

## Thermochemistry of double carbonates in the $K_2CO_3$ - $CaCO_3$ system

ALEXANDRA NAVROTSKY,<sup>1</sup> ROBERT L. PUTNAM,<sup>1</sup> CAMILLA WINBO,<sup>2</sup> AND ERIK ROSÉN<sup>2</sup>

<sup>1</sup>Department of Geosciences and Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544-1003, U.S.A.

<sup>2</sup>Department of Inorganic Chemistry, Umeå University, S-90187 Umeå, Sweden

### ABSTRACT

Enthalpies of formation,  $\Delta H_f$ , of the double carbonates  $K_2Ca(CO_3)_2$  (with two polymorphs, bütschliite and fairchildite) and  $K_2Ca_2(CO_3)_3$  from the components  $K_2CO_3$  and  $CaCO_3$  were determined at 298 K by drop solution calorimetry in molten  $2PbO \cdot B_2O_3$  at 974 K. The enthalpies of formation were  $-38.7 \pm 3.2$  kJ/mol for bütschliite,  $-5.1 \pm 3.3$  kJ/mol for fairchildite and  $-7.2 \pm 5.8$  kJ/mol for  $K_2Ca_2(CO_3)_3$ . The entropy changes for the formation,  $\Delta S_f$ , were also evaluated for the double carbonates. Assuming  $\Delta S_f(\text{bütschliite}) = 0$ , because of its ordered structure, the entropy of formation of fairchildite is  $40.9 \pm 5.1$  J/mol·K and of  $K_2Ca_2(CO_3)_3$  is  $39.4 \pm 7.3$  J/mol·K.

### INTRODUCTION

In the binary system  $K_2CO_3$ - $CaCO_3$ , three intermediate phases exist (Cooper et al. 1975). Two of these double carbonates have the composition  $K_2Ca(CO_3)_2$ , named bütschliite and fairchildite, with bütschliite as the low-temperature polymorph and the transition occurring at 820 K. The third double carbonate, with the composition  $K_2Ca_2(CO_3)_3$ , is an incongruently melting phase (1083 K), which below 800 K decomposes to bütschliite and  $CaCO_3$ . The phases bütschliite and fairchildite have been found in wood ash in partly burned fir, hemlock, and other trees in the western United States (Milton and Axelrod 1947). Fairchildite has also been identified in ash from the combustion of biomass fuels (Olanders and Steenari 1995). It is plausible that  $K_2Ca_2(CO_3)_3$  also occurs in combustion products.

The three double carbonates have different structures. In bütschliite all atoms are centered on mirror planes and the  $CO_3$  groups are situated on threefold axes, oriented normal to the  $c$  axis (Pabst 1974). In fairchildite and  $K_2Ca_2(CO_3)_3$ ,  $\frac{1}{4}$  of the cations are situated on the threefold axes and surrounded by  $CO_3$  groups, which in fairchildite form a layered structure, where half of the  $CO_3$  groups are disordered (Pertlik 1981). In  $K_2Ca_2(CO_3)_3$ , the  $CO_3$  groups are ordered but inclined relative to the (001) plane (Winbo et al., unpublished data).

The determination of the enthalpy change of a chemical reaction can be used to relate the thermodynamic properties of a given substance to those of other substances, and thus to obtain heats of formation, of mixing, and of solid state reactions. Thermodynamic data for carbonates can be obtained by several methods: analysis of phase relations, measurements of heterogeneous equilibria using gas mixtures, or calorimetry. The calorimetric methods can be classified as direct, in which the reaction studied is the one of interest, or indirect, in which a thermochemical cycle is used to obtain the enthalpy of inter-

est (Navrotsky 1994). High-temperature drop-solution calorimetry is an indirect method, where the sample is dropped into a molten solvent where it dissolves (Navrotsky 1977; Navrotsky et al. 1994). This technique is used for substances that would decompose to an ill-defined state using ordinary calorimetric methods. Volatile components from the dissolution of the sample must be both reproducible in quantity and well characterized in terms of final state. By using high-temperature drop-solution calorimetry under a flowing gas atmosphere, reproducible final states can be obtained and well-defined thermodynamic cycles written (Navrotsky et al. 1994).

The aim of the present work is to determine the heat of formation, from the components  $K_2CO_3$  and  $CaCO_3$ , of the three double carbonates, using high-temperature drop-solution calorimetry in molten  $2PbO \cdot B_2O_3$ . Entropy values for the double carbonates are calculated on the basis of these thermochemical data and observed phase transitions and then related to their different structures.

### EXPERIMENTAL METHODS

#### Preparation of the solids

The double carbonates were synthesized by grinding appropriate amounts of dried  $K_2CO_3$  (Baker) and  $CaCO_3$  (Riedel-deHaën) and heating the mixtures in a  $CO_2$ -atmosphere. The mixtures for bütschliite, fairchildite, and  $K_2Ca_2(CO_3)_3$  were heated at 750 K, 920 K, and 1020 K, respectively. The high-temperature phases fairchildite and  $K_2Ca_2(CO_3)_3$  could easily be quenched to room temperature. The phases were verified with X-ray powder diffraction by comparison with existing literature data (Pabst 1974; Balascio and White 1972; Swanson et al. 1970). All materials were single phase.

#### Solution Calorimetry

The enthalpies of drop solution for the three double carbonates were determined by high-temperature oxide

**TABLE 1.** Drop-solution enthalpies in molten lead borate (2PbO·B<sub>2</sub>O<sub>3</sub>) at 974 K. Uncertainties are reported as two standard deviations of the mean

K <sub>2</sub> Ca <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>		Bütschliite		Fairchildite	
Mass (mg)	ΔH <sub>dr</sub> (kJ/mol)	Mass (mg)	ΔH <sub>dr</sub> (kJ/mol)	Mass (mg)	ΔH <sub>dr</sub> (kJ/mol)
14.26	637.03	15.99	468.25	14.64	437.42
15.22	619.28	14.52	467.18	15.09	437.05
14.66	625.32	14.93	468.08	14.41	437.79
14.47	638.79	14.63	464.56	14.47	430.46
14.04	615.51	14.18	463.91	14.83	428.35
14.38	639.10	15.17	469.29	14.44	427.09
14.92	617.65	14.86	462.32	14.66	433.99
14.80	639.10	14.71	473.99	14.49	434.84
14.45	620.47	14.73	460.45	14.45	428.94
14.76	637.11				
14.76	625.74				
14.78	625.58				
mean 628.4 ± 5.6		mean 466.5 ± 2.9		mean 432.9 ± 3.0	

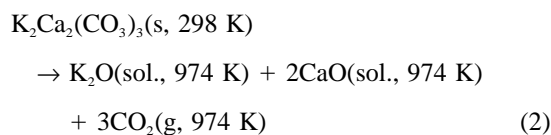
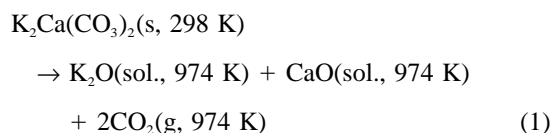
melt calorimetry in molten 2PbO·B<sub>2</sub>O<sub>3</sub> at 974 K in twin Calvet calorimeters (Navrotsky 1977). The quartz glassware used in the drop-solution experiments consisted of an outer liner in which the platinum crucible containing the solvent was placed. A dry air flow (30–40 cm<sup>3</sup>/min) passed through an inner tube which ended 1 cm above the crucible. The dry air had to pass out through the drop tube, which was located in the center of the quartz set up and which ended 1.5 cm above the solvent surface. The sample pellet was dropped through the drop tube into the solvent.

A typical experiment started with a drop of a 15 mg pellet from room temperature (298 K) into a platinum crucible containing the solvent, kept at 974 K. Before the experiment, the sample pellets were tempered to 298 K by placing the pellets on a piece of metal in the thermostated calorimeter room. The heat flow resulting from the drop was measured as a voltage change in the thermopile. The duration (61–65 minutes) included 10 min before the drop of the sample (initial baseline) and 10 min after the return of the signal to the final baseline. The initial baseline and the final baseline were used to determine the small drift of the baseline during the experiment. The integral of the voltage reading was converted into reaction enthalpy using a calibration factor, determined by dropping pellets of α-Al<sub>2</sub>O<sub>3</sub>, with the same weight and shape as the sample, from room temperature into the calorimeter. The known heat content of Al<sub>2</sub>O<sub>3</sub> was used to calculate the calibration factor. Examination of the solvent after the experiments showed that the samples were dissolved completely. This methodology is standard practice in our laboratory (Navrotsky 1977; Chai and Navrotsky 1993; Navrotsky et al. 1994; Kiseleva et al. 1996).

At 974 K, the three double carbonates decomposed to K<sub>2</sub>O and CaO (which are dissolved), and CO<sub>2</sub>, which is evolved according to the following reactions

**TABLE 2.** Calculated values of the enthalpy of formation, ΔH<sub>f</sub>, for Reactions 3 and 4

Enthalpy	Bütschliite	Fairchildite	K <sub>2</sub> Ca <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>
ΔH <sub>f</sub> (kJ/mol)	−38.7	−5.1	−7.2
Error in ΔH <sub>f</sub> (kJ/mol)	±3.2	±3.3	±5.8

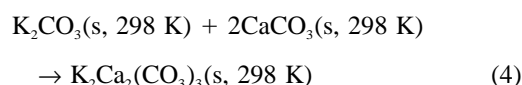
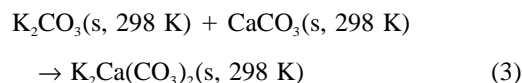


where s and g represent crystal and gas, respectively, and sol. stands for dilute solution in the molten solvent, 2PbO·B<sub>2</sub>O<sub>3</sub>. It should be noticed that Reaction 1 describes the decomposition reaction of bütschliite as well as fairchildite.

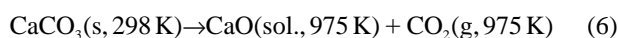
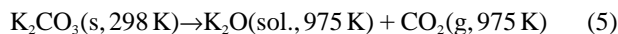
## RESULTS AND DISCUSSION

The results of the drop-solution experiments for Reaction 1 and 2 are presented in Table 1. The error (two standard deviations of the mean) for K<sub>2</sub>Ca<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> is somewhat larger than for bütschliite and fairchildite but still less than 1%, indicating a consistent dissolution reaction.

To calculate the enthalpy of formation of the double carbonates



the heats of drop-solution are needed not only for the three double carbonates, Reactions 1 and 2, but also for the components K<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub>. Recent enthalpies of drop-solution for Reactions 5 and 6



were determined in our laboratory by Kiseleva et al. (1996) to 234.4 ± 1.1 kJ/mol and 193.4 ± 0.7 kJ/mol, respectively. The enthalpy of formation, ΔH<sub>f</sub>, for Reactions (3) and (4) was calculated by the following equations:

$$\Delta H_f(\text{III}) = \Delta H_{\text{dr}}(\text{V}) + \Delta H_{\text{dr}}(\text{VI}) - \Delta H_{\text{dr}}(\text{I}) \quad (7)$$

$$\Delta H_f(\text{IV}) = \Delta H_{\text{dr}}(\text{V}) + 2\Delta H_{\text{dr}}(\text{VI}) - \Delta H_{\text{dr}}(\text{II}). \quad (8)$$

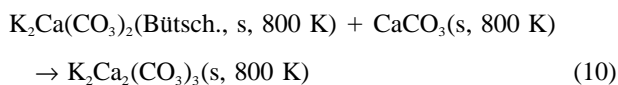
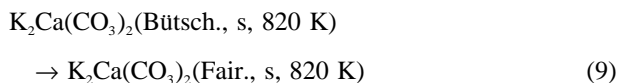
The results obtained are shown in Table 2. The uncertainties of ΔH<sub>f</sub> are reported as two standard devia-

**TABLE 3.** Enthalpy and entropy changes for Reactions 9 and 10

Parameter	Reaction (9)	Reaction (10)
$\Delta H$ (kJ/mol)	33.6	31.5
Error in $\Delta H$ (kJ/mol)	$\pm 4.2$	$\pm 6.5$
$T$ (K)	820	800
$\Delta S$ (J/mol-K)	40.9	39.4
Error in $\Delta S$ (J/mol-K)	$\pm 5.1$	$\pm 7.3$

tions of the mean with the error in  $\Delta H_{dr}$  for  $K_2CO_3$  and  $CaCO_3$ , according to Kiseleva et al. (1996), included.

The enthalpies of reaction,  $\Delta H$ , were calculated for the following reactions



by assuming  $\Delta H$  for the reactions to be constant in the temperature range 298–974 K. The entropy changes for Reactions (9) and (10) were then calculated by using the relationship:

$$\Delta S = \frac{\Delta H}{T}. \quad (11)$$

The phase transition temperatures, 820 K (9) and 800 K (10), given by Cooper et al. (1975) at 1 kbar, are assumed to be representative also at 1 bar. The enthalpy and entropy values thus calculated are given in Table 3. The uncertainties of  $\Delta H$  and  $\Delta S$  are reported as two standard deviations of the mean.

Bütschliite has ordered carbonate groups in a layered structure and the entropy change of its formation from the components,  $K_2CO_3$  and  $CaCO_3$ , can therefore be assumed to be close to zero. If this entropy value,  $\Delta S_f$ , for bütschliite formation is set equal to 0, then the  $\Delta S_f$  values 40.9 J/mol-K and 39.4 J/mol-K are obtained from Reactions (9) and (10) for fairchildite and  $K_2Ca_2(CO_3)_3$ , respectively. To be able to relate entropy values and structures of fairchildite and  $K_2Ca_2(CO_3)_3$ , the entropy values per mole of carbonate ion,  $\Delta S_{fc}$ , were calculated. These values are presented in Table 4 together with the enthalpies of formation per mole of carbonate ion,  $\Delta H_{fc}$ .

As seen from Table 4,  $\Delta H_{fc}$  is essentially zero for fairchildite and  $K_2Ca_2(CO_3)_3$ . The large positive entropy changes for fairchildite and  $K_2Ca_2(CO_3)_3$  are in line with their structures. In fairchildite half of the carbonate groups are slightly disordered (Pertlik 1981), whereas  $K_2Ca_2(CO_3)_3$  has ordered carbonate groups displaced from the (001) plane (Winbo et al., unpublished data). The  $\Delta S_{fc}$

**TABLE 4.** Enthalpy of formation,  $\Delta H_{fc}$ , and entropy change,  $\Delta S_{fc}$ , calculated per mole of carbonate group. The  $\Delta S_{fc}$  for bütschliite is assumed to be equal to zero

Phase	$\Delta H_{fc}$ (kJ/mol)	$\Delta S_{fc}$ (J/mol-K)
Bütschliite	-19.3	0.0
Fairchildite	-2.5	20.5
$K_2Ca_2(CO_3)_3$	-2.4	13.1

values indicate that the arrangement of carbonate groups in fairchildite gives a higher entropy compared with the ordered but displaced carbonate groups in  $K_2Ca_2(CO_3)_3$ . Because the  $\Delta H_{fc}$  values of the double carbonates fairchildite and  $K_2Ca_2(CO_3)_3$  are close to zero, though slightly exothermic, the stabilities are significantly enhanced by the contribution of the  $T\Delta S$  term.

#### ACKNOWLEDGMENT

This work was financially supported by the Royal Swedish Academy of Sciences, the Swedish Natural Science Research Council and the U.S. Department of Energy (grant DE-FG02-85ER 13437).

#### REFERENCES CITED

- Balascio, J.F. and White, W.B. (1972) Hydrothermal growth of calcite from alkali carbonate solutions. *Materials Research Bulletin*, 7, 1461–1471.
- Chai, L. and Navrotsky, A. (1993) Thermochemistry of carbonate-pyroxene equilibria. *Contributions to Mineralogy and Petrology*, 114, 139–147.
- Cooper, A.F., Gittins, J., and Tuttle, O.F. (1975) The system  $Na_2CO_3$ - $K_2CO_3$ - $CaCO_3$  at 1 kilobar and its significance in carbonatite petrogenesis. *American Journal of Science*, 275, 534–560.
- Kiseleva, I., Navrotsky, A., Belitsky, I.A., and Fursenko, B.A. (1996) Thermochemistry of natural potassium sodium calcium leonhardite and its cation-exchanged forms. *American Mineralogist*, 81, 668–675.
- Milton, C. and Axelrod, J. (1947) Fused wood-ash stones: fairchildite (n. sp.)  $K_2CO_3 \cdot CaCO_3$ , bütschliite (n. sp.)  $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$  and calcite,  $CaCO_3$ , their essential components. *American Mineralogist*, 32, 607–624.
- Navrotsky, A. (1977) Progress and new directions in high temperature calorimetry. *Physics and Chemistry of Minerals*, 2, 89–104.
- (1994) *Physics and Chemistry of Earth Materials*. Chap. 4. Cambridge University Press, New York.
- Navrotsky, A., Rapp, R.P., Smelik, E., Burnley, P., Circone, S., Chai, L., Bose, K., and Westrich H.R. (1994) The behavior of  $H_2O$  and  $CO_2$  in high-temperature lead borate solution calorimetry of volatile-bearing phases. *American Mineralogist*, 79, 1099–1109.
- Olanders, B. and Steenari, B.-M. (1995) Characterization of ashes from wood and straw. *Biomass and Bioenergy*, 8, 105–115.
- Pabst, A. (1974) Synthesis, properties, and structure of  $K_2Ca(CO_3)_2$ , bütschliite. *American Mineralogist*, 59, 353–358.
- Pertlik, F. (1981) Structural investigations of synthetic fairchildite,  $K_2Ca(CO_3)_2$ . *Zeitschrift für Kristallographie*, 157, 199–205.
- Swanson, H.E., McMurdie, H.F., Morris, M.C., and Evans, E.H. (1970) Standard X-ray diffraction powder patterns. National Bureau of Standards, Monograph 25 Section 8, 48.

MANUSCRIPT RECEIVED SEPTEMBER 9, 1996

MANUSCRIPT ACCEPTED JANUARY 21, 1997