Equilibrium Dissociation Pressures of Molten Lithium Carbonate

G. J. JANZ and M. R. LORENZ
Rensselaer Polytechnic Institute, Troy, N. Y.

Equilibrium carbon dioxide dissociation pressures are reported for Li_2CO_3 (m.p. 726° C.) in the molten state for the temperature range, 735° to 845° C. Some results for Na_2CO_3 (m.p. 858° C.) in the range 840° to 885° C. are also given. The displacement of the results of earlier studies from the present data and the influence of cation polarization effects are briefly considered.

THERMAL STABILITIES of the molten alkali carbonates, Li_2CO_3, Na_2CO_3 and K_2CO_3 have been investigated by Lebeau (*5*), Johnston (*4*), and Howarth and Turner (*3*) using various modifications of fundamentally the same technique—*i.e.*, a static vapor pressure measurement. The spread in the results from these studies for molten Li_2CO_3—*e.g.*, at 776° C. dissociation pressures from 1 mm. to 24 mm. of Hg—indicated need for additional data preferably by a different experimental approach. This article reports equilibrium dissociation pressures for molten Li_2CO_3 at temperatures up to 843° C. using the dynamic technique of this laboratory (*7*). Some results for molten sodium carbonate are also given.

EXPERIMENTAL

The experimental arrangement and procedure of the dynamic technique for equilibrium dissociation pressures have been described elsewhere in detail (*7*). In contrast to the static method where the CO_2 pressure of a sealed sample is taken as the equilibrium pressure at a fixed temperature, the principle of the dynamic method consists of a temperature cycle at precisely controlled partial pressures of CO_2 above the sample to observe the "equilibrium temperature." This is achieved by an adaptation of the thermogravimetric principle with temperature as a variable.

In this method the samples were contained in a 10-ml. crucible (80% Pd-20% Au alloy) freely suspended in the hot zone from a precision semi-micro single pan analytical balance with an optical scale (Mettler). A metered gas stream (N_2-CO_2mixtures, pre-dried) at a total pressure corresponding to atmospheric pressure was used to achieve a controlled partial pressure of CO_2 in the hot zone. The temperature was then raised while the sample weight was observed continually. When the onset of a weight change (loss) was detected, the temperature was decreased until the sample began to gain weight. This temperature "cycle" was repeated as required several times to determine the equilibrium temperature (the temperature for the selected partial pressure of CO_2 at which no weight change occurs). The furnace was capable of a uniform temperature zone (±0.2° C. at 700°-900° C.) in the sample region. Sample weight changes as small as 1.7 mg./per hr. were readily detectable. The dry gases were metered through sensitive flowmeters having sapphire and/or stainless steel floats (E. Greiner, type G9143B) and high precision needle valves (Edwards). The accuracy of the CO_2 pressure values is ±0.5 mm. of Hg. The gas flow rate was varied in the range of 150 to 450 cc./per min. to ascertain that the results were unaffected by this parameter.

RESULTS

The temperature range investigated and the results for Li_2CO_3 and Na_2CO_3 are given in Table I. No measurements were made for K_2CO_3, but its thermal stability is recognized (*8*) as equal to, and probably greater than, that of Na_2CO_3. A comparison of the present results for molten Li_2CO_3 and previous data is illustrated in Figure 1.

A series of calibration tests using $CaCO_3$ (for which the equilibrium dissociation pressures are well known) were undertaken as part of this work. The results gained by the present dynamic technique fall well within the limits of uncertainty of the established CO_2 dissociation pressures of $CaCO_3$—*e.g.*, pCO_2 = 1 atm. observed at 899° C.; literature values (*1*, *2*) 895° to 902° C. An interesting feature was that the equilibrium pressure was attained in a relatively short time (approximately one-half to one hour) relative to the comparable measurements using static techniques.

DISCUSSION

The displacement of the results of earlier studies from the present data (Figure 1) should be commented upon in light of the different experimental techniques. For carbonates, the following mass law-controlled equilibria are recognized:

$$M_2CO_3(l) \rightleftarrows M_2O(l) + CO_2(g) \tag{1}$$

$$CO_2(g) \rightleftarrows CO(g) + \tfrac{1}{2}\,O_2(g) \tag{2}$$

$$M_2O(l) \rightleftarrows 2M(g) + \tfrac{1}{2}\,O_2(g) \tag{3}$$

$$M_2O(l) \rightleftarrows M_2O(g) \tag{4}$$

$$M_2CO_3(l) \rightleftarrows M_2CO_3(g) \tag{5}$$

Processes 2 to 5 are assumed neglibible relative to the CO_2-M_2O dissociation below 1000° C. Thus, for carbonates in the molten state, the expression for the free energy change for reaction 1 is given by:

$$\Delta G^\circ = -RT \ln \frac{A_{M_2O} P_{CO_2}}{A_{M_2CO_3}}$$

Table I. Equilibrium Dissociation Pressures

	Temp., ° C.	CO_2 Press., mm. Hg
Li_2CO_3[a] (m.p. 726° C.)	735	11.6
	776	53.2
	797	111
	821	247
	843	501
Na_2CO_3 (m.p. 858° C.)	840	0
	858	8
	885	15

[a] Li_2O content of sample about 2.3×10^{-3} moles per mole Li_2CO_3.

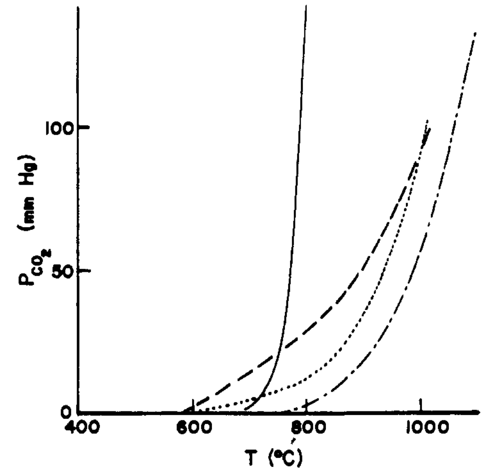

Figure 1. Comparison of equilibrium dissociation pressures for Li_2CO_3 gained by the dynamic method and from static technique Static techniques: data of Lebeau (5), — — — —; Johnston (4) ......; and Howarth and Turner (3), — · — · — · — · Dynamic technique; present investigation ————————.

where cognizance of the activities of the oxide and the carbonate in the liquid mixture as well as the CO_2 pressure in the reaction equilibrium is important. The significance of this point seems to have escaped the earlier experimentalists (*3*, *4*, *5*). The vacuum drying techniques at elevated temperatures for removal of water vapor, common practice in the preparation of dry samples for static measurements, introduce a factor of uncertainty by simultaneous removal of CO_2 and consequent formation of M_2O in the sample. The displacement of the curves in Figure 1 is understood in large part from this viewpoint. At 775° C. for example, the results of Lebeau (*5*), Johnston (*4*), and Howarth and Turner (*3*) can be brought into accord with the present data if a correction for 0.004, 0.02, and 0.1 mole Li_2O/per mole Li_2CO_3 is made for the equilibria in the molten specimens.

Both Li_2CO_3 and Na_2CO_3 show first appreciable dissociation just above their respective melting points. This may be attributed in part to the smaller interatomic distances in the molten salts compared with the solid state (*6*).

Effectively, this predicts a sudden increase in the polarizing effect of the cationic species at the melting point of the inorganic salt with the transition of the salt through fusion from the solid state to the liquid state. For both Li_2CO_3 and Na_2CO_3, the first appreciable dissociation pressures are observed on fusion. This factor, and the significantly greater dissociation pressures of Li_2CO_3 relative to Na_2CO_3 correlate with the polarizing power of the cationic species.

The following points should be noted relative to the dynamic and static methods in such studies. When measuring dissociation pressures by the dynamic method, the effects of any residual water and impurities present in the sample are of little importance. The rate of dissociation may be affected but not the equilibrium. In the case of the static pressure method, any impurity leading to a stable gas phase will contribute an error to the measured dissociation pressure. By contrast, a finite vapor pressure of the salt would contribute to an error in the dynamic, but not in the static method.

LITERATURE CITED

(1) Baker, E.H., *J. Chem. Soc. (London)* **1962**, 464.
(2) Hill, K.J., Winter, E.R.S., *J. Phys. Chem.* **60**, 1361 (1956).
(3) Howarth, J.T., Turner, W.E.S., *J. Soc. Glass Technol.* **14**, 394 (1930); *Ibid.* **15**, 360 (1931).
(4) Johnston, J., *Z. physik. Chem.* **62**, 330 (1908).
(5) Lebeau, P., *Ann. chim. et phys.* **6**, 422 (1905).
(6) Levy, H.A., Gron, P.A., Bredig, M.A., Danford, M.D., *Ann. N. Y. Acad. Sci.* **79**, 762 (1960).
(7) Lorenz, M.R., Janz, G.J., *J. Chem. Ed.* **40**, 611 (1963).
(8) Motzfeldt, K., *J. Phys. Chem.* **59**, 139 (1955).

RECEIVED for review April 30, 1963. Accepted August 9, 1963. This work was made possible, in large part, from support received from the Department of the Navy, Office of Naval Research, Chemistry Branch, Washington, D. C.

Fused Salt Distribution Studies

Distribution of TlBr Between KNO_3 and AgBr

JOHN H. KENNEDY[1]
University of California, Santa Barbara, Calif.

IN A PREVIOUS PUBLICATION (*3*), the distribution constant for TlCl between KNO_3 and AgCl:

$$K = [\mathrm{TlCl}]_{KNO_3}/[\mathrm{TlCl}]_{AgCl}$$

and the association constant, *k*, for:

$$\mathrm{Tl}^+ + \mathrm{Cl}^- \xrightarrow{k} \mathrm{TlCl}$$

in molten KNO_3 were obtained from the following equation:

$$K_o = K + (K/k)[X^-]^{-1} \qquad (1)$$

K_o was the observed distribution coefficient, *K* the distribution constant for TlCl, *k* the association constant, and $[X^{-1}]$ was the halide ion concentration in the KNO_3 phase.

The same relationship was displayed by the TlBr distribution between KNO_3 and AgBr, and in this study the temperature dependence of *K* and *k* was investigated.

EXPERIMENTAL

The same apparatus used for TlCl distribution (*3*) was used for the TlBr distributions. However, a Vycor flask was used in place of the borosilicate glass flask for distributions at temperatures above 500° C. Normally, 50 grams

---

[1] Present address: Boston College, Chestnut Hill, Mass.