

DIFFERENTIAL THERMAL ANALYSIS OF PHASE EQUILIBRIA IN MIXTURES OF ANHYDROUS CARBONATES.

II. Na_2CO_3 – BaCO_3

ROGER E. MILLS * and R. THOMAS COYLE **

Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401 (U.S.A.)

(Received 21 April 1987)

ABSTRACT

The mixtures $(\text{Na}_2\text{CO}_3)_{1-x}-(\text{BaCO}_3)_x$ were studied in a Perkin–Elmer DTA 1700 instrument operated in the DSC mode. A region of solid solution was observed for $x < 5$ mol%. An eutectic transition at $702 \pm 2^\circ\text{C}$ was found for $x > 5$ mol% with $x_{\text{eu}} = 34.6$ mol%. Polymorphic transitions were observed at $805 \pm 1^\circ\text{C}$ for $x > 50$ mol%, and at $965 \pm 2^\circ\text{C}$ for $x > 60$ mol%.

INTRODUCTION

The previously-initiated investigation [1] of phase equilibria in mixtures of barium carbonate with alkali carbonates has been continued with studies of barium carbonate mixed with sodium carbonate.

The data for phase transitions in BaCO_3 compiled by Stern and Weise [2] were reviewed in ref. 1. The melting temperature of Na_2CO_3 is given as $856 \pm 2^\circ\text{C}$, with a latent heat of 31 kJ mol^{-1} being required. The most extensive prior work on melting characteristics of mixtures of Na_2CO_3 and BaCO_3 was reported by Belyaev and Sholohovich [3] in 1953. Their measurements were made as part of an investigation of the reciprocal ternary system $\text{Na,Ba}||\text{CO}_3,\text{Cl}$ using the visual polythermal technique. The salts were melted in a corundum crucible. The temperatures of initial crystallization were observed and measured with a Pt–Rh/Pt thermocouple. From the intersection of portions of the liquidus curves, Belyaev and Sholohovich inferred a eutectic composition of 37 mol% of BaCO_3 , with melting at 686°C .

* Permanent address: Department of Physics, University of Louisville, Louisville, KY 40292, U.S.A.

** Present address: UNOCAL Science & Technology Division, UNOCAL Corporation, 376 S. Valencia Avenue, Brea, CA 92621, U.S.A.

Earlier reports of restricted observations on these mixtures are summarized in the Gmelin Handbuch [4]. In 1984, Le Chatelier [5] had reported observation of an equi-molecular double salt, $\text{Na}_2\text{Ba}(\text{CO}_3)_2$ with a melting temperature of 740°C . (Le Chatelier's temperature scale standard was not concordant with that in present use.) This report was later disputed by M. Barre [6]. The liquidus curves of Belyaev and Sholohovich are also not compatible with the existence of an equi-molecular double salt.

EXPERIMENTAL

Materials

Anhydrous barium carbonate and sodium carbonate of the Gold Label standard series (99.999%) were obtained from the Aldrich Chemical Company. The materials were kept in a dry box except during sample mixing and weighing. Exceptionally dry laboratory conditions inhibited hydration or formation of bicarbonates. Instrumental traces obtained on heating of specimens of the pure reagents showed no appreciable peaks below 400°C which might be attributable to dehydration, and sample masses of about 25 mg were typically stable to ± 0.1 mg.

Procedure

Samples were prepared by weighing the constituents in proportion to the composition desired to a total mass of about 40 mg. The materials were mixed mechanically by grinding with an agate mortar and pestle. Approximately 25 mg of the mixtures were placed in crucibles and heated in the apparatus to about 950°C , well above the melting temperature of pure Na_2CO_3 (856°C), so that further mixing by diffusion in the melt could take place. The melting peaks after the melting run were very consistent and supported an inference that concentration equilibration had been obtained. At the lowest concentrations, increments of the minority component were added successively to an initially prepared sample. An initial melting run was conducted to permit mixing to occur. Subsequent runs were highly consistent and were used as data runs. Peak distortions which might indicate inhomogeneities were not observed. All data runs were conducted as heating runs at $+10^\circ\text{C min}^{-1}$ in the presence of a flow of dry CO_2 at about 40 ml min^{-1} . The stability of sample masses during heating runs was taken as evidence that decomposition of the carbonate ions was negligible.

In initial runs, alumina crucible were used, but penetration of the porous walls by the molten carbonates produced serious mechanical problems, and later runs were made using platinum crucibles. The overall traces obtained from the equipment were slightly less noisy using the platinum crucibles, but

comparison of data from samples of like composition showed that no significant differences in temperature characteristics were observed. Peak areas were also consistent. Temperature calibration curves prepared using melting points of pure aluminum, silver, and gold were only slightly different for the two types of crucibles.

RESULTS

Traces recorded from the runs were based on conversion by machine firmware of DTA data (ΔT vs. T) into a DSC format (C_p vs. T). Onset temperatures, temperatures of peak minima, and peak areas were determined using software provided by Perkin-Elmer.

Typical traces for the mixtures are shown in Fig. 1. Figs. 1(a)–(c) show that a single melting peak persists up to 4 mol% of BaCO_3 . The peak broadens and weakens slightly in a manner characteristic of melting of solid solutions. When the BaCO_3 concentration reaches 6 mol% and higher, a peak characteristic of an isothermal event occurs at about 700°C . The peak increases in strength as x_{BaCO_3} increases to about 35 mol%, and then

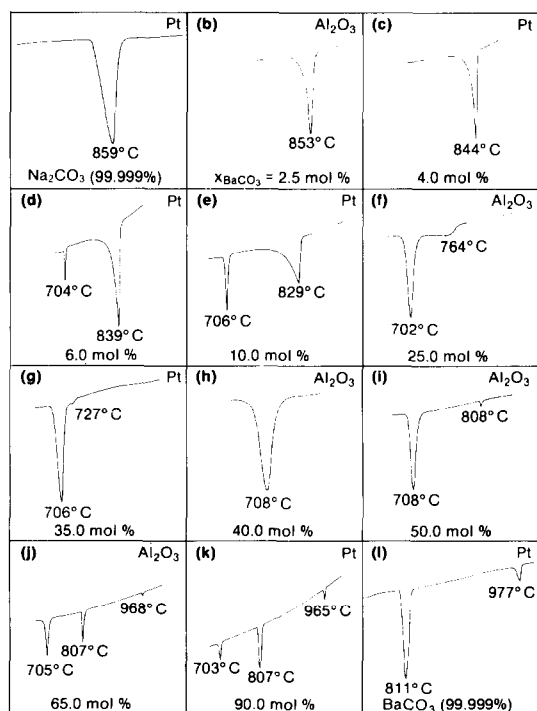


Fig. 1. DSC traces typical of Na_2CO_3 - BaCO_3 mixtures. Not all vertical scales are the same.

decreases at higher BaCO_3 concentrations. This isothermal event is followed in Figs. 1(d)–(f) by a weak, broadened feature characteristic of a continuous melting. This second feature becomes indistinguishable from the lower temperature isothermal event at 40 mol% BaCO_3 . At BaCO_3 concentrations of 50 mol% and higher (Figs. 1(i)–(l)), higher temperature isothermal features appear at temperatures consistent with the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions of unassociated BaCO_3 . In both cases, the actual onset temperature was slightly below that usually accepted for these transitions in pure BaCO_3 .

For the mixture with the least non-zero Na_2CO_3 concentration, for x_{BaCO_3} equal to 97.2 mol%, the amount of Na_2CO_3 involved was 0.38 mg. It was not practical to attempt to mix mechanically such a small amount of material and still to consider the composition to be reasonably well known. Hence the Na_2CO_3 was added directly to a previously prepared sample of pure BaCO_3 , and a sequence of melting runs were conducted, so that mixing could occur through diffusion. After an initial run in which the material remained above 700°C for two hours, a timed run was conducted at $10^\circ\text{C min}^{-1}$ from below the eutectic temperature ($\sim 700^\circ\text{C}$) to above the temperature at which the $\beta \rightarrow \alpha$ transition was observed. Figure 2 shows the history of the $\beta \rightarrow \alpha$ transition in these controlled runs. In the first $10^\circ\text{C min}^{-1}$ run, labeled 2 h, two peaks are observed. The lower one at about 965°C is clearly distinguishable from the upper one, at about 970°C . The latter corresponds well to the temperature observed for the $\beta \rightarrow \alpha$ peak in the original pure BaCO_3 sample. It can be seen that on subsequent runs, the lower temperature peak became enhanced, while the upper temperature peak was reduced. That the distortion was not totally eliminated is an indication

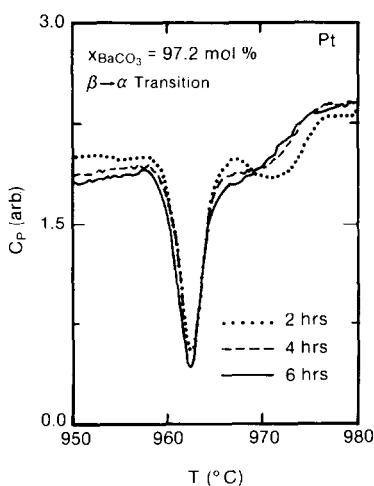


Fig. 2. DSC traces for the $\beta \rightarrow \alpha$ polymorphic transition at x_{BaCO_3} equal to 97 mol%, taken during heat treatment.

that some slight inhomogeneity still remained. (A similar distortion was not observed in other samples at lower x_{BaCO_3} .) The degree of resolution evidenced by these peak separations gives assurance that the reduction in the temperature at which this polymorphic transition occurred in the mixtures compared with the temperature for the transition in pure BaCO_3 is real and not some systematic error.

The data recorded for the various Na_2CO_3 - BaCO_3 mixtures are listed in Table 1. The total peak area for the melting of pure Na_2CO_3 is listed with the liquidus temperatures, while the total peak area of the solid solutions (up to x_{BaCO_3} equal to 4 mol%) are listed in the solidus column. Of course in those latter cases the enthalpy of melting is associated with neither liquidus nor solidus individually. All transition temperatures refer to the extrapolated onset temperatures, and average over data from at least three runs.

The phase diagram for the mixtures $(\text{Na}_2\text{CO}_3)_{1-x}-(\text{BaCO}_3)_x$ is shown in Fig. 3. The liquidus curve shown as a full line for lower values of x_{BaCO_3} is consistent with that of Belyaev and Sholohovich [3], and the portion of the liquidus curve inferred, shown as a dashed line, is qualitatively consistent. The eutectic transition, determined from the present data, is 16°C higher and the eutectic composition is slightly lower than in the earlier work.

The visual polythermal technique is better adapted to observation of the liquidus characteristics than is the present technique, but it is not as satisfactory for location of the solidus or other features below the liquidus.

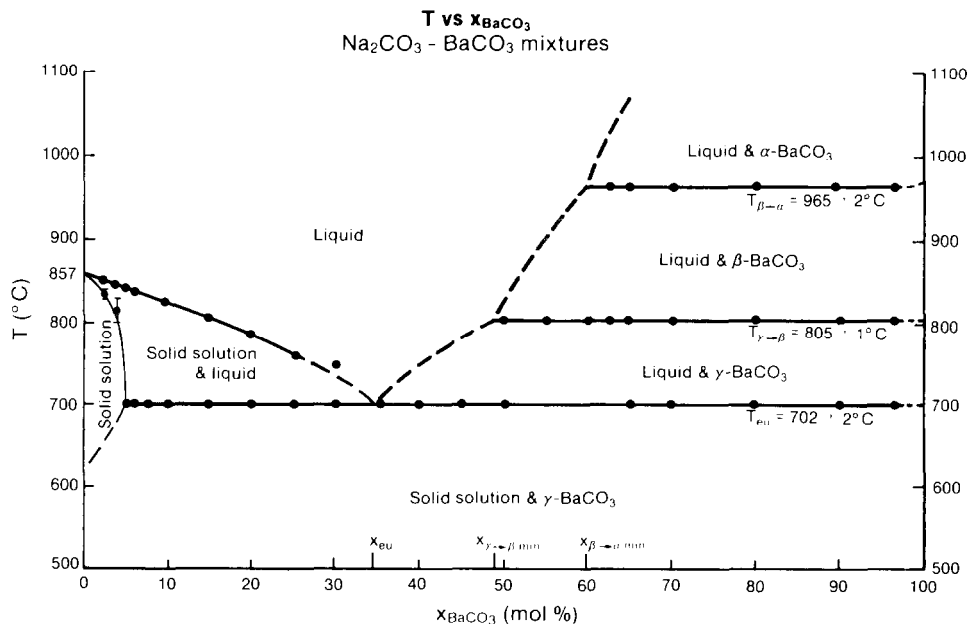


Fig. 3. Phase diagram for Na_2CO_3 - BaCO_3 mixtures.

TABLE 1
Phase transitions in Na_2CO_3 - BaCO_3 mixtures

Transition x_{BaCO_3} (mol%)	Solidus		Liquidus		γ - $\text{BaCO}_3 \rightarrow \beta$ - BaCO_3		β - $\text{BaCO}_3 \rightarrow \alpha$ - BaCO_3		Crucible		
	T ($^\circ\text{C}$)	Δh (arb)	T ($^\circ\text{C}$)	Δh (arb)	T ($^\circ\text{C}$)	Δh (arb)	T ($^\circ\text{C}$)	Δh (arb)	Al_2O_3	Pt	
0.00			857	18.7					×		
0.00			854	21.4						×	
0.00			857	21.3						×	
1.9	845	18.9	851							×	
2.5	836 ± 4	14.6	853						×		
4.0	815 ± 15	16.4	848						×		
4.0	815 ± 15	15.9	844							×	
	Eutectic										
5.0	701	0.11	846						×		
6.0	702	0.81	842						×		
6.0	702	0.83	839							×	
7.5	704	2.0	834						×		
8.1	701	1.8	832							×	
10.0	701	2.8	825						×		
10.0	704	3.1	829							×	
15.0	705	6.0	811						×		
20.0	703	8.9	787						×		
25.0	702	11.8	763						×		

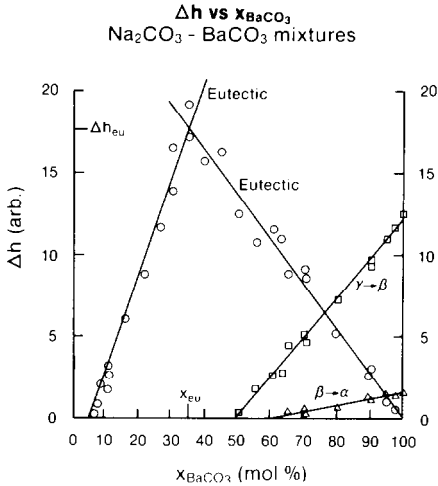


Fig. 4. Latent heats in isothermal transitions in Na_2CO_3 - BaCO_3 mixtures.

Location of the eutectic temperature is more readily done with heating runs, especially when irregular supercooling is a problem, as with carbonates. Determination of the eutectic temperature is based, with heating runs, along the entire extent of the eutectic lines rather than on only a few liquidus data points in the immediate vicinity of the eutectic point as required by the visual polythermal technique. Similar improvements occur in observation of the temperatures of the polymorphic transitions using heating runs.

Peak area data proportional to the enthalpies of the first-order transitions are plotted in Fig. 4 as functions of x_{BaCO_3} . The solid lines, consistent with Tammann's Rule [1,7], are also plotted and have the following equations

Eutectic ($701.8 \pm 1.9^\circ\text{C}$, 114 data points)

$$\Delta h = 0.600x - 2.88 \quad 4.8 < x \leq 34.6 \quad (1a)$$

$$\Delta h = -0.0272x + 27.2 \quad 34.6 \leq x \leq 100 \quad (1b)$$

$\gamma\text{-BaCO}_3 \rightarrow \beta\text{-BaCO}_3$ ($804.9 \pm 1.4^\circ\text{C}$, 45 data points)

$$\Delta h = 0.236x - 11.5 \quad 49 < x \leq 100 \quad (2)$$

$\beta\text{-BaCO}_3 \rightarrow \alpha\text{-BaCO}_3$ ($964.8 \pm 1.5^\circ\text{C}$, 34 data points)

$$\Delta h = 0.040x - 2.4 \quad 60 < x \leq 100 \quad (3)$$

where Δh is the fractional molar enthalpy discussed in ref. 1.

From the intersection of the eutectic lines, one infers a eutectic composition $x_{\text{eu}} = 34.6$ mol%, with $\Delta h(x_{\text{eu}}, T_{\text{eu}})$ equal to 17.8 arbitrary units. The calculated $\gamma \rightarrow \beta$ transition enthalpy of 12.1 arbitrary units (from eqn. (2)) agrees well with the value of 12.4 arbitrary units observed for pure BaCO_3 . Similarly the calculated $\beta \rightarrow \alpha$ transition enthalpy of 1.6 arbitrary units (from eqn. (3)) agrees well with the value of 1.52 arbitrary units observed for pure BaCO_3 . (If desired, multiplication of $\Delta h(\text{arb})$ by a factor of 1.5

converts these data approximately to Δh (kJ mol^{-1}). The accuracy of the conversion varies with the transition, however.)

It should be noted that the eutectic fractional molar enthalpy data displayed in Fig. 4 are non-zero in the vicinity of x_{BaCO_3} equal to 50 mol%. This is significant evidence that no double salt, or coordinated compound, was present in this range of temperatures. If there were such a coordinated compound, the eutectic enthalpy would go to zero at that concentration.

DISCUSSION

The insensitivity of the Perkin–Elmer DTA 1700 equipment to small gradual changes in heat capacity during heating runs has made it difficult to establish liquidus lines for higher x_{BaCO_3} with any confidence. Although the liquidus does show more clearly on cooling runs in this equipment, with the present carbonate salts there is irregular supercooling of considerable extent which precludes accurate determination of liquidus temperatures appropriate to equilibrium situations. It is possible that such supercooling may have led Belyaev and Sholohovich [3] to assign a lower eutectic temperature upon observation of initial crystallization that we have found here by observation of initial melting. The excellent consistency of the eutectic temperatures observed on heating mixtures over a large range of composition (see Table 1) gives confidence that superheating, which would be irregular, is not a significant contributor to the observed difference in eutectic temperatures.

If the double salt $\text{Na}_2\text{Ba}(\text{CO}_3)_2$ reported by Le Chatelier [5] were real, it would show in thermal analysis as a change in the eutectic line at x_{BaCO_3} equal to 50 mol%, and as a vanishing of the transition enthalpy for the eutectic at that same concentration. In the absence of any evidence of either signal, it should be concluded that at that concentration there is only a mixture and not a coordinated compound.

The depression of the temperatures at which the polymorphic transitions occur for high x_{BaCO_3} compared to the temperatures for those transitions for pure BaCO_3 is similar to the phenomena observed for the mixtures $(\text{Li}_2\text{CO}_3)_{1-x}-(\text{BaCO}_3)_x$ [1]. The reduction of the eutectic enthalpy line to zero at a value of x_{BaCO_3} consistent with 100 mol% (see Fig. 4 and eqn. (1b)) argues that if the depression of temperatures is an indicator of a narrow zone of solid solubility for very high x_{BaCO_3} , that zone must begin above the eutectic temperature. Further study by X-ray diffraction of the zone of solid solution observed at low x_{BaCO_3} and the possible zone of solid solution at high x_{BaCO_3} would help considerably in verifying the accuracy of these interpretations of the thermal data. Such studies should also be of value in specifying more precisely the position of the liquidus curves.

ACKNOWLEDGMENTS

We are grateful to G. Gross and P. Schissel of SERI for support and encouragement of this work, and to R.W. Burrows for much helpful advice during the experiments. One of us (R.E.M.) is most grateful to SERI for excellent professional hospitality and support, to the Associated Western Universities and the University of Louisville for sabbatical leave support, and to the American Society of Engineering Education for a Summer Grant all of which were important to the completion of this work. This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-83CH10093.

REFERENCES

- 1 R.E. Mills and R.T. Coyle, *Thermochim. Acta*, 124 (1987) 65.
- 2 K.H. Stern and E.L. Weise, *NSRDS-NBS 30, High Temperature Properties and Decomposition of Inorganic Salts, Part 2, Carbonates*, 1969.
- 3 I.N. Belyaev and M.L. Sholohovich, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, 1 (1953) 134.
- 4 *Gmelin Handbuch der Anorganischen Chemie*, Springer-Verlag, Berlin, 1932, Vol. 30, p. 365.
- 5 H. Le Chatelier, *C. R. Acad. Sci.*, 118 (1894) 415.
- 6 M. Barre, *C. R. Acad. Sci.*, 154 (1912) 279.
- 7 G. Tammann, *Z. Anorg. Chem.*, 37 (1903) 303.