

New aspects of the decomposition kinetics of calcite. Part 1. Isothermal decomposition

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Abstract

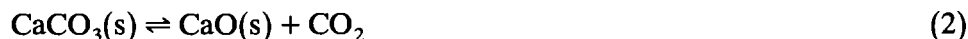
Under experimental conditions which tend to minimise the effects of heat and mass transfer, the kinetics of the decomposition of calcite according to $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is split by the restriction of CO_2 transport at the degree of conversion α_t when the channels in the $\text{CaO}(\text{s})$ surrounding the reactant provide the only diffusion path. Because of the resulting convective cooling beyond α_t , the phase boundary reaction proceeds initially with the reaction-only activation energy $E_a(1) = 192.89 \text{ kJ mol}^{-1}$ up to α_t , after which the reaction proceeds with an apparent activation energy of $E_a(2) = 210.33 \text{ kJ mol}^{-1}$. The diffusion-controlled reaction proceeds with the mean value of the activation energy $E_a(D_1) = 0.5(E_a(1) + E_a(2)) = 201.65 \text{ kJ mol}^{-1}$. The activation energies differ by the same amount, i.e. $E_a(D_1) - E_a(1) = E_a(2) - E_a(D_1) = 8.72 \text{ kJ mol}^{-1}$, equivalent to the degenerate deformation vibration $\nu_4 = \delta(\text{O}-\text{C}-\text{O})$ of calcite observed at 706 cm^{-1} (infrared) and 714 cm^{-1} (Raman), which for a transition state sensitive to the instantaneous transport of CO_2 , complements the cage effect exercised by the lattice, thus giving strong evidence supporting our mechanistic interpretation of the decomposition kinetics.

INTRODUCTION

Solid state decomposition reactions of the type



tend to show variable kinetic parameters. An exemplary case is the decomposition of calcite



which has frequently been studied and for which the activation energy is variably reported from the lowest value of 147 kJ mol^{-1} up to 220 kJ mol^{-1} [1–19]. Values several times higher than 220 kJ mol^{-1} can also be obtained, depending on the CO_2 content of the purge gas [20,21].

In view of the large fluctuation in these results, the physical meaning of the kinetic parameters for solid state decompositions can be challenged [22], because under these circumstances the activation energy cannot be

assigned to a specific activated state. The suggestion has also been made that the Arrhenius equation which is invariably used to evaluate the kinetic measurements, is an inadequate tool for handling heterogeneous kinetics [22].

A plausible explanation for the variation of the kinetic parameters is the contributions of heat and mass transfer to the kinetics of the phase boundary reaction, as these physical processes present a significant problem which is not encountered in homogeneous kinetics, where consistent kinetic parameters are normally obtained.

We believe that a decomposing solid presents variable vibrational states of the reacting groups, depending on the prevailing conditions of heat and mass transfer. This follows from the fact that vibrational motion provides the only significant means of the exchange of thermal energy among the reacting groups in a solid. To test this proposition, we have studied the kinetics of calcite decomposition under isothermal and dynamic heating. Our results from the isothermal decomposition of calcite single crystals in a stream of nitrogen are reported here. These results show our approach to be correct.

Gallagher and Johnson have demonstrated that the kinetics of calcite decomposition are sensitive to the heat conductivity of the purge gas [11]. The authors concluded from this observation that the decomposition was controlled by the transmission of heat to the endothermic reactant. As the problem of heat transfer under isothermal heating is reduced to the lowest possible level, the variation of the decomposition kinetics which may arise due to the formation and growth of the solid reaction product around the reactant should give activation energies $E_a(1)$ and $E_a(2)$ which differ by the lowest terms of the vibrational states. For the phase boundary reaction, the activation energy $E_a(1) = 192.89 \text{ kJ mol}^{-1}$ is obtained during the first phase of the reaction up to a degree of conversion α of between 0.45 and 0.69, and a larger value $E_a(2) = 210.33 \text{ kJ mol}^{-1}$ is obtained above this.

The activation energies differ by the amount $E_a(2) - E_a(1) = 17.44 \text{ kJ mol}^{-1}$, the equivalent of twice the frequency of the degenerate vibration ν_4 observed in the spectra of calcite at 706 cm^{-1} (infrared) and 714 cm^{-1} (Raman) [23].

Under the conditions of the experiment, however, the reaction rate is clearly diffusion-controlled beyond $\alpha = 0.4$, proceeding with the activation energy $E_a(D_1) = 201.65 \text{ kJ mol}^{-1}$, the mean value of $E_a(1)$ and $E_a(2)$. Accordingly, the kinetics of the phase boundary reaction is split by the restriction of CO_2 transport into two phases, the first proceeding with the activation energy $E_a(1) = E_a(D_1) - E_{\nu_4}$ and the other with the activation energy $E_a(2) = E_a(D_1) + E_{\nu_4}$.

The vibrational spectra support our interpretation of the kinetic decomposition behaviour of calcite that the deformation vibration $\nu_4 = \delta(\text{O}-\text{C}-\text{O})$ is complementary to the cage effect exercised by the lattice with respect to

the transition state, which is sensitive to the instantaneous transport of CO_2 away from the phase boundary.

EXPERIMENTAL

Calcite single crystals in the form of flat chips were polished to give final sample weights of 34–36 mg. The quality of the sample was ensured by comparing the TG and DTG curves of the powdered material with those of AnalaR grade precipitated CaCO_3 .

In order to eliminate the influence of nucleation (and the induction period), the sample was heated in a Metler TG 50 thermal balance at a selected heating rate to the desired isothermal temperature and the time zero was taken to be the time when the reaction temperature was reached. The amount decomposed before reaching the reaction temperature was kept to below 2% by appropriate selection of the heating rate whilst the sample was being heated to the desired reaction temperature.

The decomposition was carried out in a stream of dry nitrogen flowing at the rate of 100 ml min^{-1} . In order to improve heat transmission to the reactant, the sample was placed directly on the metallic sample carrier, thus avoiding the use of the Al_2O_3 crucible. A typical decomposition curve is shown in Fig. 1.

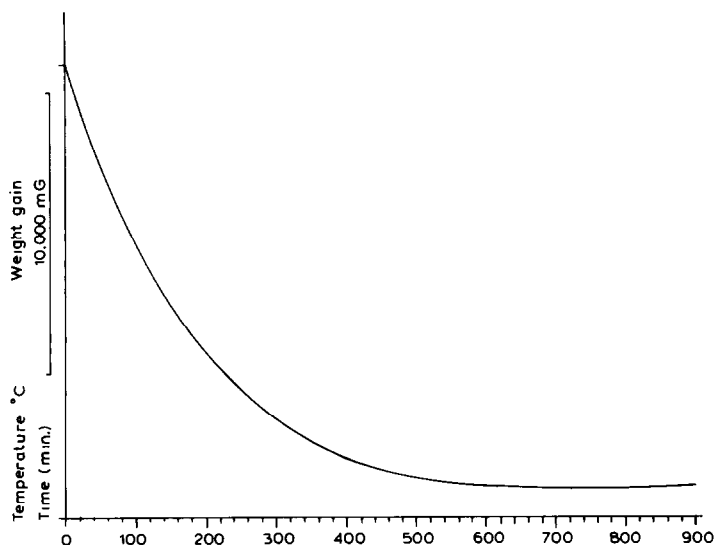


Fig. 1. A typical thermal decomposition curve for calcite single crystals: isothermal temperature, 670°C ; heating rate to reaction temperature, 30 K min^{-1} ; reaction time at 670°C , 900 min; sample wt., 34.223 mg.

RESULTS AND DISCUSSION

The experimental results of the kinetic measurements are summarised in the plots of α versus t shown in Fig. 2. These results are compatible with the mechanism of a two-dimensional phase boundary reaction (R_2) according to

$$g(\alpha) = 2(1 - (1 - \alpha)^{1/2}) = k_1 t \quad (3)$$

and the mechanism of one-dimensional diffusion according to

$$g(\alpha) = \alpha^2 = k_2 t \quad (4)$$

Representative plots of $g(\alpha)$ versus t are shown in Fig. 3.

For the phase boundary reaction mechanism (R_2), the plots of $g(\alpha)$ showed a characteristic drop in rate constant k_1 at a transition value α_t of the degree of conversion, observed between $\alpha = 0.45$ and 0.69 . The variation of α_t in the given limits is random, which suggests the possibility of the formation of pores in the CaO(s) of slightly variable sizes. The formation of these closely spaced pores, $2 \mu\text{m}$ or less in diameter, is supported by our own microscopic observations and those of Beruto and Searcy [18]. The Arrhenius plots for the two mechanisms (R_2 and D_1) are shown in Fig. 4. The corresponding slopes are labelled R'_2 , R''_2 and D_1 for easy identification.

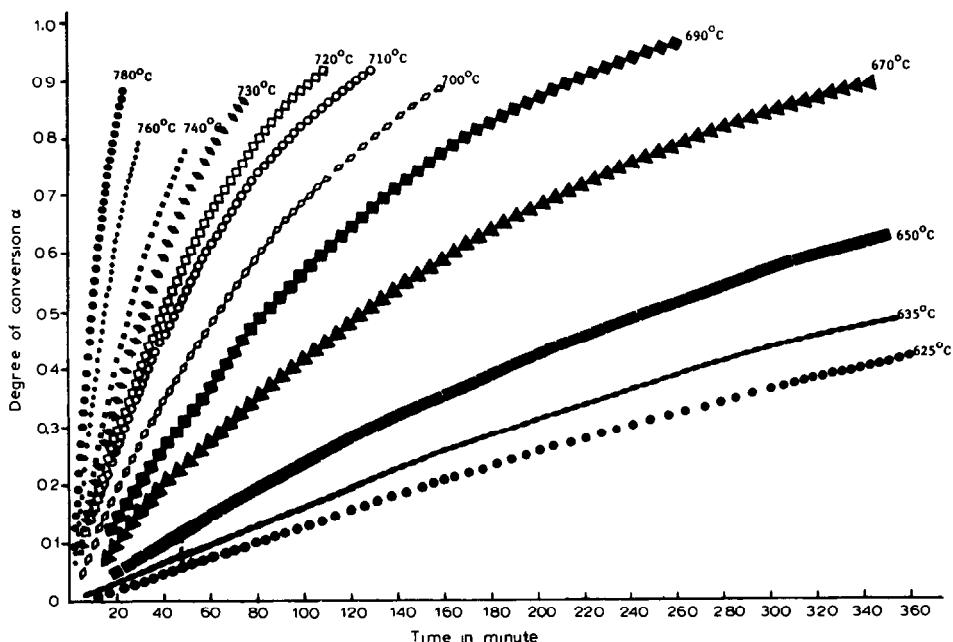


Fig. 2. Plots of α vs. time (min).

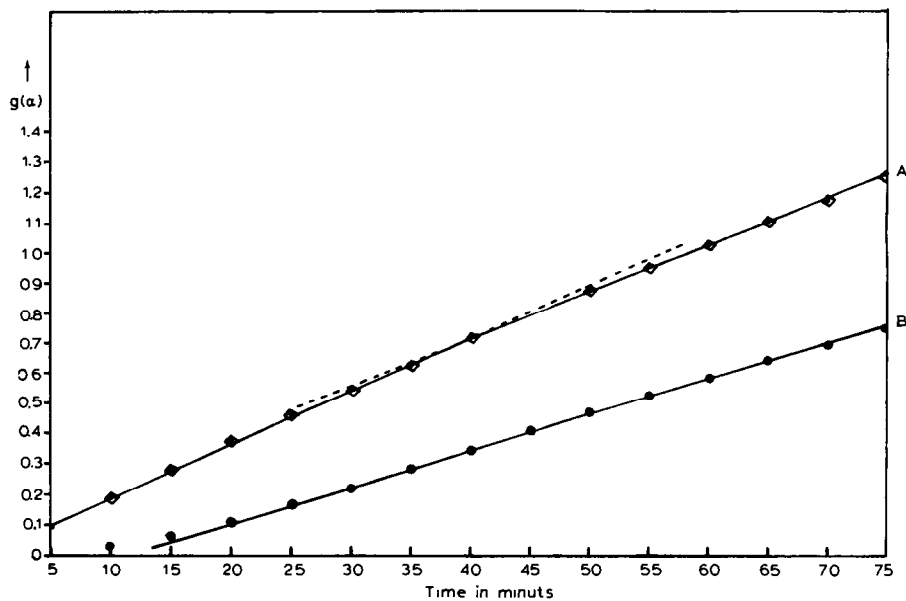


Fig. 3. Plots of $g(\alpha)$ vs. time: A, phase boundary reaction mechanism (R_2); B, one-dimensional diffusion mechanism (D_1).

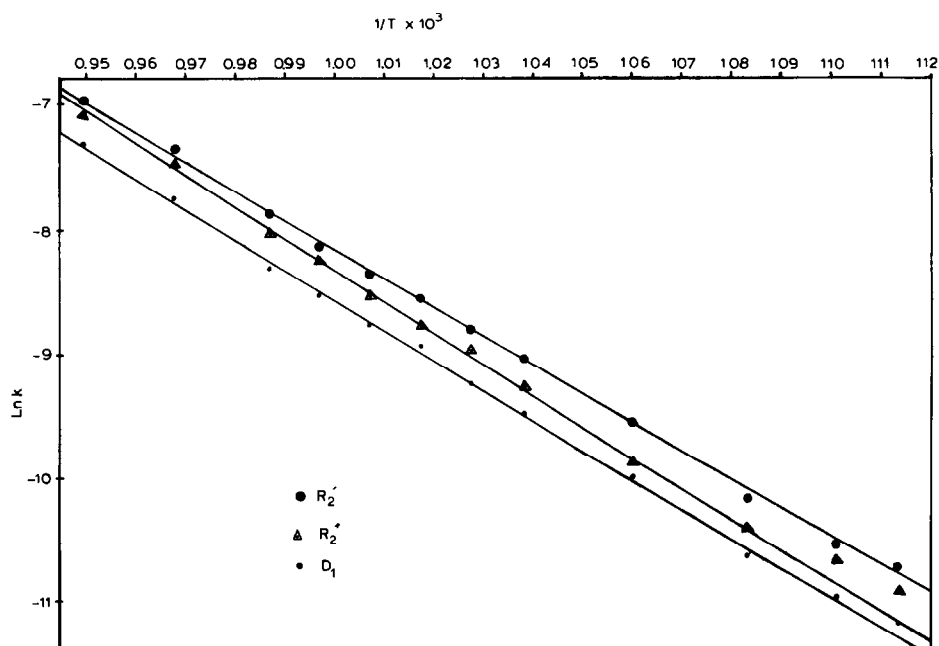


Fig. 4. The Arrhenius plots for the mechanisms R_2 and D_1 .

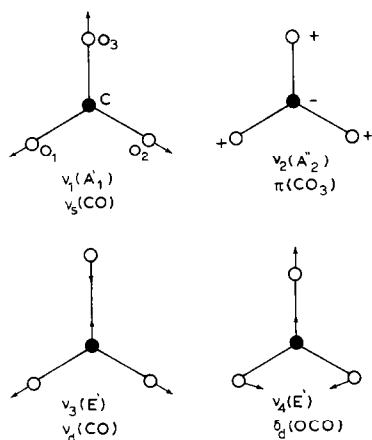


Fig. 5. Normal modes of vibration of planar CO_3^{2-} .

The activation energies derived from the slopes are $E_a(1) = 192.89 \text{ kJ mol}^{-1}$ and $E_a(2) = 210.33 \text{ kJ mol}^{-1}$ for the phase boundary reaction (R_2) mechanism and $E_a(D_1) = 201.65 \text{ kJ mol}^{-1}$ for the one-dimensional diffusion mechanism.

MOLECULAR VIBRATION AND THE DECOMPOSITION OF CALCITE

In order to explain the experimental results, each energy barrier is assumed to be the sum of an invariant component ΔH , the reaction enthalpy change, and a variable component ϵ which gives the energy required to overcome the obstruction of heat and mass transfer.

The energy $\epsilon = z\nu$ is determined by the frequency ν of a specific vibration consistent with the decomposition mechanism, and z , the number of vibrations required before the reactant attains the energy level of the activated state, thus achieving the infinite separation of the reaction products at the end of the z th vibration.

The four modes of vibration for planar CO_3^{2-} (D_{3h} symmetry) are shown in Fig. 5. The symmetric bond stretching, $\nu_5(C-O)$, should contribute considerably to the vibrational states relevant to the transition state involving the breaking of the carbonate C-O bond. On the other hand, the degenerate O-C-O deformation band (ν_4) should be important for the transition state of a diffusion-controlled reaction since it complements the cage effect of the lattice. Thus the differences in the activation energies $E_a(2) - E_a(D_1) = E_a(D_1) - E_a(1) = 8.76 \text{ kJ mol}^{-1}$, give the energy equivalent of the degenerate deformation band ν_4 observed in the spectra of calcite at 706 cm^{-1} (infrared) and 714 cm^{-1} (Raman), being a manifestation of the complementary effect of CO_2 transport on the mechanisms (R_2 and D_1).

The Arrhenius plots (Fig. 4) represents the three energy barriers for the phase boundary reaction (R'_2 and R''_2) and the one dimensional diffusion

TABLE 1

Values of the degree of conversion α_t at which the rate constant K_1 of the phase boundary reaction drops, apparently because of the restriction of CO_2 transport by CaO(s) around the reactant

Isothermal reaction temperature (°C)	α_t
625	0.520
635	0.630
650	0.469
670	0.640
690	0.552
700	0.539
710	0.682
720	0.620
730	0.557
740	0.490
760	0.524
780	0.696
Average	0.58

mechanism (D_1). The intersections of the slopes give the characteristic temperatures $T = 1086.2 \text{ K}$ (R'_2 and R''_2) and $T_0 = 812.5 \text{ K}$ (D_1 and R''_2) for the mechanistic transitions from one energy barrier to another. Whereas at 812.5 K the rate constants k_1 and k_2 are equal, below this temperature the chemical reaction is a rate determining step ($k_1 < k_2$).

The decomposition rate below 812.5 K is sufficiently small as to render the cage effect of the lattice of no kinetic consequence. The cage effect determines the decomposition kinetics above 812.5 K .

The cage effect exercised by the lattice obviously influences the equilibrium with respect to the recombination of CaO(s) and $\text{CO}_2(\text{g})$ which we can treat as an adsorption phenomenon for which the relationship

$$\frac{\ln p_{\text{CO}_2}}{\Delta T} = - \frac{\Delta E_a}{RT^2} \quad (5)$$

holds. The partial pressure p_{CO_2} of carbon dioxide can be considered to be numerically identical with the transition value α_t of the degree of conversion. The mean value of $\alpha_t = 0.58$ is taken from the experimental data in Table 1. The characteristic temperatures T_0 and T give a temperature difference $\Delta T = 273.7 \text{ K}$ and putting $T = 1086.2 \text{ K}$ in eqn. (5) we obtain $\Delta E_a = 19.52 \text{ kJ mol}^{-1}$ which agrees well with the difference in the activation energies $E_a(2) - E_a(1) = 17.44 \text{ kJ mol}^{-1}$ (corresponding to $2\nu_4$).

When $T_0 = 812.5 \text{ K}$ is put in eqn. (5), we obtain $\Delta E_a = 10.92 \text{ kJ mol}^{-1}$ which is the difference $E_a(\text{D}_1) - E_a(1) = 8.76 \text{ kJ mol}^{-1}$. The values of ΔE_a calculated according to eqn. (5) are consistently higher by 2.12 kJ mol^{-1} , which is a result of random variation in α_t within the range observed, i.e. $\alpha = 0.45-0.69$.

A comparison of the activation energies for the decomposition of calcite and potassium oxalate is interesting.

In the two compounds, the decomposing groups, CO_3^{2-} and $\text{C}_2\text{O}_4^{2-}$, are assumed to be fully ionic and the breaking of a C–O bond, which is the rate-determining step, is in each case opposed by the resonance energy. The activation energy $E_a = 257 \text{ kJ mol}^{-1}$ is obtained for the decomposition of oxalate when the restriction of heat and mass transfer is a minimum. As there are four independent ways of selecting a single C–O bond among 4 in the oxalate ion, the activation energy should be 4/3 times that for calcite decomposition. The activation energy for the decomposition of $\text{K}_2\text{C}_2\text{O}_4$ agrees excellently with $\frac{4}{3}E_a(1) = 257.2 \text{ kJ mol}^{-1}$ [24,25].

The activation energy of calcite decomposition

The understanding of the effects of heat and mass transfer problems on the kinetics of heterogeneous reactions has encouraged recent investigators to take experimental precautions so that they are minimised.

Beruto and Searcy [18] improved heat transmission to the reactant calcite single crystal by employing tubular nickel shields to improve heat conductance.

By keeping the reaction rate fairly low, the heat transmission can be made to match and neutralise the self-cooling of an endothermic reactant. In the present investigation, isothermal measurements were extended down to quite low reaction temperatures where complete decomposition would take more than 18 hours. Reading et al. [19] have also employed rate jump constant-rate thermal analysis (CRTA), permitting low decomposition rates.

The activation energy $E_a = 205 \text{ kJ mol}^{-1}$ was calculated by Berruto and Searcy [18] from their experimental measurements, while Reading et al. [19] give a mean value of $210 \pm 10 \text{ kJ mol}^{-1}$ from their CRTA experiments, which is in agreement with $E_a(2) = 210.33 \text{ kJ mol}^{-1}$ obtained for the phase boundary reaction at $\alpha > 0.4$, thus suggesting that the results are affected by the transport of CO_2 . This is easily established by close examination of the activation energies of Reading et al. [19] obtained from rate jump CRTA. Their values at $\alpha < 0.3$ are close to $E_a(1) = 192.89 \text{ kJ mol}^{-1}$ obtained in this work as the reaction-only activation energy for the decomposition of calcite. Their values at $\alpha > 0.3$ are close to $E_a(2) = 210.33 \text{ kJ mol}^{-1}$.

An important conclusion from the present study is that a heterogeneous reaction may not always give a single phase of the reaction with uniform kinetics with which the entire kinetic behaviour can be adequately described. The activation energies for various phases of the reaction are determined by the respective vibrational states of the groups undergoing decomposition. The consistency of the results of the experiment with the vibrational model for the activation of the reactant provides a reliable

guide to the decomposition mechanism, and gives a physical meaning to the activation energies obtained.

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