Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Solid-Liquid Phase Equilibria for Mixtures of Lithium, Sodium, and Potassium Carbonates

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IN STUDIES on physicochemical and electrochemical aspects of molten carbonates, knowledge of the liquid-solid phase equilibria for binary and ternary systems of the alkali metal carbonates is essential. The high reactivity and thermal instability of molten alkali carbonates, and the consequent experimental problems, undoubtedly contribute in large part to uncertainties in the published data for these systems.

A comprehensive review of the knowledge of the phase equilibria up to 1958 has been recently published (*2*). Results for the three binary systems and the ternary system based on the use of the visual technique have recently been published by Volkova (*7*). While the general features of the binary liquid-solidus equilibria are qualitatively confirmed, the results contribute little to the accurate knowledge of these systems, since the data of Volkova for the liquidus temperatures, eutectic compositions, and temperatures differ appreciably from the earlier work. For the ternary system, with the exception of a passing reference by Tamaru and Kamada (*6*) which mentions a mixture melting at 380° C., without specifying the composition, knowledge is limited to the results of Volkova. For the Na_2CO_3-K_2CO_3 solid-liquid phase equilibria, the recent publication by Reisman (*4*) settles the outstanding uncertainties for this binary system. This article reports the results of studies for the Li_2CO_3-Na_2CO_3, Li_2CO_3-K_2CO_3, and Li_2CO_3-Na_2CO_3-K_2CO_3 systems undertaken to establish accurately the liquid-solid phase equilibria in mixtures.

EXPERIMENTAL

The Li_2CO_3, Na_2CO_3, and K_2CO_3 (analytical reagent grade chemicals) were dried to constant weight under a CO_2 atmosphere at 600° C., and stored over P_2O_5 in desiccators until used.

A 50-cc. gold (or gold–20% palladium alloy) crucible was used to contain the molten carbonates for the thermal analyses experiments. Preliminary corrosion tests showed that these metals suffered no attack after contact with molten carbonates for periods up to 60 hours at temperatures up to 950° C. The experimental arrangement consisted of the crucible supported on an alundum pedestal enclosed in a 96% silica glass tube. Alundum baffles prevented excessive heat losses. A motor-driven rotating stirrer maintained homogeneity in the melt. The low torque motor stopped automatically with thickening of the solid-liquid mixture. A gold-sheathed 96% silica glass thermocouple tube was immersed in the melt. A recording differential potentiometer (*5*) and a Pt-Pt, 10% Rh thermocouple were used to trace the temperature time curves. The × 20 range on this instrument, corresponding to approximately 100° C. for full scale deflection, was used to follow the temperature-time histories for most experiments. Temperatures could readily be read to the nearest 0.1° C. Critical points were checked with the next more sensitive range (20° for full scale deflection). At all times an atmosphere of CO_2 was maintained above the sample by a controlled flow of the gas into the sample housing through a 96% silica glass tube.

Various cooling rates, from 0.5° to 2.0° C. per minute, were used. At least two cooling curves for every composition point were observed: in doubtful cases as many as six indepentently prepared mixtures were investigated. Freezing points were reproducible to within 1° C.

Melts were seeded to avoid excessive supercooling—i.e., > 2° to 3° C. For the Li_2CO_3-K_2CO_3 system, it was essential to seed with crystals of the intermediate compound, $LiKCO_3$, at the approximate liquidus temperatures to define the nature of the curve accurately in the 40 to 65% Li_2CO_3 composition region. In the Li_2CO_3-Na_2CO_3 system, for compositions in the range 30 to 70% Li_2CO_3, even with the most careful seeding efforts, a relatively large uncertainty remained relative to the first halt temperature in the cooling curves. The maximum uncertainty is shown in Figure 1,B, by the dotted lines below the liquidus curves.

The experimental compositions investigated for the two binary systems, and the liquidus-solidus curves and eutectic halts are illustrated in Figure 1, *A* and *B*. From large-scale graphs of the results, and those of earlier contributions, a comparison of liquidus temperatures at uniform composition increments was compiled (Table I).

Data for the experimental compositions investigated, and temperatures at which inflections and halts were noted in

the cooling curves for six cuts across the field of the ternary are summarized in Table II. From these data, and the knowledge of the three binary systems, a large scale model of the composition-temperature phase equilibria was constructed and the liquidus surface isothermals as illustrated in Figure 2 were developed. The composition and melting point for the apparent ternary eutectic are (mole %): Li_2CO_3, 43.5; Na_2CO_3, 31.5; and K_2CO_3, 25.0; m.p. 397° ± 1° C., respectively.

DISCUSSION

Li_2CO_3-K_2CO_3. A compound $LiKCO_3$, congruently melting at 504.5° ± 1° C. is formed. Two eutectic mixtures at 42.7 and 62.0 mole % Li_2CO_3, and melting at 498° and 488° C., respectively, are present. Unless the melts were seeded with crystals of $LiKCO_3$ in the region of these eutectics, the samples would cool beyond the above temperatures to a second set of eutectic halts at 460° and 465° C., respectively. This set is shown by the dotted horizontal lines in Figure 1, *A*. For mixtures of compositions in the region 45 to 60 mole % Li_2CO_3, the separation of $LiKCO_3$ was readily induced by simple cooling, without seeding.

Table I. Liquidus Temperatures for Li_2CO_3-Na_2CO_3, and Li_2CO_3-K_2CO_3 Binary Systems

Li_2CO_3, Mole %	T_1, ° C. Le Chatelier (3)	Volkova (7)	Present authors
	Li_2CO_3-K_2CO_3 System		
0.00	860	896	899
10.0	776	810	829
20.0	687	716	742
30.0	600	611	644
40.0	511	496	533
42.0	503	497	508
44.0	505	498	500
50.0	508	499	505
60.0	504	497	503
62.0	498	493	498
72.0	552	552	557
80.0	618	625	625
90.0	671	683	683
100.0	710	732	726
	Li_2CO_3-Na_2CO_3 System		
0.00	(858)[a]	860	858
10.0	(808)	798	806
20.0	(749)	(732)	(746)
30.0	(683)	660	678
40.0	(596)	585	598 ± 2
45.0	548	545	557 ± 3
48.0	(519)	520	530 ± 5
50.0	513	500	512 ± 5
52.0	(515)	500	500
55.0	543	498	516
60.0	576	516	544
70.0	620	570	597
80.0	662	624	646
90.0	699	678	689
100.0	735	732	726

[a] Eitel and Skaliks (*1*) given for the balance of this column.

Table II. Thermal Analysis Data for Li_2CO_3-Na_2CO_3-K_2CO_3 System

Composition, Mole % Li_2CO_3	Na_2CO_3	K_2CO_3	Crystallization Temp., ° C. T_1	T_2	T_3
		Series I			
60.9	0.00	39.1	490	...	...
57.1	6.3	36.6	476	...	...
57.5	15.5	33.0	453	...	399
47.7	21.7	30.6	436	...	399
43.3	29.0	27.7	419	...	397
39.8	34.7	25.5	475	...	398
38.2	37.0	24.8	452	...	398
30.0	50.5	19.5	568	...	391
0.00	100	0.00	858	...	...
		Series II			
0.00	60.0	40.0	710	...	...
6.7	56.0	37.3	669	451	399
12.6	52.5	34.9	632	450	399
19.2	48.5	32.3	590	450	399
26.0	44.4	29.6	542	...	398
32.6	40.4	27.0	492	...	397
48.6	30.8	20.6	470	418	393
54.7	27.1	18.2	494	...	393
59.8	24.1	16.1	518	417	392
64.4	21.4	14.2	549	417	392
68.6	18.8	12.6	579	417	392
73.0	16.2	10.8	605	415	392
76.4	14.1	9.5	624	409	392
100	0.00	0.00	726	...	...
		Series III			
0.00	72.3	27.7	740	...	...
14.8	61.6	23.6	663	...	...
22.3	56.2	21.5	617	...	390
27.9	52.1	20.0	580	...	390
33.6	48.0	18.4	541	411	391
38.9	44.2	16.9	498	421	391
44.4	40.2	15.4	448	441	392
49.1	36.8	14.1	480	445	392
53.1	33.9	13.0	503	444	391
100	0.00	0.00	726	...	...
		Series IV			
43.1	0.00	56.9	499	...	...
37.5	13.0	49.5	462	...	...
32.8	23.9	43.3	452	435	390
29.7	31.2	39.1	475	(419) 454	...
23.3	46.0	30.7	561	...	399
17.5	59.6	22.9	648	...	390
0.00	100	0.00	858	...	...
		Series V			
58.0	42.0	0.00	533	500	...
47.6	34.4	18.0	434	...	395
40.6	29.3	30.1	415	406	397
36.7	26.6	36.7	424	...	...
43.5	31.5	25.0	...	...	397
0.00	0.00	100	...	898	...
		Series VI			
48.7	51.3	0.00	525	500	...
26.8	28.2	45.0	510	420	...
19.5	20.5	60.0	638	429	...
14.3	15.0	70.7	725	...	...
40.8	42.8	16.4	480	...	395
36.4	38.1	25.5	465	...	397

Inspection of data in Table I shows that the present results entirely confirm the nature of the liquidus-solidus phase equilibria of the earlier studies of Le Chatelier (*3*) and Volkova (*7*) for this system. The consistently lower values of Volkova (at 35 mole % Li_2CO_3, the liquidus-temperature is as much as 35° C. lower than that observed in the present work) may be attributed as a consequence of the visual method used by Volkova to detect the temperatures of first crystallization and the high degree of supercooling possible on these systems. Inspection of the work of Le Chatelier (*3*) shows that the melting point of pure K_2CO_3 is reported as 860° C., some 40° below accepted values; therefore agreement of those data with present results, except in a qualitative way, would not be anticipated.

An interesting feature in the present system is the second set of eutectic halts that are attained in a range of compositions as shown in Figure 1, *A*. One possibility is that $LiKCO_3$ has a crystalline modification which is stable at lower temperatures and it is this phase which freezes out at the second set of eutectics.

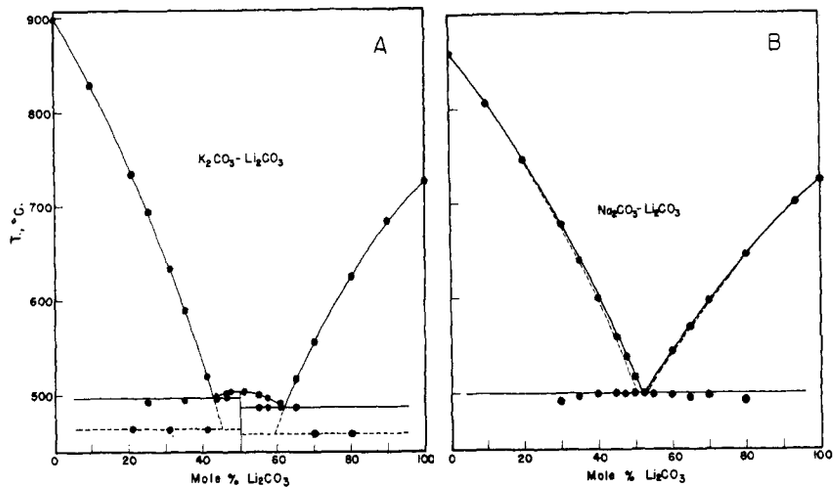

Figure 1. Temperature-composition diagrams of the liquid-solid phase equilibria in binary carbonate systems

A. K_2CO_3-Li_2CO_3

B. Na_2CO_3-Li_2CO_3

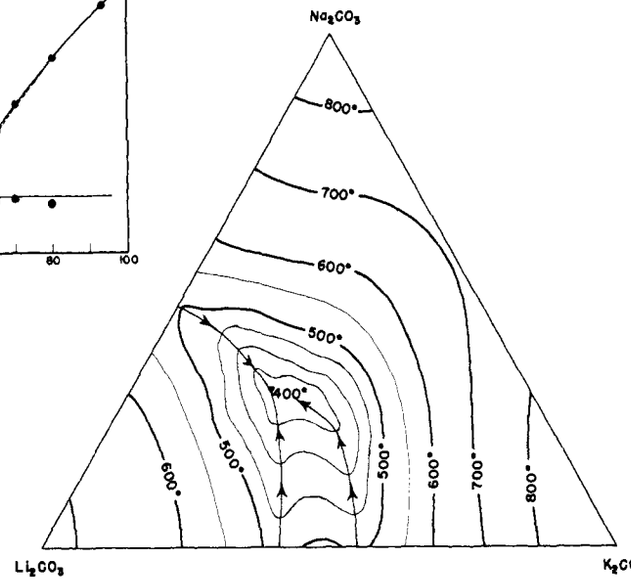

Figure 2. Temperature isothermals for liquid-solid equilibria in the ternary Li_2CO_3-Na_2CO_3-K_2CO_3 system

Exact composition of the ternary eutectic, m.p. 397 ± 1° C., is (mole %), Li_2CO_3:Na_2CO_3:K_2CO_3; 43.5:31.5:25.0, respectively

Li_2CO_3-Na_2CO_3. Inspection of the thermal analysis in which Eitel and Skaliks (*1*) first advanced the suggestion that a congruently melting compound $LiNaCO_3$ occurs in this system shows clearly that the limited number of experimental compositions and the scatter in the data are insufficient to support this claim. Evidence is based entirely on supporting results of x-ray analysis and index of refraction data (*1*) obtained from melts cooled to room temperature. Consideration of the present thermal analysis data shows clearly that the Na_2CO_3-Li_2CO_3 system is of the simple eutectic type. The dotted lines (Figure 1, *B*) give the maximum uncertainty and rule out the separation of the congruently melting compound, $LiNaCO_3$, previously suggested (*6, 7*). Although the eutectic region was investigated repeatedly, the early work (*6, 7*) could not be confirmed. The rather unambiguous thermal data show that the confusion in this region is due to the conclusions based on the x-ray data obtained at room temperature relative to the status of the system above this temperature. Inspection of the limited thermal data of Eitel and Skaliks (*1*) shows that interpretation of the results as a simple liquid-solid eutectic type diagram is possible. The thermodynamically improbable x-ray data may be interpreted equally well due to polymorphic transitions with composition and/or solid solution effects arising in the solid system on cooling from the simple eutectic system at 501° C. to room temperature. Experimental data concerning the solid state diagram of the system are required to resolve this point. The existence of a simple eutectic is strongly supported by the unambiguous thermal data for the liquidus region.

Li_2CO_3-Na_2CO_3-K_2CO_3. According to the three binary systems which bound this ternary system, the latter is expectedly complex. The present investigation is mainly concerned with the liquidus surface and not with complete accurate characterization of the ternary system. Inspection of the liquidus surface shown in Figure 2 indicates three fields of crystallization—i.e., that of Li_2CO_3, $LiKCO_3$, and solid solution Na_2CO_3-K_2CO_3. At the intersection of the three lines of demarcation, there exists the lowest melting mixture of the ternary system. Interpretation of this point, m.p. 397° ± 1° C., composition (mole %), Li_2CO_3:Na_2CO_3:K_2CO_3 is 43.5:31.5:25.0, respectively, as a simple ternary eutectic is supported by thermal data (Table II, Series V, 5th entry).

Molar ratio of the three carbonates in this mixture approximates very nearly the simple ratio: 1.00:1.25:1.75 for K_2CO_3:Na_2CO_3:Li_2CO_3. The composition of a low-melting ternary mixture (390° C.) in this system as reported by Volkova (*7*) was (mole %); Li_2CO_3:Na_2CO_3:K_2CO_3; 27:45:28. Inspection of present results shows that for a point of this composition, the first crystallization temperature is 480° C. (Table II, Series VI), with cooling to the ternary eutectic composition and temperature following. The erroneous composition cited by Volkova is thus understood, if the cooling curve had been initiated at temperatures less than 480° C. under which circumstances the first arrest in the cooling curve to solid phase separation would not have been observed. The somewhat lower melting points, 390° and 380° C., reported in the earlier investigations (*6, 7*) could not be reproduced in the present work. Errors due to supercooling effects and thermometry in the earlier studies could well account for temperature differences of this magnitude. There are insufficient details given in the original publications to resolve these points further.

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