

ON THE CHANGES OF THE ACTIVATION ENERGY WITH THE CONVERSION DEGREE IN NON-ISOTHERMAL KINETICS

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(Received 18 April 1985)

ABSTRACT

The authors present their results concerning the changes of activation energy determined under non-isothermal conditions with the conversion degree. An interpretation of this effect is suggested.

INTRODUCTION

In a previous note, a method to evaluate the non-isothermal kinetic parameters using integration over small temperature intervals and several heating rates was described [1]. For the activation energy, we obtained the approximate formula

$$E = R \frac{T_{1ik} T_{2ik}}{T_{2ik} - T_{1ik}} \ln \frac{\beta_{2ik} (T_{1k} - T_{1i})}{\beta_{1ik} (T_{2k} - T_{2i})} \quad (1)$$

where T_{1i} and T_{1k} are the temperatures corresponding to the conversion degree values α_i and α_k for the heating rate β_1 ; T_{2i} and T_{2k} are the temperatures corresponding to the conversion degree values α_i and α_k for the heating rate β_2 ($\beta_2 > \beta_1$); β_{1ik} and β_{2ik} are the local (corrected) heating rates in the interval $\alpha \in [\alpha_i, \alpha_k]$ and

$$T_{lik} = \frac{T_{li} + T_{lk}}{2} \quad (l = 1, 2) \quad (2)$$

The method is based on the assumption that $f(\alpha)$ does not change its form for various heating rates and conversion degree values in the interval $\alpha \in [\alpha_i, \alpha_k]$.

Taking into account that

$$\beta_{lik} = \frac{T_{lk} - T_{li}}{\Delta t_l} \quad (3)$$

where Δt_l is the time difference corresponding to the interval $\alpha \in [\alpha_i, \alpha_k]$,

TABLE 1

Values of the conversion degree for two heating rates and various temperatures

No.	α	T (K) $\rightarrow \beta_2 = 5$ (K min ⁻¹)	T (K) $\rightarrow \beta_1 = 1$ (K min ⁻¹)
1	0.0417	416.0	406.4
2	0.0833	423.0	411.0
3	0.1667	431.5	416.8
4	0.2500	437.8	421.0
5	0.3333	442.0	424.2
6	0.4167	446.2	427.0
7	0.5000	449.2	429.2
8	0.5833	452.6	431.2
9	0.6667	456.0	433.2
10	0.7500	459.0	435.2
11	0.8333	462.2	437.3
12	0.9167	466.3	439.8
13	0.9583	469.0	441.2

relationship (1) becomes

$$E = R \frac{T_{1ik} T_{2ik}}{T_{2ik} - T_{1ik}} \ln \frac{\Delta t_1}{\Delta t_2} \quad (4)$$

The activation energy calculated either by eqns. (1) or (4) corresponds most probably to the conversion degree, α , given by

$$\alpha = \frac{\alpha_i + \alpha_k}{2} \quad (5)$$

The method will be used for the dehydration of calcium oxalate monohydrate as well as for the decomposition of potassium permanganate.

THE DEHYDRATION OF $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

The experimental data for the heating rates $\beta_1 = 1$ K min⁻¹ and $\beta_2 = 5$ K min⁻¹ and the corresponding values of the activation energy are given in Tables 1 and 2. The changes in the activation energy with the conversion degree are given graphically in Fig. 1.

DECOMPOSITION OF POTASSIUM PERMANGANATE

The experimental data, for the heating rates $\beta_1 = 1.5$ K min⁻¹ and $\beta_2 = 3$ K min⁻¹ and the corresponding values of the activation energy are given in Tables 3 and 4. The changes in the activation energy with the conversion degree are presented in Fig. 2.

TABLE 2
Activation energy values for various values of the conversion degree

No.	α_i	α_k	α	Δt_1 (min)	Δt_2 (min)	$\ln \frac{\Delta t_1}{\Delta t_2}$	$T_{1k} - T_{1i}$	$T_{2k} - T_{2i}$	$T_{2ik} - T_{1ik}$	E (kcal mol ⁻¹)
1	0.0417	0.1667	0.1042	10.30	3.08	1.207	10.4	15.5	12.15	34.43
2	0.0833	0.2500	0.1667	10.12	2.93	1.240	10.0	14.8	14.40	30.64
3	0.1667	0.4167	0.2917	10.30	3.12	1.194	10.2	14.7	16.95	25.94
4	0.2500	0.5000	0.3750	8.68	2.57	1.217	8.2	11.4	18.40	24.78
5	0.3333	0.5833	0.4583	7.30	2.21	1.195	7.0	10.6	19.60	23.18
6	0.4167	0.6667	0.5417	6.95	2.00	1.246	6.2	9.8	21.00	22.87
7	0.5000	0.7500	0.6250	6.20	1.82	1.226	6.1	9.8	21.85	21.88
8	0.5833	0.8333	0.7083	6.30	1.84	1.231	6.1	9.6	23.15	20.98
9	0.6667	0.9167	0.7917	6.05	1.85	1.185	6.6	10.3	24.65	19.23
10	0.7500	0.9583	0.8542	5.70	1.73	1.192	5.9	10.0	25.75	18.71

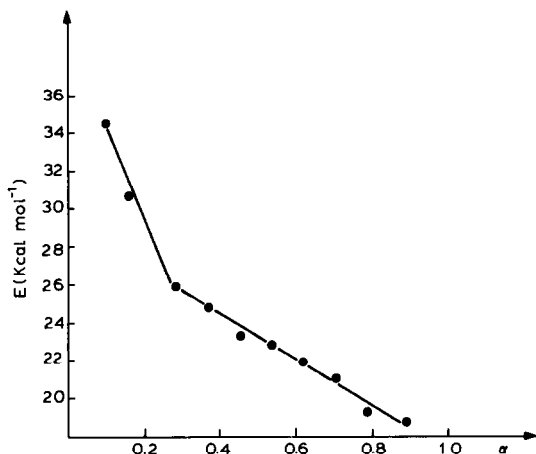


Fig. 1. Plot of E versus conversion degree for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ dehydration.

TABLE 3

Values of the conversion degree for two heating rates and various temperature values

No.	α	T (K) $\rightarrow \beta_2 = 3$ (K min ⁻¹)	T (K) $\rightarrow \beta_1 = 1.5$ (K min ⁻¹)
1	0.15	499.0	479.5
2	0.20	511.5	492.5
3	0.30	518.5	500.5
4	0.35	525.0	509.4
5	0.40	527.0	511.6
6	0.45	529.5	514.0
7	0.55	531.0	516.4
8	0.80	534.5	520.5
9	0.90	536.0	522.0

DISCUSSION

From the data presented one can easily notice significant changes in the activation energy with the conversion degree. For the decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ the activation energy decreases with α whereas for the decomposition of potassium permanganate the activation energy increases with the conversion degree. The activation energy varies linearly with the conversion degree. In each case two straight lines were obtained for the following intervals of the conversion degree

$$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \begin{cases} \alpha \in [0.1-0.3] \\ \alpha \in [0.3-0.85] \end{cases}$$

$$\text{KMnO}_4 \begin{cases} \alpha \in [0.175-0.450] \\ \alpha \in [0.450-0.675] \end{cases}$$

TABLE 4
 Activation energy values for various values of the conversion degree

No.	α_i	α_k	α	Δt_1 (min)	Δt_2 (min)	$\ln \frac{\Delta t_1}{\Delta t_2}$	$T_{1k} - T_{1i}$	$T_{2k} - T_{2i}$	$T_{2ik} - T_{1ik}$	E (kcal mol ⁻¹)
1	0.150	0.200	0.175	8.74	4.15	0.745	13.0	12.5	19.25	18.88
2	0.200	0.300	0.250	5.28	2.24	0.857	8.0	7.0	18.50	23.49
3	0.300	0.450	0.375	8.88	3.60	0.903	13.5	11.0	16.75	28.44
4	0.350	0.550	0.450	4.51	1.74	0.952	7.0	6.0	15.10	33.87
5	0.400	0.800	0.600	5.26	2.01	0.962	8.9	7.5	14.70	35.56
6	0.450	0.900	0.675	5.16	1.95	0.973	8.0	6.5	14.75	36.13

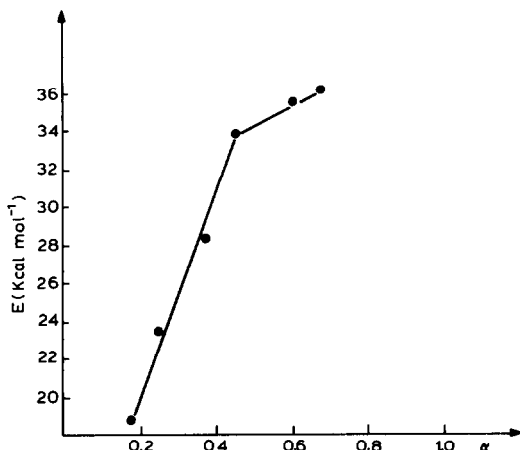


Fig. 2. Plot of E versus conversion degree for KMnO_4 decomposition.

The slope changes for the $E(\alpha)$ straight lines could eventually suggest a change in the reaction mechanism.

From the data presented it turns out that

$$E = E_0 + E_1\alpha \quad (6)$$

with $E_0 > 0$ and $E_1 < 0$ for the dehydration of calcium oxalate monohydrate and $E_1 > 0$ for the decomposition of potassium permanganate. Relationship (6) can be generalized in the form

$$E = E_0 + E_1\alpha + E_2\alpha^2 + E_3\alpha^3 + \dots \quad (7)$$

where E_0 , E_1 , E_2 , etc., are real constants.

The average values of E for both temperature intervals are:

(1) dehydration of calcium oxalate monohydrate

$$E(0.1-0.3) \approx 30.3 \text{ kcal mol}^{-1}$$

$$E(0.3-0.85) \approx 22.2 \text{ kcal mol}^{-1}$$

the last value being in close agreement with the literature data [2-4];

(2) decomposition of potassium permanganate

$$E(0.175-0.450) \approx 26.2 \text{ kcal mol}^{-1}$$

$$E(0.450-0.675) \approx 35.2 \text{ kcal mol}^{-1}$$

both values being in close agreement with the literature data [5].

As far as the reasons for such an opposite $E(\alpha)$ dependence are concerned, let us analyse from this standpoint eqn. (4), which contains three terms.

(a) The product $T_{1,k}T_{2,k}$, which increases insignificantly with α

(b) The term $\ln \Delta t_1/\Delta t_2$ which does not change significantly with α .

For the decomposition of potassium permanganate, $\ln(\Delta t_1/\Delta t_2)$ monotonously increases with α , and thus influences the increase of E with α .

(c) The term $T_{2ik} - T_{1ik}$ is the most significant as the determinant for the change of E with α . For the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, as one can see from Table 2, the difference $T_{2ik} - T_{1ik}$ increases with α , thus, determining a decrease in the activation energy with respect to the same variable. As far as the decomposition of potassium permanganate is concerned, the difference $T_{2ik} - T_{1ik}$ decreases with α (Table 4) and, thus, the activation energy increases with α ; this effect being amplified by the increase of $\ln(\Delta t_1/\Delta t_2)$ with α .

CLASSIFICATION OF THE REACTIONS IN NON-ISOTHERMAL KINETICS

As shown in Tables 2 and 4, an increase of the conversion degree, $\Delta\alpha = \alpha_k - \alpha_l$, for two heating rates, corresponds to the temperature increases $\Delta T_1 = T_{1k} - T_{1l}$ and $\Delta T_2 = T_{2k} - T_{2l}$. If $\Delta\alpha$ and ΔT_l ($l = 1, 2$) are small enough, then

$$\frac{\Delta\alpha}{\Delta T_l} \approx \left(\frac{d\alpha}{dT} \right)_{\beta_l} \quad (l = 1, 2) \quad (8)$$

From Table 2 one can see that for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ the inequalities

$$\left. \begin{array}{l} \frac{\Delta\alpha}{\Delta T_1} > \frac{\Delta\alpha}{\Delta T_2} \\ \text{and, consequently} \\ \left(\frac{d\alpha}{dT} \right)_{\beta_1} > \left(\frac{d\alpha}{dT} \right)_{\beta_2} \end{array} \right\} \quad (9)$$

are valid at least for $\alpha \in [0.1-0.85]$. Thus, for a given α value, $d\alpha/dT$ depends on β , and $d\alpha/dT$ (β) decreases when β increases at least for $\beta \in [1, 5 \text{ K min}^{-1}]$.

For the decomposition of potassium permanganate, as shown in Table 4

$$\left. \begin{array}{l} \frac{\Delta\alpha}{\Delta T_1} < \frac{\Delta\alpha}{\Delta T_2} \\ \left(\frac{d\alpha}{dT} \right)_{\beta_1} < \left(\frac{d\alpha}{dT} \right)_{\beta_2} \end{array} \right\} \quad (10)$$

at least for $\alpha \in [0.15-0.9]$, i.e., $d\alpha/dT$ (β) increases with β at least for $\beta \in [1.5, 3 \text{ K min}^{-1}]$.

These two kinds of $d\alpha/dT$ (β) dependencies could be used for a classification of chemical reactions according to their non-isothermal kinetic behaviour.

DERIVATION OF A MORE GENERAL RATE EQUATION

The fundamental rate equation of non-isothermal kinetics

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) e^{-E/RT} \quad (11)$$

with relationship (6), takes the form

$$\frac{d\alpha}{dT} = \frac{A(p)}{\beta} f(\alpha) e^{-E_0/RT} e^{-E_1\alpha/RT} \quad (12)$$

Introducing the notation

$$g(\alpha, T) = e^{-E_1\alpha/RT} \quad (13)$$

one obtains the equation

$$\frac{d\alpha}{dT} = \frac{A(p)}{\beta} f(\alpha) e^{-E_0/RT} g(\alpha, T) \quad (14)$$

A more general equation than eqn. (12) should probably have the form

$$\frac{d\alpha}{dT} = \frac{A(p)}{\beta} f(\alpha) e^{-\frac{E_0 + E_1\alpha + E_2\alpha^2 + E_3\alpha^3 + \dots}{RT}} \quad (15)$$

where p is a set of variables which will be analyzed in a future work.

AN ATTEMPT TO EXPLAIN THE OPPOSITE DEPENDENCIES, $d\alpha/dT$ (β), IN THE FRAMEWORK OF CLASSICAL NON-ISOTHERMAL KINETICS

In the rate equation (11) with $E = \text{const}$ and $A = \text{const}$, a given value of α will be considered. Through the separation of variables and integration, eqn. (11) becomes

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_\alpha} e^{-E/RT} dT \quad (16)$$

where T_α is the temperature corresponding to the given α value. Introducing the notation

$$\frac{d\alpha}{dT} = \alpha^*(\beta) \quad (17)$$

and taking the derivative of eqn. (11) with respect to β (taking into account that $T = T_\alpha$), it turns out that

$$\frac{d\alpha^*(\beta)}{d\beta} = -\frac{A}{\beta^2} f(\alpha) e^{-E/RT_\alpha} + \frac{A}{\beta} f(\alpha) e^{-E/RT_\alpha} \frac{E}{RT_\alpha^2} \frac{dT_\alpha}{d\beta} \quad (18)$$

or

$$\frac{d\alpha^*(\beta)}{d\beta} = \frac{A}{\beta} f(\alpha) e^{-E/RT_\alpha} \left[\frac{E}{RT_\alpha^2} \frac{dT_\alpha}{d\beta} - \frac{1}{\beta} \right] \quad (19)$$

Introducing a new notation

$$\frac{E}{RT_{\alpha}^2} \frac{dT_{\alpha}}{d\beta} - \frac{1}{\beta} = D(\beta) \quad (20)$$

it follows that: for $D(\beta) > 0$, $\alpha(\beta)$ increases when β increases; for $D(\beta) < 0$, $\alpha(\beta)$ decreases when β increases. Let us introduce a new variable Z defined by the relationship

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = Z \quad (21)$$

which shows that for a given α value, Z depends of the form of $f(\alpha)$. In terms of Z , relationship (16) becomes

$$\beta Z = A \int_0^{T_{\alpha}} e^{-E/RT} dT \quad (22)$$

As a solution of eqn. (22)

$$T_{\alpha} = T_{\alpha}(\beta, Z) \quad (23)$$

Taking the derivative of eqn. (22) with respect to β , one obtains

$$Z = A e^{-E/RT_{\alpha}} \frac{dT_{\alpha}}{d\beta} \quad (24)$$

or

$$\frac{dT_{\alpha}}{d\beta} = \frac{Z}{A} e^{E/RT_{\alpha}} \quad (25)$$

Introducing this result into eqn. (20) we obtain

$$D(\beta) = \frac{E}{RT_{\alpha}^2} \frac{Z}{A} e^{E/RT_{\alpha}} - \frac{1}{\beta} \leq 0 \quad (26)$$

and

$$Z \leq \frac{ART_{\alpha}^2}{E\beta} e^{-E/RT_{\alpha}} \quad (27)$$

This last result allows us to establish, in principle, the form of $f(\alpha)$.

CONCLUSIONS

(1) An opposite dependence of the activation energy on the conversion degree was shown for the dehydration of calcium oxalate monohydrate and the decomposition of potassium permanganate

(2) An explanation of the above experimental data was given.

(3) For the systems studied the meaning of $g(\alpha, T)$ in the rate equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha)g(\alpha, T)$$

was established.

REFERENCES

- 1 E. Urbanovici and E. Segal, *Thermochim. Acta*, in press.
- 2 E.S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
- 3 A.W. Coats and J.P. Redfern, *Nature (London)*, 201 (1964) 68.
- 4 E. Segal, *Thermochim. Acta*, 53 (1982) 365.
- 5 J. Šesták, V. Šatava and W.W. Wendlandt, *Thermochim. Acta*, 7 (1973) 333.