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ON THE CHANGE OF THE ACTIVATION ENERGY WITH CONVERSION DEGREE AND HEATING RATE FOR THE NON-ISOTHERMAL DEHYDRATION OF $CaC_2O_4 \cdot H_2O$

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ABSTRACT

The authors present their results concerning the approximate dependence of the activation energy of $CaC_2O_4 \cdot H_2O$ on the conversion degree and heating rate.

INTRODUCTION

In our previous papers and notes [1–3] some methods have been described to obtain the non-isothermal kinetic parameters using several heating rates and integration over small changes of the variables, or in short $-\!\!(\!\!-\!\!-\!\!-\!\!)\!\!-$ [4]. One of the methods allowed us to prove a significant change of the activation energy with conversion degree for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O(s)$ and decomposition of $KMnO_4(s)$ [5].

This paper aims to present our results concerning the change of the activation energy of dehydration of $CaC_2O_4 \cdot H_2O(s)$, with conversion degree and heating rate.

METHOD AND CALCULATION PRINCIPLES

"Classical" non-isothermal kinetics uses the fundamental equation [6]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha)\, e^{-E/RT} \tag{1}$$

where α stands for the conversion degree, T for the temperature, A for the pre-exponential factor, $f(\alpha)$ for the conversion function, E for the activation energy and R for the gas constant, with $A = \text{const}$, $E = \text{const}$ and $f(\alpha)$ keeping the same form for all the values of the conversion degree. In the following, we shall use the same equation but in the more general form:

$$\frac{d\alpha}{dT} = \frac{A(v)}{\beta} f(v, \alpha)\, e^{-E(v)/RT} \tag{2}$$

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where v is a set of variables on which the pre-exponential factor, the activation energy and the conversion function could depend. In the most general case,

$$v = (\alpha, T, \beta \ldots) \tag{3}$$

We shall consider several approximately constant heating rates β_l ($l = 1, 2, 3, \ldots, h$). The values β_l correspond to average values calculated for the whole range of values. Taking into account that β_l ($l = 1, 2, 3, \ldots, h$) values are not rigorously constant, some local heating rates $\beta_{l_{ik}}$ ($l = 1, 2, 3, \ldots, h$) corresponding to the closed interval $\alpha \in [\alpha_i, \alpha_k]$ should be introduced.

The following notations will be introduced for the isoconversion temperatures and times:

$$\alpha = \alpha_i \begin{cases} T_{1_i}, T_{2_i}, \ldots, T_{r_i} \\ t_{1_i}, t_{2_i}, \ldots, t_{r_i} \end{cases}$$

The local heating rates can be calculated from the formula:

$$\beta_{l_{ik}} = \frac{T_{lk} - T_{li}}{t_{lk} - t_{li}} \tag{4}$$

Integration of the differential equation (2) over the interval $\alpha \in [\alpha_i, \alpha_k]$ for two heating rates β_x and β_y gives:

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(v, \alpha)} = \frac{1}{\beta_{x_{ik}}} \int_{T_{x_i}}^{T_{x_k}} A(v)\, \mathrm{e}^{-E(v)/RT}\, \mathrm{d}T \tag{5}$$

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(v, \alpha)} = \frac{1}{\beta_{y_{ik}}} \int_{T_{y_i}}^{T_{y_k}} A(v)\, \mathrm{e}^{-E(v)/RT}\, \mathrm{d}T \tag{6}$$

The difficulty in solving the integrals from eqns. (5) and (6) arises because the analytical dependences $A(v)$, $\mathrm{f}(v, \alpha)$ and $E(v)$ are unknown.

In order to solve this problem we should use for the moment a first rough approximation by substituting in the integrals from (5) and (6) the functions $A(v)$, $\mathrm{f}(v, \alpha)$ and $E(v)$ with some average constant values corresponding to an average conversion degree given by

$$\alpha = \frac{\alpha_i + \alpha_k}{2} \tag{7}$$

as well as to an average heating rate $\beta_{xy_{ik}}$ given by:

$$\beta_{xy_{ik}} = \frac{\beta_{x_{ik}} + \beta_{y_{ik}}}{2} \tag{8}$$

with $x < y$.

For the interval:

$$\Delta\alpha_{ik} = \alpha_k - \alpha_i \tag{9}$$

we recommend such values that the condition:

$\Delta\alpha_{ik} \leq 0.3\text{–}0.4$

is fulfilled.

Thus, according to our first approximation

$$A(v) \rightarrow A(\bar{v}) \equiv A \tag{10}$$

$$\mathrm{f}(v, \alpha) \rightarrow \mathrm{f}(\bar{v}, \alpha) \equiv \mathrm{f}(\alpha) \tag{11}$$

$$E(v) \rightarrow E(\bar{v}) \equiv E \tag{12}$$

keeping in mind that without considering identical notations the right-hand side values are average values and should not be confused with those from eqn. (1).

Taking into account (10), (11) and (12), from (5) and (6) it turns out that:

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{\beta_{xik}} \int_{T_{xi}}^{T_{xk}} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{13}$$

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{\beta_{yik}} \int_{T_{yi}}^{T_{yk}} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{14}$$

Thus the first rough approximation led to results which are equivalent to those obtained by applying the classical model. As far as the interpretation is concerned our nonclassical model shows that $E = E(\alpha, \beta)$. The same dependence is exhibited by the classical model, thus showing its inconsistency.

Using the results obtained in the first rough approximation, by applying the nonclassical model, a second approximation can be obtained.

From (13) and (14) one gets:

$$\frac{\displaystyle\int_{T_{yi}}^{T_{yk}} \mathrm{e}^{-E/RT}\,\mathrm{d}T}{\displaystyle\int_{T_{xi}}^{T_{xk}} \mathrm{e}^{-E/RT}\,\mathrm{d}T} = \frac{\beta_{yik}}{\beta_{xik}} \tag{15}$$

a relationship which allows evaluation of the activation energy E. Depending on the approximations used to solve the temperature integral we get various formulae to evaluate E.

A good approximation uses the average theorem to solve the temperature integral [7,8]. In this case one gets the following formula:

$$E = R\frac{T_{xik}T_{yik}}{T_{yik} - T_{xik}} \ln\frac{t_{xk} - t_{xi}}{t_{yk} - t_{yi}} \tag{16}$$

with

$$T_{xik} = \frac{T_{xk} + T_{xi}}{2}$$
$$T_{yik} = \frac{T_{yk} + T_{yi}}{2} \tag{17}$$

A very good approximation for the temperature integral can be obtained by using Simpson's formula for $n = 2$ [8,9]. Introducing this approximation in (15) it turns out that,

$$\frac{(T_{yk} - T_{yi}/6)(\mathrm{e}^{-E/RT_{yi}} + 4\mathrm{e}^{-E/RT_{yik}} + \mathrm{e}^{-E/RT_{yk}})}{(T_{xk} - T_{xi}/6)(\mathrm{e}^{-E/RT_{xi}} + 4\mathrm{e}^{-E/RT_{xik}} + \mathrm{e}^{-E/RT_{xk}})} = \frac{\beta_{yik}}{\beta_{xik}} \tag{18}$$

or taking into account relationship (4),

$$\frac{\mathrm{e}^{-E/RT_{yi}} + 4\mathrm{e}^{-E/RT_{yik}} + \mathrm{e}^{-E/RT_{yk}}}{\mathrm{e}^{-E/RT_{xi}} + 4\mathrm{e}^{-E/RT_{xik}} + \mathrm{e}^{-E/RT_{xk}}} = \frac{t_{xk} - t_{xi}}{t_{yk} - t_{yi}} \tag{19}$$

The differences $T_{xk} - T_{xi}$ and $T_{yk} - T_{yi}$ should not be higher than 15–20 K or lower than 4–5 K.

Although the errors concerning the values of the determined activation energy are beyond the aim of this article, one should emphasize that:

(a) the errors due to the mathematical approximations are not essential;

(b) the errors due to the inaccuracy of the measurements of the variables are quite significant, the most dangerous being the inaccurate determination of the temperature.

As an example let us consider formula (16) and suppose that the difference $T_{yik} - T_{xik}$ was erroneously evaluated with ΔT. The relative error of the difference $T_{yik} - T_{xik}$, e_r, is given by:

$$e_r \approx \frac{\Delta T}{T_{yik} - T_{xik} + \Delta T} \tag{20}$$

were ΔT can be either positive or negative.

For $T_{yik} - T_{xik} = 6$ K and $\Delta T = 1$ K

$e_r \approx \frac{1}{7} \times 100 = 14.3\%$

thus a significant error.

Formula (20) shows that e_r, and correspondingly the error in the evaluation of the activation energy, decreases with the increase of the difference $T_{yik} - T_{xik}$. This is why the results obtained for close β_y and β_x (to which correspond small values of the difference $T_{yik} - T_{xik}$) should be carefully considered.

APPLICATIONS

The method was applied for the dehydration of $CaC_2O_4 \cdot H_2O$ using four heating rates: $\beta_1 = 0.987$ K min^{-1}, $\beta_2 = 2.353$ K min^{-1}, $\beta_3 = 4.988$ K min^{-1}, $\beta_4 = 9.573$ K min^{-1}. The thermogravimetric curves have been recorded with a Du Pont 1090 thermal analyser.

The experimental data are listed in Table 1.

TABLE 1

Experimental data for the dehydration of $CaC_2O_4 \cdot H_2O(s)$

No.	α	$\beta_1 = 0.987$ K min^{-1}		$\beta_2 = 2.353$ K min^{-1}		$\beta_3 = 4.988$ K min^{-1}		$\beta_4 = 9.573$ K min^{-1}	
		T (K)	t (min)	T (K)	t (min)	T (K)	t (min)	T (K)	t (min)
1	0.10	412.2	119.95	420.9	27.02	425.3	26.40	430.8	13.96
2	0.20	418.4	126.30	428.1	30.14	434.0	28.27	441.1	15.02
3	0.30	422.8	130.60	433.1	32.30	440.2	29.54	447.6	15.76
4	0.40	426.2	134.00	437.2	34.04	445.3	30.58	453.2	16.35
5	0.50	429.2	137.10	441.0	35.58	449.2	31.46	458.0	16.87
6	0.60	431.9	139.65	443.8	36.92	453.1	32.21	462.4	17.31
7	0.70	434.0	142.05	446.6	38.18	456.8	32.92	466.2	17.75
8	0.80	436.2	144.55	449.6	39.36	460.5	33.63	470.6	18.18
9	0.90	439.0	147.10	452.9	40.62	465.1	34.38	475.6	18.64

In Table 2 the local heating rates β_{lik} ($l = 1, 2, 3, 4$) for several intervals $\alpha \in [\alpha_i, \alpha_k]$ are given. The results of the calculations using formulae (16) and (19) as well as the values β_{xyik} for various combinations between x and y ($x \neq y$; $x < y$; $x, y = 1, 2, 3, 4$) are listed in Tables 3–8. The calculated values of the activation energy using formula (16) have been noted by E' and those calculated with formula (19) have been noted by E. From Tables

TABLE 2

Local heating rates β_{lik} ($l = 1, 2, 3, 4$) for pairs α_i, α_k

No.	α_i	α_k	α	β_{1ik} (K min^{-1})	β_{2ik} (K min^{-1})	β_{3ik} (K min^{-1})	β_{4ik} (K min^{-1})
1	0.10	0.20	0.15	0.976	2.308	4.652	9.717
2	0.10	0.30	0.20	0.995	2.311	4.745	9.333
3	0.20	0.30	0.25	1.023	2.315	4.882	8.784
4	0.20	0.40	0.30	1.013	2.333	4.892	9.098
5	0.20	0.50	0.35	1.000	2.371	4.765	9.135
6	0.30	0.40	0.35	1.000	2.356	4.904	9.492
7	0.30	0.50	0.40	0.985	2.409	4.688	9.369
8	0.30	0.60	0.45	1.006	2.316	4.832	9.584
9	0.30	0.70	0.50	0.978	2.296	4.911	9.347
10	0.40	0.60	0.50	1.009	2.292	4.785	9.583
11	0.40	0.70	0.55	0.969	2.271	4.915	9.286
12	0.40	0.80	0.60	0.948	2.331	4.984	9.508
13	0.50	0.70	0.60	0.970	2.154	5.206	9.318
14	0.50	0.80	0.65	0.940	2.275	5.207	9.618
15	0.50	0.90	0.70	0.980	2.361	5.445	9.944
16	0.60	0.80	0.70	0.878	2.377	5.211	9.425
17	0.60	0.90	0.75	0.953	2.460	5.530	9.925
18	0.70	0.90	0.80	0.990	2.582	5.685	10.562

TABLE 3

E' and E values for $x=1$ and $y=2$

No.	α_i	α_k	α	E' (kcal mol^{-1})	E (kcal mol^{-1})	β_{12ik} (K min^{-1})
1	0.10	0.20	0.15	27.06	26.98	1.642
2	0.10	0.30	0.20	26.16	25.97	1.653
3	0.20	0.30	0.25	24.78	24.75	1.669
4	0.20	0.40	0.30	23.86	23.78	1.673
5	0.20	0.50	0.35	23.34	23.16	1.686
6	0.30	0.50	0.40	22.90	22.82	1.697
7	0.30	0.60	0.45	22.55	22.45	1.661
8	0.30	0.70	0.50	21.79	21.63	1.637
9	0.40	0.60	0.50	22.10	22.07	1.651
10	0.40	0.70	0.55	21.28	21.21	1.620
11	0.40	0.80	0.60	21.32	21.17	1.640
12	0.50	0.70	0.60	20.09	20.07	1.562
13	0.50	0.80	0.65	20.62	20.56	1.608
14	0.50	0.90	0.70	20.56	20.46	1.671
15	0.60	0.90	0.75	21.05	20.97	1.707
16	0.70	0.90	0.80	21.41	21.38	1.786

3–8 one can conclude that the values E' and E are very close, most of the differences not exceeding 0.05–0.50 kcal mol^{-1}. Thus formula (16) leads to correct results, as the errors with respect to the exact value of E calculated according to formula (19) are exceptionally higher than 3%, most of them being 0.05–1.5%.

TABLE 4

E' and E values for $x=1$ and $y=3$

No.	α_i	α_k	α	E' (kcal mol^{-1})	E (kcal mol^{-1})	β_{13ik} (K min^{-1})
1	0.10	0.20	0.15	30.20	30.00	2.814
2	0.10	0.30	0.20	28.75	28.27	2.870
3	0.20	0.30	0.25	27.00	26.93	2.953
4	0.20	0.40	0.30	25.60	25.40	2.953
5	0.20	0.50	0.35	25.48	25.16	2.883
6	0.30	0.50	0.40	24.55	24.45	2.837
7	0.30	0.60	0.45	23.99	23.80	2.919
8	0.30	0.70	0.50	23.17	22.88	2.945
9	0.40	0.60	0.50	23.62	23.57	2.897
10	0.40	0.70	0.55	22.73	22.61	2.942
11	0.40	0.80	0.60	22.19	21.98	2.966
12	0.50	0.70	0.60	22.16	22.11	3.088
13	0.50	0.80	0.65	21.78	21.65	3.074
14	0.50	0.90	0.70	21.06	20.84	3.213
15	0.60	0.90	0.75	20.72	20.59	3.242
16	0.70	0.90	0.80	20.29	20.24	3.338

TABLE 5

E' and E values for $x = 1$ and $y = 4$

No.	α_i	α_k	α	E' (kcal mol^{-1})	E (kcal mol^{-1})	β_{14ik} (K min^{-1})
1	0.10	0.20	0.15	31.19	30.92	5.347
2	0.10	0.30	0.20	29.85	29.30	5.164
3	0.20	0.30	0.25	27.52	27.46	4.904
4	0.20	0.40	0.30	26.51	26.34	5.056
5	0.20	0.50	0.35	25.94	25.62	5.068
6	0.30	0.50	0.40	25.28	25.16	5.177
7	0.30	0.60	0.45	24.66	24.44	5.277
8	0.40	0.60	0.50	24.06	23.88	5.296
9	0.40	0.70	0.55	23.22	23.08	5.128
10	0.40	0.80	0.60	22.58	22.35	5.228
11	0.50	0.70	0.60	22.44	22.39	5.144
12	0.50	0.80	0.65	21.96	21.84	5.279
13	0.50	0.90	0.70	21.32	21.12	5.462
14	0.60	0.80	0.70	21.43	21.38	5.152
15	0.60	0.90	0.75	20.84	20.73	5.439
16	0.70	0.90	0.80	20.61	20.56	5.776

Besides, one notices that when working with two pairs of values α_{i1}, α_{k1} and α_{i2}, α_{k2} such as:

$$\alpha = \frac{\alpha_{i1} + \alpha_{k1}}{2} = \frac{\alpha_{i2} + \alpha_{k2}}{2} \tag{21}$$

TABLE 6

E' and E values for $x = 2$ and $y = 3$

No.	α_i	α_k	α	E' (kcal mol^{-1})	E (kcal mol^{-1})	β_{23ik} (K min^{-1})
1	0.10	0.20	0.15	36.02	35.47	3.480
2	0.10	0.30	0.20	33.19	32.00	3.528
3	0.20	0.30	0.25	30.56	30.39	3.599
4	0.20	0.40	0.30	28.28	27.84	3.613
5	0.20	0.50	0.35	28.87	28.27	3.568
6	0.30	0.50	0.40	27.03	26.91	3.549
7	0.30	0.60	0.45	26.02	25.69	3.574
8	0.30	0.70	0.50	25.09	24.58	3.604
9	0.40	0.60	0.50	25.72	25.63	3.539
10	0.40	0.70	0.55	24.70	24.47	3.593
11	0.40	0.80	0.60	23.37	23.04	3.658
12	0.50	0.70	0.60	25.06	24.91	3.680
13	0.50	0.80	0.65	23.39	23.15	3.741
14	0.50	0.90	0.70	21.73	21.34	3.903
15	0.60	0.80	0.70	21.73	21.66	3.794
16	0.60	0.90	0.75	20.30	20.13	3.995
17	0.70	0.90	0.80	18.89	18.82	4.134

TABLE 7

E' and E values for $x = 2$ and $y = 4$

No.	α_i	α_k	α	E' (kcal mol^{-1})	E (kcal mol^{-1})	β_{24ik} (K min^{-1})
1	0.10	0.20	0.15	34.67	34.17	6.013
2	0.10	0.30	0.20	32.87	31.92	5.822
3	0.20	0.30	0.25	29.62	29.53	5.550
4	0.20	0.40	0.30	28.52	28.25	5.716
5	0.20	0.50	0.35	27.91	27.47	5.753
6	0.30	0.50	0.40	27.05	26.90	5.889
7	0.30	0.60	0.45	26.16	25.85	5.932
8	0.40	0.60	0.50	25.46	25.33	5.938
9	0.40	0.70	0.55	24.59	24.39	5.779
10	0.40	0.80	0.60	23.47	23.17	5.920
11	0.50	0.70	0.60	24.12	24.04	5.736
12	0.50	0.80	0.65	22.91	22.75	5.947
13	0.50	0.90	0.70	21.85	21.58	6.153
14	0.60	0.80	0.70	21.57	21.51	5.901
15	0.60	0.90	0.75	20.70	20.58	6.193
16	0.70	0.90	0.80	20.07	20.00	6.572

the E values calculated for the two intervals are in good agreement in most cases. If (21) is valid the values of E', E and β_{xyik} will be considered as averaged for the two cases.

TABLE 8

E' and E values for $x = 3$ and $y = 4$

No.	α_i	α_k	α	E' (kcal mol^{-1})	E (kcal mol^{-1})	β_{34ik} (K min^{-1})
1	0.10	0.20	0.15	33.54	33.08	7.185
2	0.10	0.30	0.20	32.58	31.85	7.039
3	0.20	0.30	0.25	28.75	28.74	6.833
4	0.20	0.40	0.30	28.75	28.65	6.995
5	0.20	0.50	0.35	27.03	26.72	6.950
6	0.30	0.40	0.35	29.36	29.32	7.198
7	0.30	0.50	0.40	27.07	26.89	7.029
8	0.30	0.60	0.45	26.30	26.01	7.190
9	0.40	0.60	0.50	25.15	25.03	7.184
10	0.40	0.70	0.55	24.47	24.31	7.101
11	0.40	0.80	0.60	23.59	23.31	7.246
12	0.50	0.70	0.60	23.14	23.12	7.262
13	0.50	0.80	0.65	22.41	22.32	7.413
14	0.50	0.90	0.70	22.00	21.85	7.695
15	0.60	0.80	0.70	21.38	21.36	7.318
16	0.60	0.90	0.75	21.16	21.09	7.728
17	0.70	0.90	0.80	21.46	21.40	8.124

DISCUSSION: AN APPROXIMATE DEPENDENCE $E = E(\alpha, \beta)$

To find an approximate dependence $E = E(\alpha, \beta)$ we shall start with $\alpha = ct$, and study how the values of E calculated with formula (19) depend on β, i.e. the dependence $E = E(\beta)$. The next step is to establish the dependence $E = E(\alpha)$ for an approximately constant β_{xy} $(x, y = 1, 2, 3, 4)$ with $\beta_{yy} = (\beta_x + \beta_y)/2$ for $x < y$.

Before giving the solution of our problem, we take the liberty of removing the unreliable pairs of data (as for example the combination $x = 2$, $y = 3$, due to the fact that β_2 and β_3 are quite close).

To consider the dependence $E = E(\beta)$ for $\alpha = ct$, in a first approximation we shall admit that with the exception of one point (E, β_{23ik}) or (E, β_{12ik}) the remaining points lie on a straight line. The results obtained using the least-squares method [10] as well as β_{xyik} values for which the pair of data (E, β) is removed as statistically unreliable, are listed in Table 9. As seen from these data, in a first approximation E depends linearly on β, i.e.

$$\alpha = ct \quad E = a_1 + b_1\beta \tag{22}$$

A linear dependence can be obtained for $E = E(\alpha)$ too, when $\beta_{xy} = ct$ $(x, y = 1, 2, 3, 4)$. The results using the linear regression method are given in Table 10. There are no pairs of data to be removed as statistically unreliable. The linearity $E(\alpha)$ is better than the linearity $E(\beta)$. This statement is supported by the values of the correlation coefficients. Thus, for $\beta = ct$

$$E = a_2 + b_2\alpha \tag{23}$$

TABLE 9

Constants a_1 and b_1 of the linear dependence $E(\beta)$

No.	α	r_{xy}	a_1 (kcal mol^{-1})	b_1 (kcal mol^{-1} K^{-1} min)	β_{xyik} for which the point is removed
1	0.15	0.9083	25.93	1.11	β_{23ik}
2	0.20	0.9504	24.56	1.09	β_{23ik}
3	0.25	0.8992	23.97	0.80	β_{23ik}
4	0.30	0.9692	22.40	0.91	β_{23ik}
5	0.35	0.9537	22.07	0.85	β_{23ik}
6	0.40	0.9530	21.86	0.75	β_{23ik}
7	0.45	0.9606	21.61	0.63	β_{23ik}
8	0.50	0.9390	21.17	0.59	β_{23ik}
9	0.55	0.9444	20.58	0.56	β_{23ik}
10	0.60	0.9068	20.23	0.47	β_{23ik}
11	0.65	0.8754	20.37	0.31	β_{23ik}
12	0.70	0.9823	20.16	0.21	β_{23ik}
13	0.75	0.7427	19.86	0.15	β_{12ik}
14	0.80	0.6740	18.36	0.33	β_{12ik}

[a] r_{xy} is the correlation coefficient.

TABLE 10

Constants a_2 and b_2 of the linear dependence $E(\alpha)$

No.	β_{xy} (K min^{-1})	r_{xy}	a_2 (kcal mol^{-1})	b_2 (kcal mol^{-1})
1	$\beta_{12} = 1.670$	−0.9155	26.96	−9.10
2	$\beta_{13} = 2.987$	−0.9754	30.50	−13.81
3	$\beta_{23} = 3.670$	−0.9762	36.20	−21.50
4	$\beta_{14} = 5.280$	−0.9777	31.58	−14.92
5	$\beta_{24} = 5.960$	−0.9835	35.20	−19.63
6	$\beta_{34} = 7.281$	−0.9808	34.45	−18.05

Taking in (22) the derivative of E with respect to β it turns out that

$$\frac{\partial E}{\partial \beta} = b_1 \tag{24}$$

Taking into account that for every value of α one gets a particular value of $\partial E/\partial \beta = b_1$, one concludes that $\partial E/\partial \beta$ should depend on α, i.e.

$$\frac{\partial E}{\partial \beta} = \frac{\partial E}{\partial \beta}(\alpha) = b_1(\alpha) \tag{25}$$

As seen from Fig. 1 the plot of $\partial E/\partial \beta$ against α is a straight line, whose parameters, obtained using the least-squares method, are given in Table 11. Thus,

$$\frac{\partial E}{\partial \beta} = a_3 + b_3\alpha \tag{26}$$

Now taking in (23) the derivative of E with respect to α, one gets:

$$\frac{\partial E}{\partial \alpha} = \frac{\partial E}{\partial \alpha}(\beta) = b_2(\beta) \tag{27}$$

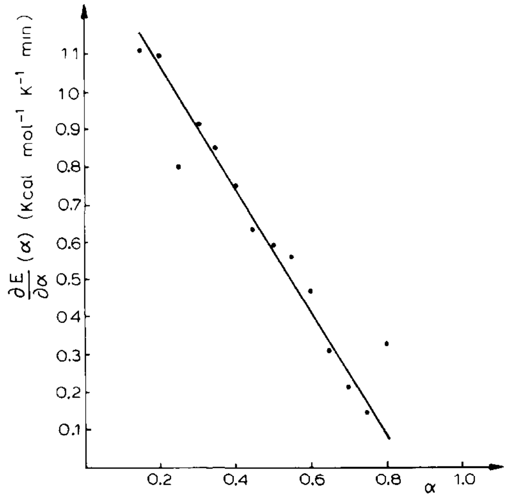

Fig. 1. The dependence $[(\partial E/\partial \beta), \alpha]$.

TABLE 11

The constants a_3 and b_3 of the linear dependence (26)

No.	r_{xy}	a_3 (kcal mol^{-1} K^{-1} min)	b_3 (kcal mol^{-1} K^{-1} min)	α for which points are removed
1	-0.9940	1.4023	-1.6425	0.25 0.80

where

$$\beta = \beta_{xy} = \frac{\beta_x + \beta_y}{2} \tag{28}$$

As shown in Fig. 2, the plot $[(\partial E/\partial \alpha), \beta]$ is quite linear with the exception of one point (b_2, β_{23}) which lies far away from the straight line. The parameters of the straight line obtained using the least-squares method are listed in Table 12. Thus in a first approximation,

$$\frac{\partial E}{\partial \alpha} = a_4 + b_4 \beta \tag{29}$$

In order to obtain the dependence $E = E(\alpha, \beta)$ through integration of the differential equations (26) and (29) one gets the following two particular solutions:

$$E_1 = a' + b'\beta + c'\alpha\beta \tag{30}$$

$$E_2 = a'' + b''\beta + c''\alpha\beta \tag{31}$$

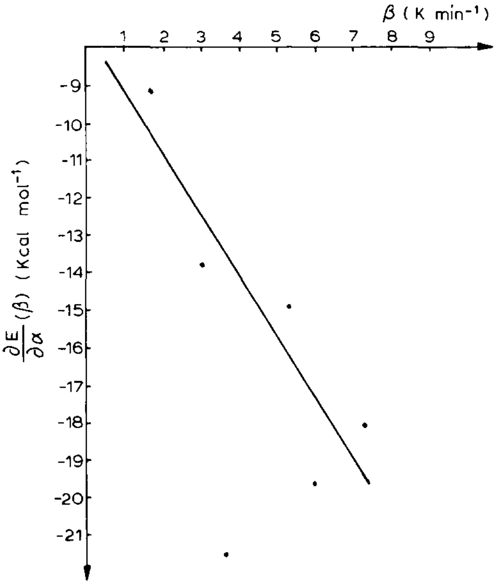

Fig. 2. The dependence $[(\partial E/\partial \alpha), \beta]$.

TABLE 12

Constants a_4 and b_4 of the linear dependence (29)

No.	r_{xy}	a_4 (kcal mol^{-1})	b_4 (kcal mol^{-1} K^{-1} min)	β_{xy} for which points are removed
1	−0.9034	−7.5686	−1.6251	β_{23}

where a', b', c', a'', b'', c'' are constants. A general solution can be obtained as a linear combination of E_1 and E_2.

$$E(\alpha, \beta) = C_1 E_1(\alpha, \beta) + C_2 E_2(\alpha, \beta) \tag{32}$$

or taking into account (30) and (31),

$$E(\alpha, \beta) = E_0 + E_1\alpha + E_2\beta + E_3\alpha\beta \tag{33}$$

where E_0, E_1, E_2 and E_3 are real constants.

To confirm our results, the derivatives of relationships (26) and (29) with respect to α and β, respectively, should be considered. One gets:

$$\frac{\partial^2 E}{\partial\alpha\,\partial\beta} = b_3 \tag{34}$$

$$\frac{\partial^2 E}{\partial\beta\,\partial\alpha} = b_4 \tag{35}$$

As the two variable functions $E(\alpha, \beta)$ fulfil the conditions of Schwarz's theorem [11], it follows that:

$$\frac{\partial^2 E}{\partial\alpha\,\partial\beta} = \frac{\partial^2 E}{\partial\beta\,\partial\alpha} \tag{36}$$

or

$$b_3 = b_4 \tag{37}$$

Our results are in fair agreement with (37), as

$b_3 = -1.6425$ kcal mol^{-1} K^{-1} min

and

$b_4 = -1.6251$ kcal mol^{-1} K^{-1} min

SUGGESTION FOR A NEW EQUATION IN NON-ISOTHERMAL KINETICS

If one supposes that:

$$\ln A = a + bE \tag{38}$$

then for E given by (33) it follows that:

$$A = A_0\, e^{E'_1\alpha}\, e^{E'_2\beta}\, e^{E'_3\alpha\beta} \tag{39}$$

where A_0, E_1', E_2' and E_3' are real constants. Taking into account relationships (33) and (39) from eqn. (2) one gets:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A_0}{\beta} \mathrm{f}(\upsilon, \alpha)\, \mathrm{e}^{E_1'\alpha}\, \mathrm{e}^{E_2'\beta}\, \mathrm{e}^{E_3'\alpha\beta}\, \mathrm{e}^{-E_0/RT}\, \mathrm{e}^{-E_1\alpha/RT}\, \mathrm{e}^{-E_2\beta/RT}\, \mathrm{e}^{-E_3\alpha\beta/RT} \quad (40)$$

which is the equation we have been looking for.

CONCLUSIONS

The experimental data and the method of working them, presented in this paper, should be considered as an illustration of an idea which has penetrated non-isothermal kinetics according to which the non-isothermal kinetic parameters are, to a certain extent, influenced by the experimental conditions [12].

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