

## The thermal decomposition kinetics of $\text{CdCO}_3$ powder

Adolf M. Mulokozi

*Department of Chemistry, University of Dar es Salaam, P.O. Box 35061,  
Dar es Salaam (Tanzania)*

(Received 27 September 1991)

### Abstract

In previous publications (*Thermochimica Acta*, 194 (1992) 375; 197 (1992) 363), we suggested the theoretical foundation for the interpretation of the decomposition kinetics of crystalline compacts. A solid AB decomposing according to an endothermic reaction  $\text{AB(s)} \rightarrow \text{A(s)} + \text{B(g)}$  absorbs from the thermal reservoir the energy  $\varepsilon = z\nu$  in excess of the reaction enthalpy change  $\Delta H$ , which allows the reactant to overcome the effects of heat and mass transfer and leads to the infinite separation of the reaction products in the  $z$ th vibration of frequency  $\nu$ . The vibrational quantum number  $z$  is not the same for compacts and powders. Covalent bonding in  $\text{CdCO}_3$  also influences the decomposition kinetics.

### INTRODUCTION

Unlike solution and gas phase kinetics where the reactant has unrestricted translational degrees of freedom, the decomposition kinetics of solids is affected by the rigid lattice. In order to overcome the obstruction of heat and mass transfer by the lattice, a solid reactant AB decomposing according to an endothermic reaction  $\text{AB(s)} \rightarrow \text{A(s)} + \text{B(g)}$  absorbs from the thermal reservoir the energy  $\varepsilon = \nu z$  in excess of the enthalpy change  $\Delta H$  of the reaction, before the infinite separation of reaction products is possible in the  $z$ th vibration of the frequency  $\nu \text{ cm}^{-1}$ . The energy barrier is therefore

$$E_a = \Delta H + z\nu \quad (1)$$

The validity of eqn. (1) is established from the determination of  $\nu$  from the difference of the activation energies  $E_a(2) - E_a(1) = \nu\Delta z$  [1,2]. Because  $z$  is a vibrational quantum number defining the number of possible transitions from  $z_0$  to  $z = z_0 + \Delta z$ , where  $\Delta z = 1, 2, 3, 4$ , etc., the activation energy can assume variable values, which is consistent with experience [3].

---

*Correspondence to:* A.M. Mulokozi, Department of Chemistry, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania.

The present theoretical approach is of interest in chemical technology, because energy costs in operation of kilns and other industrial devices are dependent on the energy barrier of the chemical reaction.

Because with solid reactants the application of a catalyst is impracticable, the reduction of the energy barrier is exclusively dependent on optimization of heat and mass transfer processes. For the theoretical treatment of heat and mass transfer in decomposing crystalline compacts, reference is made to our previous papers [1,2].

The behaviour of powders must differ appreciably, because the intergranular spaces offer diffusion channels of infinitely large dimensions compared to the diffusion channels in a continuous lattice network. This becomes important because of convective heat transmission to the reactant by hot furnace gas or, in the present case, the nitrogen, used as purge gas. The purge gas, initially at the temperature of the furnace, loses heat to the solid phases as it penetrates into the interior of the sample. Therefore as the reaction spreads towards the interior, most of the freely available heat of the purge gas is increasingly spent heating the solid reaction product A, and increasingly less heat is available for heating the reactant. Again the partial pressure of the purge gas is decreasing while that of the gaseous reaction product is increasing. Under these circumstances, the increasing temperature gradient in the solid phases enhances self-cooling of an endothermic reactant. Therefore, the reaction spread, which in bulk proceeds uniformly towards the interior, is no longer uniform in the reactant grains which, for simplicity, are assumed to be spherical. The layer of solid product on the reactant grains will grow faster along the side exposed to the intergranular diffusion channels.

Because the rate of heat demand of an endothermic reactant increases with increasing reaction rate, self-cooling and, in turn, the temperature gradient in the solid phases of the reactant grains will increase with increasing temperature. Also the temperature gradient will be large when  $\Delta H$ , the enthalpy change of the reaction, is large. Therefore the decomposition behaviour of  $\text{CaCO}_3$  powder with a large enthalpy change,  $\Delta H = 167 \text{ kJ mol}^{-1}$ , is unlikely to be comparable with that of  $\text{CdCO}_3$  powder where the enthalpy change is  $98 \text{ kJ mol}^{-1}$ . Because there is least tendency for the formation of a stable continuous layer of  $\text{CaO}$  on the grains of  $\text{CaCO}_3$ , the chemical reaction is the rate-determining step giving the characteristic vibration  $\nu_{\text{R}} = \nu(\text{C-O})$  observed at  $1088 \text{ cm}^{-1}$  [4]. The reduction of the energy barrier on going from calcite to  $\text{CaO}_3$  powder is considerable, despite the change in the characteristic vibration from  $\nu = 710 \text{ cm}^{-1}$  [1,2] to  $1088 \text{ cm}^{-1}$ , because there is less obstruction of convective heat transport, reducing  $z$  to 1. However the decomposition of  $\text{CdCO}_3$  powder would tend to give a continuous stable solid layer of the reaction product around the reactant grains because of the very low enthalpy change compared to that of  $\text{CaCO}_3$  decomposition, and the effect should be pronounced at low reaction temperatures.

TABLE 1

The  $\text{CO}_3^{2-}$  vibrations in calcite and  $\text{CdCO}_3$ 

Vibration mode	$\text{CaCO}_3$	$\text{CdCO}_3$ in the infrared (IR)
O–C–O deformation	$\nu_4$ 706 $\text{cm}^{-1}$ (IR) 714 $\text{cm}^{-1}$ (R)	$\nu_6$ ( $\text{B}_2$ ) 650 $\text{cm}^{-1}$ $\nu_3$ ( $\text{A}_1$ ) 738 $\text{cm}^{-1}$
II ( $\text{CO}_3$ )	$\nu_2$ 879 $\text{cm}^{-1}$ (IR)	$\nu_8$ ( $\text{B}_1$ ) 870 $\text{cm}^{-1}$
$\nu$ (C–O)	$\nu_1$ 1088 $\text{cm}^{-1}$ (R) $\nu_3$ 1492–1429 $\text{cm}^{-1}$ (IR)	$\nu_1$ ( $\text{A}_1$ ) and $\nu_5$ ( $\text{B}_2$ ) 1485–1390 $\text{cm}^{-1}$

R is Raman spectroscopy and A and B have the usual spectroscopic meaning.

Although diffusion of  $\text{CO}_2$  becomes a rate-determining step giving a lower frequency of the characteristic vibration, the reduction of the energy barrier is not as large, because of the increase in  $z$ .

The decomposition behaviour of  $\text{CdCO}_3$  is also different from that of  $\text{CaCO}_3$  because of the covalent bonding which is manifest in the splitting of the degenerate O–C–O deformation vibration giving  $\nu_1 = 738 \text{ cm}^{-1}$  and  $\nu_2 = 650 \text{ cm}^{-1}$  in the infrared spectrum. The vibrations are given a different numbering from that commonly used in vibrational spectroscopy [5] as a convenient measure for the present purpose. The covalence of  $\text{CdCO}_3$  is further shown by the appearance of  $\nu(\text{Cd–O})$  at  $290 \text{ cm}^{-1}$ . The  $\text{CO}_3^{2-}$  vibrations in  $\text{CdCO}_3$  are listed in Table 1, allowing a comparison with those of calcite.

A mechanistic transition at the degree of conversion  $\alpha_d$  when the temperature gradient becomes critical, will involve  $\nu_2 \rightarrow \nu_1$ , requiring  $\Delta z = 2$  because  $\nu_1 \gg \nu_2$ . The energy difference  $2\nu_2 - \nu_1$  would reduce self-cooling and increase the reaction rate after  $\alpha_d$ . Accordingly at a temperature  $T_t$  of the mechanistic transition (D  $\rightarrow$  R) the number of the reactant groups attaining the energy level of the activated state in the time interval of one second is no longer  $k_0(\text{D})$  calculated from  $\nu_2$  but  $[(2\nu_2 - \nu_1)/\nu_2]k_0(\text{D})$  (D and R refer to the diffusion and phase boundary reaction mechanisms respectively). The transition temperature  $T_t$  is given by the intersection of the Arrhenius slopes D and R(1) of Fig. 3.

Because a mechanistic transition must give the two mechanisms equal reaction rates ( $k(1) = k(\text{D})$ ), the number of reactant groups attaining the energy of the activated state per second must also be the same, i.e.

$$[(2\nu_2 - \nu_1)/\nu_2]k_0(\text{D}) = k_0(1) \quad (2)$$

Obviously eqn. (2) is only valid for the transition temperature  $T_t$ .

If for the rate constants  $k(1) = k(\text{D})$  the Arrhenius equation is given in the logarithmic form, we obtain

$$\ln k_0(\text{D}) - \ln k_0(1) = \frac{E_a(\text{D}) - E_a(1)}{RT_t} \quad (3)$$

where  $k_0(\text{D})$  and  $k_0(1)$  are the frequency factors obtained from the Arrhenius slopes D and R for the two mechanisms.

Because there are equal numbers of reactant groups with the energy of the activated state per second for the two mechanisms, the relationship

$$\ln k_0(1) - \ln k_0(\text{D}) = \frac{E_a(\text{D}) - E_a(1)}{RT_t} \quad (4)$$

should also be valid.

The expressions (2)–(4) allow the consistency of the observed frequency factor with the characteristic vibrations to be established and provide the theoretical basis of the equilibrium factor with which we previously explained the effect of self cooling [2].

## EXPERIMENTAL

The preparation of  $\text{CdCO}_3$  was according to a standard procedure [6]. The purity of the product was established by chemical analysis and X-ray diffraction of the preparation,  $\text{CdO}$  being obtained as the decomposition product.

A single decomposition step was indicated by thermogravimetry of the sample. For kinetic studies, the powdery product was used without additional grinding. The decomposition was carried out in a platinum crucible in a stream of dry nitrogen, using the same sample mass (34–36 mg) as in our previous studies [1,2].

## RESULTS AND DISCUSSION

The results from isothermal kinetic measurements at various temperatures are shown in Fig. 1 in the form of plots of  $\alpha$  against time.

The evaluation was according to the contracting cylinder model and one-dimensional diffusion, as in our previous studies [1,2].

Typical features of the  $g(\alpha)$  versus  $t$  plots are demonstrated in Fig. 2 for a decomposition temperature of 663.15 K. The increase in the rate constant in the second kinetic phase was explained in the theoretical introduction above. The Arrhenius plots of  $\ln k$  versus  $1/T$  shown in Fig. 3 give the activation energies  $E_a(1) = 124.71$ ,  $E_a(2) = 128.87$  and  $E_a(\text{D}) = 129.33$   $\text{kJ mol}^{-1}$ . Assuming  $E_a(\text{D}) = E_a(2)$ ,  $\Delta H = 98.23$   $\text{kJ mol}^{-1}$  is calculated for  $E_a(1) = \Delta H + 3\nu_1$  and  $E_a(\text{D}) = E_a(2) = \Delta H + 4\nu_2$ .

The transition temperature  $T_t = 786.16$  K is derived from the intersection of the Arrhenius slopes R(1) and D (Fig. 3). Using the transition temperature and the activation energy difference  $E_a(\text{D}) - E_a(1) = 4620$  J, eqn. (4) gives

$$\ln k_0(1) - \ln k_0(\text{D}) = 0.7066706 \quad (5)$$

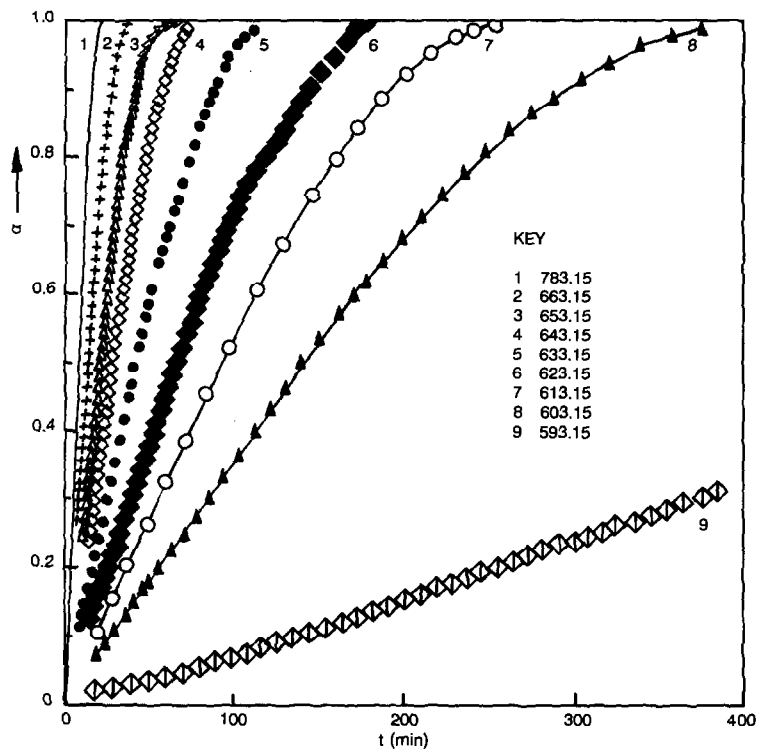


Fig. 1. Plots of  $\alpha$  vs time (min) for the decomposition of  $\text{CdCO}_3$  powder.

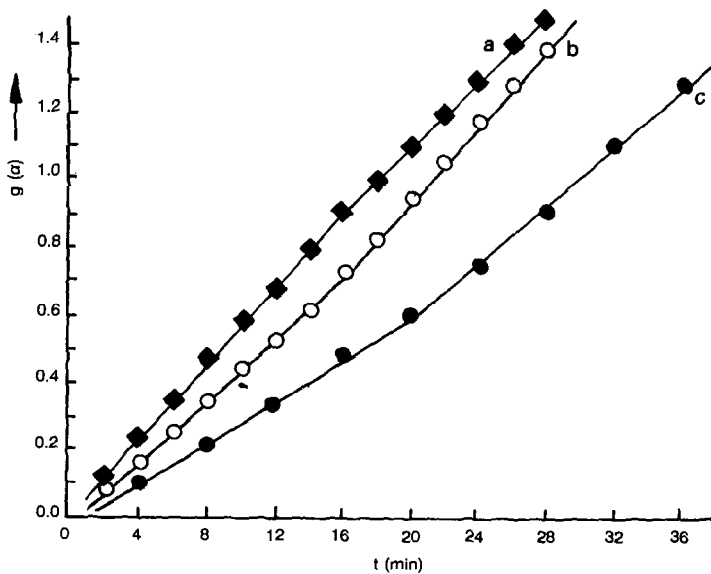


Fig. 2. The effect of sample subdivision on the features of the  $g(\alpha)$  vs  $t$  plots. Curve a,  $\text{CaCO}_3$  crystalline compact decomposed at 1053.15 K; curve b,  $\text{CdCO}_3$  powder decomposed at 663.15 K; curve c,  $\text{CaCO}_3$  powder decomposed at 973.15 K.

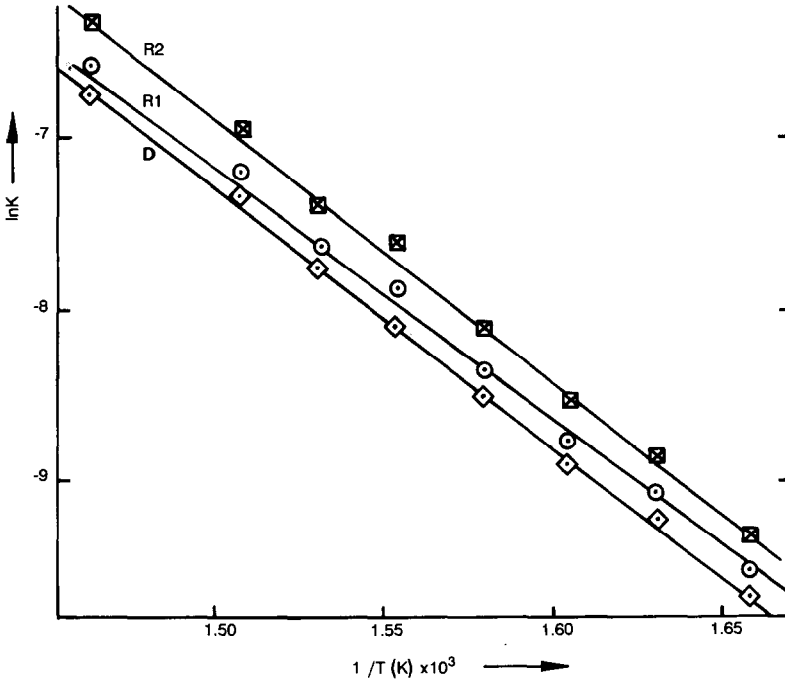


Fig. 3. The Arrhenius plots of  $1/T$  vs  $\ln k$  for isothermal decomposition of  $\text{CdCO}_3$  powder. The slopes for the phase boundary reaction mechanism are marked R(1) and R(2). D is the slope for a diffusion controlled reaction.

The natural logarithms of the frequency factors obtained from the Arrhenius plots are  $\ln k_0(1) = 15.36$  and  $\ln k_0(D) = 16.07$ . Using  $\ln k_0(D) = 30.60$  calculated from  $\nu = 650 \text{ cm}^{-1}$  and  $\ln k_0(D) = 16.07$ , we obtain  $\ln k_0(D) = 14.53$  and  $\ln k_0(1) = 15.24$  according to eqn. (5). The calculated natural logarithm of the frequency factor  $\ln k_0(1) = 30.60 - 15.24 = 15.36$ , is found to be identical with that found from the experiment.

Accordingly, the decomposition kinetics of  $\text{CdCO}_3$  powder is determined by the vibrations  $\nu_1 = 738 \text{ cm}^{-1}$  and  $\nu_2 = 650 \text{ cm}^{-1}$  of the O-C-O deformation vibrations of covalently bonded  $\text{CO}_3^{2+}$ . The mechanistic transition is in accordance with the vibrational transition  $\nu_2 \rightarrow \nu_1$  with  $\Delta z = 2$ . The excess energy  $2\nu_2 - \nu_1$  is responsible for the observed increase in the reaction rate constant in the second kinetic phase.

We can therefore conclude from the results that a  $\alpha_d$ , a stable continuous layer of  $\text{CdO}$  is formed around the  $\text{CdCO}_3$  grains. All the reaction temperatures are well below the transition temperature. Accordingly the sample retains the porosity necessary for the penetration of the hot furnace gas. The resulting efficient convective heat transport to the reactant by the furnace gas cancels the contribution  $\nu\Delta_2 z$  by the obstruction of convective heat transfer within the grains. As a result the energy barrier for the

second kinetic phase,  $\Delta H + 4\nu_2$ , is less than the  $\Delta H + 5\nu_2$  expected for  $\text{CdCO}_3$  crystalline compact. The reduction of the energy barrier by the subdivision of solid reactant is a matter of basic chemical experience.

The value of  $\Delta H = 98.23 \text{ kJ mol}^{-1}$  for the decomposition of  $\text{CdCO}_3$  at 768.16 K obtained from this study is identical with the value calculated with the thermochemical data according to Kubaschewski and Alcock [7]. Our approach to the energy barrier for the reactions of solids is thus neatly confirmed by our experimental results for the decomposition kinetics of  $\text{CdCO}_3$  powder.

#### ACKNOWLEDGEMENT

This work was supported with a generous financial support from NO-RAD, the Norwegian Agency for International Development.

#### REFERENCES

- 1 A.M. Mulokozi and E. Lugwisha, *Thermochim. Acta*, 194 (1992) 375.
- 2 A.M. Mulokozi (1991) *Thermochim. Acta*, 197 (1992) 363.
- 3 P.D. Garn, *J. Therm. Anal.*, 13 (1978) 581–593.
- 4 A.M. Mulokozi, in preparation.
- 5 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination compounds*, 3rd edn., Wiley, New York, 1978.
- 6 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. 2, 2nd edn., Academic Press, New York, 1965.
- 7 O. Kubaschewski and C.B. Alcock, *Metallurgical Thermochemistry*, 5th edn., Pergamon, Oxford, 1979.