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Kinetic parameters in heterogeneous kinetics

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Abstract

The energy barrier model, which has been quite successful in describing homogeneous kinetics, also applies in heterogeneous kinetics. This becomes evident when the activation energy E_a is split into an invariant component ΔH, the enthalpy change of the reaction, and a variable term $z_i\nu$ which gives the variation of the vibrational states according to a characteristic vibration of the reactant. The activation energy becomes $E_a = \Delta H + z_i\nu$, where z_i is a multiple of the characteristic vibration. The energy barrier models are described for the decomposition of calcite according to $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ and potassium oxalate according to $K_2C_2O_4 \rightarrow K_2CO_3(s) + CO(g)$. The results show that the activation energy and the frequency factor k_0 are consistent with the chemical reactions under the prevailing reaction conditions.

INTRODUCTION

Two important criteria can be employed to assess the physical significance of kinetic parameters. The first concerns the relevance of the activation energy E_a to the chemical transformations of the rate-determining step. The second is the consistency of the frequency factor k_0 with the characteristic vibration of the decomposing group. Typical vibrations have frequencies in the infrared and Raman spectra between 200 and 1800 cm^{-1} and hence reasonable frequency factors should be in range of 6×10^{12}–5.4×10^{13} s^{-1}.

In heterogeneous kinetics, the activation energy may show a variation too large to ignore. As an example, values between 147 and 217 kJ mol^{-1} have been reported for the decomposition of calcite [1,2]. Reaction orders between 0.1 and 1.0 can be found. Frequency factors of 10^6–10^8 s^{-1} are not uncommon [3,4]. Also for some reactions, frequency factors as high as 10^{92} can be obtained [5]. These observations raise doubts regarding the physical meaning of the kinetic parameters in heterogeneous kinetics [6].

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They are therefore conveniently called apparent kinetic parameters, because their variation obviously precludes a uniquely describable activated state [6].

We can now show that the variations are determined by the actual physical conditions of the experiments, which are controllable only to within certain limits. These physical conditions are a product of the restriction of heat and mass transport in the solid phases, and they modify the vibrational states and the internal energy of the reactant.

For their quantitative assessment it is convenient to split the activation energy E_a into an invariant component ΔH, the enthalpy change of the reaction, and a variable term $z_i\nu$ describing the variation of the vibrational states. Then the activation energy becomes

$$E_a = \Delta H + z_i\nu \tag{1}$$

where $z_i\nu$ is a multiple of a characteristic vibration of the decomposing group. From eqn. (1), we can give a quantitative description of the effects of the physical conditions in terms of the characteristic vibration ν.

The variation in the physical conditions leads to corresponding variations in the internal energy of the reactant and the vibrational states, the consequence of which is the variation in the energy barrier height to the activated complex.

Let us consider the variation of the barrier height for an endothermic reaction

$$\mathrm{AB(s)} \rightarrow \mathrm{A(s)} + \mathrm{B(g)} - \Delta H \tag{2}$$

Such reactions are frequently encountered and are of great technical importance in extraction metallurgy and in a variety of chemical processes in industry. With increasing reacting mass per unit time, self-cooling of the reactant increases. This necessarily lowers the internal energy and vibrational states of the reactant.

Because A(s) is frequently a denser solid than the reactant AB(s), the restriction of the transport of B(g) by diffusion, initially determined by AB(s), increases at the degree of conversion α_d when a stable layer of the dense product A(s) has formed around the reactant. These variations in the physical conditions have mechanistic implications because a reaction initially proceeding according to a phase boundary reaction (R) tends to be diffusion controlled after α_d.

The effect of the physical conditions of the experiment is the increase in the energy barrier height. Quantum mechanical considerations allow jumps of $\Delta z = 1,2,3$, etc., and no fractional values of Δz.

Under the mild experimental conditions prevailing in isothermal studies at low reaction temperatures, jumps of $\Delta z > 2$ can be considered unlikely. Accordingly, a significant variation of each of the physical conditions can increase the barrier height by $\Delta z = 1$.

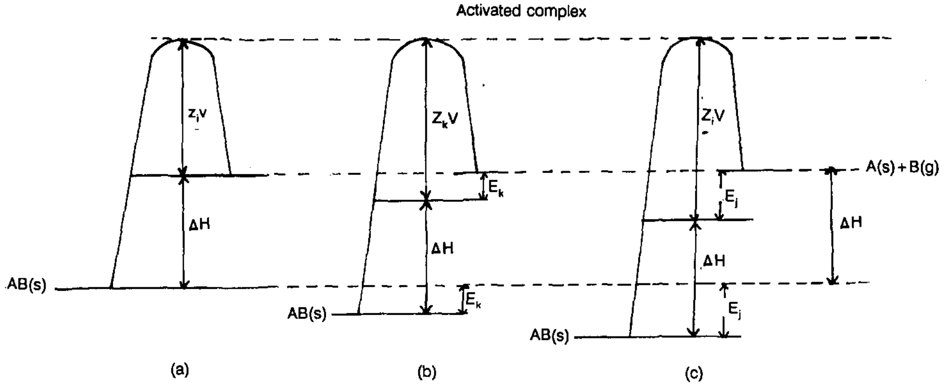

Fig. 1. The energy barriers for the isothermal reaction, AB(s) → A(s) + B(g) when A(s) forms a stable layer around AB(s) at $\alpha = \alpha_d$: (a) before α_d, $z_i = 3$, mechanism R; (b) after α_d, mechanism D, $E_k = \nu$ cm^{-1}; (c) after α_d, mechanism R, $E_j = 2\nu$ cm^{-1}.

When a stable layer of solid reaction product has formed around the reactant at $\alpha = \alpha_d$, the obstruction of conductive heat transmission to the reactant is a maximum as a result of the added new solid phase between the reactant and furnace. Also the restriction of the diffusion of B(g) now taking place in a denser solid A(s) is increased.

Hence, $\Delta z = 1$ applies for each of the two, i.e. conductive and convective heat transfer. Accordingly, for the phase boundary reaction mechanism (R) the energy barrier is increased by $\Delta z\nu = 2\nu$ after $\alpha = \alpha_d$.

The effect of self-cooling on the kinetics of a diffusion-controlled reaction mechanism is insignificant compared to the relative sizes of a diffusing molecule B(g) and the diffusion channels in the solid lattice. Therefore the kinetics of a diffusion-controlled mechanism (D) is determined by the cage effect produced by a dense solid product A(s). Hence the energy barrier for a diffusion mechanism will increase by $\nu\Delta z = \nu$ after $\alpha = \alpha_d$.

Accordingly, we obtain the activation energies $E_a(1)$, $E_a(D) = E_a(1) + \nu$, and $E_a(2) = E_a(1) + 2\nu$. The resulting energy barriers applicable when a stable layer of A(s) forms around AB(s) are shown in Fig. 1.

The activation energies predicted when a porous, (i.e. discontinuous) layer of A(s) forms around the reactant are $E_a(1) = E_a(2) + \nu$, and $E_a(2) = E_a(D)$.

The energy barriers of Fig. 1 apply for the decomposition of calcite. On the basis of these results we are able to draw certain valid conclusions. Because the reaction rate must be sensitive to the spacing of the vibrational states of the reactant and its activated complex:

1. At low reaction temperatures the rate constants must increase in the order $k(2) < k(D) < k(1)$.

2. At high reaction temperatures, increases in z_i greater than 1, i.e. 2, 3, etc., will occur. This will raise the rate constant $k(2)$ because for $E_a(2)$, a jump of 2 reduces the spacing of the vibrational states of the reactant and

its activated complex to the spacing of $E_a(1)$, i.e. making $k(1) = k(2)$. At very high reaction temperatures we predict $k(2) < k(1)$. These conclusions were shown by the experiment to be valid.

When ν refer to degenerate vibrations, those of higher energy will be frozen at low temperatures.

High reaction temperatures tend to activate the dormant vibrations. This may also happen for a vibration frozen at low reaction temperatures on grounds of symmetry. These possibilities influence the finer details of the barrier model.

To demonstrate our new approach to heterogeneous kinetics, we have selected two reactions:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \tag{3}$$

and

$$K_2C_2O_4(s) \rightarrow K_2CO_3(s) + CO(g) \tag{4}$$

because they provide all possible kinetic situations encountered with an endothermic reaction of the type in reaction (2).

The kinetics of reaction (3) has been studied and the results have been reported by us before [4]. A detailed discussion of the results was, however, reserved, pending our study of reaction (4) which allows interesting comparisons to be made.

EXPERIMENTAL

Isothermal decomposition kinetic studies were carried out using $K_2C_2O_4 \cdot H_2O$ single crystals of 34–35 mg weight. The dehydration occurred when the sample was being heated at 30 K min^{-1} from room temperature to a programmed reaction temperature. Other details of the experimental procedure are described elsewhere [4].

RESULTS AND DISCUSSION

The thermal decomposition kinetics of calcite according to reaction (3) is typical of the energy barrier model described and illustrated in Fig. 1. For the isothermal decomposition of calcite in a stream of dry nitrogen, activation energies $E_a(1) = 192.89$, $E_a(\text{D}) = 201.65$ and $E_a(2) = 210.33$ kJ mol^{-1} were obtained [4]. The characteristic vibration ν is determined by the activation energy differences $E_a(\text{D}) - E_a(1) = \nu$, $E_a(2) - E_a(\text{D}) = \nu$ and $E_a(2) - E_a(1) = 2\nu$. The best value of the characteristic vibration is $\nu = 710$ cm^{-1}, identical with the mean of the degenerate deformation vibration (O–C–O) of the carbonate ion in calcite observed at 706 cm^{-1} (infrared) and 714 cm^{-1} (Raman) [7]. Their small difference does not allow their differentiation experimentally. Using the data from suitable thermochemi-

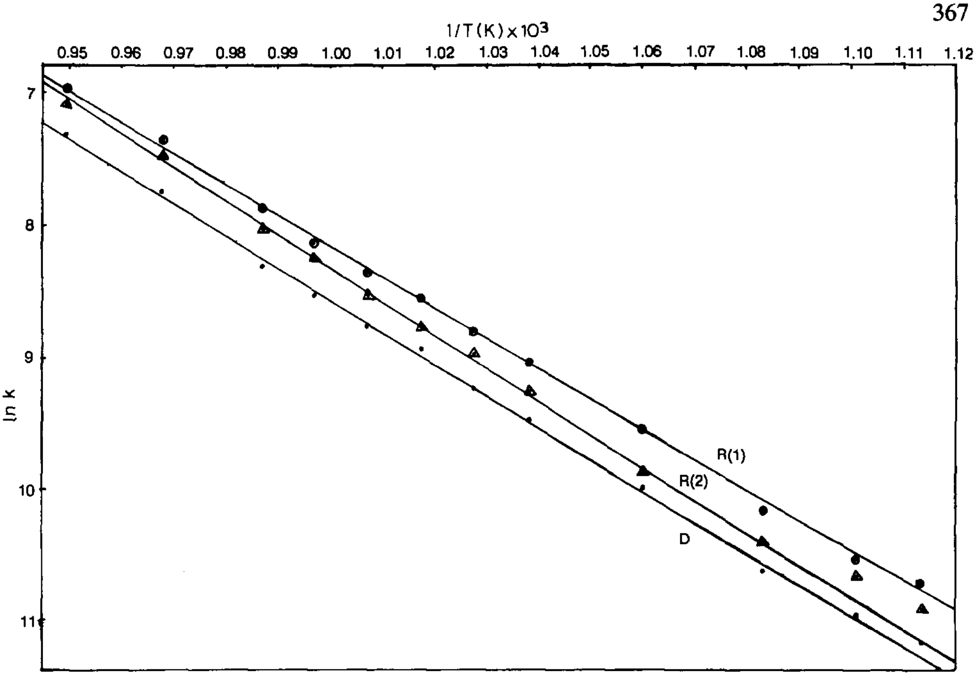

Fig. 2. The Arrhenius plots for isothermal decomposition of calcite. The rate constant $k(2)$ refers to the slope R(2), $k(\mathrm{D})$ to D and $k(1)$ to R(1).

cal tables [8], $\Delta H = 167$ kJ mol^{-1} was calculated for reaction (3) for a temperature of 1171 K where the dissociation pressure of CO_2 is one atmosphere. This gives $z_i = 3$ and a spacing of 3ν between the vibrational states of the reactant and its activated complex.

A complete kinetic description of reaction (3) is not possible without involving the two mechanisms (R and D). For example the order of the rate constants, $k(2) < k(\mathrm{D}) < k(1)$, found to hold at temperatures below 812.5 K, no longer applies above this temperature. At 812.5 K, $k(2) = k(\mathrm{D}) = 7.08 \times 10^{-7}$ and $k(1) = 1.39 \times 10^{-6}$. This information can be derived from the Arrhenius plots (Fig. 2). The data used to construct the plots is given elsewhere [4]. The energy barrier increases by ν from $E_a(1)$ to $E_a(\mathrm{D})$ and by 2ν from $E_a(1)$ to $E_a(2)$. Hence the ratio of the rate constants $k(1)/k(2) = 2\nu/\nu = 2$ should apply at 812.5 K. This is in agreement with the results of the experiment (Fig. 2). At low temperatures $k(1) > k(2)$ applies because R(1) gives the narrower spacing for the vibrational states of the reactant and its activated complex. At higher temperatures the dormant degenerate vibration becomes increasingly active thus increasing the exchange of energy among the reacting groups, hence raising the number of groups with energy in excess of $\Delta H + 5\nu$. This increases the rate constant $k(2)$. At 1086.2 K, $k(1) = k(2)$ and above, $k(2) > k(1)$ applies.

An important kinetic characteristic of reaction (3) arises from the influence of the reaction reversibility. We shall call this the equilibrium factor. The reverse reaction with a rate constant $\underleftarrow{k}$ as opposed to $\underrightarrow{k}$ for the dissociation of calcite, is responsible for the low values of the frequency factor. For R(1) the frequency factor $k_0 = 3.37 \times 10^6$ is obtained from the respective Arrhenius slope, in contrast to 2.13×10^{13} calculated from the characteristic frequency $\nu = 710$ cm^{-1}. The rate constant is given by the Arrhenius equation

$$k = k_0 \, \mathrm{e}^{-E_a/RT} \tag{5}$$

for which k becomes $k_{\rightarrow}/k_{\leftarrow}$ and $k_0 = k_{0\rightarrow}/k_{0\leftarrow}$ applies for the decomposition of calcite. The equilibrium factor hidden in the Arrhenius equation may be verified by means of the well known thermodynamic relationship

$$\frac{\mathrm{d}(\ln k)}{\Delta T} = -\frac{E_{a\rightarrow} - E_{a\leftarrow}}{RT_1T_2} \tag{6}$$

where by definition $E_{a\rightarrow} - E_{a\leftarrow} = E_a$. when two ln k values for the temperatures T_1 and T_2 are taken from the Arrhenius slope of R(1), d(ln k) becomes $\ln k_2 - \ln k_1$ and $\Delta T = T_2 - T_1$. Both equations (5) and (6) are found to give identical values of the activation energy $E_a(1) = 192.89$ kJ mol^{-1}.

THE KINETIC BEHAVIOUR OF $K_2C_2O_4$

Interpreting the kinetic results from the decomposition of potassium oxalate is more challenging than in the previous example of calcite. The complicating feature arises from the disproportionation of CO according to

$$2CO(g) \rightleftharpoons C(s) + CO_2(g) \tag{7}$$

which is exothermic. This affects the internal energy and vibrational states of the reactant and its transition state complex in a peculiar way.

The kinetic measurements for reaction (4) are summarised in Fig. 3 for α versus t. The same mechanisms are found to apply as those which were observed for reaction (2) [4].

The two-dimensional phase boundary reaction mechanism (R_2) gives the typical splitting of the decomposition kinetics, resulting in a second kinetic phase [4] after a stable layer of a denser solid product has formed around the reactant. This is shown in Fig. 4 for the plot of $g(\alpha)$ versus t. However the splitting is accompanied by an increase in the rate constant, instead of a decrease as observed for reaction (3) [4]. The plots of $g(\alpha)$ versus t for all reaction temperatures employed show the same features as Fig. 4 given for a reaction temperature of 520°C. The splitting occurs at the degree of conversion α_d between 0.41 and 0.51. The decomposition kinetics is also found to obey the mechanism of one-dimensional diffusion (D_1) in the

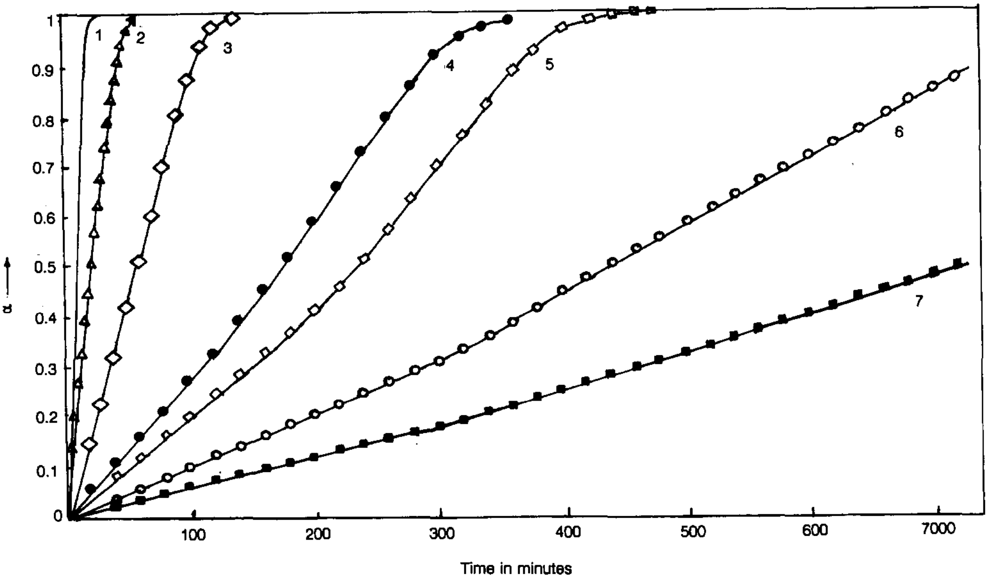

Fig. 3. Plots of α vs. *t* (in minutes) for the isothermal decomposition of potassium oxalate: (1) at 560°C, (2) at 540°C, (3) at 522°C, (4) at 500°C, (5) at 490°C, (6) at 480°C and (7) at 470°C. The sigmoid shapes of (4) and (5) have nothing to do with nucleation. For explanation, see text.

second kinetic phase. The plot of $g(\alpha)$ versus t for this mechanism is also given in Fig. 4.

The Arrhenius plots (Fig. 5) give the activation energies $E_a(1) = 291.00$ and $E_a(2) = 254.86$ kJ mol^{-1} for the phase boundary reaction and 252.03 kJ mol^{-1} for D_1.

Based on our previous experience we can make the following observations and comments:

1. The Arrhenius plots give the order of the rate constants $k(1) < k(D) < k(2)$ at low reaction temperatures. This is a complete reversal of the order observed for calcite decomposition. Here, therefore, the activation of a frozen vibration ν_2 does not require high reaction temperatures as was the case with calcite decomposition. The activation of ν_2 is facilitated by the heat of the disproportionation of CO according to reaction (7). Because the rate constants show that the heat of the disproportionation of CO is available to the main reaction (4) only in the second phase after $\alpha = \alpha_d$, at this degree of conversion, K_2CO_3 forms a coherent layer around the reactant. Complete disproportionation at the phase boundary is favoured by the resulting compression of CO.

2. The rate constants $k(1)$ and $k(D)$ are identical at 844.88 K. At this temperature the ratio of the rate constants $k(2)/k(1)$ gives the ratio of the characteristic vibrations, i.e. $\nu_2/\nu_1 = 1.41$.

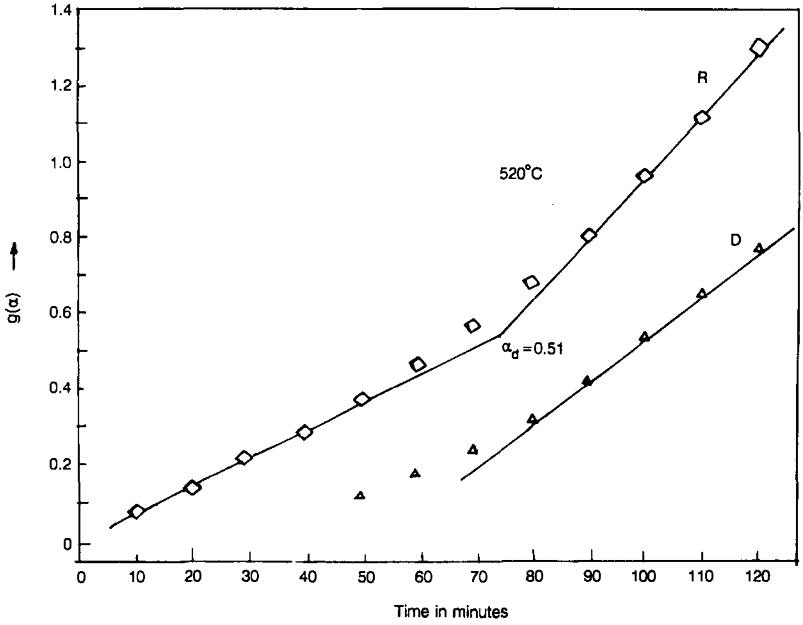

Fig. 4. A typical plot of $g(\alpha)$ vs. time (in minutes) for the isothermal decompositions of $K_2C_2O_4$. The reaction splits into two kinetic phases. The second phase of higher rate constant is due to additional heating of the reactant by the disproportionation of CO at the phase boundary.

3. Because the phase boundary reaction mechanism gives the most appropriate rate-determining step, ν_1 and ν_2 must be the stretching frequencies of the C–O and C–C bonds in oxalate.

The enthalpy change $\Delta H(7) = -80.62$ kJ mol^{-1} is calculated for reaction (7) using the thermochemical data for 850 K [8]. Let $\Delta H(4)$ be the corresponding enthalpy change for reaction (4). The same energy barriers of Fig. 1 are applicable after modification to accommodate the effect of CO disproportionation. The characteristic vibrations are $\nu_1 = 3200$ cm^{-1} composed of ν(C–C) observed at 881 and 875 cm^{-1}, ν_s(C–O) observed as very strong bands at 1444 cm^{-1} in the Raman spectrum of $K_2C_2O_4$ [9], and $\nu_2 = \nu_1 + \nu_s$(C–O) observed at 1313 cm^{-1} as a strong band in the infrared spectrum [10]. The ratio $\nu_2/\nu_1 = 4513/3200 = 1.41$ agrees with the ratio of the rate constants $k(2)/k(1)$ at 844.88 K.

The heat of disproportionation gives a lowering effect of the energy barrier height by 1313 cm^{-1} for $E_a(2)$ and a raising effect of the same amount for $E_a(1)$. Accordingly, the relationships

$$-80.62 + \Delta H(4) + 5\nu_2 - 1313 \text{ cm}^{-1} = E_a(2)$$

and

$$80.62 + \Delta H(4) + 3\nu_1 + 1313 \text{ cm}^{-1} = E_a(1)$$

apply.

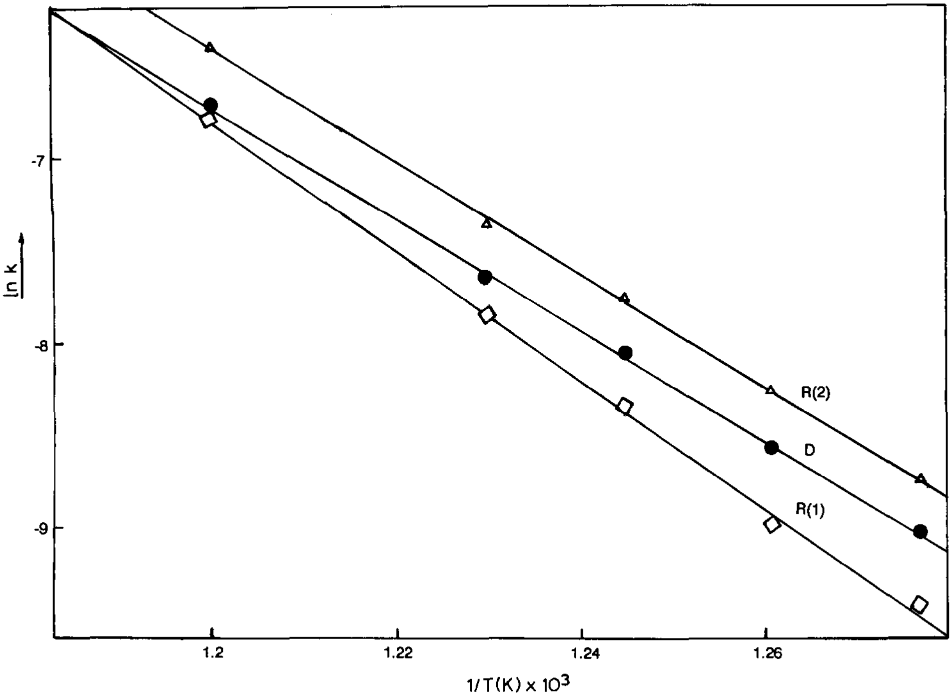

Fig. 5. The Arrhenius plots for isothermal decomposition of $K_2C_2O_4$. R(1) and R(2) refer to the first and second kinetic phases of the phase boundary reaction. D refers to the diffusion-controlled reaction mechanism.

These two expressions give the activation energy difference, $E_a(1)-E_a(2)=37.57$ kJ mol^{-1}. The activation energies obtained from the Arrhenius plots are $E_a(1)=291$ kJ mol^{-1} and $E_a(2)=254.86$ mol^{-1}, giving a difference of 36.14 kJ mol^{-1}.

It is reasonable to assume that $E_a(2)=E_a(\mathrm{D})$ because for both energy barriers the effects of heat and mass transfer are a minimum. When the average, 253.4 kJ mol^{-1}, is taken as $E_a(2)$ and $E_a(1)=291$ kJ mol^{-1}, we obtain $\Delta H(4)=79.85$ kJ mol^{-1}.

Except for the sign, the enthalpy changes $\Delta H(4)$ and $\Delta H(7)$ are identical at 298 K. Our results suggest that the situation does not change appreciably at 850 K.

Indeed the enthalpy change $\Delta H(4)$ at 298 K is larger by about 5.5 kJ mol^{-1} which is not at all unreasonable. Although we could not obtain $\Delta H(4)$ for 850 K (using thermochemical tables) the results of our calculations suggest that our approach is essentially correct even in the complex situation given by the thermal decomposition of $K_2C_2O_4$.

CONCLUSIONS

We have shown that the concept of the energy barrier is applicable in heterogeneous kinetics. This has been a controversial subject. The variation of the energy barrier, for which Garn concluded that there can be no "uniquely describable activated state" [6], is a consequence of the experimental physical conditions which, as we have seen, can be accounted for. The average frequency factor obtained for the decomposition of potassium oxalate is 9.78×10^{14} which compares favourably with the average of 1.15×10^{14} obtained from the characteristic vibrations ν_1 and ν_2.

The low value of the frequency factor obtained for calcite decomposition was explained by the equilibrium factor.

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