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Note

NEW EQUATIONS IN NON-ISOTHERMAL KINETICS TAKING INTO ACCOUNT THE DEPENDENCES $A(\alpha)$ AND $E(\alpha)$

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In previous papers [1,2] we presented two new methods to estimate the values of non-isothermal kinetic parameters. We applied integration over small temperature intervals with several linear heating rates. In the first paper [1] the conversion function, $f(\alpha)$, was determined using small intervals of the conversion degree, α, whereas in the second one [2] an average function, $\bar{f}(\alpha)$, was determined using a larger interval of α values. Following these investigations, this paper deals with estimating the pre-exponential factor and $\bar{f}(\alpha)$ using the second method [2] for the dehydration of $CaC_2O_4 \cdot H_2O$ and the decomposition of $KMnO_4$. Results concerning the activation energy of these two reactions were presented in a previous paper [3].

FORMULAE USED [1–3]*

$$E = R\frac{T_{1ik}T_{2ik}}{T_{2ik} - T_{1ik}} \ln \frac{\Delta t_1}{\Delta t_2} \tag{1}$$

To obtain $f(\alpha)$ the following formulae should be used

$$\frac{\int_{\alpha_a}^{\alpha_b} \frac{d\alpha}{f(\alpha)}}{\int_{\alpha_b}^{\alpha_c} \frac{d\alpha}{f(\alpha)}} = R \tag{2}$$

where

$$R = \frac{R_1 + R_2}{2} \tag{3}$$

* To understand the meanings of the notations, refs. 1–4 should be consulted.

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and

$$R_i = \frac{\beta_{ibc}}{\beta_{iab}} \frac{\int_{T_{ia}}^{T_{ib}} e^{-E/RT} dT}{\int_{T_{ib}}^{T_{ic}} e^{-E/RT} dT} \tag{4}$$

The integrals were evaluated by using Simpson's method [4]

$$\int_{x_0}^{x_2} y\, dx = \frac{h}{3}(y_0 + 4y_1 + y_2) \tag{5}$$

$$h = \frac{x_2 - x_0}{2} \tag{6}$$

Using the average theorem to calculate the temperature integral [4] we obtained for the pre-exponential factor

$$A_l \approx \frac{e^{E/RT_{lik}}}{\Delta t_{lik}} \int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} \tag{7}$$

$$\log A = \frac{\log A_1 + \log A_2}{2} \tag{8}$$

THE FUNCTION $\bar{f}(\alpha)$

Dehydration of $CaC_2O_4 \cdot H_2O$

$\bar{E} = 24.26$ kcal mol^{-1}
$\alpha_a = 0.0417$, $\alpha_b = 0.5000$, $\alpha_c = 0.9583$
$T_{1a} = 406.4$ K, $T_{1b} = 492.2$ K, $T_{1c} = 441.2$ K
$\Delta t_{1ab} = 23.20$ min, $\Delta t_{1bc} = 11.90$ min
$\beta_{1ab} = 0.983$ K min^{-1}, $\beta_{1bc} = 1.008$ K min^{-1}
$R_1 = 0.652$,
$T_{2a} = 416.0$ K, $T_{2b} = 449.2$ K, $T_{2c} = 469.0$ K
$\Delta t_{2ab} = 6.90$ min, $\Delta t_{2bc} = 3.55$ min
$\beta_{2ab} = 4.812$ K min^{-1}, $\beta_{2bc} = 5.577$ K min^{-1}
$R_2 = 0.433$, $R = 0.543$

The average value of n from $f(\alpha) = (1-\alpha)^{\bar{n}}$ can be obtained by using the equation

$$\frac{0.9583^{1-\bar{n}} - 0.5000^{1-\bar{n}}}{0.5000^{1-\bar{n}} - 0.0417^{1-\bar{n}}} = 0.543 \tag{9}$$

whose solution is $\bar{n} = 0.5$. Although this value is smaller with respect to that reported in the literature [5,6], one has to take into account that it is an average value for $0.0417 \le \alpha \le 0.9583$.

$\bar{E} = 29.40$ kcal mol^{-1}
$\alpha_a = 0.150$, $\alpha_b = 0.450$, $\alpha_c = 0.900$
$T_{1a} = 479.5$ K, $T_{1b} = 514.0$ K, $T_{1c} = 522.0$ K
$\Delta t_{1ab} = 22.91$ min, $\Delta t_{1bc} = 5.16$ min
$\beta_{1ab} = 1.506$ K min^{-1}, $\beta_{1bc} = 1.549$ K min^{-1}
$R_1 = 1.526$,
$T_{2a} = 499.0$ K, $T_{2b} = 529.5$ K, $T_{2c} = 536.0$ K
$\Delta t_{2ab} = 10.00$ min, $\Delta t_{2bc} = 1.95$ min
$\beta_{2ab} = 3.050$ K min^{-1}, $\beta_{2bc} = 3.326$ K min^{-1}
$R_2 = 2.096$, $R = 1.811$

For $\bar{f}(\alpha) = (1-\alpha)^{\bar{n}}$ one obtains $\bar{n} = -1.35$, whereas for $\bar{f}(\alpha) = \alpha^{\bar{m}}$ one obtains $\bar{m} = 1.15$ which is more probable, thus

$$\bar{f}(\alpha) = \alpha^{1.15} \qquad (10)$$

This conversion function is quite different from that reported in the literature [7]. Nevertheless, such a function was tried because of its simplicity as well as of its dependence on only one parameter.

PRE-EXPONENTIAL FACTORS

The values of pre-exponential factors for different values of the conversion degree are listed in Table 1

As shown in Figs. 1 and 2 the dependences (log A, E) are linear. Thus, the data exhibit a particular kind of apparent mathematical compensation effect. The equations of the two straight lines are for dehydration of $CaC_2O_4 \cdot H_2O$

$$\log A = -3.06 + 0.51E \qquad r_{xy} = 0.9997 \qquad (11)$$

and for decomposition of $KMnO_4$

$$\log A = -2.51 + 0.42E \qquad r_{xy} = 0.9989 \qquad (12)$$

where r_{xy} are the corresponding correlation coefficients.

Generally, a dependence of the form

$$\log A = a + bE \qquad (13)$$

should be considered.

Concerning the dependence $E(\alpha)$, as shown in a previous paper [3], this could be described by

$$E = \mathrm{P}(\alpha) \qquad (14)$$

where $\mathrm{P}(\alpha)$ is a general polynomial in α. For a degree higher than that of the polynomial, one has to handle a large , inconvenient number of parameters

TABLE 1

Pre-exponential factors for various values of the conversion degree

(A) Dehydration of $CaC_2O_4 \cdot H_2O$										
α	0.1042	0.1667	0.2917	0.3750	0.4583	0.5417	0.6250	0.7083	0.7917	0.8542
A (s^{-1})	4.10×10^{14}	3.77×10^{12}	1.32×10^{10}	3.36×10^{9}	5.47×10^{8}	3.74×10^{8}	1.29×10^{8}	4.55×10^{7}	6.77×10^{6}	3.72×10^{6}
log A	14.61	12.58	10.12	9.53	8.74	8.57	8.11	7.66	6.83	6.57
(B) Decomposition of $KMnO_4$										
α	0.175	0.250	0.375	0.450	0.600	0.675				
A (s^{-1})	2.21×10^{5}	3.46×10^{7}	1.59×10^{9}	5.13×10^{11}	2.76×10^{12}	4.21×10^{12}				
log A	5.34	7.54	9.20	11.71	12.44	12.62				

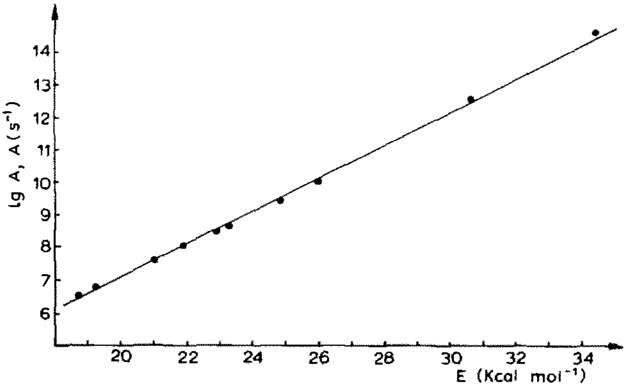

Fig. 1. Plot of log A vs. E for dehydration of $CaC_2O_4 \cdot H_2O$.

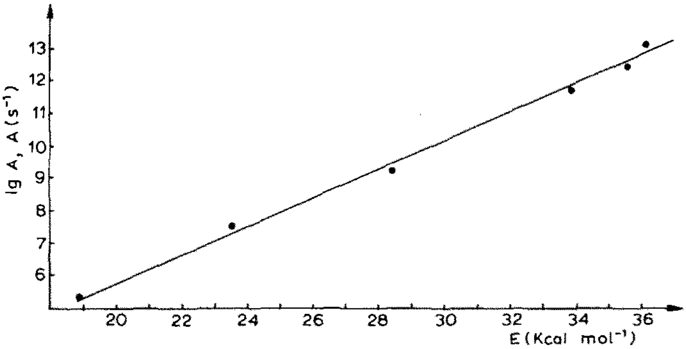

Fig. 2. Plot of log A vs. E for decomposition of $KMnO_4$.

in the corresponding equations. Thus two kinds of linear dependences of the form

$$y = a + bx \tag{15}$$

where $y = E$ and $x = \alpha$ or $1/\alpha$ will be considered. The results are listed in Table 2.

As seen from Table 2 in a first approximation the following dependences should be considered

$$E \approx a_1 + b_1\alpha \tag{16}$$

$$E \approx a_2 + b_2\frac{1}{\alpha} \tag{17}$$

Taking into account eqn. (13) it follows that

$$\log A \approx a_1' + b_1'\alpha \tag{18}$$

$$\log A \approx a_2' + b_2'\frac{1}{\alpha} \tag{19}$$

TABLE 2

Values of the constants a and b for $y = E$ and $x = \alpha$ or $x = 1/\alpha$ in eqn. (14)

No.	Decomposition of	The dependence $E(\alpha)$ or $E(1/\alpha)$	r_{xy}	a	b
1	$CaC_2O_4 \cdot H_2O$	(E, α)	0.9514	33.29	−18.35
2	$CaC_2O_4 \cdot H_2O$	$(E, 1/\alpha)$	0.9657	18.71	1.78
3	$KMnO_4$	(E, α)	0.9577	14.79	34.79
4	$KMnO_4$	$(E, 1/\alpha)$	−0.9779	42.00	4.26

By introducing in the fundamental rate equation of non-isothermal kinetics

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

From eqns. (16) and (18), and (17) and (19) it turns out that

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \bar{f}(\alpha)\, e^{(m\alpha + n/T + p\alpha/T)} \tag{20}$$

and

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \bar{f}(\alpha)\, e^{(m'/\alpha + n'/T + p/\alpha T)} \tag{21}$$

CONCLUSIONS

Equations (20) and (21) take into account the dependences $A(\alpha)$ and $E(\alpha)$. That is the reason for proposing them as new rate equations in non-isothermal kinetics. Future papers will deal with the methods of mathematical working of these equations.

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