus combining density measurement with subsequent dilution of a sample for analysis. The pH of the concentrated solution was measured on a glass electrode system at the working temperature.