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DIFFERENTIAL THERMAL ANALYSIS OF PHASE EQUILIBRIA IN MIXTURES OF ANHYDROUS CARBONATES.
I. Li_2CO_3–$BaCO_3$

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ABSTRACT

The mixtures $(Li_2CO_3)_{1-x}$–$(BaCO_3)_x$ were studied in a Perkin–Elmer DTA 1700 Instrument operated in the DSC mode. An eutectic transition was observed at $640 \pm 3°C$ for x in the interval (2.55, 96.4) mol% with $x_{eu} = 39.4$ mol%. A solid solution may exist for $x > 96.4$ mol%. Polymorphic transitions were observed at $807 \pm 1°C$ for $x > 53$ mol%, and at $966 \pm 1°C$ for $x > 64$ mol%.

INTRODUCTION

In recent years, several studies have been conducted of the use of molten salts as heat transfer and storage media for solar thermal central receivers. One of the mixtures of salts with attractive properties is the ternary eutectic of carbonates of lithium, sodium, and potassium. This mixture melts at 397°C, [1] but the anticipated operating range is 500–1000°C. Since the lithium component is more expensive than the others, the question has been raised about the practicality of replacement of at least some of the lithium carbonate by barium carbonate. There was little information in the literature regarding mixtures of $BaCO_3$ with the other constituents, and so a series of measurements was begun using current techniques and equipment to determine the properties of some of those mixtures. This paper is concerned with a discussion of the technique and its application to a study of phase transitions in binary mixtures of Li_2CO_3 and $BaCO_3$. Data on transitions in the other mixtures will be reported separately.

$BaCO_3$ melts only under high pressures, at 1400°C, and at lower pressures it decomposes before melting [2]. It experiences two polymorphic

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transformations at higher temperatures. γ-$BaCO_3$ is an orthorhombic material (similar to the $CaCO_3$ phase aragonite) which is stable up to 803 ° C. There it undergoes a transformation to β-$BaCO_3$, a hexagonal phase, which persists up to 976 ° C. At that temperature, the material transforms to α-$BaCO_3$, a face-centered cubic phase. (There is some uncertainty in the literature concerning the exact transition temperatures.) Several melting points are given for pure Li_2CO_3 [2], 720, 725, and 734 ° C, and the reference to melting at 725 ° C also indicates that a latent heat of 42 kJ mol^{-1} is required. Previous observations of $BaCO_3$ mixtures with Li_2CO_3 were reported by Bellanca [3], as part of a series of observations on the ternary system $CaCO_3$–$BaCO_3$–Li_2CO_3. He observed solidification from a melt for pure Li_2CO_3 and binary mixtures at values of x_{BaCO_3} of 25, 35, 50, and 60 mol% $BaCO_3$.

In the present work, observations of the phase transitions have been made for mixtures in the range 2.5–95 mol% using Perkin–Elmer DTA 1700 equipment operating in a mode giving calculated DSC data. An adaptation of Tammann's Rule [4] to this equipment is used in interpretation of the data.

THEORY

Tammann's Rule

The empirical rule established by Tammann [4] relates the extent of isothermal halts at phase transitions of binary mixtures to the compositions of those mixtures. The use of this rule facilitates determination of eutectic or peritectic compositions as well as the range of compositions over which those and other isothermal transitions occur. In practice, zero quantities cannot be measured and so it is impossible to determine precisely the composition at which a given transition begins or ends. Similarly, experimental error bounds make it difficult to determine directly the composition at which a transition is strongest, e.g., the eutectic composition. Tammann's Rule holds that the heat required to effect a transition at a given composition is a linear function of the composition. The use of this rule makes it possible to extrapolate from data taken across the entire range of the transition to determine the extrema with accuracy. Although Tammann's Rule is well-known, an analytical basis for the rule does not appear to be readily available. Such a basis, therefore is given here, both for its own sake and to make apparent how data obtained using the Perkin–Elmer DTA 1700 equipment is to be interpreted in order to apply the rule.

Suppose that two materials A and B are present in varying proportions in the samples. If M_i is the molecular weight of species i, and m_i is the mass of that species, then the number of moles of the species, n_i and the mole fraction, x_i, are defined in the usual manner. The mean molecular weight of the sample, M_s, is given by

$$M_S = x_A M_A + x_B M_B \tag{1}$$

and the mass of the sample, m_s, and the number of moles of the sample, n_s, are the sums of the corresponding quantities for each species.

Figure 1 is a hypothetical phase diagram for mixtures of species A and B. At low concentrations of B, the materials experience mutual solubility in the solid state. Beginning at a composition x_{min}, the material experiences partial melting at a eutectic temperature T_{eu}, and the system consists of a solid phase in equilibrium with a liquid phase for temperatures from T_{eu} to T_A, the latter being the melting temperature of pure species A. The amount of liquid formed at T_{eu} increases from zero at x_{min} to the total mass m_s at the eutectic composition, x_{eu}. The mixture with composition x_c forms a coordinated compound which melts incongruently at a peritectic temperature T_{per}. This first-order transition is first seen at T_{per} in samples of composition x_{per}. The amount of liquid formed at T_{eu} decreases from m_s at composition x_{eu} to zero at composition x_c. At the peritectic temperature, the incongruent melting produces a transition which increases in strength from x_{per}, reaching a maximum at x_c, and thereafter decreasing as x_B increases to one. A solid–solid transition is observed at T_{ss} for concentrations x_B in the interval $(x_{ss},1)$.

Consider first the melting at T_{eu}. The total number of moles of species B is given by

$$n_B = x_B n_s = x_{min} n^{(s)}(x_B,T_{eu}) + x_{eu} n^{(l)}(x_B,T_{eu}) \tag{2}$$

where $n^{(s)}(x_B,T_{eu})$ is the number of moles of solid which are produced in the

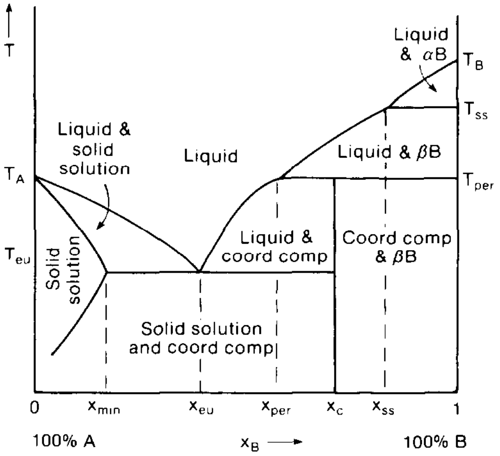

Fig. 1. Hypothetical phase diagram for binary mixtures of species A and B.

phase separation at T_{eu} when the overall sample composition is x_B. Similarly $n^{(l)}(x_B,T_{eu})$ is the amount of liquid which occurs under these conditions. Since n_s is also the sum of $n^{(s)}(x_B,T_{eu})$ and $n^{(l)}(x_B,T_{eu})$, the lever rule follows

$$n^{(l)}(x_B,T_{eu})(x_{eu}-x_B)=n^{(s)}(x_B,T_{eu})(x_B-x_{min}) \tag{3}$$

From eqns. (2) and (3)

$$n^{(l)}(x_B,T_{eu})=n_s\left(\frac{x_B-x_{min}}{x_{eu}-x_{min}}\right) \tag{4}$$

If the molar enthalpy of melting at composition x_{eu} is Δh_{eu}, then the total enthalpy needed to produce the liquid fraction at x_B is

$$\Delta H(x_B,T_{eu})=\Delta h_{eu}n^{(l)}(x_B,T_{eu})=\Delta h_{eu}n_s\left(\frac{x_B-x_{min}}{x_{eu}-x_{min}}\right) \tag{5}$$

ΔH depends on x_B not only through the explicit factor, but also through a dependence implicit in n_s. Dividing ΔH by n_s then gives a fractional molar enthalpy, Δh, which is a linear function of x_B

$$\begin{aligned}\Delta h(x_B,T_{eu})&=\Delta H(x_B,T_{eu})/n_s\\&=\Delta h_{eu}\left(\frac{x_B-x_{min}}{x_{eu}-x_{min}}\right)\qquad x_{min}\leqslant x_B\leqslant x_{eu}\end{aligned} \tag{6}$$

Similarly, one finds for x_B in the interval (x_{eu}, x_c)

$$\Delta h(x_B,T_{eu})=\Delta h_{eu}\left(\frac{x_c-x_B}{x_c-x_{eu}}\right)\qquad x_{eu}\leqslant x_B\leqslant x_c \tag{7}$$

From experimental data, one can find the reduced enthalpies, Δh, and then the equations of straight lines which are best fits. The intersections of the lines provide the eutectic composition, x_{eu}, and eutectic molar enthalpy, Δh_{eu}. From the intersection of the lines with the composition axis ($\Delta h=0$), one determines x_{min} and x_c.

The fractional molar enthalpy associated with the incongruent melting at T_{per} is found in an analogous manner

$$\begin{aligned}\Delta h(x_B,T_{per})&=\Delta H(x_B,T_{per})/n_s\\&=\Delta h_{per}\left(\frac{x_B-x_{per}}{x_c-x_{per}}\right)\qquad x_{per}\leqslant x_B\leqslant x_c \qquad (8)\\&=\Delta h_{per}\left(\frac{1-x_B}{1-x_c}\right)\qquad x_c\leqslant x_B\leqslant 1 \qquad (9)\end{aligned}$$

As is the case with the eutectic, the peritectic parameters x_{per}, x_c, and Δh_{per} can be inferred from straight lines fitted to the data observed at T_{per}.

Assessment of fractional molar enthalpy data with regard to Tammann's Rule also is very useful in discovering the presence or absence of congruent melting. For, if a eutectic line were to terminate on one end at a composition x_{con} corresponding to congruent melting at a temperature T_{con}, one would find that the fractional molar enthalpy at T_{eu} would satisfy

$$\Delta h(x_{\mathrm{B}},T_{\mathrm{eu}}) = \Delta h_{\mathrm{eu}}\left(\frac{x_{\mathrm{con}} - x_{\mathrm{B}}}{x_{\mathrm{con}} - x_{\mathrm{eu}}}\right) \qquad x_{\mathrm{eu}} \leqslant x_{\mathrm{B}} \leqslant x_{\mathrm{con}} \tag{10}$$

Thus, $\Delta h(x_{\mathrm{con}},T_{\mathrm{eu}})$ vanishes, a feature which would be quite clear from the data if it were so. Of course, $\Delta h(x_{\mathrm{con}},T_{\mathrm{con}})$ is non-zero.

Consider now the polymorphic transition in which species B undergoes a solid–solid transition at temperature T_{ss}. The liquidus at this temperature is associated with a concentration x_{ss}. At T_{ss}, the relation of moles of A in the liquid to moles of B in the liquid is

$$n_{\mathrm{A}}^{(\mathrm{l})}(T_{\mathrm{ss}})x_{\mathrm{ss}} = n_{\mathrm{B}}^{(\mathrm{l})}(T_{\mathrm{ss}})(1 - x_{\mathrm{ss}}) \tag{11}$$

regardless of the actual composition of the sample, x_{B}. At the actual composition, x_{B}, the amount of solid B which undergoes the solid–solid transition is, since species A is entirely liquid

$$\begin{aligned} n_{\mathrm{B}}^{(\mathrm{s})}(x_{\mathrm{B}},T_{\mathrm{ss}}) &= n_{\mathrm{B}} - n_{\mathrm{B}}^{(\mathrm{l})}(x_{\mathrm{B}},T_{\mathrm{ss}}) = x_{\mathrm{B}}n_{\mathrm{s}} - n_{\mathrm{A}}^{(\mathrm{l})}(x_{\mathrm{B}},T_{\mathrm{ss}})x_{\mathrm{ss}}/(1 - x_{\mathrm{ss}}) \\ &= [x_{\mathrm{B}} - x_{\mathrm{ss}}(1 - x_{\mathrm{B}})/(1 - x_{\mathrm{ss}})]\,n_{\mathrm{s}} \end{aligned} \tag{12}$$

or

$$n_{\mathrm{B}}^{(\mathrm{s})}(x_{\mathrm{B}},T_{\mathrm{ss}}) = \left(\frac{x_{\mathrm{B}} - x_{\mathrm{ss}}}{1 - x_{\mathrm{ss}}}\right)n_{\mathrm{s}} \tag{13}$$

The fractional molar enthalpy, Δh, associated with the first-order solid state polymorphic transition is then found, as before, to be

$$\Delta h(x_{\mathrm{B}},T_{\mathrm{ss}}) = \Delta h_{\mathrm{ss}}\left(\frac{x_{\mathrm{B}} - x_{\mathrm{ss}}}{1 - x_{\mathrm{ss}}}\right) \tag{14}$$

where Δh_{ss} is the molar enthalpy of the transition at pure B.

The Perkin–Elmer DTA 1700 system can be operated in a mode in which the ΔT vs. T data are converted to heat flux vs. T, simulating the output of a differential scanning calorimeter (DSC). The conversion is performed by proprietary firmware. The support software includes subroutines which perform analysis of the peaks associated with first-order phase changes to yield information concerning the interpolated temperature of onset of the leading edge of the peak, the temperature at which the peak has its largest amplitude, maximum or minimum, and the area enclosed by the peak and the extrapolated baseline. The area information is quite useful since that area is proportional to the latent heat or enthalpy of the transition, and knowledge of its value permits application of Tammann's Rule [4].

In actual operation, the sample mass is one of the parameters specified when the program is run. After peak analysis, a datum is displayed which is proportional to peak area per unit sample mass. If suitable conversion factors are established by calibration against standard materials, the read-out can be converted directly into enthalpy per unit mass (e.g., J/kg^{-1}). It has been observed in these experiments that the calibration factors vary slightly and direct comparison of specific enthalpy data taken at different temperatures does not provide the same accuracy obtained in the temperature measurements themselves ($<0.5\%$). However, in these experiments using tall cups (100 mm^3), a calibration factor of 1.5 was found to give a relative accuracy of 3–4%.

The datum Δh_m provided by the machine analysis is proportional to the enthalpy per unit mass, $\Delta H/m_s$, involved in the transition at that composition. If the constant of proportionality is denoted α, then the fractional molar enthalpy Δh is related to Δh_m in a simple way

$$\Delta h = \Delta H/n_s = (\Delta H/m_s)M_s = \alpha\ \Delta h_m M_s \tag{15}$$

If α can be determined through calibration, then Δh is readily determined from the data for Δh_m. If α cannot be determined satisfactorily, then setting it to unity gives Δh in arbitrary units. The relative data which result are adequate for the extrapolation to x_{min}, x_{eu}, etc. for a given transition.

EXPERIMENTAL

Materials

Anhydrous barium carbonate and lithium carbonate reagents of the Gold Label standard (99.999%) series were obtained from the Aldrich Chemical Company. The reagents were stored in a dry box and were tested periodically for possible hydration by observation of heating of the pure reagents. The traces observed showed little or no signs of peaks below 400 ° C which might be indicative of dehydration. Samples masses of 25 mg or more were consistent before and after heating, usually to within ± 0.1 mg and rarely to -0.4 mg. Exceptionally low laboratory humidity helped avoid hydration during brief exposure of the reagents to the ambient environment during sample preparation.

Procedure

All measurements were made by heating runs, at $+10\,^\circ C\ min^{-1}$, in a Perkin–Elmer DTA 1700 apparatus operated in the DSC mode. All runs were conducted using a purge gas of dry CO_2 at a flow rate of 40 ml min^{-1}. The preservation of surface finish and masses of platinum crucibles containing the carbonate mixtures were evidence that the gas flow successfully inhibited decomposition of the carbonate ions at the temperatures reached in the experiments. All masses were determined to 0.01 mg with a Mettler

H51AR balance. Instrumental temperature readings were converted to the Celsius scale using a calibration curve based on the melting points of pure aluminum, silver, and gold. Samples with $BaCO_3$ concentrations in the range 20–90 mol% were prepared by measuring a total mass of about 40 mg of reagents weighted to give the desired molar composition. The reagents were mixed by grinding and a platinum crucible loaded with about 25 mg of material. The sample was heated to well above the observed melting temperature of pure Li_2CO_3 (728°C) to achieve more complete and uniform mixing. Subsequent runs showed no signs of further change. It was necessary when the amount of the minority component was very small to avoid losses in mixing or transfer which might have a significant effect on the accuracy of compositions. Such samples were prepared by adding the minority component directly to a crucible containing a known amount of the majority component. In the range where eutectic melting persisted, this melting promoted sufficient diffusion during the initial melt that no history dependence of traces was observable on subsequent runs. In a sample of specially low Li_2CO_3 composition, a special problem was encountered which will be discussed below. All data reported were taken only after sample stability was established.

RESULTS

The phase diagram for binary mixtures of Li_2CO_3 and $BaCO_3$ is mainly of the simple eutectic type, complicated only by the presence of polymorphic transformations of the remnant solid $BaCO_3$ at high concentrations of that reagent, and the possible existence of a narrow range of solid solution for x_{BaCO_3} greater than 96 mol%.

DSC traces characteristic of those observed for the Li_2CO_3–$BaCO_3$ mixtures are shown in Fig. 2. At low $BaCO_3$ concentrations a nearly isolated peak characteristic of an isothermal event is observed at essentially the same temperature regardless of concentration. The return to baseline is not complete, and the curve leads into a second broader peak, at variable temperatures, which then terminates with a rapid return to steady baseline.

In the calibration procedure, the melting temperature of the metal standards was taken as the temperature at which the DTA/DSC data began to show the endothermic peak characteristic of melting. The temperature scale thus relates to the hottest part of the sample. (The non-zero heating rate makes unavoidable the presence of a temperature gradient in the sample.) The onset temperature of the initial peak for the carbonate mixtures was thus interpreted as the eutectic temperature. With a temperature gradient present, the liquidus is first seen when the last bit of solid disappears in the hottest part of the sample. Since this produces a decrease in the mass to which latent heat must be provided, this point is evident in the DTA/DSC

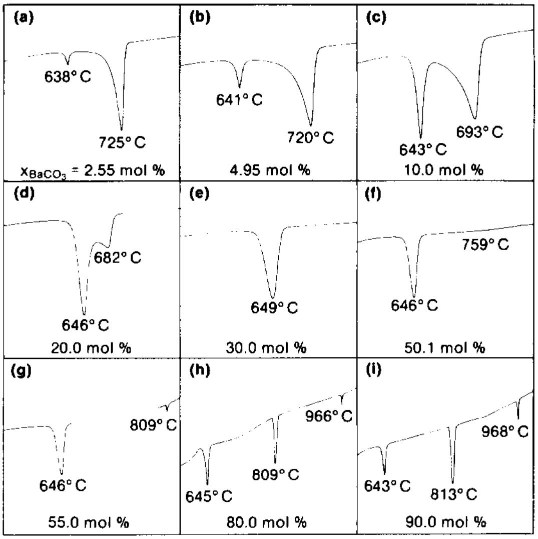

Fig. 2. DSC traces typical of the Li_2CO_3–$BaCO_3$ mixtures. Not all vertical scales are the same.

data as the peak minimum, the onset of return to baseline, and so the peak temperature has been interpreted as the liquidus temperature. (The return to baseline of the trailing edge of the peak corresponds to the final disappearance of solid in the coolest part of the sample. Since at that moment the coolest part would be at the liquidus temperature, the calibrated temperature, at the hottest point, would be several degrees too high to provide a liquidus datum.) Figures 2(a)–(e) show the development of the eutectic feature and the decrease of the associated continuous melt as x_{BaCO_3} increases toward the eutectic composition, x_{eu}. Instrumental broadening and growth of the eutectic feature precludes observation of the continuous melt (and the liquidus) near x_{eu}. As shown in Fig. 2(f), the continuous melt feature is very weak and broad for x_{BaCO_3} above, but still near x_{eu}. As x_{BaCO_3} increases past the values where the polymorphic transformations appear, the continuous melt and the liquidus become unobservable by this technique. (Traces of the liquidus appear much more clearly as an exothermic feature in cooling runs at some of the higher $BaCO_3$ concentrations, but because of irregular supercooling, the positions of the peak are not good indicators of the liquidus temperature in those cases.) Figures 2(g)–(i) illustrate the appearance and growth of peaks associated with the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations of the residual solid $BaCO_3$, and the accompanying dwindling of the eutectic feature as the Li_2CO_3 concentration decreases.

The data taken from the temperature at which these transitions occurred, and the Δh data obtained for the corresponding peak areas are listed in Table 1. All data in Table 1 are averages of measurements from at least

TABLE 1

Phase transitions in Li_2CO_3–$BaCO_3$ mixtures

Transition	Eutectic		Liquidus		γ-$BaCO_3$ $\rightarrow \beta$-$BaCO_3$		β-$BaCO_3$ $\rightarrow \alpha$-$BaCO_3$	
x_{BaCO_3} (mol%)	T (°C)	Δh (arb)	T (°C)	Δh (arb)	T (°C)	Δh (arb)	T (°C)	Δh (arb)
0.00			728	31				
2.55	634	1.5	725					
4.95	637	3.4	719					
10.0	642	7.3	710					
20.0	641	14	682					
30.0	640	20						
40.0	642	28						
50.1	641	22	760±15					
55.0	642	19			808	0.7		
60.0	643	19			809	2		
70.0	639	12			808	5	965	0.3
79.9	639	7.8			807	7	966	0.8
89.9	637	1.6			807	12	966	1.6
95.1	638	2.0			807	11	968	1.7
100.0					810	13	976	1.8

T (°C) is the calculated temperature of onset of the leading edge of the endothermic DSC peak associated with the transition. Δh(arb) is the calculated peak area in arbitrary units. Multiplication of Δh(arb) by 1.5 gives, approximately, Δh (kJ mol^{-1}). Standard deviations for all temperatures are within ±0.5 °C unless otherwise noted.

three runs. It should be noted that the overall variation of the temperatures of the eutectic and $\gamma \rightarrow \beta$ transitions are small across the entire range of observed compositions. It is a peculiar feature that variation of the temperature of the $\beta \rightarrow \alpha$ transition is small across the range of compositions of the mixture samples, but the temperature of that transition for the mixtures is noticeably lower than the temperature for that transition in pure $BaCO_3$. This difference in temperature is well outside the resolution of the instrument, and it is believed to be a real feature.

The temperature and composition data presented in Table 1 are plotted in Fig. 3 showing the phase diagram for the Li_2CO_3–$BaCO_3$ mixtures. The liquidus curve is sketched as a dashed line beyond the points where it is supported by direct observation. The data of Bellanca [3] are included for comparison. Figure 3 shows clearly the simple progression of phase changes for this series of mixtures. Data obtained from other techniques would be needed to augment this diagram, particularly in establishing better the location of the liquidus at higher $BaCO_3$ concentrations. The depression in the $\beta \rightarrow \alpha$ transition temperature by nearly 9 °C for the mixtures is clear. The similar, but smaller, depression in the $\gamma \rightarrow \beta$ transition temperature should also be noted. The agreement of the present data with those reported

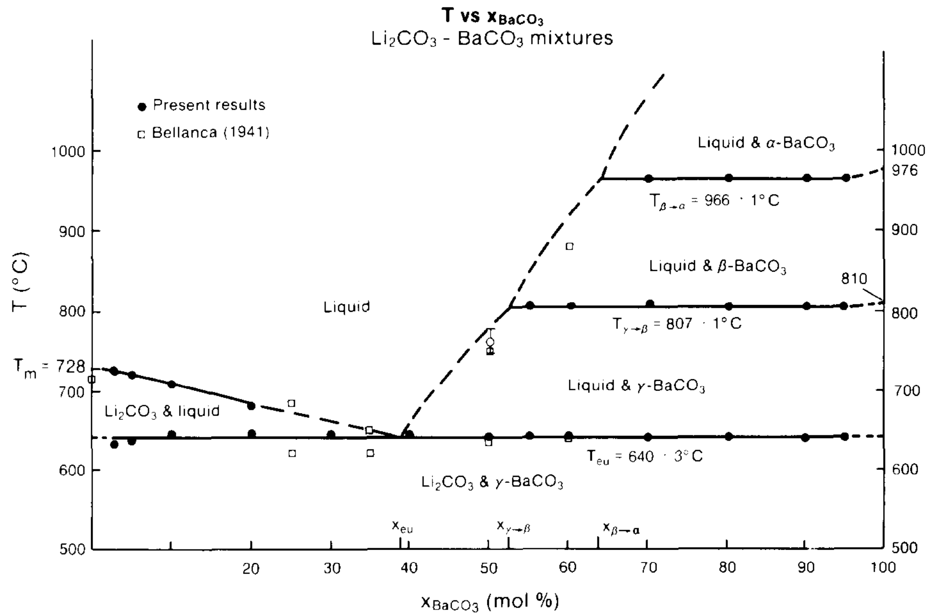

Fig. 3. Phase diagram for Li_2CO_3–$BaCO_3$ mixtures. Solid lines imply regions of established data. Broken lines imply inferences from data.

by Bellanca [3] is quite reasonable in view of the differences in technique.

The peak area–composition data are plotted in Fig. 4 together with straight lines fitted to the data in application of Tammann's Rule [4]. These lines, as determined by least-squares fits to the data, are as follows

Eutectic (639.5 ± 2.6 ° C, 42 data points)

$$\Delta h = 0.692x - 0.025 \qquad 0 \leqslant x_{BaCO_3} < 39.4 \tag{16}$$

$$\Delta h = -0.477x + 46.0 \qquad 39.4 < x_{BaCO_3} \leqslant 100 \tag{17}$$

γ-$BaCO_3$ → β-$BaCO_3$ (807.2 ± 1.1° C, 24 data points)

$$\Delta h = 0.278x - 14.6 \qquad 52.5 < x_{BaCO_3} \leqslant 100 \tag{18}$$

β-$BaCO_3$ → α-$BaCO_3$ (965.5 ± 1.0 ° C, 18 data points)

$$\Delta h = 0.053x - 3.4 \qquad 64 < x_{BaCO_3} \leqslant 100 \tag{19}$$

One infers from the eutectic lines that x_{eu} has the value 39.4 mol%, with $\Delta h(x_{eu}, T_{eu})$ equal to 27.2 in arbitrary units. From the lines associated with the polymorphic transitions, one infers that the liquidus curve reaches the 807 ° C temperature of the $\gamma \to \beta$ transition at x_{BaCO_3} equal to 52.5 mol%, and the 966 ° C temperature of the $\beta \to \alpha$ transition at x_{BaCO_3} equal to 64 mol%. It also follows from these lines that the latent heat of the $\gamma \to \beta$ transition is 13.2 compared to the value of 13 arbitrary units observed for

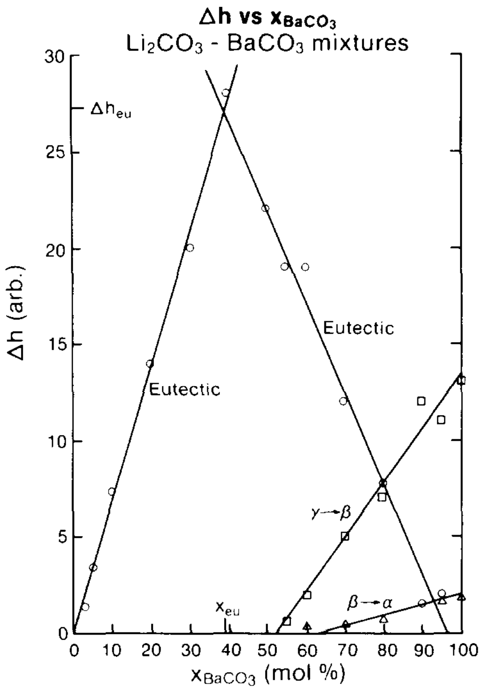

Fig. 4. Latent heats in isothermal transitions in Li_2CO_3–$BaCO_3$ mixtures.

pure $BaCO_3$, and of the $\beta \rightarrow \alpha$ transition 1.9 arbitrary units compared to the value of 1.8 arbitrary units observed for pure $BaCO_3$. The good agreement of the values of Δh_{ss} observed directly in each of these transitions with the values calculated using Tammann's Rule supports the assumption that use of Δh_{ss} regardless of concentration is valid.

In an attempt to calibrate the peak area data, it was found that a factor of 1.5 gives an approximate conversion of Δh(arb) into Δh(kJ mol^{-1}). Such conversion suggests that the present data are commensurate with the data reported by Stern and Weise [2].

It should be noted in Fig. 4 that the enthalpy line for low $BaCO_3$ concentrations extrapolates to zero molar enthalpy for a value of x_{BaCO_3}, 0.036 mol%, which is consistent with zero, suggesting that no solid solution occurs at T_{eu} for low x_{BaCO_3}. However, for high $BaCO_3$ concentrations, the fitted line extrapolates to zero enthalpy for a value of x_{BaCO_3} of 96.4 mol%. This suggests that a solid solution may exist in this narrow range of concentrations. In an attempt to verify this, 0.23 mg of Li_2CO_3 were added to 39.70 mg of $BaCO_3$ and heated to promote mixing. As mentioned above, a melt at the eutectic temperature was noted on the initial run, but after time was allowed for diffusion of the Li^+ ions, no further sign of eutectic melting was seen. Had a homogeneous sample been obtained, the masses would give x_{BaCO_3} a value of 98.5mol%. Even after 7 h of heating, distortions in the shape of the $\beta \rightarrow \alpha$ peak suggested that at least some $BaCO_3$ remained unassociated with Li_2CO_3, and that x_{BaCO_3} was somewhat less than 98.5 mol% in part of the sample. In view of this uncertainty, it did not seem appropriate to report quantitatively on this sample. Qualitatively, the absence of signs of an eutectic transition after extended heat preparation is in accord with the solid solution hypothesized above. The difference in the temperature of the polymorphic transitions in the mixed and the pure materials may be further evidence for a solid solution.

DISCUSSION

The measurement of phase transition characteristics using very small samples has the advantage that effects of non-zero temperature gradients which are inevitable in heating or cooling can be reduced substantially in comparison with what is experienced in large samples. Thus, the data may be more nearly representative of those which would be observed in quasi-static experiments. In these experiments however, direct observation of the sample was impossible and there is no immediate verification that some of the transitions inferred from the thermal data actually did take place. While there is little reason to doubt the data for the first-order isothermal eutectic or polymorphic transitions, the observation of continuous melts with large dT/dx is difficult in the DTA 1700 instrument. It was found that residual continuous melting persisted for the heavier samples for some compositions in ranges of temperature where one would infer from the DTA 1700 traces that the melting had been complete. Gradual small changes of heat capacity of the small samples were indistinguishable in the traces from a true baseline.

As stated above, the interpretation of fractional molar enthalpy data using Tammann's Rule does strengthen inferences drawn about the isothermal first-order transitions which have been observed. At low x_{BaCO_3}, the termination of the continuous melt feature is also unambiguous. But, as shown in Fig. 2(e)–(i), at concentrations near and above x_{eu}, evidence for the liquidus is uncertain in these experiments and should be supplemented by data in experiments where more direct observation is possible. Hot stage or visual polythermal experiments or measurements using X-ray diffraction would be helpful. Such techniques might also be helpful in clarifying both the existence of a solid solution region for very high x_{BaCO_3} and the differences in temperatures at which the polymorphic transitions occur in the mixtures and in pure $BaCO_3$.

It was observed above that the calibration factor for conversion of peak areas to enthalpy, based on metal standards, appeared to be less precise (3–4%) than were the data for temperatures ($< 0.5\%$). The latent heats for the pure salts, given in Stern and Weise [2], are not all that accurate. Better measurement of those latent heats for the pure salts could be helpful as reference data and would then provide a basis for improvement in conversion of the peak area data to enthalpy data.

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