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

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ABSTRACT

Enthalpies of formation, ΔH_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 ± 3.2 kJ/mol for bütschliite, -5.1 ± 3.3 kJ/mol for fairchildite and -7.2 ± 5.8 kJ/mol for $K_2Ca_2(CO_3)_3$. The entropy changes for the formation, ΔS_f, were also evaluated for the double carbonates. Assuming ΔS_f(bütschliite) = 0, because of its ordered structure, the entropy of formation of fairchildite is 40.9 ± 5.1 J/mol·K and of $K_2Ca_2(CO_3)_3$ is 39.4 ± 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 $K_2Ca_2(CO_3)_3$, ¼ 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 In $K_2Ca_2(CO_3)_3$, the CO_3 groups are ordered but inclined relative to the (001) plane (Winbo et al., unpublished data).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 interest (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

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Table 1. Drop-solution enthalpies in molten lead borate ($2PbO{\cdot}B_2O_3$) at 974 K. Uncertainties are reported as two standard deviations of the mean

$K_2Ca_2(CO_3)_3$		Bütschliite		Fairchildite	
Mass (mg)	ΔH_{dr} (kJ/mol)	Mass (mg)	ΔH_{dr} (kJ/mol)	Mass (mg)	ΔH_{dr} (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	

Table 2. Calculated values of the enthalpy of formation, ΔH_f, for Reactions 3 and 4

Enthalpy	Bütschliite	Fair-childite	$K_2Ca_2(CO_3)_3$
ΔH_f (kJ/mol)	−38.7	−5.1	−7.2
Error in ΔH_f (kJ/mol)	±3.2	±3.3	±5.8

melt calorimetry in molten $2PbO{\cdot}B_2O_3$ 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^3/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_2O_3, with the same weight and shape as the sample, from room temperature into the calorimeter. The known heat content of Al_2O_3 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_2O and CaO (which are dissolved), and CO_2, which is evolved according to the following reactions

$$\begin{aligned} &K_2Ca(CO_3)_2(\text{s, 298 K}) \\ &\quad \rightarrow K_2O(\text{sol., 974 K}) + CaO(\text{sol., 974 K}) \\ &\quad\quad + 2CO_2(\text{g, 974 K}) \qquad (1) \end{aligned}$$

$$\begin{aligned} &K_2Ca_2(CO_3)_3(\text{s, 298 K}) \\ &\quad \rightarrow K_2O(\text{sol., 974 K}) + 2CaO(\text{sol., 974 K}) \\ &\quad\quad + 3CO_2(\text{g, 974 K}) \qquad (2) \end{aligned}$$

where s and g represent crystal and gas, respectively, and sol. stands for dilute solution in the molten solvent, $2PbO{\cdot}B_2O_3$. 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 $K_2Ca_2(CO_3)_3$ 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

$$\begin{aligned} &K_2CO_3(\text{s, 298 K}) + CaCO_3(\text{s, 298 K}) \\ &\quad \rightarrow K_2Ca(CO_3)_2(\text{s, 298 K}) \qquad (3) \end{aligned}$$

$$\begin{aligned} &K_2CO_3(\text{s, 298 K}) + 2CaCO_3(\text{s, 298 K}) \\ &\quad \rightarrow K_2Ca_2(CO_3)_3(\text{s, 298 K}) \qquad (4) \end{aligned}$$

the heats of drop-solution are needed not only for the three double carbonates, Reactions 1 and 2, but also for the components K_2CO_3 and $CaCO_3$. Recent enthalpies of drop-solution for Reactions 5 and 6

$$K_2CO_3(\text{s, 298 K}) \rightarrow K_2O(\text{sol., 975 K}) + CO_2(\text{g, 975 K}) \qquad (5)$$

$$CaCO_3(\text{s, 298 K}) \rightarrow CaO(\text{sol., 975 K}) + CO_2(\text{g, 975 K}) \qquad (6)$$

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_f, for Reactions (3) and (4) was calculated by the following equations:

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

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

The results obtained are shown in Table 2. The uncertainties of ΔH_f are reported as two standard devia-

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

Parameter	Reaction (9)	Reaction (10)
ΔH (kJ/mol)	33.6	31.5
Error in ΔH (kJ/mol)	±4.2	±6.5
T (K)	820	800
ΔS (J/mol·K)	40.9	39.4
Error in ΔS (J/mol·K)	±5.1	±7.3

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

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

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

The enthalpies of reaction, ΔH, were calculated for the following reactions

$$K_2Ca(CO_3)_2(\text{Bütsch., s, 820 K}) \rightarrow K_2Ca(CO_3)_2(\text{Fair., s, 820 K}) \quad (9)$$

$$K_2Ca(CO_3)_2(\text{Bütsch., s, 800 K}) + CaCO_3(\text{s, 800 K}) \rightarrow K_2Ca_2(CO_3)_3(\text{s, 800 K}) \quad (10)$$

by assuming ΔH 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 ΔH and ΔS 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, ΔS_f, for bütschliite formation is set equal to 0, then the ΔS_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, $\Delta S_{f/c}$, were calculated. These values are presented in Table 4 together with the enthalpies of formation per mole of carbonate ion, $\Delta H_{f/c}$.

As seen from Table 4, $\Delta H_{f/c}$ 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 $\Delta S_{f/c}$ 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 $\Delta H_{f/c}$ 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.

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