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THE KINETIC COMPENSATION EFFECT IN THE DECOMPOSITION OF CALCIUM CARBONATE

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Some specific factors which may cause the kinetic compensation effect (k.c.e.) during the decomposition of $CaCO_3$ are identified. The role of the CO_2 equilibrium pressure is examined in relation to the k.c.e. The article also shows why non-isothermal experiments must sometimes necessarily yield a value of activation energy different from the value obtained from isothermal experiments.

It is known that the experimentally determined value of activation energy depends on several factors associated with the experimental technique and sample characteristics, especially when kinetic experiments are carried out under rising temperature conditions [1]. It has often been noted that the variation of the experimentally determined value of E is accompanied by a corresponding variation in the experimentally determined value of the pre-exponential factor A and there is a linear relationship between log A and E. This is called the kinetic compensation effect (k.c.e.). In recent years, this effect has been the subject of several investigations [2–8]. However, it has not yet been properly explained and considerable confusion persists regarding its origin and implications.

For calcium carbonate decomposition, the experimentally determined apparent values of E and A can vary in the ranges 100–4000 kJ/mole and 10^2-10^{69}, respectively [1]. Such variations cannot be arbitrary and must be attributed to specific factors. The aim of the present work is to re-examine the origins of the k.c.e. critically, identify some specific factors and then show why variations of A and E follow a compensation law. In this article, the role of the CO_2 pressure, among others, is brought out in explaining the k.c.e. The article also shows why non-isothermal experiments must sometimes necessarily yield a value of activation energy significantly different from the value obtained from isothermal experiments.

Arrhenius equation for $CaCO_3$ decomposition

The Arrhenius expression for variation of the rate constant with temperature is written as

$$k = A \,.\, \exp\,(-E/RT) \tag{1}$$

where k is the rate constant and A and E are the Arrhenius parameters, both assumed constant. During actual reactions, such as the decomposition of $CaCO_3$, k is not determined by temperature alone. Amongst other factors, the particle size as well as the thermodynamic driving force of a reaction influence k. For $CaCO_3$ decomposition the thermodynamic driving force is described in terms of the concentration of CO_2 in the ambient atmosphere and the equilibrium concentration of CO_2 at the gas/solid interface where thermodynamic equilibrium for decomposition prevails, the exact form of the equation being dependent on the reaction mechanism.

Modification of Eq. (1)

Equation (1) can be modified to account for the effects of various factors on the rate constant. Thus, if the reaction rate is proportional to the surface area of the particles, then k can be shown to be proportional to $1/r_0$, where r_0 is the initial radius of the particles, all assumed spherical and uniform. Again, if the rate is proportional to the thermodynamic driving force, then k will be proportional to $(C^e - C)$, where C^e is the equilibrium concentration of CO_2 at the gas/solid interface and C is the concentration in the bulk gas at a given temperature. We can therefore write

$$\begin{aligned} k &= \frac{A}{r_0}(C^e - C)e^{E/RT} \\ &= \frac{A}{r_0}\frac{(p^e - p)}{RT}e^{-E/RT} \qquad (2) \end{aligned}$$

where p^e = equilibrium pressure of CO_2
p = pressure of CO_2 in gas stream

The possible effects of several other factors can similarly be incorporated. It should be noted that Eq. (2) has been written for a sample in which all particles are spherical and of uniform radius. In an actual situation a size distribution will be involved. The effect of the particle size distribution on the reaction rate has recently been discussed by Lahiri [9]. This article is concerned with variations in the apparent values of Arrhenius parameters because of changes in the value p^e.

Apparent values of Arrhenius parameters

Suppose that the apparent values of the Arrhenius parameters are A' and E'. That is

$$k = A' \cdot e^{-E'/RT} = \frac{A}{r_0}\,\frac{(p^e - p)}{RT} \cdot e^{-E/RT} \qquad (3)$$

We can calculate values of A' and E' (to examine their relationship) for given values of A/r_0, p^e, p, T, etc.

Consider first the decomposition of $CaCO_3$ in a CO_2-free atmosphere, i.e. when $p = 0$. Let us also assume, arbitrarily, that A/r_0 equals 10^{14}. Then

$$A' e^{-E'/RT} = \frac{10^{14} \cdot p^e}{RT} e^{-E/RT} \tag{4}$$

The equilibrium CO_2 pressures over $CaCO_3$ at various temperatures are available in the literature [10]. One can thus calculate values of E' for arbitrary values of A' using Eq. (4). Some calculated values for $E = 209.2$ kJ/mole and three temperatures are shown in Table 1. Figure 1 shows that semi-log plots of these values conform to the compensation law. The linearity is obvious in Eq. (4) itself. At a particular temperature and for an assumed value of E the right-hand side of Eq. (4) is a constant (k). Obviously, therefore, if one varies A', E' must also vary according to the compensation law.

Consider now the decomposition of $CaCO_3$ in a pure CO_2 atmosphere at 1 atm. There will, of course, be no decomposition until the equilibrium pressure p^e exceeds 1 atm, i.e. until about 900°. Consider a temperature of 1100°, at which p^e is about 1.6 atm and $(p^e - p)$ is about 0.6 atm. The values of E' for some assumed values of A' are shown in Table 1. A semi-log plot of these values is shown in Fig. 1. This linearity should also be obvious from Eq. (3), where the right-hand side becomes constant (k) for assumed values of A/r_0, p and tempera-

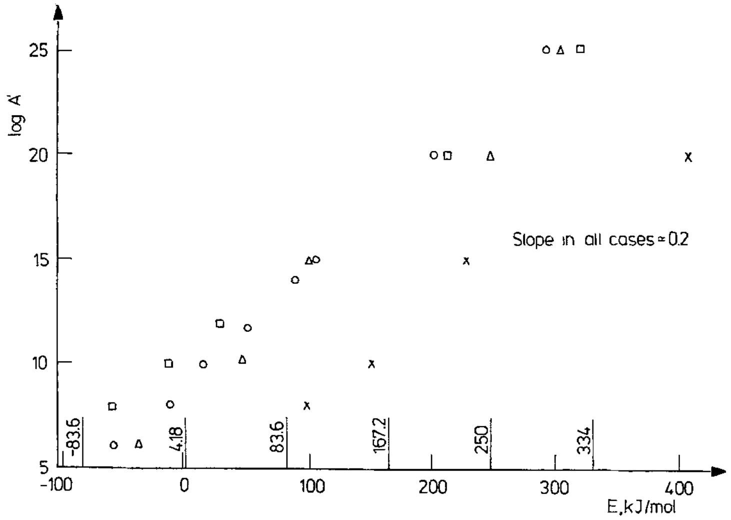

Fig. 1. The kinetic compensation effect

CO_2-free atm
○ 973 K $p^e_{CO_2} = 0.04$ atm
△ 1073 K $p^e_{CO_2} = 0.20$ atm
□ 1173 K $p^e_{CO_2} = 0.95$ atm
$A = 10^{14}$ $E = 209.2$ kJ/mole

CO_2 atm
1073 K $p^e_{CO_2} = 1.6$ atm
$A = 10^{14}$ $E = 209$ kJ/mol

ture, provided E is constant. The slopes of the lines shown in Fig. 1 agree closely with those reported in the plots given by Gallagher and Johnson [1]. In these calculations the pre-exponential factor is being changed because of the variation of some parameters and we are essentially calculating apparent values A' and E' (both variable) by assuming that the Arrhenius type expression still holds. The question, however, remains as to why A' should vary at all. Perhaps it so varies because A/r_0, which is assumed to be constant in the derivation, is not constant due to progressive decrease in the particle size.

Apparent activation energy

Consider now the non-isothermal decomposition of $CaCO_3$ so that p^e changes continuously during heating. Assuming that A/r_0 is constant at 10^{14}, the $\log_e k$ values at different temperatures can be calculated. These values are shown in Table 2.

We can plot an 'Arrhenius plot' using these values of $\log_e k$, i.e. plot $\log_e k$ values against reciprocal absolute temperature. The plot is shown in Fig. 2. Sur-

Table 1

Calculation of apparent activation energy E′ for varying values of A′ using Eq. (5)

$A = 10^{14}$, $E = 209.2$ kJ/mole; CO_2-free atmosphere (i. e. $p_{CO_2} = 0$)

T, K	$p^e_{CO_2}$, atm	A'	E', kJ/mole
973	0.04	10^6	−61.9
		10^8	−24.4
		10^{12}	50.6
		10^{15}	106.7
		10^{25}	294.3
1073	0.20	10^8	−40.6
		10^{12}	42.3
		10^{20}	207.5
		10^{25}	310.9
1173	0.95	10^8	−61.2
		10^{12}	31.7
		10^{20}	212.5
		10^{25}	325.5
CO_2 atm. (i. e. $p_{CO_2} = 1$ atm)		10^4	8.7
1373	1.6	10^{10}	149.8
		10^{20}	414.6
		10^{25}	546.8

Table 2

Apparent activation energy during non-isothermal decomposition ($p^e_{CO_2}$ varying)

$A/r_0 = 10^{14}$, $E = 209.2$ kJ/mole, $p_{CO_2} = 0$

T, K	$p^e_{CO_2}$, atm	k	$\log_e k$	$1000/T$, K
973	0.04	2.0033×10^9	21.418	1.0277
1073	0.20	9.105×10^9	22.932	0.93197
1173	0.95	3.964×10^{10}	24.403	0.8525

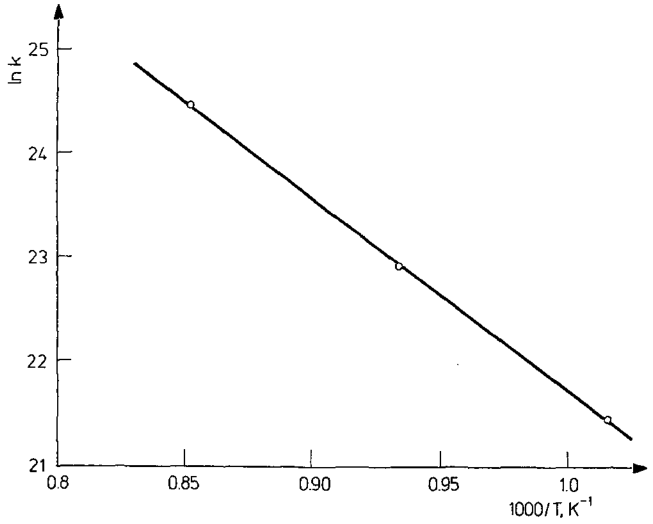

Fig. 2. The Arrhenius plot

prisingly, even with variations of p^e the plot comes out linear. However, the slope yields for the value of E' a much smaller value, approximately 154.8 kJ/mole, as compared to the value 209.2 kJ/mole assumed for E. This shows why one may get a different value of activation energy from the analysis of non-isothermal data. The data for Table 2 assume that A/r_0 is constant. If there is a change in the size distribution of the particles, and therefore, the average size during the course of heating, then this condition will no longer hold. Recently, Dollimore [11] has pointed out that many decomposition reactions can be accompanied by splitting of particles and consequently a decrease in the particle size and an increase in the particle number. This, of course, will introduce some scatter of the data in the compensation plot.

Conclusions

It is shown that the kinetic compensation effect can be explained if one takes proper account of the various factors which influence the rate constant of a decomposition reaction. One must consider, amongst other factors, the dynamic driving force. It is also found that if one takes into account the variation of the equilibrium CO_2 pressure during the heating of $CaCO_3$, then one can show that the apparent value of the activation energy for decomposition would be different from the true value determined from isothermal experiments.

Symbols

A = Pre-exponential factor in Arrhenius expression
A' = Apparent value of A
C = Concentration of CO_2 in bulk gas
C^e = Concentration of CO_2 at gas/solid interface at equilibrium
E = Activation energy
E' = Apparent value of activation energy
k = Rate constant
p = Partial pressure of CO_2 in bulk gas
p^e = Equilibrium partial pressure of CO_2
r_0 = Radius of particles (all assumed spherical and uniform)
R = The gas constant
T = Temperature, K.

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Zusammenfassung — Einige spezifische Faktoren, welche den sogenannten kinetischen Kompensationseffekt (k. c. e.) während der Zersetzung von $CaCO_3$ herbeiführen können, werden identifiziert. Die Rolle des Gleichgewichtsdruckes des CO_2 wird im Zusammenhang mit dem k. c. e. geprüft. Der Beitrag zeigt, warum die nicht-isothermen Versuche manchmal zwangläufig zu einem von den isothermen Versuchen abweichenden Wert der Aktivierungsenergie führen.

Резюме — Установлены некоторые специфические факторы, вызывающие так называемый кинетический компенсационный эффект (к. к. э) при разложении карбоната кальция. Исследована роль давления CO_2 в равновесной системе по отношению к к. к. э. Показано, что вследствии чего неизотермические измерения иногда дают значения энергии активации, отличающиеся от значений, полученных при изотермически измерениях.