Thermochimica Acta, 5 (1973) 365–367

Letters to the Editor

Dear Sir,

We would like to draw the attention of you and your readers to some factual errors in a paper entitled "thermal synthesis of sodium calcium carbonate—a potential thermal analysis standard" in *Thermochimica Acta*, 2 (1971) 305–312. We have written to Smith *et al.* concerning this matter but feel that attention should be brought to those readers who might consider using sodium calcium carbonate ($Na_2CO_3 \cdot CaCO_3$) as a DTA standard.

In the introduction to the paper it was stated the new compound is a previously unrecognised double carbonate, $Na_2CO_3 \cdot CaCO_3$. However, there are several literature references[1–4] to $Na_2CO_3 \cdot CaCO_3$ as far back as 1916. The formation by powder reaction has been discussed by Jagitsch[5], who also determined the rate of diffusion of Na^+ and Ca^{2+} ions. Incidentally, work on the effect of particle size on the production of $Na_2CO_3 \cdot CaCO_3$ has been carried out in these laboratories (R.M.M. and F.W.W.). Furthermore, the DTA curves for mixtures in the system Na_2CO_3–$CaCO_3$, including the 1:1 molar ratio were given in a paper by Wilburn *et al.*[6]. Billhardt[7] has given the X-ray data for the compound at room temperature and at temperatures above and below the inversion temperatures given by Wilburn *et al.*[6]. The melting point of $Na_2CO_3 \cdot CaCO_3$ has been given variously as 812–814 °C; the decomposition in carbon dioxide (1 atm.) at 750 °C is a little surprising considering most workers have prepared $Na_2CO_3 \cdot CaCO_3$ in CO_2 (1 atm.) at 800–850 °C. Billhardt[7], on the other hand, considers Na_2CO_3–$CaCO_3$ mixtures to be solid solutions with a maximum in the melting point for the 1:1 molar ratio. The authors apparently neglected the additional complication of the crystal transformations in sodium carbonate reported by many workers[8–11].

A considerable amount of work has been carried out on the Na_2CO_3–$CaCO_3$ system in these laboratories much of which is unpublished. The work carried out here has confirmed that the crystal transformations in Na_2CO_3 are at ~354 °C and ~481 °C, whilst those for $Na_2CO_3 \cdot CaCO_3$ occur at 395 °C and 437 °C. Four peaks were not observed even on the most sensitive DTA setting. However, in a 1:1 molar mixture heated below the melting point four peaks are discernible at 354°, 397°, 432° and 443 °C on DTA with a heating rate of 10 °C min^{-1}. The 354 °C peak can be attributed to Na_2CO_3 and that at 397 °C to $Na_2CO_3 \cdot CaCO_3$. The peaks at 432° and 443 °C only appear, in our experience, in incompletely reacted Na_2CO_3–$CaCO_3$ mixtures. The decomposition of shortite ($Na_2CO_3 \cdot 2CaCO_3$), has also been the subject of a thermal investigation (MF) and appears to dissociate into $Na_2CO_3 \cdot CaCO_3$ and $CaCO_3$ and this was confirmed by infrared spectral analysis.

Under the circumstances, we feel it is inadvisable to use $Na_2CO_3 \cdot CaCO_3$ as a standard for DTA, notwithstanding the excellent peaks obtained for the 1:1 compound.

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Dear Sir,

We certainly thank Finch and his co-workers for pointing out our error in describing sodium calcium carbonate ($Na_2CO_3 \cdot CaCO_3$) as a "previously unrecognized double carbonate"[1]. We took our inability to find earlier discussions of this compound as proof that they didn't exist. We apologize to our readers for any misconceptions caused by our failure to find this background information, which unfortunately is an extremely sparse collection for the 56-year span since Niggli[2] first reported the compound's existence.

In spite of the statement by Finch *et al.*, we feel that we made no other errors in our description of the thermal synthesis of sodium calcium carbonate and in our recommendation of it as a thermal analysis standard. The compound's decomposition temperature in CO_2 we stated only as "above 750°". At temperatures above this the sodium carbonates wreak havoc on sample holders. For purposes of our report we limited the temperatures investigated in detail to those significant to the solid-state formation of sodium calcium carbonate and to the detection and evaluation of its crystal transformations by DTA.

We neither neglected nor ignored the crystal transformations of Na_2CO_3 in studying the DTA-detected inversions of sodium calcium carbonate. Samples of Na_2CO_3 identical to the material we used to generate the double carbonate produce *no* DTA inversion responses from 390° to 450°, the temperature range where the double carbonate inversions occur. In addition, the Na_2CO_3 transformations appear to be at least an order of magnitude less energetic than those of the double carbonate.