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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA

VII. THERMAL DECOMPOSITION OF CALCIUM CARBONATE

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Fifteen thermogravimetric curves of the thermal decomposition of $CaCO_3$ reported in the literature have been analysed and kinetic parameters have been derived by means of Coats and Redfern's method. The activation energy varies between 26 and 377 kcal/mole, and the pre-exponential factors between 10^2 and 10^{69}, as functions of the working conditions. The kinetic compensation effect has been observed, and the results are well described by the following empirical compensation law: $\log Z = 0.195E - 1.86$.

The kinetics of the thermal decomposition of $CaCO_3$ have been studied by many authors. This process cannot generally be described by means of a simple kinetic law [1, 2]. Many attempts have been made to elucidate the mechanism of the thermal decomposition [3–7]. The activation energy is presumed by some authors to equal the reaction enthalpy, which is about 40 kcal/mole [8]. On the basis of isothermal kinetic measurements, various values have been reported for the activation energy, e.g. 35–42 [9], 40.8–44.3 [10], 48.7 [11] and 37.0 kcal/mole [12], which are indeed close to the reaction enthalpy. Experiments with marble blocks have given 38.4 and 41.6 kcal/mole in a N_2 atmosphere and 29.3 kcal/mole in vacuo [13].

In the case of calcite monocrystals two kinetic stages have been observed. The first stage has $E_a = 38$ kcal/mole in the case of untreated crystals, and $E_a = 27$ kcal/mole for quenched ones. The second stage needs $E_a = 51$ and $E_a = 48$ kcal/mole for the untreated and quenched crystals, respectively [14]. These values are rather scattered and clearly show the dependence of the activation energy on the working conditions, the source of the sample, etc. Obviously, it is not a simple task to elucidate the clear physical significance of the activation energies obtained.

In the past 10–15 years the "non-isothermal" methods have largely been used to derive kinetic parameters from experimental data obtained under dynamic temperature conditions, mainly from thermogravimetric data. It is well-known that the shapes of thermogravimetric curves, and consequently also the values of the kinetic parameters derived from these curves, depend very much on procedural variables such as the heating rate, the shape and material of the sample holder, the sample weight, the nature of the atmosphere, etc. [15]. It is not surprising that activation energies derived by means of different calculation techniques from thermogravimetric data are much more scattered than those obtained from isothermal studies. Values reported for E_a oscillate between 11 and 95 kcal/mole [7, 16–18]. It is clear that this E_a cannot have the same meaning as the activation energy in homogeneous kinetics. In a previous paper [19] we have discussed the basic principles of non-isothermal kinetics and have shown that "kinetic parameters" derived from TG curves have only the value of variational parameters, which enables us to give the approximate equation of the TG curves. The physical meaning of these parameters is rather obscure and, based on TG measurements only, one can tell nothing about them.

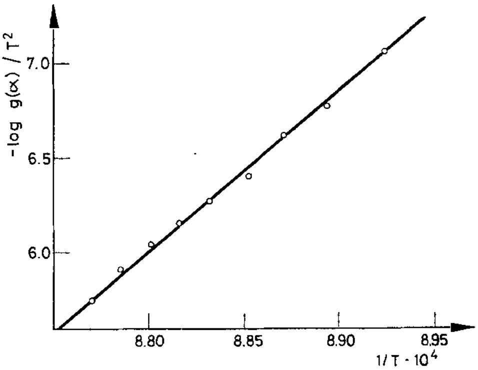

Fig. 1. Coats–Redfern linearization of a TG curve [7]
p_{CO_2} = 200 mmHg; q = 0.83°C/min; n = 1

The "thermal decomposition of $CaCO_3$ under dynamic temperature conditions" cannot be characterized by means of a single set of kinetic parameters such as activation energy E, pre-exponential Arrhenius factor Z and reaction order n. These parameters will vary between very wide limits depending on the working conditions.

In the present paper 15 thermogravimetric curves, published by different authors, have been analysed. 5 curves have been taken from [20] (Diagrams 20, 21 and 35), 4 from [21] (Fig. 7, curves 4, 5, 6 and 8) and 6 from [7]. These curves were recorded under very different conditions and the sample was synthetic $CaCO_3$ in some cases, and dolomite or calcium oxalate monohydrate in others, where the last stage of reaction is also the decomposition of $CaCO_3$.

Calculations have been carried out by means of Coats and Redfern's method [16], which has been shown to be correct and rapid [19]. Conversion functions of the type

$$f(\alpha) = (1 - \alpha)^n \tag{1}$$

have been tried with n = 0, 1/3, 1/2, 2/3, 1 and 2 (α stands for the transformation degree).

For the calculation of Z the following equation has been used [22]:

$$\log Z = \log g(\alpha) - \log p(x) + \log Rq - \log E_a \tag{2}$$

where $g(\alpha)$ stands for the conversion function given in [22], $p(x)$ for the exponential integrals tabulated in [22, 23], x for E_a/RT and q for the heating rate.

In the majority of the cases the Coats–Redfern graphical representation yields a single straight line for a given n value.

The rather good linearity shows the possibility of characterizing *TG* curves by means of 3 variational parameters. One example of this linearization is given in Fig. 1.

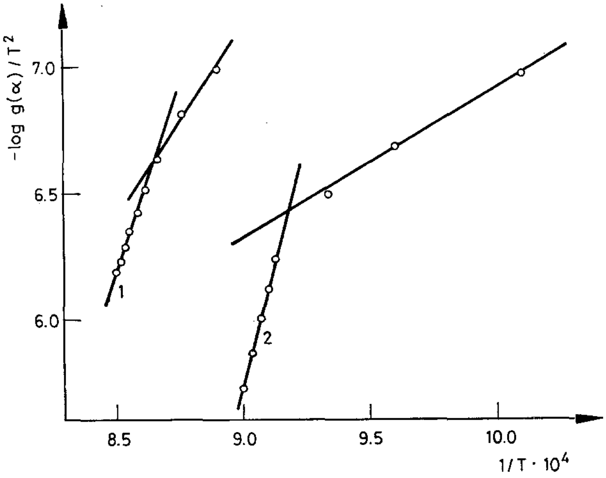

Fig. 2. Coats–Redfern linearization
1 — curve 6 from [21], $n = 0$; 2 — curve 4 from [21], $n = 1$

In two cases, curves 4 and 6 from [21], the process seems to be composed of two distinct kinetic stages, as seen from Fig. 2. Kinetic parameters have been derived for both stages.

Results are presented in Table 1, where the working conditions are also indicated.

As seen from this Table, n varies between 0 and 1. The activation energy and the pre-exponential factor exhibit very large variations and can have enormous values. Surprisingly high values have been obtained for the thermal decomposition in a CO_2 atmosphere at low pressures, where the reaction is very fast and occurs in a very narrow temperature interval.

In all cases when only the heating rate is different, one can observe the decrease of the activation energy and of Z with increasing heating rate, as reported earlier for other compounds [24, 25].

Table 1

Kinetic parameters of the thermal decomposition of $CaCO_3$, derived from TG curves

Atmosphere	p, mmHg	q, °C/min	n	E kcal/mole	log Z	Source
Air	760	10	0	37.1	4.2	[20], diagr. 20
Air	760	3	1	58.7	10.0	[20], diagr. 20
Air	760	10	1/3	52.7	8.4	[20], diagr. 21
Air	760	3	0	61.6	9.8	[20], diagr. 21
Air	760	10	1	75.5	12.9	[20], diagr. 35
Air	760	10	1	26.3	2.2	[21], curve 4, stage 1
Air	760	10	1	177.3	33.5	[21], curve 4, stage 2
Air	769	10	0	41.9	5.3	[21], curve 5
Air	760	10	0	70.9	10.6	[21], curve 6, stage 1
Air	760	10	0	132.7	22.6	[21], curve 6, stage 2
Air	760	10	0	79.6	16.7	[21], curve 8
CO_2	200	0.83	1	377.5	68.9	[7]
CO_2	75	1.22	1	251.7	47.3	[7]
CO_2	75	0.36	2/3	310.0	58.5	[7]
CO_2	43	0.43	1	289.4	55.7	[7]
CO_2	23.5	2	1	169.3	32.2	[7]
CO_2	23.5	0.93	1	201.3	39.2	[7]

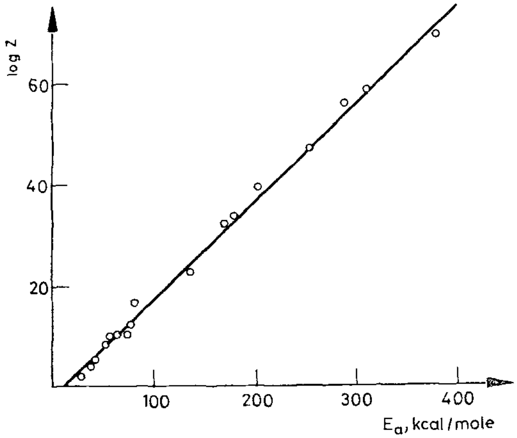

Fig. 3. Kinetic compensation effect in the thermal decomposition of $CaCO_3$

It is obvious that the great differences in the kinetic parameters do not arise because of the calculation techniques. They are inherent in the process and characterize not only the substance decomposed but also the working conditions used.

Although the activation energies show a variation exceeding one order of magnitude, and the pre-exponential factors vary by more than 60 orders of magnitudes, these parameters are not independent of each other. If higher activation energies are obtained, the pre-exponential factors are higher too. This is a manifestation of the kinetic compensation effect [26–28].

The graphical plot of $\log Z$ versus E (Fig. 3), shows the validity of a linear kinetic compensation law of the following type

$$\log Z = aE + b \tag{3}$$

The following values of the parameters a and b of this straight line have been obtained by means of the least square method:

$$a = 0.195 \text{ mole/kcal}, \quad b = -1.86$$

These values are very close to those derived by Pavlyuchenko et al. [26] by using literature data obtained under isothermal conditions, but much smaller than those reported earlier for the thermal decomposition of certain cobalt complexes [27, 28].

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RÉSUMÉ — On a calculé les paramètres cinétiques de la décomposition thermique de $CaCO_3$ en suivant la méthode de Coats et Redfern et en utilisant 15 courbes thermogravimétriques publiées dans la littérature. L'énergie d'activation varie entre 26 et 377 kcal/mol, les fac teurs préexponentiels entre 10^2 et 10^{69}, suivant les conditions opératoires. On a observé l'effet de compensation cinétique et les résultats peuvent être décrits par la loi empirique suivante: $\log Z = 0.195E - 1.86$.

ZUSAMMENFASSUNG — Fünfzehn, in der Literatur veröffentlichte thermogravimetrische Kurven der thermischen Zersetzung des $CaCO_3$ wurden analysiert und kinetische Parameter unter Anwendung der Methode von Coats und Redfern abgeleitet. Die Aktivierungsenergie schwankt zwischen 26 und 377 kcal/Mol, die prä-exponentiellen Faktoren zwischen 10^2 und 10^{69}, je nach den Arbeitsbedingungen. Der kinetische Kompensationseffekt wurde beobachtet und die Ergebnisse lassen sich mit dem folgenden empirischen Kompensationsgesetz gut beschreiben: $\log Z = 0.195E - 1.86$.

Резюме — Проанализированы 15 термогравиметрических кривых термораспада $CaCO_3$, опубликованных в литературе, и по методу Котса и Редферна рассчитаны кинетические параметры в зависимости от условий эксперимента. Энергия активации колеблется между 26 и 377 ккал/мол, преэкспоненциальные факторы — между 10^2 и 10^{69}. Наблюдается эффект кинетической компенсации и результаты удовлетворительно описываются следующим эмпирическим законом компенсации: $\log Z = 0{,}195\, E - 1{,}86$.