# Thermal Analytical Study of the Decomposition of K$_2$Ca$_2$(CO$_3$)$_3$

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The thermal stability of the double carbonate K$_2$Ca$_2$(CO$_3$)$_3$ was studied by means of thermal gravimetry, differential thermal analysis and separate equilibration experiments in atmospheres with various partial pressures of CO$_2$ (0.03–0.20 bar). The decomposition reactions for the carbonate phases K$_2$Ca$_2$(CO$_3$)$_3$ and K$_2$Ca(CO$_3$)$_2$ (fairchildite) were determined by equilibration experiments and X-ray powder diffraction. The experimental results were used to calculate the equilibrium pressures of CO$_2$ for the decomposition reaction

$$K_2Ca_2(CO_3)_3(s) \rightleftharpoons K_2Ca(CO_3)_2(s) + CaO(s) + CO_2(g)$$
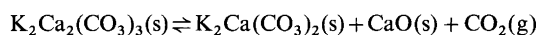
in the temperature range 980–1080 K, giving the following relationship

$$\lg(p_{CO_2}/bar) = -9695/T + 8.35$$

with an estimated uncertainty of ± 0.04 lg units. The enthalpy of this decomposition reaction was calculated to 185.6 ± 0.8 kJ.

The binary system K$_2$CO$_3$–CaCO$_3$ is of considerable importance in several technological processes, especially in combustion of biomass fuels. According to the study by Cooper et al.[1] at 1 kbar, there exist three double carbonates of which two have the phase composition K$_2$Ca(CO$_3$)$_2$, i.e. fairchildite and bütschliite. Fairchildite is the high-temperature polymorph, melting at 1095 K. The transition from bütschliite to fairchildite occurs at 820 K. The third double carbonate, with the composition K$_2$Ca$_2$(CO$_3$)$_3$, is an incongruently melting (1083 K) high-temperature phase which, below 800 K, decomposes to bütschliite and CaCO$_3$.

In 1966 the double carbonates bütschliite and fairchildite were found in wood ashes of partly burned fir, hemlock, and other trees in the western United States.[2,3] Recently fairchildite has been found also in ashes from wood and straw.[4,5] It seems plausible, but not yet proved, that K$_2$Ca$_2$(CO$_3$)$_3$ can also occur in ashes from wood.

The crystal structures of bütschliite and fairchildite have been described by Pabst[6] and Pertlik,[7] respectively, and of K$_2$Ca$_2$(CO$_3$)$_3$ by Winbo et al.[8] In a recent investigation, Navrotsky et al.[9] determined ΔH and ΔS for the formation of all three double carbonates from the components K$_2$CO$_3$ and CaCO$_3$ by high-temperature drop-solution calorimetry.

The present work is part of an ongoing effort to obtain accurate basic data of the intermediate phases in the system K$_2$CO$_3$–CaCO$_3$, and aims to study the thermal decomposition of K$_2$Ca$_2$(CO$_3$)$_3$ in atmospheres with various partial pressures of CO$_2$, p_{CO_2}. This study includes thermochemical measurements, using a thermobalance, and separate phase equilibrations in atmospheres with various p_{CO_2}.

Experimental

Materials. The double carbonates K$_2$Ca$_2$(CO$_3$)$_3$ and K$_2$Ca(CO$_3$)$_2$ (fairchildite) were synthesized by grinding stoichiometric mixtures of dried K$_2$CO$_3$ (Baker *p.a.*) and CaCO$_3$ (Riedel–deHaën *p.a.*) and by heating the mixtures in a CO$_2$ atmosphere at 650 °C for 7 days. These two double carbonates, which are high-temperature phases, could easily be quenched to room temperature and then verified with X-ray powder diffraction.[8,10]

Thermoanalytical measurements. The thermal gravimetric analysis, TGA, and differential thermal analysis, DTA, were carried out with two different types of thermobalance. The investigations at lower partial pressures of CO$_2$ (0.03 and 0.06 bar) were performed with a vertical set-up (Mettler, TA1), while at higher CO$_2$ pressures horizontal equipment (TA Instruments, SD 2960) was used. Both these instruments allowed the TGA and DTA curves to be recorded simultaneously, as a function of temperature and time.

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In order to study the thermochemical properties of the double carbonate $K_2Ca_2(CO_3)_3$, the samples were heated in an atmosphere with various prefixed p_{CO_2} in the temperature range 298–1223 K. For every gas composition, the weight change and the temperature difference were recorded continuously. The different p_{CO_2} were accomplished by mixing N_2 and CO_2 using calibrated flow meters. The gas flow was about 100 ml min^{-1}. The solid samples were kept in platinum crucibles, and their weights were 80–100 mg (Mettler) and 10 mg (TA Instruments). Dried alumina powder was used as reference material. The effect of the heating rate on the TGA curve was studied at a number of different heating rates. The rate 5 °C min^{-1} was found to be optimal in the temperature range of interest.

Equilibration experiments. The sample, which consisted of either $K_2Ca_2(CO_3)_3$ or fairchildite, was heated in a platinum crucible, placed in a closed alumina tube, to 923 K in a CO_2 atmosphere. After 12 h, a gas mixture of argon and CO_2 with a specified p_{CO_2} was led into the alumina tube, and the temperature was increased to a constant pre-set value. The sample was then equilibrated at this constant temperature for 24 h, before it was quenched to room temperature. The composition of the sample phases thus formed was analyzed with X-ray powder diffraction and identified using data from the JCPDS Powder diffraction files[10] and from Winbo *et al.*[8] for $K_2Ca_2(CO_3)_3$.

The temperature of decomposition was determined by equilibration experiments at a number of different temperatures, but at constant p_{CO_2}, until the decomposition temperature was found. The different p_{CO_2} were accomplished by mixing Ar and CO_2 using calibrated flow meters. The gas flow used was about 40 ml min^{-1}.

Results and calculations

In the present work the thermal decomposition of $K_2Ca_2(CO_3)_3$ was studied by means of equilibration experiments, TGA, and DTA, while fairchildite was studied only by equilibration experiments.

Results from equilibration experiments. Equilibration of samples containing $K_2Ca_2(CO_3)_3$ were performed at three different partial pressures of CO_2, $p_{CO_2} = 0.06$, 0.09 and 0.19 bar. The results obtained at various temperatures are shown in Table 1. The decomposition temperature, indicated at each p_{CO_2} value, was evaluated from the highest temperature where $K_2Ca_2(CO_3)_3$ still is stable and the lowest temperature with the solid products fairchildite and CaO.

The following decomposition reaction for $K_2Ca_2(CO_3)_3$ was proved to occur at $p_{CO_2} \leqslant 0.19$ bar:

$$K_2Ca_2(CO_3)_3(s) \rightarrow K_2Ca(CO_3)_2(s) + CaO(s) + CO_2(g) \quad (I)$$
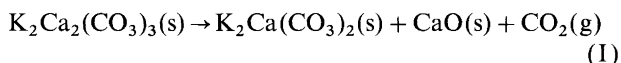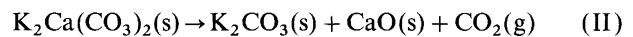
The melting point for $K_2Ca_2(CO_3)_3$ at $p_{CO_2} = 1$ bar

Table 1. Results from equilibration experiments with $K_2Ca_2(CO_3)_3$.

p_{CO_2}/ bar	lg p_{CO_2}	T/K	Solid product(s) obtained	Decomposition temperatures/K
0.06	−1.22	1022	Fairchildite + CaO	
		1016	$K_2Ca_2(CO_3)_3$	1019±3
		1001	$K_2Ca_2(CO_3)_3$)	
0.09	−1.05	1074	Fairchildite + CaO	
		1043	Fairchildite + CaO	
		1038	$K_2Ca_2(CO_3)_3$	1041±3
		1032	$K_2Ca_2(CO_3)_3$	
0.19	−0.72	1074	Fairchildite + CaO	
		1063	$K_2Ca_2(CO_3)_3$	1069±5
		1043	$K_2Ca_2(CO_3)_3$	

obtained in the present work, 1080 ± 5 K, is very close to the melting point at 1 kbar, 1083 K, as Cooper *et al.*[1] reported.

Equilibration experiments at $p_{CO_2} \geqslant 0.03$ bar showed that fairchildite melted before decomposition. Therefore, decomposition measurements in the range $0.03 \leqslant p_{CO_2} \leqslant 0.19$ could not be performed. It was however found that in air $(p_{CO_2} = 3.5 \times 10^{-4}$ bar) fairchildite decomposed according to:

$$K_2Ca(CO_3)_2(s) \rightarrow K_2CO_3(s) + CaO(s) + CO_2(g) \quad (II)$$

Its melting point at $p_{CO_2} = 1$ bar found in the present work, 1075 ± 5 K, is somewhat lower than the value 1085 K reported by Cooper *et al.*[1] at 1 kbar.

Results from thermal analytical experiments. The thermal decomposition of $K_2Ca_2(CO_3)_3$ was, in addition to the equilibration experiments, investigated by thermal gravimetric and differential thermal analytical methods. The temperatures of decomposition were mainly evaluated from the TGA curves, as these were more pronounced than corresponding DTA curves. The temperatures of the decomposition obtained at various fixed p_{CO_2} for $K_2Ca_2(CO_3)_3$ and for $CaCO_3$ are given in Table 2. $CaCO_3$ was used both as an equilibrium reference substance and for temperature 'calibration' of the TGA/DTA apparatus.

In Fig. 1 the experimental values of $lg(p_{CO_2}/bar)$ are plotted as a function of $1/T$. The solid line shown in

Table 2. Measured (T_d) and adjusted (T_{ad}) temperatures (in K) of decomposition for $K_2Ca_2(CO_3)_3$ and $CaCO_3$ determined by TGA at various p_{CO_2} (in bar).

p_{CO_2}/ bar	lg p_{CO_2}	T_d/K CaCO$_3$	T_{ad}/K CaCO$_3$	T_d/K K_2Ca_2-(CO$_3$)$_3$	T_{ad}/K K_2Ca_2-(CO$_3$)$_3$
0.028	−1.55	971±6	970±6	982±5	980±6
0.054	−1.27	1018±5	1001±5	1023±5	1006±5
0.070	−1.15	1065±2	1014±2	1076±2	1025±2
0.094	−1·02	1074±2	1029±2	1081±2	1036±2
0.126	−0.90	1091±2	1044±2	1091±2	1045±2
0.200	−0.70	1101±2	1069±2	1106±2	1073±2
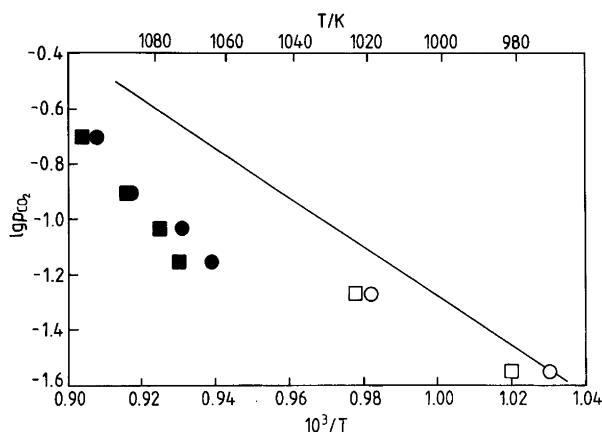
Fig. 1. Diagram with results obtained from the TGA measurements: ($\blacksquare$, $\square$), results from $K_2Ca_2(CO_3)_3$ samples; ($\bullet$, $\bigcirc$), results from $CaCO_3$ samples. Open symbols denote results from the vertical instrument (Mettler) and filled symbols denote results from the horizontal instrument (TA Instruments). The solid line represents the equilibrium decomposition values for $CaCO_3$.

Fig. 2. Diagram with adjusted results from the TGA measurements and results from the equilibrium studies. The symbols ($\blacksquare$, $\square$, $\bullet$, $\bigcirc$) and solid line are defined in Fig. 1. The symbol ($\triangle$) denotes results from equilibration experiments. The broken line represents the equilibrium decomposition values for $K_2Ca_2(CO_3)_3$.

Fig. 1:

$$\lg p_{CO_2}(III) = -9075/T + 7.80 \qquad (1)$$

was calculated using thermodynamic data from literature[11] for the equilibrium decomposition reaction

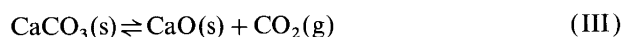$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad (III)$$

Figure 1 shows that the experimental values obtained for the $CaCO_3$ decomposition deviate from the calculated equilibrium values. This is partly due to the fact that the samples were not fully thermally equilibrated during the heating procedure, and partly due to incorrect temperature readings. To overcome these problems, the experimental $CaCO_3$ decomposition values are adjusted to coincide with the corresponding equilibrium values. An equivalent deviation was assumed to occur also for the decomposition of $K_2Ca_2(CO_3)_3$, due to the similarity of reactions (I) and (III). The experimental decomposition temperatures for $K_2Ca_2(CO_3)_3$ are therefore corrected by the same extent as for the decomposition values of $CaCO_3$. The results of these transformations are given in Table 2 and illustrated in Fig. 2. The experimental value for the $CaCO_3$ decomposition at 970 K came surprisingly close to the corresponding calculated equilibrium value. The values obtained from the equilibration measurements of $K_2Ca_2(CO_3)_3$ are also plotted in Fig. 2. As it can be seen, these equilibrium values agree well with the adjusted TGA results.

Equilibrium relationship for the decomposition of $K_2Ca_2(CO_3)_3$. The data points for the decomposition of solid $K_2Ca_2(CO_3)_3$, $\lg(p_{CO_2}/bar)$ and T/K, given in Table 1 for the equilibration values, in Table 2 for the adjusted TGA values, and shown in Fig. 2, were evaluated by a least squares treatment to give the following relationship:
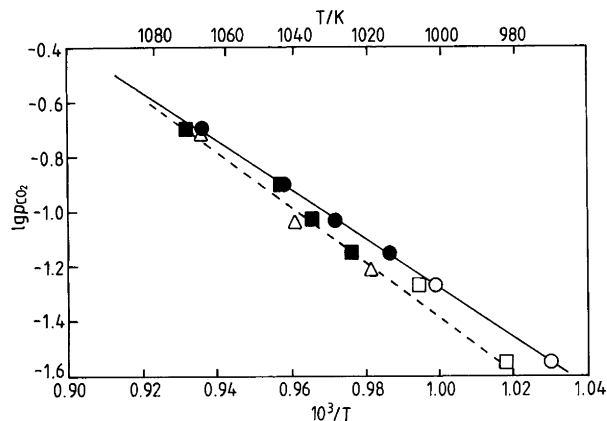
$$\lg p_{CO_2}(I) = -9695/T + 8.35 \qquad (2)$$

This equation represents the equilibrium decomposition conditions of reaction (I). The estimated uncertainty of $\lg p_{CO_2}(I)$ is ± 0.04 lg units.

Calculation of enthalpies. The law of mass action applied to the equilibrium reaction (I) gives the relation

$$\lg K = \lg p_{CO_2} \qquad (3)$$

By assuming the enthalpy and entropy change of reaction (I), $\Delta H(I)$ and $\Delta S(I)$, to be constant in the temperature interval studied, the temperature dependence of $\lg K$ can be written as

$$\lg K = -\frac{\Delta H}{R \ln 10} \times \frac{1}{T} + \frac{\Delta S}{R \ln 10} \qquad (4)$$

From eqns. (2)–(4) it follows that $\Delta H(I) = 185.6 \pm 0.8$ kJ and $\Delta S(I) = 159.8 \pm 0.8$ J K^{-1}.

The enthalpy change of reaction (I) can be written accordingly as

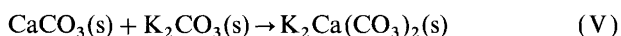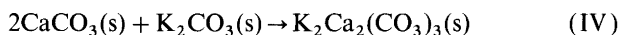$$\Delta H(I) = \Delta_f H[K_2Ca(CO_3)_2] + \Delta_f H(CaO) + \Delta_f H(CO_2)$$
$$- \Delta_f H[K_2Ca_2(CO_3)_3] \qquad (5)$$

By rearranging eqn. (5), the following expression is derived:

$$\Delta_f H[K_2Ca(CO_3)_2] - \Delta_f H[K_2Ca_2(CO_3)_3]$$
$$= \Delta H(I) - \Delta_f H(CaO) - \Delta_f H(CO_2) \qquad (6)$$

It could be of some interest to calculate the difference indicated on the left-hand side of eqn. (6), ΔH[left, eqn. (6)], at 298 K. This can be done assuming the derived $\Delta H(I)$-value, 185.6 kJ, in the present work to be constant down to 298 K. The literature values[12] of $\Delta_f H(CaO)$ and $\Delta_f H(CO_2)$ are -635.09 ± 0.88 kJ mol^{-1} and -393.51 ± 0.05 kJ mol^{-1}, respectively, and thus ΔH[left, eqn. (6)] will equal 1214 ± 1 kJ. This enthalpy difference can also be calculated using values from the

recent study by Navrotsky *et al.*[9] for reactions (IV) and (V) at 298 K and literature data[11,13] for $\Delta_f H(CaCO_3)$:

$$2CaCO_3(s) + K_2CO_3(s) \rightarrow K_2Ca_2(CO_3)_3(s) \qquad (IV)$$

$$CaCO_3(s) + K_2CO_3(s) \rightarrow K_2Ca(CO_3)_2(s) \qquad (V)$$

The values given for $\Delta H(IV)$ and $\Delta H(V)$ are -7.2 ± 5.8 kJ and -5.1 ± 3.3 kJ, respectively, and the value for $\Delta_f H(CaCO_3)$ is -1206.7 ± 1 kJ. Recombination of reactions (IV) and (V) will give reaction (VI) and eqn. (7):

$$CaCO_3(s) + K_2Ca(CO_3)_2(s) \rightarrow K_2Ca_2(CO_3)_3(s) \qquad (VI)$$
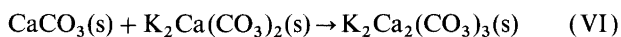
$$\Delta_f H[K_2Ca(CO_3)_2] - \Delta_f H[K_2Ca_2(CO_3)_3]$$

$$= \Delta H(VI) - \Delta_f H(CaCO_3) \qquad (7)$$

The value of ΔH [left, eqn. (7)] is then 1209 ± 7 kJ, which agrees well with the value of 1214 ± 1 kJ from the present work.

Conclusions

In the present work the thermal stability of the double carbonate $K_2Ca_2(CO_3)_3$ was determined by means of equilibration experiments and thermogravimetric analysis (TGA). The results of the experiments showed that solid $K_2Ca_2(CO_3)_3$ will decompose to the solid products fairchildite and CaO in atmospheres where $0.03 \leqslant p_{CO_2} \leqslant 0.20$ bar. In addition, calculations using eqn. (2) and the melting point of 1080 K, determined in the present work, suggest that $K_2Ca_2(CO_3)_3$ will melt before decomposition at $p_{CO_2} > 0.23$ bar. These results support the suggestion that solid $K_2Ca_2(CO_3)_3$ can be formed in a combustion process of biomass fuels ($p_{CO_2} = 0.10$–0.15 bar) in the temperature range 800–1060 K (530–790 °C). An investigation concerning the possible presence of $K_2Ca_2(CO_3)_3$ in some ashes of biomass fuels is in progress.

The equilibration experiments also showed that in air ($p_{CO_2} = 3.5 \times 10^{-4}$ bar), the double carbonate fairchildite will decompose to the solid products K_2CO_3 and CaO. At pressures of $p_{CO_2} \geqslant 0.03$ bar, however, it was found that fairchildite melted before decomposing.

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