[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

The Equilibrium $Li_2CO_{3(s)} + CO_2 + H_2O \rightleftarrows 2\ Li^+ + 2HCO_3^-$ at High Temperature and Pressure[1]

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The solubility of lithium carbonate in carbonic acid solutions has been measured at 200, 250 and 290°, respectively, and under CO_2 partial pressures up to nearly 200 atmospheres. The data are shown to be consistent with the assumption that the only ionic species present in significant concentrations are Li^+ and HCO_3^-. Equilibrium constants calculated from concentration units are very constant over a wide range of CO_2 pressures and a moderate range of Li^+ concentrations. These studies support a contention that the activity coefficient factors of the equilibrium constants in this system are remarkably constant. These observations may apply to aqueous systems in general at high temperature.

The solubility of lithium carbonate in carbonic acid solutions as a function of CO_2 pressure has been explored at low temperature by Haehnel.[2] He reports that bicarbonate ions are formed in solution; however, no attempt is made to interpret the solubility data on the basis of equilibrium constants. The purpose of this paper is to present solubility data for lithium carbonate in carbonic acid solutions as a function of CO_2 pressure at several high temperatures and to show that the solubility relationships can be explained readily by an equilibrium involving lithium and bicarbonate ions. Furthermore, equilibrium constants based on analytical concentrations and pressures rather than activities and fugacities agree for the most part within ±5% at any one temperature over a fourfold change in CO_2 pressure and up to 0.8 *m* lithium. These data are presented as evidence that aqueous solutions at elevated temperature show markedly different properties than at low temperature and in this case indicate an isothermal constancy in the activity coefficient factor of the equilibrium constant over the concentration ranges considered. The extension of studies of this type at high temperature is indicated as an important field of investigation for aqueous systems.

Experimental

An apparatus and thermostat controller for solubility determinations at high temperature has been described previously.[3] This apparatus was modified in order to be able to introduce CO_2 gas pressure to the equilibration pressure bomb and also to be able to read the total pressure of the system under study by means of a 0–340 atm. "Acragage" pressure gage. A schematic drawing of the modified apparatus is shown in Fig. 1. All parts were constructed of Type 347 stainless steel. Since the critical pressure of CO_2 is 72.9 atm. at 31° and since higher pressures were desired, liquid CO_2 tank pressure at room temperature could not be utilized. Therefore, an additional pressure bomb constructed to withstand 1000 atm. was connected to the pressure system. Commercial solid CO_2 was added to this pressure bomb which was then placed in a water-bath. The water was heated to the boiling point thereby obtaining CO_2 pressures in excess of the critical pressure. This CO_2 gas was introduced to the equilibration bomb containing the solution and solid components until the desired total pressure was attained.

Lithium was determined by standard acid–base titration of LiOH after first removing all carbonate and bicarbonate ion by the use of Dowex A-1 anion exchange resin. This method was shown to give quantitative values within ±0.2% by determining lithium in control solutions of LiOH and Li_2CO_3. However, in the runs at 250°, lithium was analyzed with an accuracy of ±3% by photometry.

Analyses for total carbonate content were made by collecting liquid–gas samples in a specially devised 250-cc. flask, weighing the flask, acidifying with H_2SO_4 and boiling out the CO_2 from the acidified solution. The CO_2 gas was absorbed on "Ascarite" and weighed by following the standard gas analysis procedure for CO_2. Similar procedures were used for the analysis of the residual solid phase for CO_2 content after the completion of a run.

Standard 3 mm. o.d. Pyrex tubes of one-meter length were employed in another analytical method for CO_2. A clean, dry tube was attached to the sampling tip from the equilibration pressure bomb, and a solution sample was withdrawn. As the pressure on the liquid sample fell to atmospheric during the sampling process, CO_2 gas was evolved from the solution to form relatively small gas and liquid segments in the long tube. The liquid and gas segments were allowed to flow through the tube until the walls were wet and sufficient holdup solution had been withdrawn and discarded. The tube was removed from the sampling tip and each end was sealed with a torch at an equal distance between two segments of liquid. The liquid portion was shaken or vibrated to the lower end, and the total gas-to-liquid-length ratio was measured after allowing the tube to remain in a vertical position for 24 hr. By the use of the standard gas equation, an approximation was made of the wt. % CO_2 gas which evolved from the solution sample upon releasing the CO_2 pressure. In this case the total CO_2 content (all species) of the solution at equilibrium was estimated by adding the analyzed weight of CO_2 remaining in a given weight of solution (at atmospheric pressure) to the weight of gas released.

During a run the total gas pressure was read on the gage, and the approximate CO_2 pressure was determined by subtracting saturated steam pressure from this gage pressure. The resulting values, then, are only approximations to the true CO_2 pressure since the liquid is not pure water but rather a Li_2CO_3–CO_2–H_2O solution. It was felt that corrections for the differences in water vapor pressure between the solutions and H_2O were negligible at these high total pressures.

Procedure for Making a Run.—A known weight of Baker and Adamson C.P. Li_2CO_3 was added to 60 cc. of "ion-exchange purified" distilled water in a 100-cc. capacity pressure bomb. The temperature was raised, and, at approximately 100°, carbon dioxide gas was bled into the equilibration bomb from the auxiliary gas pressurizer bomb to approximate the highest desired total pressure at the equilibration temperature. The equilibration bomb was heated to the desired temperature, the solution and solid were thermostated within ±1°, and both the bomb and thermostat were rocked between ±30° angles from the horizontal position. After equilibration, the bomb was set in a vertical position and the solid phases were allowed to settle. The total pressure was read from the gage, a holdup sample was removed, and a final sample of the clear liquid phase was withdrawn for analysis. Each sample volume was of the order of 3 cc. which included the holdup portion; therefore, many samples at varying total pressures could be obtained per run.

The pressure of CO_2 was lowered by bleeding sufficient CO_2 and water vapor from the system through the gas inlet tube (Fig. 1) while the bomb was still in the vertical position. For raising the total pressure, CO_2 was added at tempera-

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[1] This paper is based upon work performed at Oak Ridge National Laboratory which is operated by Union Carbide Nuclear Company for the Atomic Energy Commission.

[2] O. Haehnel, *J. prakt. chem.*, (2) **148**, 295 (1937).

[3] W. L. Marshall, *Anal. Chem.*, **27**, 1923 (1955).

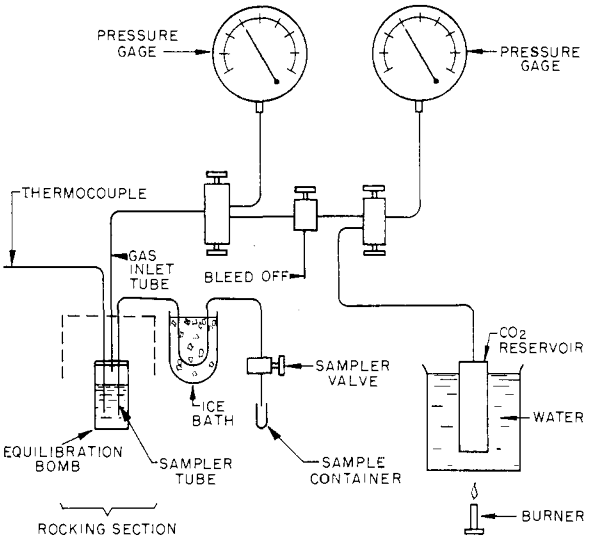

Fig. 1.—Schematic diagram of solubility apparatus.

ture in the same manner as in the initial addition. The system was then ready for equilibration at a lower or higher CO_2 pressure. Equilibrium was attained within 5 to 10 minutes after raising or lowering the CO_2 pressure as evidenced by agreement of results obtained over this time interval compared with data at the same pressure obtained 16 hr. later. These observations indicated complete and relatively fast reversibility of the over-all equilibrium.

Results

Solubility of Li_2CO_3 in Aqueous Solution.—The solubility of Li_2CO_3 in water as a function of temperature and as a function of CO_2 pressure at 40, 200, 250 and 290°, respectively, is given in Table I. The solubility values at 40° are those from the data of Haehnel[2] and do not approach the precision of our high temperature data. Haehnel reported his results as wt. % Li_2CO_3. We have recalculated these values as molality Li^+.

The solid phase was shown to be Li_2CO_3 by rapidly cooling the pressure vessel after several of the runs, separating the white solid from the supernatant, drying the solid between filter paper and analyzing it for lithium and total CO_2. The mole ratio, Li/CO_2, was found to be 2.00 ± 0.01 and the average analysis gave 99.7% Li_2CO_3.

The solubility of Li_2CO_3 at constant temperature is increased greatly as the pressure of CO_2 is raised. This increase in the solubility of Li_2CO_3 with CO_2 pressure is attributed entirely to the formation of HCO_3^- ions as will be demonstrated.

For saturation with Li_2CO_3, combination of K_{SP} (solubility product of Li_2CO_3), K_1 and K_2 (first and second ionization constants of CO_2) gives

$$\frac{(a_{Li^+})^2(a_{HCO_3^-})^2}{(a_{CO_2})(a_{H_2O})} = \frac{K_{SP}K_1}{K_2} = K_a \qquad (1)$$

In absence of information on activity coefficients or fugacities we can test this expression only in terms of concentrations. We assume that m_{CO_2} is proportional to $P_{CO_2}k'$ (Henry's law) and that $CO_3^=$ is negligible compared to HCO_3^-, so that $m_{HCO_3^-}$ is taken as essentially equal to m_{Li^+}. Hence, with $a_{H_2O} \cong 1$, we write

$$\frac{(m_{Li^+})^4}{P_{CO_2}} = K_m \qquad (2)$$

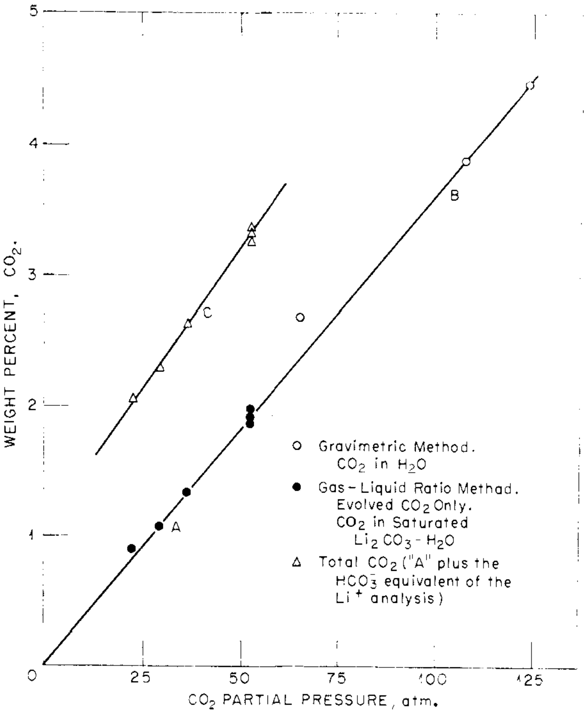

Fig. 2.—Solubility of CO_2 in H_2O and saturated Li_2CO_3 solution at 250°.

The K_m's so calculated are given in Table I and indicate excellent agreement over a wide concentration range which approaches one molal in lithium at 200°. The constancy of K_m at a given temperature indicates the probable correctness of the postulated equilibrium.

Solubility of CO_2 in H_2O and in Solutions Saturated with Li_2CO_3.—Table II and Fig. 2 give the

TABLE I

SOLUBILITY OF Li_2CO_3 IN H_2O–CO_2 SOLUTIONS

CO_2, atm.	40°[a] Li^+, m	$K_m \times 10^{+1}$	CO_2, atm.	250° Li^{+b}, m	$K_m \times 10^{+4}$
5.0	1.40	7.68	0	0.0639	...
10.0	1.40	3.84	0	.0655	...
20.0	1.92	6.79	22.7	.265	2.17
30.0	2.06	6.00	28.9	.283	2.22
34.0	2.06	5.29	38.4	.299	2.07
			40.8	.296	1.88
(Av. K_m = 5.92 × 10^{-1})			53.4	.316	1.87
			61.6	.336	2.07
			66.3	.347	2.19
			(Av. K_m = 2.07 × 10^{-4})		

CO_2, atm.	200° Li^+, m	$K_m \times 10^{+3}$	CO_2, atm.	290° Li^+, m	$K_m \times 10^{+4}$
0	0.0824[b]	...	25.2	0.1151	6.96[c]
0	.0829[b]	...	37.1	.1475	12.75
41.8	.556	2.28	49.3	.1596	13.16
70.8	.635	2.29	62.9	.1661	12.10
72.5	.640	2.31	76.9	.1764	12.59
76.5	.645	2.26	91.9	.1828	12.15
102.1	.703	2.39	102.7	.1898	12.63
126.2	.744	2.42	115.3	.1912	11.58
152.8	.776	2.38	130.6	.1962	11.35
188.8	.814	2.32			
(Av. K_m = 2.33 × 10^{-3})			(Av. K_m = 12.29 × 10^{-6})		

[a] K_m's calculated from data of Haehnel (see ref. 2). [b] Flame spectrophotometer analyses. [c] Not included in the average.

TABLE II

THE SOLUBILITY OF CO_2 IN H_2O AND IN SATURATED Li_2CO_3 SOLUTIONS AT 250°

CO_2 pressure, atm.	CO_2, wt. % evolved from Li_2CO_3 soln.	CO_2, tot. wt. % in Li_2CO_3 soln.	CO_2, tot. wt. % in H_2O
22.9	0.90	2.05	
29.7	1.07	2.29	
36.7	1.34	2.63	
52.7	1.87	3.26	
52.7	1.98	3.37	
52.7	1.92	3.32	
65.3			2.686
107.1			3.881
123.1			4.473

solubility of CO_2 in H_2O and in solutions saturated with solid Li_2CO_3 at 250°. Curve AB fits data for CO_2 in pure water (determined by the gravimetric method) and for non-ionic CO_2 in the saturated Li_2CO_3 solution (determined by the gas–liquid ratio method). This indicates the solubility of non-ionic CO_2 in the lithium carbonate solution is essentially independent of the concentration of the ionic species. Curve C gives the total CO_2 content of the Li_2CO_3 saturated solutions calculated by adding the HCO_3^- equivalent of the Li^+ analysis to the CO_2 determined by the gas–liquid ratio method.

The Henry's law constant k' ($k' = m_{CO_2}/P_{CO_2}$, where m_{CO_2} = molality of non-ionic CO_2 and P_{CO_2} is the partial pressure of CO_2 in atmospheres) is calculated from line AB to be 8.69×10^{-3} at 250° Substituting for P_{CO_2} in equation 2, we obtain

$$K' = \frac{K_m}{k'} = \frac{(m_{Li^+})^4}{m_{CO_2}} = 2.38 \times 10^{-2} \text{ (at 250°)} \quad (3)$$

The adherence to Henry's law at elevated temperatures is not paralleled at lower temperatures[4,5] where there are significant deviations from linearity at comparable pressures. This observation concurs with our previous comment supporting an isothermal constancy of the activity coefficient in this aqueous system at high temperature. If approximate Henry's law constants calculated from the data of Wiebe and Gaddy are plotted, along with the value of the constant at 250°, a minimum in the solubility of CO_2 in H_2O occurs at approximately 180°.

In conclusion, the data presented give evidence that, in general, aqueous solutions at high temperature are probably much simpler to interpret than similar systems at low temperature, as had been pointed out previously by Gibson and Loeffler.[6]

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(4) R. Wiebe and V. L. Gaddy, THIS JOURNAL, **63**, 475 (1941).

(5) R. Wiebe and V. L. Gaddy, *ibid.*, **62**, 815 (1940).

(6) R. E. Gibson and O. H. Loeffler, *Ann. N. Y. Acad. Sci.*, **51**, 727 (1949).

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Water Vapor Pressures above Sodium Hydroxide and Mixtures of Sodium Hydroxide and Sodium Oxide in the Vicinity of 300°

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An effusion study of the $NaOH–Na_2O–H_2O$ system between 260 and 310° yields water pressures significantly higher than expected from reported thermodynamic properties. Vaporization of NaOH was not detected below 310°. Limited solubility of Na_2O in NaOH in the solid phase, less than 10% at 305°, is indicated.

Published thermodynamic data predict that the decomposition of sodium hydroxide to sodium oxide will give an equilibrium pressure of water vapor of *ca.* 10^{-11} atmosphere in the vicinity of 300°, if both solid phases are at unit activity. Hence direct study of this equilibrium below the melting point of sodium hydroxide (319°) does not appear practical. However, on investigation of the behavior of sodium hydroxide in effusion cells, water pressures above 10^{-8} atmosphere have been observed for prolonged periods. An extended study of the system between 260 and 310° has been made in an effort to ascertain whether pressures of this magnitude actually are established by the decomposition equilibrium.

Experimental

The effusion apparatus and techniques used were basically those described for a study of magnesium hydroxide[1] with the exception that the sample was not subjected to continuous evacuation but remained isolated in a closed vacuum system during the short time necessary for determination of the quantity of effusate collected in a given run. Water vapor removed from the cell at reaction temperature during the measurement was collected in a liquid oxygen cooled trap. The trap was then isolated from the effusion cell by means of a large bore stopcock and the collected water transferred to a small calibrated volume where it was allowed to vaporize and the quantity determined by *PVT* measurements near room temperature. The identity of the vapor frequently was confirmed by checking the vapor pressure of the condensate at the ice point. Thus the water leaving the cell was determined directly, independent of any other species which may also have effused.

Baker C.P. sodium hydroxide sticks (analyzed lot no. 4231, 98.9% NaOH, 0.9% Na_2CO_3) were used. Sodium oxide was prepared by reaction of sodium (present in excess) with sodium peroxide at 500° in an argon atmosphere. After the reaction the excess sodium was distilled away *in vacuo*. Weighed samples of oxide, hydroxide and mixtures of the two were analyzed by titration with standard HCl solution to phenolphthalein and methyl orange endpoints and Na_2O, NaOH and Na_2CO_3 contents evaluated in the conventional way. For several samples, Na_2CO_3 also was determined independently by release of carbon dioxide, the latter measured gravimetrically in a standard Ascarite absorption train. Carbonate content was generally between 1 and 2%. When samples of sodium oxide were dissolved in water in evacuated containers, no gas was

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(1) E. Kay and N. W. Gregory, *J. Phys. Chem.*, **62**, 1079 (1958).