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THE USE OF A METHOD FOR EVALUATING THE NON-ISOTHERMAL ACTIVATION ENERGY BY MODELLING A NON-ISOTHERMAL CHANGE WITH KINETIC PARAMETERS DEPENDENT ON THE DEGREE OF CONVERSION

E. URBANOVICI

*Research Institute for Electrotechnics, Sfîntz Gheorghe Branch, Str. Josef Attila Nr. 4,
Sfîntu Gheorghe 4000, Judeţul Covasna (R.S. Romania)*

A. VARHELYI

*Computing Centre of I.A.C.M. Sfîntu Gheorghe, Str. Progresului 2, Sfîntu Gheorghe 40000,
Judeţul Covasna (R.S. Romania)*

E. SEGAL

*Department of Physical Chemistry and Electrochemical Technology,
Faculty of Chemical Technology, Polytechnic Institute of Bucharest, Bulevardul Republicii 13,
Bucharest (R.S. Romania)*

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ABSTRACT

A method for determining the non-isothermal activation energy, elucidated previously by the present authors, was used to evaluate the change in this kinetic parameter with the degree of conversion.

INTRODUCTION

A method for evaluating the non-isothermal activation energy, which uses the integration over small ranges of variables and two heating rates, has been determined and applied previously by the present authors [1–4]. The working formula is

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

where T_{1i} and T_{2i} and T_{1k} and T_{2k} are the temperatures (K) corresponding to the degrees of conversion $\alpha = \alpha_i$ and $\alpha = \alpha_k$ for the two heating rates β_1 and β_2, respectively,

$$T_{1ik} = (T_{1k} + T_{1i})/2 \tag{2}$$

$$T_{2ik} = (T_{2k} + T_{2i})/2 \tag{3}$$

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and β_{1ik} and β_{2ik} are the local heating rates [1–4]. The use of eqn. (1) allowed us to show a significant change in the activation energy with the degree of conversion [1–4].

As the activation energy depends on α, the activation energy evaluated using eqn. (1) is an average value in the range $\alpha \in [\alpha_i, \alpha_k]$, i.e. the activation energy calculated according to eqn. (1) corresponds to an α_{ik} value given by [5]

$$\alpha_{ik} = (\alpha_i + \alpha_k)/2 \qquad (4)$$

In order to show that this method is useful in determining the change in activation energy with the degree of conversion, it was applied to some data obtained through modelling a kinetic equation with parameters which are dependent on the degree of conversion.

THE MODELLING OF SOME NON-ISOTHERMAL CURVES WHICH CONTAIN KINETIC PARAMETERS DEPENDING ON THE DEGREE OF CONVERSION

Three curves with $\beta_1 = 2$ K min^{-1}, $\beta_2 = 6$ K min^{-1} and $\beta_3 = 12$ K min^{-1} were modelled. For the activation energy, the following linear variation with the degree of conversion

$$E(\alpha) = 40\,000 - 20\,000\alpha (\text{cal mol}^{-1}) \qquad (5)$$

was considered. This linear dependence was shown by determining some experimental data [4,6].

For the pre-exponential factor $A(\alpha)$ the dependence on the degree of conversion was taken as

$$\log A(\alpha) = 15 - 10\alpha \qquad (6)$$

or

$$A(\alpha) = 10^{15-10\alpha}\ (\text{s}^{-1})$$

A similar relationship to that of eqn. (7) has been found in a previous work [6].

The conversion function $f(\alpha)$ of the reaction-order model was taken as

$$f(\alpha) = (1 - \alpha)^{(1.5-\alpha)} \qquad (8)$$

i.e.

$$n(\alpha) = 1.5 - \alpha \qquad (9)$$

where $n(\alpha)$ is the reaction order which depends on the degree of conversion. Taking into account eqns. (5) to (9) the non-isothermal differential kinetic equation can be written

$$\frac{d\alpha}{dT} = \frac{10^{15}}{\beta}(1 - \alpha)^{(1.5-\alpha)}10^{-\alpha} - \exp(40\,000\text{–}20\,000\alpha/RT) \qquad (10)$$

TABLE 1

Values of the degree of conversion and the temperature corresponding to the integral form of eqn. (10) ($R = 1.981$ cal mol^{-1} K^{-1})

α	T (K)		
	$\beta = 2$ K min^{-1}	$\beta = 6$ K min^{-1}	$\beta = 12$ K min^{-1}
0.05	465.924	477.694	485.413
0.10	474.125	486.475	494.586
0.20	483.939	497.192	505.924
0.30	491.277	505.413	514.742
0.40	497.894	513.000	523.000
0.50	504.440	520.648	531.448
0.60	511.277	528.796	540.537
0.70	518.706	537.834	550.717
0.80	527.164	548.265	562.578
0.90	537.414	561.097	577.293
0.95	543.960	569.355	586.792

Equation (10) cannot be integrated directly; to perform the integration it is necessary to apply numerical methods. The Runge–Kutta method in the form modified by Gill [7] led to the results given in Table 1 for the initial values at $\alpha_0 = 0$, $T_0 = 300$ K. The numerical integration was performed using an Independent-I 102F computer.

RESULTS

The activation energies for various intervals $\alpha \in [\alpha_i, \alpha_k]$ were calculated.

In order to compare the calculated values using eqn. (1) with those given by eqn. (5), an average value of E for $\alpha \in [\alpha_i, \alpha_k]$

$$\bar{E} = \frac{1}{\alpha_k - \alpha_i} \int_{\alpha_i}^{\alpha_k} E(\alpha)\, \mathrm{d}\alpha \tag{11}$$

was considered. Introducing the $E(\alpha)$ value given by eqn. (5) into eqn. (11) gives

$$\bar{E} = 40\,000 - 20\,000 \frac{\alpha_i + \alpha_k}{2}$$

or

$$\bar{E} = 40\,000 - 20\,000\alpha_{ik} \tag{12}$$

The $\bar{E}$ values calculated using eqn. (12) and the E values calculated using eqn. (1) are compared in Table 2. The agreement between the two sets of values is very good; thus values of E calculated using eqn. (1) can be used to

TABLE 2

The values of $\bar{E}$ and E for various values of the degree of conversion

α_i	α_k	α_{ik}	$\bar{E}$, eqn. (10) (kcal mol^{-1})	E, eqn. (1) (kcal mol^{-1})		
				$\beta_1 = 2$ K min^{-1} $\beta_2 = 6$ K min^{-1}	$\beta_1 = 2$ K min^{-1} $\beta_2 = 12$ K min^{-1}	$\beta_1 = 6$ K min^{-1} $\beta_2 = 12$ K min^{-1}
0.05	0.10	0.075	38.50	38.505	38.510	38.519
0.10	0.20	0.150	37.00	36.997	36.988	36.972
0.10	0.30	0.200	36.00	35.942	35.957	35.980
0.20	0.30	0.250	35.00	34.973	35.013	35.075
0.20	0.40	0.300	34.00	33.880	33.911	33.962
0.30	0.40	0.350	33.00	32.957	32.994	33.053
0.30	0.50	0.400	32.00	31.896	31.876	31.844
0.40	0.50	0.450	31.00	31.034	30.986	30.909
0.40	0.60	0.500	30.00	29.901	29.863	29.801
0.50	0.60	0.550	29.00	29.022	28.995	28.953
0.50	0.70	0.600	28.00	27.815	27.814	27.812
0.60	0.70	0.650	27.00	26.914	26.934	26.967
0.60	0.80	0.700	26.00	25.791	25.789	25.785
0.70	0.80	0.750	25.00	24.968	24.959	24.945
0.70	0.90	0.800	24.00	23.750	23.738	23.720
0.80	0.90	0.850	23.00	22.926	22.918	22.907
0.80	0.95	0.875	22.50	22.306	22.308	22.311

determine the change in the activation energy with the degree of conversion in non-isothermal kinetics.

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