are endothermic, and that for the sulfite is exothermic. Despite the variation from endothermicity to exothermicity for the dilution processes, all the heats are exothermic for the transfer from heavy into normal water. This is interpreted as an indication that the salts all possess a structure-breaking influence (*3*). The heat of transfer decreases in absolute value with increased solution concentration, providing further confirmation of the hypothesis suggested previously (*5*), that distant hydration is responsible for the solvent structure influence exhibited by salts passing between the isotopic solvents.

LITERATURE CITED

(1) Arnett, E. M., McKelvey, D. R., "Solute-Solvent Interactions," J. F. Coetzee, C. D. Ritchie, Ed., p 371, Marcel Dekker, New York, 1969.
(2) Greyson, J., Snell, H., *J. Phys. Chem.*, **73**, 3208 (1969).
(3) Greyson, J., Snell, H., *ibid.*, p 4423.
(4) Krishnan, C. V., Friedman, H. L., *ibid.*, **74**, 2356 (1970).
(5) Snell, H., Greyson, J., *ibid.*, **74**, 2148 (1970).

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Solubility of Lithium Carbonate at Elevated Temperatures

SOMERS H. SMITH, JR., DALE D. WILLIAMS, and ROMAN R. MILLER[1]
U. S. Naval Research Laboratory, Washington, D. C. 20390

The aqueous solubility of lithium carbonate (Li_2CO_3) has been measured between 100° and 300° C. Platinum-lined nickel tubing ¼ in. in diameter was weld-sealed at the ends, thus enclosing about 1 ml liquid plus excess salt. This was equilibrated at temperature, and the supernatant liquid was isolated from the excess salt by pinching the tube at the middle. When the tube was cool, the upper part was separated, and its contents were analyzed. The data correlated well with literature values. All available data were combined and an equation was generated for calculating solubility at temperatures between 0° and 300° C.

There is a probability that lithium hydroxide (LiOH) will be used as an additive in steam generators. When this substitution is made for the presently used sodium hydroxide (NaOH), it will be necessary to discontinue the concurrent addition of phosphate for precipitation of the hard water contaminants, calcium and magnesium. Whereas these phosphates settle as a mobile mud that is easily blown out, lithium phosphate (Li_3PO_4) deposits as a hard, adherent, insoluble layer on heat exchange surfaces to cause overheating and rapid deterioration in an operating boiler. A substitute additive presently considered for use with LiOH is a chelating agent such as ethylenediaminetetraacetic acid (EDTA) which would assume the tetralithium salt form at boiler alkalinity levels (pH 10–11), and would be expected to chelate calcium and magnesium ions to prevent their deposition.

There is one negative factor in this use of EDTA; a slow thermal decomposition occurs at boiler temperature (*ca.* 300° C) which could generate carbon dioxide (CO_2). Since this would react with LiOH to form the slightly soluble lithium carbonate (Li_2CO_3), it is important to know the carbonate solubility up to 300° C.

A search of the literature revealed a number of measurements over the period from 1856 to 1961 (*1-4, 6, 7, 9, 10*), most of which were at atmospheric pressure and at temperatures up to 100° C. Elenevskaya and Ravich (*3*), however, made determinations almost to the critical point of water. Since their method involved filtration and a possible thermal disturbance by water vaporization while the sample was being withdrawn, it was decided to redetermine values up to 300° C.

EXPERIMENTAL

Lithium carbonate solubility determinations at several temperatures between 100° and 302° C were made by placing an excess of solid Li_2CO_3 in a 1-ml, water-filled container formed from a 9-cm length of quarter-inch platinum-lined nickel tubing. This tubing had been deformed into an oval-shaped cross section with an area slightly less than one-half the original to allow for liquid expansion. Air space above the sample was kept to a minimum by freezing the liquid and arc welding the pinched tube end. The tube was clamped upright at or near its lengthwise center in an isothermal zone of a furnace by a screw-operated pinching device, and the furnace heat cycle was started. For temperature readings, two calibrated Pt-Pt + 10% Rh thermocouples were used; one was firmly taped to the upper end of the sample tube, and the other near the pinch zone. The outputs were read with a precision potentiometer with an overall accuracy of ±0.5° C. The isothermicity of the tube was ±0.4° C.

After a tube had equilibrated for from 30–115 hr in the furnace, the pinching device was screwed tightly shut so as to squeeze the sides of the tube together and isolate, at temperature, the supernatant liquid in the upper half from the excess undissolved solids in the bottom. The furnace was then allowed to cool, the tube removed, and the upper and lower sections were separated with a pinch-off tool. The upper portion was then weighed, opened, and its contents were rinsed into a flask for titration. The empty tube was dried and tared.

The amount of carbonate dissolved was obtained by titration of the sample with 0.1*N* hydrochloric acid (HCl) using a 1-ml semimicro buret. Use of a double–end point technique

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[1] To whom correspondence should be addressed.

(*8*) permitted evaluation of alkalinity in addition to that of carbonation.

The stock Li_2CO_3 used for this work analyzed 99.3% as carbonate, the remainder being a difficultly soluble, but alkaline-type impurity. Spectrographic analysis indicated the presence of approximately 0.10% calcium, 0.01% silicon and magnesium, and traces of iron and aluminum. Carbonates of calcium and magnesium are suspected to be the principal impurities. The quantities involved do not affect the data significantly.

DISCUSSION

The classical treatment of solubility data (*5*), assuming that no ionization, solvation, or other anomalies are involved, makes use of the Clausius-Clapeyron relationship, wherein the logarithm of the mole fraction of solute dissolved is plotted against the reciprocal of the absolute temperature. Most, but not all, materials respond to this treatment by exhibiting a linear plot, usually with a negative slope. Li_2CO_3 is one of a number of solutes giving a positive slope (negative temperature coefficient of solubility). The limited literature values also do not give a linear curve. The data obtained in this study substantiate both of these characteristics of Li_2CO_3.

To minimize the effects of scatter, a computer program, employing the method of least squares, was used to determine the lowest order polynomial equation fitting the data with an acceptable standard deviation. Data from all quoted sources, plus that resulting from this work, were used for this analysis. The computer-selected equation is:

$$\mathrm{Log}_{10}N = -5.4439 + 1486.6/T - 176190/T^2$$

where N is the mole fraction of solute and T is degrees Kelvin.

Solubility values over the temperature range of interest, calculated from this equation, are presented in Table I, as are the experimental values from the literature and this work. The standard deviation between observed and calculated values of log N is ± 0.04665.

The average percent deviation of the experimental values from calculated values is 15.8% for this work and 6.8% for the data of Elenevskaya and Ravich (*3*), with no significant positive or negative bias. When the magnitude of the absolute solubilities involved (*ca.* 1.3 mg Li_2CO_3/ml H_2O at 300° C) are considered in the context of the experimental difficulties of working with water systems at elevated temperatures and pressures, these percent deviations become acceptable, even if they are not pleasing.

The problem of saturation in this quiescent system is somewhat complicated by the negative coefficient of solubility with temperature. If the solution becomes saturated at a low temperature, then crystallization will occur as the temperature is raised—ensuring saturation, but allowing for the possibility of crystal deposition on the upper portion of the tube, and dissolution upon cooling to give spuriously high results. If the filling technique used successfully prevented saturation at low temperature, then thermal convection and diffusion would have to be depended upon to ensure saturation at pinch-off. The internal agreement of the data, considering the varying "soak" times used, implies that saturation was accomplished, and the lack of significant bias to the high side implies that supersaturation or "seeding" on the upper walls did not occur.

Table I. Aqueous Solubility of Li_2CO_3

Temp, ° C	Mole fraction 10^{-3} Calcd	Obsd	Reference
0	3.724	3.819	(*4*)
0	3.724	3.74	(*1*)
0	3.724	3.57	(*6*)
10	3.508	3.417	(*1*)
15	3.394	3.65	(*2*)
15	3.394	3.485	(*4*)
20	3.277	3.19	(*6*)
25	3.160	3.045	(*10*)
30	3.042	3.231	(*1*)
50	2.590	2.869	(*1*)
75	2.092	2.104	(*1*)
75	2.092	2.04	(*9*)
90	1.836	2.205	(*4*)
95	1.758	1.77	(*9*)
100	1.684	1.768	(*1*)
100	1.684	1.76	(*2*)
100	1.684	1.74	(*6*)
102	1.655	1.89	(*7*)
111	1.531	1.42	[a]
144	1.159	0.908	[a]
150	1.103	1.027	(*3*)
177	0.889	0.71	[a]
200	0.746	0.6474	(*3*)
220	0.645	0.724	[a]
250	0.524	0.5253	(*3*)
293	0.401	0.51	[a]
300	0.382	0.3662	(*3*)
302	0.377	0.37	[a]

[a] This work.

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LITERATURE CITED

(1) Bevada, I., *J. Russ. Phys. Chem. Soc.*, **16**, 591 (1884).
(2) Draper, C. N., *Chem. News*, **55**, 169 (1887).
(3) Elenevskaya, V. M., Ravich, M. I., *Zh. Neorg. Khim.*, **6**, 2380 (1961).
(4) Fluckiger, F. A., *Arch. Pharm.*, **25**, 509 (1887).
(5) Glasstone, S., "Textbook of Physical Chemistry," p 732, Van Nostrand, New York, N. Y., 1946.
(6) Haehnel, Otto, *J. Prakt. Chem.*, **48**, 295 (1937).
(7) Kremers, P., *Ann. Phys. Chem.* (Leipzig), **99**, 25 (1856).
(8) "Scott's Methods of Chemical Analysis," H. N. Furman, Ed., 5th ed., Vol. 2, p 2265, Van Nostrand, New York, 1939.
(9) Tschugaeff, L., Chlopin, W., *Z. Anorg. Allg. Chem.*, **86**, 154 (1914).
(10) Urazov, G. G., Lifatova, Z. I., *Zh. Prikl. Khim.*, **17**, 16 (1944).

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