ENERGY OF ACTIVATION FOR THE DECOMPOSITION OF THE ALKALINE-EARTH CARBONATES FROM THERMOGRAVIMETRIC DATA

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(Received March 24, 1971; in revised form May 18, 1971)

Activation energies for the vacuum thermal decomposition of calcium, strontium and barium carbonates have been determined from thermogravimetric data, using the Coats and Redfern equation. A computer program, written in 4100 Algol, was used to process the data and to obtain the order (n) of the decomposition reactions. In all three cases, a value of $n = \dfrac{2}{3}$ was in closest agreement with the experimental results, suggesting that decomposition occurs at a progressively shrinking spherical interface. The energies of activation obtained were in close agreement with the corresponding values of the enthalpy of decomposition, calculated at the temperature at which half of the sample had decomposed.

The decomposition of calcium carbonate has been extensively studied from a kinetic viewpoint (see for example refs [1—6]); two alternative mechanisms have been suggested to describe the decomposition process. Most workers consider that the rate of reaction is controlled by the movement of an interface between the two solid phases and that the rate equation can be expressed in the form:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{1}$$

where k = rate constant
  n = the so called "order of reaction" and
  α = the fraction of the carbonate decomposed at time t.
In thermogravimetric (TG) studies, this can be equated to w/w_F
where w = weight loss at time t and
  w_F = total weight loss.

The reaction has been shown to proceed by a mechanism which leads to either $\dfrac{1}{2}$ or $\dfrac{2}{3}$ order kinetics [1—3]; these orders of reaction (n) correspond respectively to the inwards movement of circular interface in a disc and to a progressively shrinking spherical interace. Britton et al. [4] have described in detail the effects that such factors as sample self cooling, rate of nucleation, etc., would have on the value of n obtained. In a more recent study on the decomposition of calcium

carbonate, Hills [5] has proposed that the reaction is not controlled by a chemical step at an interface, but by the rate of transfer of heat to the boundary of the reaction zone and by the rate of transfer of carbon dioxide away from it. However, the power law equation, given above, provides a satisfactory description of the data up to high values of the percentage decomposition. Values of the activation energy calculated by previous workers lie within the range $145-210$ kJ·mol^{-1}, the actual value depending on the experimental conditions used.

Little data appear to be available on the decomposition of the corresponding carbonates of strontium and barium, but such evidence as exists leads us to suppose that the mechanism of decomposition is similar to that for calcium carbonate. Values of the activation energy have been calculated from DTA data for these compounds by Garcia-Clavel et al. [7].

Of the two equations most widely used in obtaining kinetic data from TG measurements, it has been shown [6] that the equation of Freeman and Carroll [2] is less satisfactory in several respects. The equation due to Coats and Redfern [8] is generally preferable, but assumes a prior knowledge of the order of reaction. This, in itself, is not such a problem as might be expected, since the correct value for n is assumed to be the one which leads to a rectilinear graph.

These authors [9] have also used computer programs which do not assume a prior knowledge of the order of reaction.

This paper presents a kinetic investigation into the decomposition, under vacuum, of calcium, strontium and barium carbonates. Kinetic data are calculated from TG results using the equation of Coats and Redfern, which may be written in the form:

$$\log_{10}\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303\,RT} \tag{2}$$

where α = the fraction of the sample decomposed at time t
n = the order of reaction
T = temperature (°K)
A = pre-exponential factor
R = the gas constant
E = the activation energy
a = conversion factor to transfer from a time scale to a temperature scale,

$$\text{i.e.}\quad a = \frac{dT}{dt} \tag{3}$$

The above equation (2) holds for all values of n except where $n=1$; in which case the equation becomes:

$$\log_{10}\left[-\log_{10}\frac{(1-\alpha)}{T^2}\right] = \text{R.H.S. of Eq. (2)} \tag{4}$$

If it is assumed that the expression $\log_{10} \dfrac{AR}{aE} \left[1 - \dfrac{2RT}{E} \right]$ remains constant over the temperature range of the decomposition, then a plot of either

(a) $\log_{10} \left[\dfrac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right]$ against $1/T$

or

(b) $\log_{10} \left[-\log_{10} \dfrac{(1 - \alpha)}{T^2} \right]$ against $1/T$ for $n = 1$

should result in a straight line, of slope $-E/2.303\ R$.

A computer program has been written for the calculation of kinetic data from the Coats and Redfern equation, in which the data can be cycled for any value of n until the best linear fit is obtained (by the method of least mean squares). For this program, the authors are indebted to Mr. R. K. Cosgrove. Copies of the program, written in 4100 Algol, can be obtained, upon request, from the authors.

Experimental

The samples of calcium, strontium and barium carbonate were "Spec Pure" grade supplied by Johnson Matthey & Company Limited, London. Even though the concentration of other metals present are quoted to be less than 5 p.p.m., it has been shown previously [10, 11] that both the strontium and barium carbonates contain some hydroxide impurity (approx. 5% in the case of strontium carbonate). These carbonates were therefore heated, under vacuum, to a temperature at which the hydroxides had decomposed to the oxide, and then exposed to an atmosphere of carbon dioxide. The samples were cooled to room temperature and allowed to stand overnight under carbon dioxide. This treatment has been shown [11] to give a sample free from any hydroxide impurity.

TG studies were carried out using the quartz spring balance described elsewhere [9]. Samples (ca. 500 mg) were contained in nickel buckets (15 × 13 mm dia.) and heated, under high vacuum (ca. 10^{-4} torr when no decomposition was taking place), at a heating rate of 200°/hr. The temperature was measured outside the balance tube adjacent to the sample; ideally the actual temperature of the sample should be recorded, but this proved impracticable with the existing apparatus.

Results and discussion

In published work on the thermal decomposition of calcium carbonate, two values of n appear to be most favoured. These are $n = \dfrac{1}{2}$ and $\dfrac{2}{3}$, which correspond

to the movement of an interface in a circular disc or sphere respectively. However, it has been shown [4] that the rate of the decomposition process can be affected by a variety of factors, including the mass and geometry of the sample, the dimensions of the sample container and the ambient atmosphere. Accordingly, values of n corresponding to the various possible models for the decomposition mechanism were inserted into the computer program, together with TG data for calcium carbonate. The best rectilinear graph was obtained for $n = \dfrac{2}{3}$ (see Fig. 1), while the other most probable value of $n = \dfrac{1}{2}$ gives rise to a pronounced curve. This result suggests that under the experimental conditions used, the decomposition
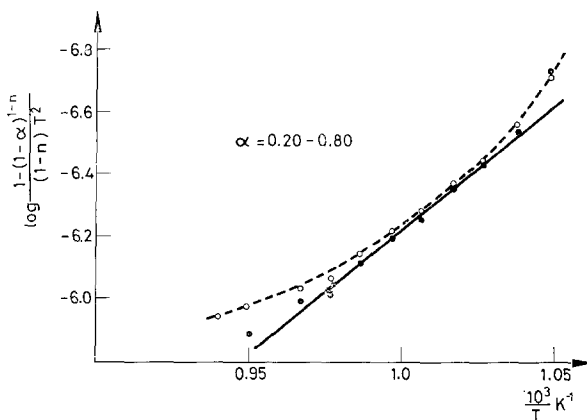

Fig. 1. Activation energy plot for calcium carbonate: $\circ\, n = \dfrac{1}{2}$; $\bullet\, n = \dfrac{2}{3}$

of calcium carbonate is more reasonably represented by the contracting sphere model. The activation energy was calculated from the slope of the best straight line, analysed by the method of least mean squares, using the computer program previously referred to. This led to a value of 180 (± 13) kJ mol^{-1} for the decomposition of calcium carbonate; the figure obtained thus lies near the mean of the range of values (145−210 kJ mol^{-1}) reported in the literature.

For the decomposition of strontium and barium carbonates, the experimental conditions were kept as near as possible to those used for calcium carbonate. The TG data were substituted into the Coats and Redfern equation using the various possible values of n; in both cases the best rectilinear graph was obtained for $n = \dfrac{2}{3}$. The calculated results for heat treated samples of strontium and barium carbonate are shown as the open points in Figs 2 and 3. As can be seen, good rectilinear plots are obtained which held over a large range of α. The

values of the activation energy calculated are 222 ($\pm$13) kJ mol^{-1} for strontium carbonate and 283 ($\pm$17) kJ mol^{-1} for barium carbonate. These figures are in reasonably good agreement with the values reported by Garcia-Clavel et al. [6] which were 224 and 258 kJ mol^{-1} respectively.
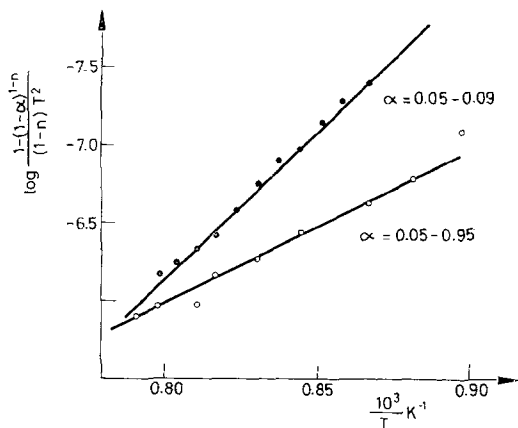
Fig. 2. Activation energy plot for strontium carbonate, $n = \dfrac{2}{3}$; $\bigcirc$ heat treated sample; ● "Spec Pure" sample
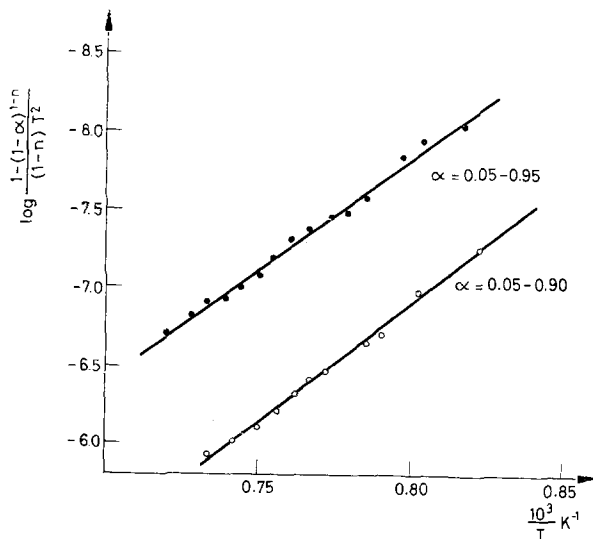
Fig. 3. Activation energy plot for barium carbonate, $n = \dfrac{2}{3}$; $\bigcirc$ heat treated sample; ● "Spec Pure" sample

3*

The closed points in Figs 2 and 3 refer to the non-heat treated samples of strontium and barium carbonate. With barium carbonate, although the carbon dioxide treatment lowers the onset temperature [11] for the decomposition, the activation energy calculated (267 ± 13 kJ mol^{-1}) agrees, within the experimental error, with that for the heat treated sample (283 ± 17). This suggests that the small amount of barium oxide, formed by decomposition of the hydroxide impurity, has little effect on the decomposition process. With strontium carbonate, however, the effect of heat treatment is much more pronounced; the energy of activation calculated for the original material (352 ± 21 kJ mol^{-1}) is considerably higher than the value (222 ± 13) for the heat treated sample. It therefore appears that the presence of strontium oxide (ca 5%) from the hydroxide impurity has in some way inhibited the decomposition process. The reasons for this marked difference are, as yet, not readily apparent. However, it may be relevant to note the work of Brown [12] who, in looking at the sintering of calcium oxide, showed that the presence of $1-5\%$ SrO in the calcium oxide increases the energy of activation for the sintering process from 184 to 322 kJ mol^{-1}.

Previous workers [1, 4, 5] have observed that the value of the activation energy for the decomposition of calcium carbonate is in close agreement with the value of the enthalpy of decomposition (ΔH). Table 1 lists the activation energy values calculated for calcium carbonate and heat treated samples of strontium and barium carbonate and compares these to values of ΔH. The figures for ΔH were

Table 1

Comparison of the calculated activation energy with the enthalpy of decomposition for the alkaline-earth carbonates

Compound	Decomposition range °C	α	Activation energy kJ mol^{-1}	*+ Enthalpy of reaction kJ mol^{-1}
CaCO$_3$	$500-1000$	$0.20-0.85$	$180\ (\pm 13)$	167 (G 750 °C)
SrCO$_3$	$750-1020$	$0.05-0.95$	$222\ (\pm 13)$	236 (G 930 °C)
BaCO$_3$	$830-1100$	$0.05-0.90$	$283\ (\pm 17)$	260 (G 1030 °C)

+ Enthalpy data were calculated from the standard values for the enthalpy of reaction, using the following equations:

lit. ref.

[14]	CaCO$_3$	$Cp = 104.42 + 21.90 \times 10^{-3}\,T + 25.92 \times 10^5\,T^{-2}$ J mol^{-1} K^{-1}
[15]	SrCO$_3$	$= 89.54 + 35.78 \times 10^{-3}\,T - 14.20 \times 10^5\,T^{-2}$,,
[15]	BaCO$_3$	$= 86.82 + 48.91 \times 10^{-3}\,T - 11.96 \times 10^5\,T^{-2}$,,
[14]	CaO	$= 48.78 + 4.51 \times 10^{-3}\,T + 6.52 \times 10^5\,T^{-2}$,,
[15]	SrO	$= 51.58 + 4.68 \times 10^{-3}\,T - 7.55 \times 10^3\,T^{-2}$,,
[15]	BaO	$= 53.25 + 4.35 \times 10^{-3}\,T - 8.29 \times 10^5\,T^{-2}$,,
[14]	CO$_2$	$= 26.83 + 43.47 \times 10^{-3}\,T - 14.80 \times 10^{-6}\,T^2$,,

* Enthalpy data refer to the temperature of the mid point of the reaction, i.e. at a value of $\alpha = 0.50$.

calculated from the standard enthalpy changes, using Kirchoff's law to obtain the values of ΔH corresponding to the reaction temperature. Since the decomposition occurs over a wide temperature range, the reaction temperature was taken as the temperature for the mid point of the decomposition, as suggested by Ingraham and Marier [1]. It can be seen that, within the experimental error, good agreement is obtained between the observed activation energy and the calculated value for ΔH.

One conclusion which has been drawn [1, 4, 13] from this apparent agreement is that the reverse reaction, i.e. the recombination of the oxide and carbon dioxide to form the carbonate, must involve zero energy of activation. In the case of zinc carbonate, where the dissociation is irreversible, the activation energy is considerably greater [13] than the heat of reaction. Hills [5] has made a theoretical study of the mechanisms of decomposition of calcium carbonate, which led him to conclude that the energy of activation is equal to the enthalpy of decomposition because the reaction rate is governed by the rate of heat transfer to the reaction zone.

Conclusion

Activation energies have been determined for the decomposition of calcium, strontium and barium carbonate. These results have been obtained by substituting TG data into the Coats and Redfern equation, using a value of $\dfrac{2}{3}$ for the order of reaction.

The activation energies so determined agree closely with calculated values of ΔH, the enthalpy of reaction at the mid point of the decomposition. It therefore appears that the mechanism, postulated by Hills [5] for calcium carbonate, may also be applicable to strontium and barium carbonates.

In the case of strontium carbonate, the value of the activation energy determined for a sample known to contain hydroxide as an impurity, is considerably higher than that for the pure carbonate. This observation accords with the work of Brown [12], who has shown that the presence of strontium oxide in the carbonate leads to a greatly increased energy of activation for sintering.

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RÉSUMÉ — On a déterminé les valeurs de l'énergie d'activation des carbonates de calcium, strontium et baryum en appliquant l'équation de Coats et Redfern aux données thermogravimétriques pendant la décomposition thermique sous vide. Le programme du calculateur a été établi en langage Algol 4100 pour le traitement des données et l'obtention de l'ordre n de la réaction de décomposition. Dans les trois cas, la valeur $n = 2/3$ a donné le meilleur accord avec les résultats expérimentaux, montrant que la décomposition se produit par contraction progressive de l'interface sphérique. Les valeurs de l'énergie d'activation obtenues sont en bon accord avec les valeurs correspondantes de l'enthalpie de décomposition calculée à la température de demi-décomposition.

ZUSAMMENFASSUNG — Die Aktivierungsenergiewerte der thermischen Zersetzung von Kalzium-, Strontium- und Bariumkarbonat im Vacuum wurden aus den thermogravimetrischen Daten mit Hilfe der Coats—Redfern Gleichung errechnet. Ein Computerprogramm in 4100 Algol wurde zur Bearbeitung der Daten und der Ermittlung der Ordnungszahl (n) der Zersetzungsreaktion gebraucht. In allen drei Fällen war der gefundene Wert $n = 2/3$ in bester Übereinstimmung mit den experimentellen Resultaten, hinweisend, daß die Zersetzung bei allmählich sinternden sphärischen Zwischenflächen verläuft. Die erhaltenen Aktivierungsenergiewerte standen im Einklang mit den Enthalpiewerten gerechnet bei der Temperatur, bei welcher die Hälfte der Probe zersetzt war.

Резюме — Определены энергии активации термораспада карбонатов кальция, стронция и бария в вакууме на основании термогравиметрических данных с использованием уравнения Котса и Редферна. Использована компьютерпрограмма, описанная в 4100 Алголь, и получен порядок (n) реакции разложения. Во всех трех случаях величина $n = 2/3$ что хорошо совпадает с экспериментальными результатами в предположении, что реакция происходит на постепенно сморщивающейся сферической предельной поверхности. Полученные величины энергии активации хорошо совпадают с соответствующими величинами энтальпии распада, расчитанной при температуре, при которой половина образца разложена.