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**Note**

# Influence of the pressure on the shape of DTA and DTG curves of reversible reactions of thermal decomposition of solids

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Bandi and Krapf have studied in a recent and interesting paper[1] the influence of the pressure of $CO_2$ on the shape of the DTA curve of dolomite. At pressures of less than 200 torr a one-step decomposition of the sample to CaO and MgO has been reported[1]. Moreover, taking into account the abrupt sharpening observed in the DTA peak of dolimite by increasing the pressure of $CO_2$ from 0 to 70 torr, it is concluded[1] that the reaction mechanism at very low pressures is different than at higher ones.

The aim of this note is to suggest another possible explanation of the above behaviour without considering any change of the reaction mechanism. In order to show this, we will try to estimate the influence of the $CO_2$ pressure on the shape of the derivatographic curve of thermal decomposition of $CaCO_3$:

$$CaCO_3 \leftrightarrows CaO + CO_2 \tag{1}$$

This reaction has been chosen because the values of its equilibrium pressure, $P_{eq}$, at different temperatures have been reported in the literature[2]. Therefore, it can be easily deduced from data of previous reference[2] that between 500 and 1000°C it is fitted very closely the equation:

$$P_{eq}(\text{torr}) = 1.4 \cdot 10^{10} \cdot e^{-39/RT} \tag{2}$$

$R$ being $1.98 \cdot 10^{-3}$ kcal $K^{-1}$ $mol^{-1}$ and $T$ the absolute temperature.

On the other hand, the same mechanism has been reported[3] for both reaction (1) and the thermal decomposition of dolomite under vacuum. Therefore, we can write:

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT}(1-\alpha)^{2/3} \tag{3}$$

$\alpha$ being the reacted fraction.

However, if the thermal decomposition of the salt is not carried out under vacuum but at a pressure $P_{CO_2}$ of $CO_2$, eqn (3) becomes, after taking into account the microreversibility principle:

$$\frac{d\alpha}{dt}=A\cdot e^{-E/RT}\left[1-\frac{P_{CO_2}}{P_{eq}}\right]\cdot(1-\alpha)^{2/3} \qquad (4)$$

Substituting eqn (2) into (4) and using for $E$ and $A$ the values of 39 kcal mol$^{-1}$ and $2\cdot10^{8}$ min$^{-1}$ reported by Morales[4], we obtain:

$$\frac{d\alpha}{dt}=\left(2\cdot10^{8}\cdot e^{-39/RT}-\frac{2\cdot10^{8}}{1.4\cdot10^{10}}P_{CO_2}\right)(1-\alpha)^{2/3} \qquad (5)$$

If the reaction rate, $d\alpha/dt$, were recorded at a heating rate $\beta=dT/dt$, the previous equation would be transformed, after rearranging, into:

$$\frac{d\alpha}{(1-\alpha)^{2/3}}=\frac{2\cdot10^{8}}{\beta}\cdot e^{-39/RT}dT-\frac{1.4\cdot10^{-2}}{\beta}\cdot P_{CO_2}dT \qquad (6)$$

that would be integrated in order to obtain the value of $\alpha$ required for calculating the reaction rate by means of eqn (4).

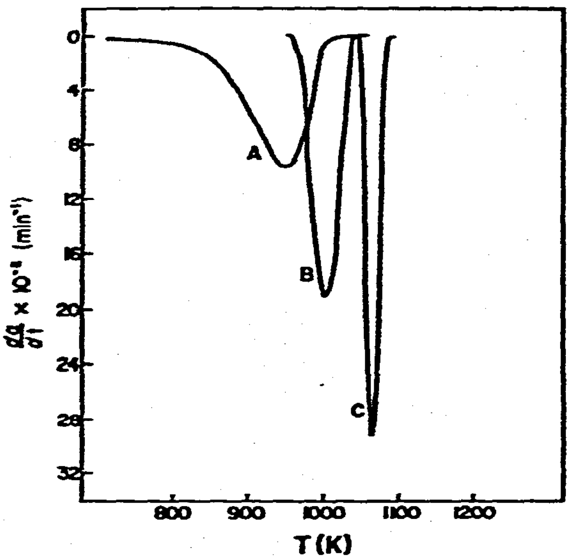

Fig. 1. Diagrams of the reaction rate of thermal decomposition of $CaCO_3$ versus temperature, calculated at a heating rate of 10°C min$^{-1}$ and different pressures of $CO_2$: (A) 0 torr; (B) 20 torr; (C) 100 torr.

Reaction (1) is not thermodynamically favoured until a temperature is reached at which the equilibrium pressure coincides with the pressure of $CO_2$ around the sample. Thus, integrating eqn (6) as described by Coats and Redfern[5], by using as lower integration limit of temperature the value of $T_0$ previously calculated from eqn (2), we obtain:

$$3[1-(1-\alpha)^{1/3}]=\frac{2\cdot 10^{8}RT^{2}}{39}\cdot e^{-39/RT}-\frac{2\cdot 10^{8}RT_0^{2}}{39\beta}\cdot e^{-39/RT_0}-$$

$$-\frac{1.4\cdot 10^{-2}}{\beta}\cdot P_{CO_2}\cdot(T-T_0) \tag{7}$$

Therefore, the plots of $d\alpha/dt$ that would be expected when performing the experiment under a particular pressure of $CO_2$ and a heating rate $\beta$ would be calculated from eqns (5) and (7). The curves determined for pressures of 0; 20 and 100 torr of $CO_2$, respectively, and at the same heating rate of 10°C $min^{-1}$ are plotted in Fig. 1. From this figure we can see that when reversible reactions of thermal decomposition of solids are concerned, an abrupt sharpening of DTA or DTG diagrams because of the pressure would be expected without assuming any change of the reaction mechanism.

## REFERENCES

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