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Non-isothermal kinetics of reactions whose activation energy depends on the degree of conversion

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Abstract

A procedure for evaluating the non-isothermal kinetic parameters of reactions for which the activation energy depends on the degree of conversion is suggested. The procedure has been applied to the dehydration of calcium oxalate monohydrate and to the thermal degradation of poly(vinyl chloride) (PVC) and polychloroprene rubber.

Keywords: Activation energy; Non-isothermal kinetics; Thermal degradation

1. Introduction

Earlier non-isothermal kinetic investigations of some heterogeneous solid–gas decompositions or thermooxidations of polymeric materials have shown that the activation energy depends on the degree of conversion [1–5]. In order to estimate the activation energy, methods due to Reich–Levi [6, 7], Flynn–Wall–Ozawa [8, 9] and Urbanovici–Segal [10–13] based on the use of different heating rates and investigation over a small range of the variable, have been applied. It has been shown that for the dehydration of calcium oxalate monohydrate [3], the decomposition of potassium permanganate [3] and the non-isothermal degradation of polychloroprene rubber [5] the activation energy, *E*, and the preexponential factor, *A*, depend on the degree of

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conversion and are related by

$$\ln A = aE + b \tag{1}$$

where a and b are constant coefficients.

Eq. (1) arises as a compensation effect between the exponential and preexponential factors in the Arrhenius equation.

This paper is dedicated to a procedure for estimating non-isothermal kinetic parameters and the compensation effect parameters of reactions for which the activation energy depends on the degree of conversion. This procedure will be applied to the dehydration of calcium oxalate monohydrate and the thermal degradation of poly(vinyl chloride) and polychloroprene rubber.

2. Estimation of the non-isothermal kinetic parameters

The procedure is based on the following assumptions:

1. the activation energy, E, and the preexponential factor, A, depend on the degree of conversion and do not depend on the heating rate, provided the rate is low;
2. the activation energy and the preexponential factor are correlated through the compensation effect described by Eq. (1);
3. the dependence of the activation energy on the degree of conversion, α, is given by

$$E = E_0 + E_1 \ln(1-\alpha) \tag{2}$$

where E_0 and E_1 are constants;

4. the differential conversion function, $\mathrm{f}(\alpha)$, has the form

$$\mathrm{f}(\alpha) = (1-\alpha)^n \tag{3}$$

where n is the reaction order.

The assumption concerning the independence of the activation energy on the heating rate is the basis of the methods derived by Reich and Levi [6, 7] and Flynn et al. [8, 9] to evaluate the activation energy.

Relationship (2) has been checked for the isothermal thermomechanical degradation of some polymeric materials [14].

From the generally accepted equation of non-isothermal kinetics

$$\beta \frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\,\mathrm{f}(\alpha) \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where β is the heating rate and T is the temperature (K), we obtain

$$\ln\left(\beta \frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln A\,\mathrm{f}(\alpha) - \frac{E}{RT} \tag{5}$$

This is the basis of Friedman's method [15] for estimating the non-isothermal kinetic parameters. For $\alpha = \text{const.}$ and using various heating rates, the plot of $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ vs.

$(1/T)$ should be linear. From the slope and the intercept of the straight line the values of activation energy and the product $Af(\alpha)$ were obtained. This enables $E(\alpha)$ and $A(\alpha)$ to be estimated using various values of α.

From the differential conversion function (3) it follows that

$$\ln Af(\alpha) = \ln A + n\ln(1-\alpha) \tag{6}$$

and from the values of $Af(\alpha)$ and α, the values of $\ln A$ corresponding to various values of n can be obtained. The plot of $\ln A$ vs. E should be linear as required by the existence of a compensation effect (Eq. (1)). The correct value of n will be that which gives a correlation coefficient closest to 1.00 for the straight line $\ln A$ vs. E.

The existence of the kinetic compensation effect presumes the existence of an isokinetic temperature which can be estimated from the slope of the straight line $\ln A$ vs. E [16]

$$T_i = \frac{1}{Ra} \tag{7}$$

From Eqs. (1)–(5) we obtain

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \left(b + aE_0 - \frac{E_0}{RT}\right) + \left(aE_1 - \frac{E_1}{RT} + n\right)\ln(1-\alpha) \tag{8}$$

For $T = T_i$, relationships (7) and (8) lead to

$$b = \left[\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\right]_{T=T_i} - n\ln(1-\alpha) \tag{9}$$

Thus the constant b can be determined from the curves $\alpha = \alpha(T)$ and $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ vs. α for a given heating rate. Obviously for all the heating rates used, values of b close to that obtained from the plot $\ln A$ vs. E should be obtained. This is a confirmation of the above procedure.

3. Applications

3.1. The dehydration of calcium oxalate monohydrate

In order to obtain the values of the non-isothermal kinetic parameters, the thermogravimetric data determined previously [4] have been used. The thermogravimetric curves for four heating rates are given in Fig. 1.

In reference [4] these curves were used to estimate the activation energy by integration over small changes of the variables. Some of the results obtained are shown in Fig. 2.

In Fig. 2 an estimate of the activation energy, using the Flynn–Wall–Ozawa method, is also shown. For all sets of α values used in the linear plot, correlation coefficient values for the linear regression were higher than 0.993. The activation energy decreased with the degree of conversion.

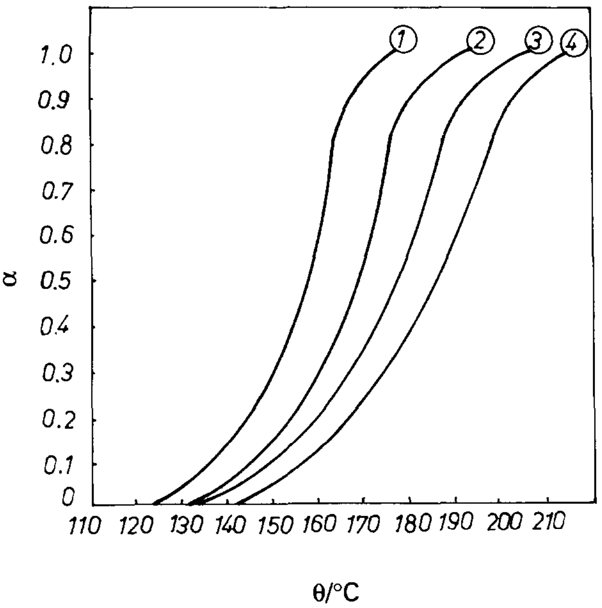

Fig. 1. The TG curves for the dehydration of calcium oxalate monohydrate. 1. $\beta = 0.987\,\mathrm{K\,min^{-1}}$; 2. $\beta = 2.353\,\mathrm{K\,min^{-1}}$; 3. $\beta = 4.998\,\mathrm{K\,min^{-1}}$; 4. $\beta = 9.573\,\mathrm{K\,min^{-1}}$.

Fig. 3 shows the curves $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ vs. α, and using these curves and TG curves shown in Fig. 1, the plots of $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ vs. $(1/T)$ for $0.15 \leqslant \alpha \leqslant 0.70$ were obtained. Some of these straight lines are given in Fig. 4.

The correlation coefficient for $\alpha = 0.15$ is 0.987; for $0.20 \leqslant \alpha \leqslant 0.70$ the values of the correlation coefficients are higher than 0.99. From the slopes of these straight lines, the values of the activation energy for each value of the degree of conversion have been obtained. According to our results the activation energy decreases from $125.0\,\mathrm{kJ\,mol^{-1}}$ (for $\alpha = 0.15$) to $93.6\,\mathrm{kJ\,mol^{-1}}$ (for $\alpha = 0.70$). These values of the activation energy (see Fig. 2) are closer to those obtained by Urbanovici and Segal [4] but lower than those obtained using the Flynn–Wall–Ozawa method. Taking into account that such a dependence of the activation energy on the degree of conversion could be described by Eq. (2), E_0 and E_1 were found to be $130.1\,\mathrm{kJ\,mol^{-1}}$ and $40.75\,\mathrm{kJ\,mol^{-1}}$ respectively with $r = 0.9800$. The linear dependence of E on $\ln(1-\alpha)$ is justified by the results shown in Table 1 where the values of E calculated using relationship (2) with determined values of E_0 and E_1 are compared with the corresponding values obtained by the above described procedure.

From the intercept of $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ vs. $(1/T)$ according to Eq. (6), the values of $\ln A$, for values of reaction order located in the range 0.5–1.2 (in steps of 0.1) were evaluated. For $n = 1$ we found that the correlation coefficient corresponding to the straight line $\ln A$ vs. E had the highest value ($r = 0.99993$). Values of r higher than 0.9998 have also been obtained for other values of n. Fig. 5 shows the straight line corresponding to the compensation effect for $n = 1$.

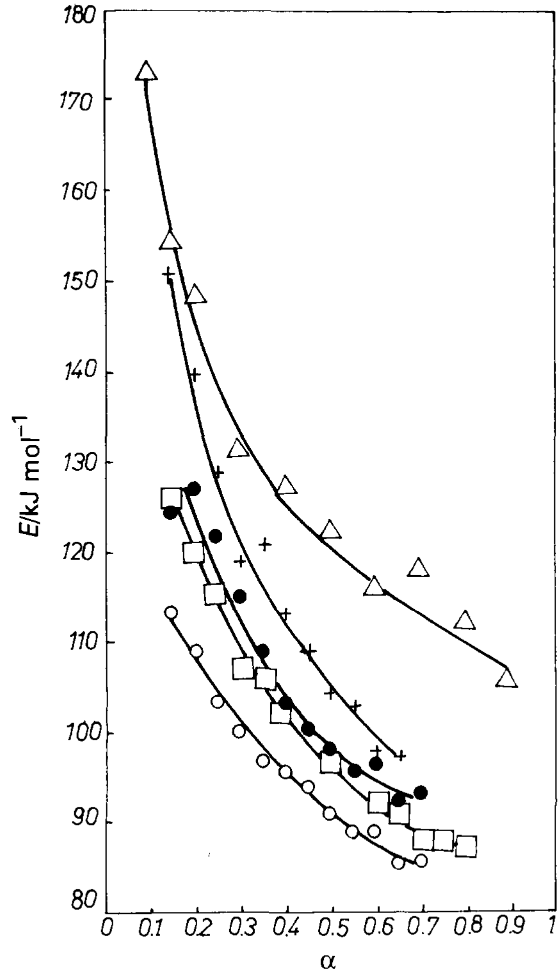

Fig. 2. The curve E (α) for the dehydration of calcium oxalate monohydrate. Method used to estimate the activation energy: ○ Urbanovici and Segal for $\beta_1 = 0.987$ K min^{-1} and $\beta_2 = 2.353$ K min^{-1}; □ Urbanovici and Segal for $\beta_1 = 0.987$ K min^{-1} and $\beta_3 = 4.988$ K min^{-1}; + Urbanovici and Segal for $\beta_2 = 2.353$ K min^{-1} and $\beta_3 = 4.988$ K min^{-1}; △ Flynn–Wall–Ozawa; ● Friedman.

The following values have been obtained for the parameters of the compensation effect: $a = 0.270$ mol kJ^{-1} and $b = -5.62$. Using Eq. (7) a value of T_i of 446 K was obtained for the isokinetic temperature. Urbanovici and Segal [3] have checked the existence of a compensation effect (Eq. (1)) in the dehydration of calcium oxalate monohydrate using values of E and $\ln A$ obtained by another method and $n = 0.5$. The values $a = 0.281$ mol kJ^{-1} and $b = -7.05$ ($r = 0.9997$) were obtained. The values obtained from our data for $n = 0.5$ are identical.

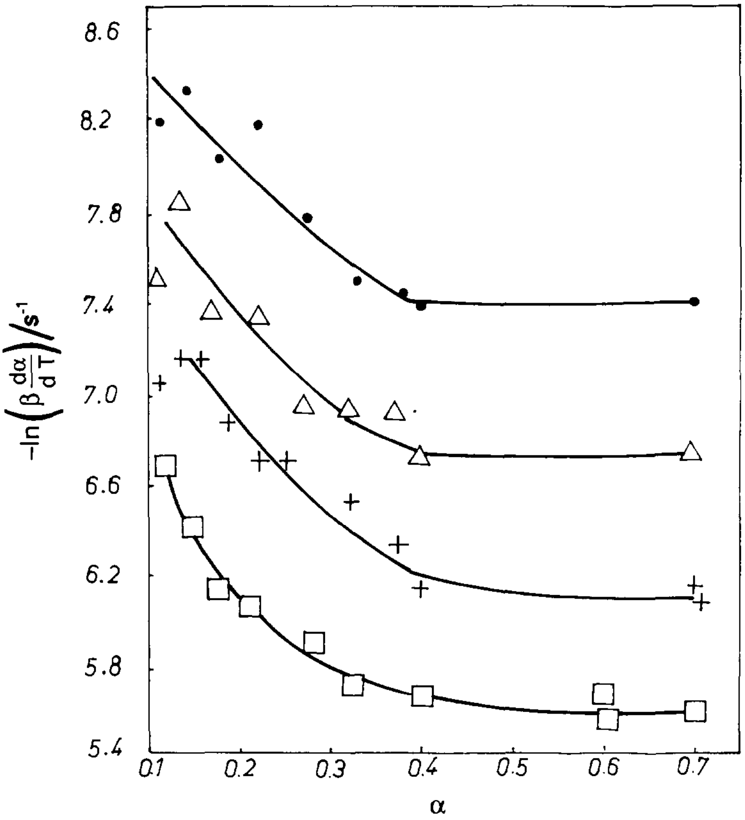

Fig. 3. The curves $\ln(\beta(d\alpha/dT))$ vs. α for the dehydration of calcium oxalate monohydrate. ● $\beta = 0.987\,K\,min^{-1}$; △ $\beta = 2.353\,K\,min^{-1}$; + $\beta = 4.998\,K\,min^{-1}$; □ $\beta = 9.573\,K\,min^{-1}$.

For $n = 1$ and $T_i = 446\,K$, using the curves from Figs. 1 and 3, the value of the parameter b has been calculated by use of Eq. (9). The results obtained for three heating rates, 2.353, 4.988 and 9.573 K min^{-1}, are listed in Table 2.

These values are close to those obtained from the linear regression $\ln A$ vs. E ($b = -5.62$).

3.2. *The thermal degradation of PVC*

The thermal degradation curves of PVC, produced by Electromures–Romania, have been recorded in a static air atmosphere at the heating rates of 0.70, 1.50, 2.70 and 5.60 K min^{-1}, using a Q-1500 D MOM Budapest-type Paulik–Paulik–Erdey derivatograph. The derivatogram corresponding to $\beta = 2.70\,K\,min^{-1}$ is shown in Fig. 6. Similar derivatograms were obtained at other heating rates.

Two degradation steps I and II were observed. For step II and using Friedman's method [15] the change of the activation energy with the degree of conversion

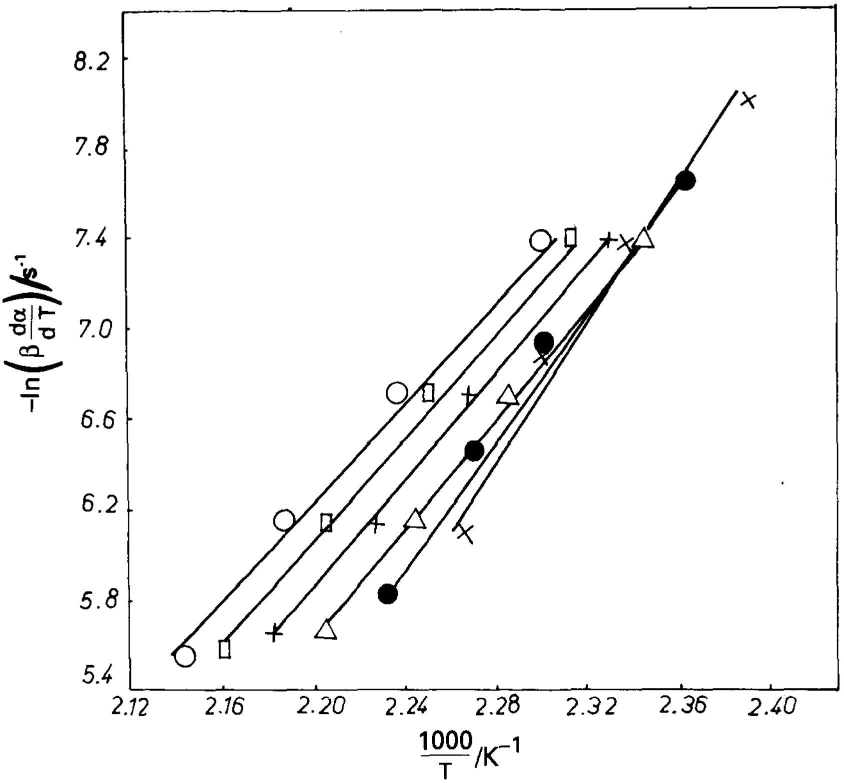

Fig. 4. The straight lines $\ln(\beta(d\alpha/dT))$ vs. $(1/T)$ for the dehydration of calcium oxalate monohydrate. × $\alpha = 0.20$; ● $\alpha = 0.30$; △ $\alpha = 0.40$; + $\alpha = 0.50$; □ $\alpha = 0.60$; ○ $\alpha = 0.70$.

Table 1
Verification of Eq. (2) applied to the dehydration of calcium oxalate monohydrate

α	0.15	0.20	0.30	0.35	0.40	0.45	0.50	0.60	0.70
E calculated/[kJ mol^{-1}]	123.3	120.2	115.4	112.4	109.1	105.75	102.0	92.8	81.1
E determined/[kJ mol^{-1}]	125.0	127.1	115.8	108.7	103.2	100.3	98.2	97.4	93.6

was investigated. In the range of α, $0.01 \leqslant \alpha \leqslant 0.30$, $\ln(\beta(d\alpha/dT))$ could be correctly estimated and the values of E increased from 105.75 kJ mol^{-1} to 153.4 kJ mol^{-1}. Using the procedure previously described, values of $E_0 = 107.6$ kJ mol^{-1}; $E_1 = -175.9$ kJ mol^{-1}; $r = 0.9804$, were obtained. The highest value of the correlation coefficient for the straight line $\ln A$ vs. E, $r = 0.999972$, was obtained for $n = 0.5$, with the following values for the compensation parameters: $a = 0.231$ mol kJ^{-1}; $b = -8.025$; $T_i = 521$ K.

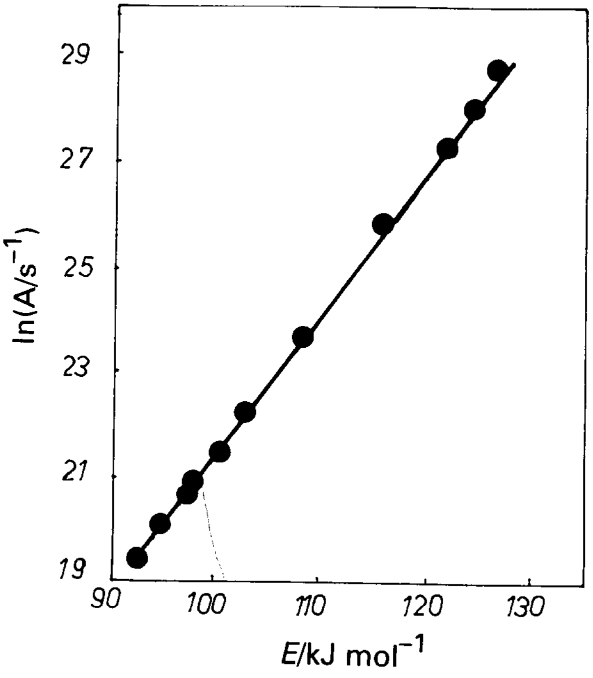

Fig. 5. The plot of ln A vs. E for the dehydration of calcium oxalate monohydrate.

Table 2
The values of b derived for the dehydration of calcium oxalate monohydrate using relationship (9)

β/[K min^{-1}]	α	$\left[\ln\left(\beta\frac{d\alpha}{dT}\right)\right]^{a}_{T=T_i}$	$b=\left[\ln\left(\beta\frac{d\alpha}{dT}\right)\right]_{T=T_i}-\ln(1-\alpha)^{a}$
2.353	0.70	−6.70	−5.50
4.998	0.42	−6.16	−5.615
9.573	0.27	−5.87	−5.555

[a] $\langle\beta\rangle = s^{-1}$.

Fig. 7 shows the straight line corresponding to the compensation effect for $n = 0.5$.

For $n = 0.5$ and $T_i = 521$ K, using relationship (9), the parameter b has been obtained. The heating rates 1.50 and 2.70 K min^{-1} for which the α values lie in the range where E has been estimated, have been considered. The values $b = -8.075$ for $\beta = 1.50$ K min^{-1} and $b = -8.080$ for $\beta = 2.70$ K min^{-1} have been obtained. These values are close to those obtained from the linear regression ln A vs. E ($b = -8.025$).

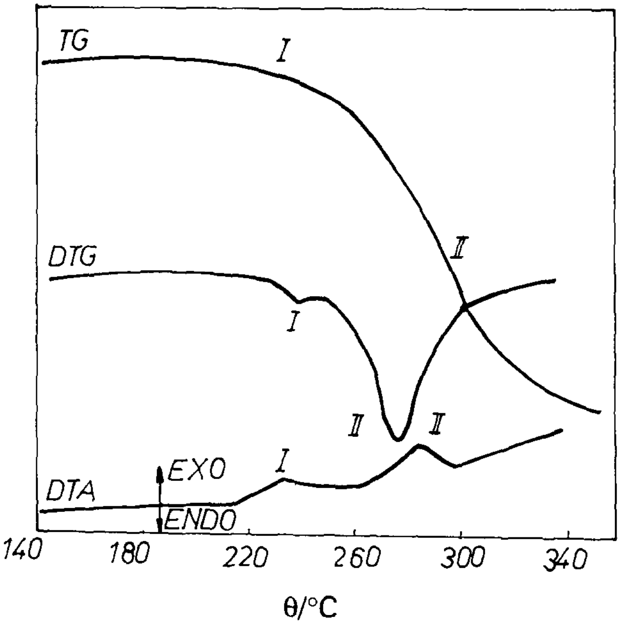

Fig. 6. Derivatogram corresponding to the thermal degradation of PVC at $\beta = 2.70\,\mathrm{K\,min^{-1}}$.

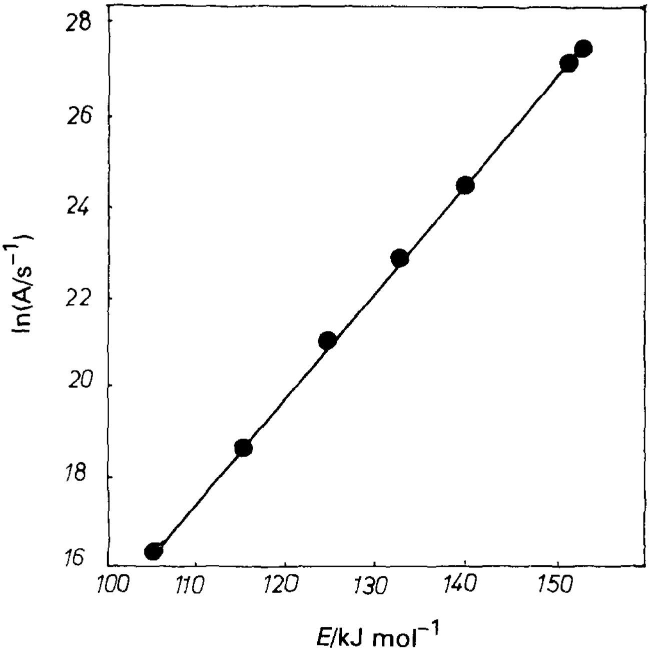

Fig. 7. The plot of ln A vs. E for the thermal degradation of PVC.

3.3. Thermal degradation of polychloroprene rubber

Some results concerning the non-isothermal kinetics of the degradation of polychloroprene rubber have been reported in a previous paper [5]. The activation energy was estimated using the Flynn–Wall–Ozawa method [8, 9] and the value of ln *A* was obtained using the values of *E* and $(\mathrm{d}\alpha/\mathrm{d}T)$ from the DTG curve. It was shown that for $0.04 \leqslant \alpha \leqslant 0.14$, the activation energy increased from 42.6 kJ mol^{-1} to 106.6 kJ mol^{-1} and that *E* and ln *A* values are correlated through the compensation effect.

The procedure described in this work gives

$$E_0 = 52.3\,\mathrm{kJ\,mol^{-1}};\quad E_1 = -297.9\,\mathrm{kJ\,mol^{-1}};\quad r = 0.9744.$$

The highest correlation coefficient of the straight line ln *A* vs. *E* was obtained for $n = 2$ ($r = 0.999772$), corresponding to $a = 0.237\,\mathrm{mol\,kJ^{-1}}$; $b = -8.085$; $T_i = 508$ K. This value of *a* is close to that obtained in the previous work [5], but the value of *b* is about one higher than that previously reported [5].

Fig. 8 shows the straight line corresponding to the compensation effect for $n = 2$.

For $n = 2$ and $T_i = 508$ K, the *b* parameter has been estimated by use of relationship (9). The heating rates 1.48, 3.08 and 6.20 K min^{-1}, for which α lies in the range used for *E* estimation, have been considered. The values $b = -8.29$ for $\beta = 1.48\,\mathrm{K\,min^{-1}}$;

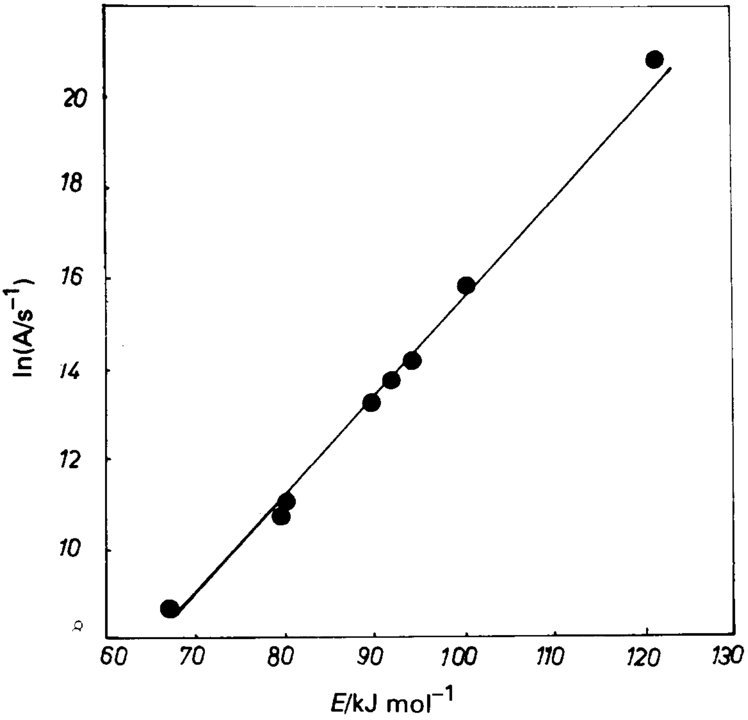

Fig. 8. The plot of ln *A* vs. *E* for the thermal degradation of polychloroprene rubber.

$b = -8.38$ for $\beta = 3.08\,\mathrm{K\,min^{-1}}$ and $b = -8.09$ for $\beta = 6.20\,\mathrm{K\,min^{-1}}$ have been obtained. These values are in good agreement with those obtained from the linear regression $\ln A$ vs. E ($b = -8.085$).

4. Conclusions

A procedure has been derived for estimating the non-isothermal kinetic parameters as well as the compensation effect parameters of reactions for which changes in the values of the activation energy depend on the degree of conversion. It has been shown that in order to estimate the activation energy corresponding to a given conversion, the Friedman method applied to a set of thermograms recorded at various heating rates is suitable. A procedure for estimating the preexponential factor was also suggested. The values of E and A can be used in order to estimate the parameters of the compensation effect.

The suggested procedure has been applied to the dehydration of calcium oxalate monohydrate and to the thermal degradation of poly(vinyl chloride) and polychloroprene rubber.

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