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Evaluation of the activation energy from derivative temperature-programmed desorption curves

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Abstract

A set of expressions for the evaluation of the activation energy from first and second derivative temperature-programmed desorption (DTPD) have been presented for different values of the order of kinetics. Taking into consideration a large number of computer generated DTPD curves of different order of kinetics it is shown that the value of the activation energy obtained by using the present set of expressions are in good agreement with its actual value. © 1998 Elsevier Science B.V.

Keywords: Derivative temperature-programmed desorption (DTPD); Activation energy; Order of kinetics; Pre-exponential factor

1. Introduction

Temperature-programmed desorption (TPD) is an indispensable tool in the field of catalytic research for the exhaustive study of the number of adsorption forms on the surface and their relative stability. The resolving power of the TPD curves can be enhanced by using a derivative TPD (DTPD). Hu et al. [1] suggested a method for the determination of activation energy and pre-exponential factor from first and second DTPD curves. In their work they have used an asymptotic expansion of the integral $\int_0^T \exp(-E/RT)\,dT$ (E=activation energy, R=Universal gas constant, T=absolute temperature) known as temperature integral. They have dealt only with two cases of order of kinetics (n), namely first and second (n=1 and n=2).

In the present paper we report a number of expressions for the determination of the activation energy from the first and second DTPD curves not only for n=1 and n=2 but also for some other values of n. The present set of expressions for the evaluation of the activation energy unlike those of Hu et al. [1] involve only the characteristic temperatures not the higher order derivatives which require a very tedious method of evaluation. The suitability of the present set of expressions have been tested by computing the activation energies of some computer generated DTPD curves.

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2. Theory

According to Hu et al. [1] the mathematical equation for TPD can be expressed as

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t}=A\exp(-E/RT)\theta^{n} \tag{1}$$

where A is the pre-exponential factor, θ the surface coverage and t the time. For a linear heating scheme one gets

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T}=\frac{A}{\beta}\exp(-E/RT)\theta^{n} \tag{2}$$

where β is the constant heating rate. The curve connecting $\theta_T=-\frac{\mathrm{d}\theta}{\mathrm{d}T}$ and T is called a TPD curve. So the curve connecting $-\frac{\mathrm{d}^2\theta}{\mathrm{d}T^2}=\dot{\theta}_T$ and T is the first DTPD curve and that connecting $-\frac{\mathrm{d}^3\theta}{\mathrm{d}T^3}=\ddot{\theta}_T$ and that T represents the second DTPD curve. Now following Hu et al. [1] one can write

$$\theta_T=\frac{A}{\beta}\exp(-E/RT)\exp[-F(T)]\theta_0(n=1) \tag{3}$$

and

$$\theta_T=\frac{A}{\beta}\exp(-E/RT)[(n-1)F(T)+\theta_0^{1-n}]^{-\frac{n}{n-1}}(n\neq 1) \tag{4}$$

where

$$F(T)=\frac{A}{\beta}\int_0^T\exp(-E/RT)\mathrm{d}T \tag{5}$$

The integral$\int_0^T\exp(-E/RT)\mathrm{d}T$ can not be evaluated exactly. Hu et al. [1] have used an asymptotic expansion of the integral in terms of $X=E/RT$. In the preset paper, following Devi [2] we express the temperature integral in terms of the second exponential integral $E_2(X)$ [3]. According to Devi [2]

$$F(T)=\frac{A}{\beta}\int_0^T\exp(-E/RT)\mathrm{d}T=\frac{AE}{\beta RX}E_2(X) \tag{6}$$

Devi [2] has also developed a rigorous computer code for the evaluation of $E_2(X)$ by expressing it in terms of continued fraction [4]. The method converges rapidly and permits a very high precision. Now after some elementary mathematical manipulations Eqs. (3) and (4) can be expressed as

$$I=\frac{\theta_T}{(\theta_T)_m}=\exp[X_m-X+F(X,X_m)]\,(n=1) \tag{7}$$

and

$$I=\frac{\theta_T}{(\theta_T)_m}=\exp(X_m-X)\times\left[1-\frac{n-1}{n}F(X,X_m)\right]^{-\frac{n}{n-1}}(n\neq 1) \tag{8}$$

where$(\theta_T)_m$ is the maximum value of$\theta_T=-\frac{\mathrm{d}\theta}{\mathrm{d}T}$ and

$$F(X,X_m)=X_m^2\exp(X_m)\left[\frac{E_2(X_m)}{X_m}-\frac{E_2(X)}{X}\right] \tag{9}$$

with $X_m=E/RT_m$. T_m is the temperature where θ_T becomes maximum.

X_m can be obtained from the following equations

$$X_m^2=\frac{AE}{\beta R}\exp(-X_m)\,(n=1) \tag{10}$$

$$(n-1)\frac{AEE_2(X_m)}{\beta RX_m}+1=\frac{nAE}{\beta RX_m^2}\exp(-X_m)\,(n\neq 1) \tag{11}$$

The equations for the first DTPD can be written as

$$\dot{I}=\frac{\mathrm{d}I}{\mathrm{d}T}=\frac{RX^2}{E}\exp(X_m-X)\left[G-\frac{\mathrm{d}G}{\mathrm{d}X}\right](n\neq 1) \tag{12}$$

and

$$\dot{I}=\frac{\mathrm{d}I}{\mathrm{d}T}=\frac{RX^2}{E}I\left[1-\frac{\mathrm{d}F}{\mathrm{d}X}\right](n=1) \tag{13}$$

For the second DTPD one can write

$$\ddot{I}=\frac{\mathrm{d}^2I}{\mathrm{d}T^2}=\frac{R^2X^3}{E^2}\exp(X_m-X)\left[X\frac{\mathrm{d}^2G}{\mathrm{d}X^2}-2(X-1)\frac{\mathrm{d}G}{\mathrm{d}X}|(X-2)G\right](n\neq 1) \tag{14}$$

and

$$\ddot{I}=\frac{d^2I}{dT^2}=\frac{R^2X^3}{E^2}I\left[\frac{d^2F}{dX^2}+\left(\frac{dF}{dX}-1\right)\times\left\{X\left(\frac{dF}{dX}-1\right)-2\right\}\right](n=1) \tag{15}$$

where

$$G=D^{-\frac{n}{n-1}} \tag{16}$$

$$D=1-\frac{n}{n-1}F \tag{17}$$

$$F=F(X,X_m) \tag{18}$$

$$\frac{dG}{dX}=-\frac{n}{n-1}\frac{G}{D}\frac{dD}{dX} \tag{19}$$

$$\frac{d^2G}{dX^2}=-\frac{n}{n-1}\left[\left(\frac{1}{D}\frac{dG}{dX}-\frac{G}{D^2}\frac{dD}{dX}\right)\frac{dD}{dX}+\frac{G}{D}\frac{d^2D}{dX^2}\right] \tag{20}$$

$$\frac{dF}{dX}=\left(\frac{X_m}{X}\right)^2\exp(X_m-X) \tag{21}$$

$$\frac{d^2F}{dX^2}=-\left(1+\frac{2}{X}\right)\frac{dF}{dX} \tag{22}$$

$$\frac{dD}{dX}=-\frac{n-1}{n}\frac{dF}{dX} \tag{23}$$

$$\frac{d^2D}{dX^2}=-\frac{n-1}{n}\frac{d^2F}{dX^2} \tag{24}$$

The peaks of the first DTPD curve is given by

$$\frac{d^2I}{dT^2}=0 \tag{25}$$

and those of the second DTPD curve is given by

$$\frac{d^3I}{dT^3}=0 \tag{26}$$

Eqs. (23) and (24) have been solved numerically by Newton–McAuley method [5] (see Appendix A).

Some simple relations were searched for connecting the quantities in each of the following pairs of variables (X_1, X_2) and (X_{d1}, X_{d2}) where $X_i=E/RT_i$ and $X_{di}=E/RT_{di}$; i=1,2. T_i and T_{di} represent respectively, the peak temperatures of the first and second DTPD curves. A plot of X_1 as a function of $X_1/(X_1-X_2)$ was found to be very linear for any value of n so that one can write

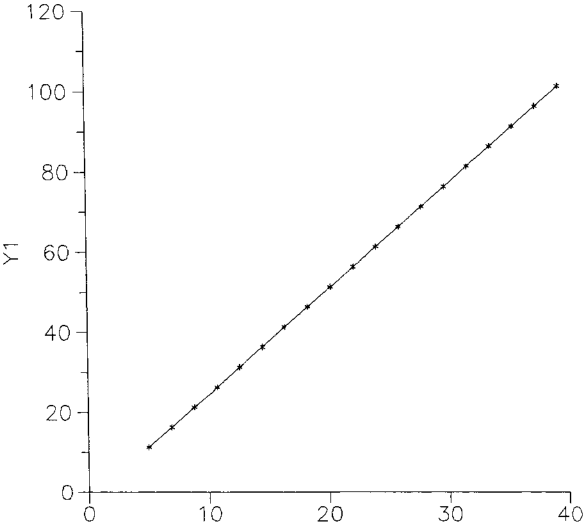

Fig. 1. Linear plot of $Y_1(=X_1)$ against $Z_1(=X_1/(X_1-X_2))$ for second order kinetics (n=2).

$$X_1=C_1\frac{X_1}{X_1-X_2}+C_0 \tag{27}$$

where C_1 and C_0 depend on the order of kinetics. We have not found out C_1 and C_0 by using the conven-

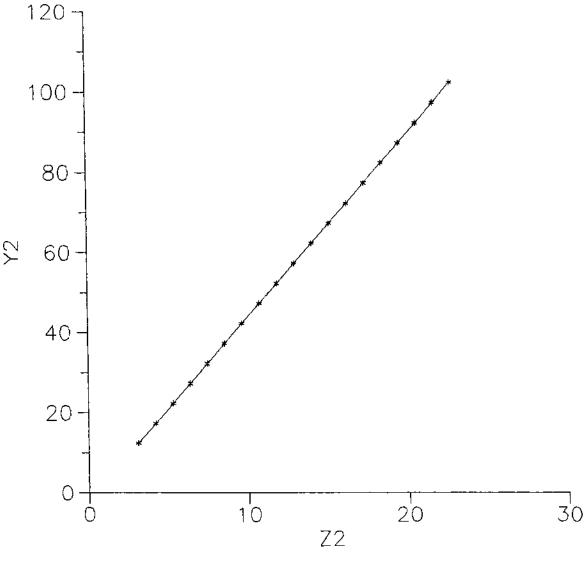

Fig. 2. Same as Fig. 1 but for $Y_2(=X_{d1})$ against $(=X_1/(X_1-X_2))$.

tional linear least square method [6] but by using the technique developed by Chakravarty [7] in which the maximum of the absolute value of the fractional error in X_1 is minimized. Similarly we can write

$$X_{d1} = C_{d1}\frac{X_{d1}}{X_{d1} - X_{d2}} + C_{d0} \qquad (28)$$

3. Results and discussions

We illustrate the linear plot of Y_1 $(=X_1)$ against $Z_1(= X_1/(X_1 - X_2))$ in Fig. 1 for n=2. In Fig. 2 we show the corresponding linear plot between $Y_2(= X_{d1})$ and $Z_2(= X_{d1}/(X_{d1} - X_{d2}))$.

Now Eqs. (27) and (28) can be written in terms of temperatures as

$$E = \frac{C_1 R T_1 T_2}{(T_2 - T_1)} + C_0 R T_1 \qquad (29)$$

$$E = \frac{C_{d1} R T_{d1} T_{d2}}{(T_{d2} - T_{d1})} + C_0 R T_{d1} \qquad (30)$$

The coefficients C_0, C_1, C_{d0} and C_{d1} are tabulated in Table 1 for different order of kinetics. We have already mentioned that the temperatures T_1, T_2, ...

Table 1
Coefficients C_0, C_1, C_{d0} and C_{d1} occuring in Eqs. (27) and (28) for the determination of activation energy (E) for various orders of kinetics (n).

n	C_0	C_1	C_{d0}	C_{d1}
0.7	−0.1409	1.6278	0.7034	2.0004
1.0	−0.5965	1.9246	0.3229	2.0895
1.5	−1.2911	2.3168	−1.0464	4.0170
2.0	−1.9172	2.6317	−1.8670	4.5769
2.5	−2.4870	2.8968	−2.5341	5.0354
3.0	−3.0092	3.1263	−3.6182	5.5487

Table 2
Comparison of the values of the activation energy and pre-exponential factor for first DTPD curves using present sets of formulas with those of Hu et al. [1]

n	Input A (s^{-1})	Values E (kJ)	A (s^{-1})	Calculated	Values E (kJ)	
			Present	Hu et al.	Present	Hu et al.
0.7	10^{13}	41.842	10^{13}	–	41.845	–
0.7	10^{13}	62.763	10^{13}	–	62.767	–
0.7	10^{13}	83.684	10^{13}	–	83.688	–
0.7	10^{13}	104.605	10^{13}	–	104.611	–
0.7	10^{13}	125.526	10^{13}	–	125.534	–
0.7	10^{13}	146.447	10^{13}	–	146.455	–
0.7	10^{13}	167.368	10^{13}	–	167.378	–
0.7	10^{5}	83.684	10^{5}	–	83.680	–
0.7	10^{8}	83.684	10^{8}	–	83.688	–
0.7	10^{10}	83.684	10^{10}	–	83.676	–
0.7	10^{15}	83.684	10^{15}	–	83.688	–
1.0	10^{13}	41.842	10^{13}	3.22×10^{13}	41.845	43.561
1.0	10^{13}	62.763	10^{13}	5.78×10^{13}	62.767	65.254
1.0	10^{13}	83.684	10^{13}	5.57×10^{13}	83.689	86.885
1.0	10^{13}	104.605	10^{13}	5.08×10^{13}	104.611	108.672
1.0	10^{13}	125.526	10^{13}	5.81×10^{13}	125.534	130.516
1.0	10^{13}	146.447	10^{13}	5.68×10^{13}	146.456	152.094
1.0	10^{13}	167.368	10^{13}	5.79×10^{13}	167.379	173.850
1.0	10^{5}	83.684	10^{5}	6.24×10^{5}	83.680	90.225
1.0	10^{8}	83.684	10^{8}	6.11×10^{8}	83.688	88.513
1.0	10^{10}	83.684	10^{10}	5.33×10^{10}	83.689	87.841
1.0	10^{15}	83.684	10^{15}	5.59×10^{15}	83.689	86.695

Table 3
Comparison of the values of the activation energy and pre-exponential factor for first DTPD curves using present sets of formulas with those of Hu et al. [1]

n	Input A (s^{-1})	Values E (kJ)	A (s^{-1})	Calculated	Values E (kJ)	
			Present	Hu et al.	Present	Hu et al.
1.5	10^{13}	41.842	10^{13}	–	41.850	–
1.5	10^{13}	62.763	10^{13}	–	62.775	–
1.5	10^{13}	83.684	10^{13}	–	83.700	–
1.5	10^{13}	104.605	10^{13}	–	104.625	–
1.5	10^{13}	125.526	10^{13}	–	125.549	–
1.5	10^{13}	146.447	10^{13}	–	146.474	–
1.5	10^{13}	167.368	10^{13}	–	167.399	–
1.5	10^{5}	83.684	10^{5}	–	83.670	–
1.5	10^{8}	83.684	10^{8}	–	83.696	–
1.5	10^{10}	83.684	10^{10}	–	83.700	–
1.5	10^{15}	83.684	10^{15}	–	83.698	–
2.0	10^{13}	41.842	10^{13}	2.25×10^{14}	41.895	44.292
2.0	10^{13}	62.763	10^{13}	2.20×10^{14}	62.789	66.384
2.0	10^{13}	83.684	10^{13}	2.20×10^{14}	83.719	88.410
2.0	10^{13}	104.605	10^{13}	2.15×10^{14}	104.648	110.425
2.0	10^{13}	125.526	10^{13}	2.15×10^{14}	125.578	132.516
2.0	10^{13}	146.447	10^{13}	2.25×10^{14}	146.507	154.671
2.0	10^{13}	167.368	10^{13}	2.15×10^{14}	167.437	176.638
2.0	10^{5}	83.684	10^{5}	2.15×10^{6}	83.649	92.628
2.0	10^{8}	83.684	10^{8}	2.15×10^{9}	83.707	90.311
2.0	10^{10}	83.684	10^{10}	2.15×10^{11}	83.717	89.402
2.0	10^{15}	83.684	10^{15}	2.25×10^{16}	83.716	87.887

etc. have been computed by Newton–McAuley method. As a further check of our computer code we have also computed those temperatures directly from first and second DTPD curves by using the Cubic Spline method [5,8] and obtained very good agreement.

In order to test the suitability of the expressions Eqs. (29) and (30) for the activation energy we evaluate the activation energies of some computer generated first and second DTPD peaks. We also calculate pre-exponential factor by using Eqs. (10) and (11). The results are presented in Tables 2–7. In these tables the values of the activation energy and pre-exponential factor obtained by Hu et al. [1] (which are in fact the average of different E and A values, respectively) are also shown. A close inspection of Tables 2–7 reveal that in all most all the cases the present values of E and A are in excellent agreement with the actual value. Moreover, when comparison of present results are made with those of Hu et al. we find that the present result exhibit superior agreement with the actual values of E and A.

4. Conclusion

In the present paper we have proposed a method for the determination of the activation energy and pre-exponential factor of first and second DTPD curves for different order of kinetics. We have applied the method to number of computer simulated first and second DTPD curves and have found that reliable values of activation energies and pre-exponential factors can be obtained. The present results are somewhat better than those of Hu et al. [1]. This might be due to the fact that in the present calculation very accurate values of temperature integral developed by Devi [2] have been employed whereas Hu et al. [1] have finally retained only two terms in the asymptotic expansion of the temperature integral in their calculation.

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Table 4
Comparison of the values of the activation energy and pre-exponential factor for first DTPD curves using present sets of formulas with those of Hu et al.

n	Input A (s^{-1})	Values E (kJ)	A (s^{-1})	Calculated	Values E (kJ)	
			Present	Hu et al.	Present	Hu et al.
2.5	10^{13}	41.842	10^{13}	–	41.871	–
2.5	10^{13}	62.763	10^{13}	–	62.807	–
2.5	10^{13}	83.684	10^{13}	–	83.742	–
2.5	10^{13}	104.605	10^{13}	–	104.678	–
2.5	10^{13}	125.526	10^{13}	–	125.613	–
2.5	10^{13}	146.447	10^{13}	–	146.549	–
2.5	10^{13}	167.368	10^{13}	–	167.484	–
2.5	10^{5}	83.684	10^{5}	–	83.619	–
2.5	10^{8}	83.684	10^{8}	–	83.718	–
2.5	10^{10}	83.684	10^{10}	–	83.738	–
2.5	10^{15}	83.684	10^{15}	–	83.739	–
3.0	10^{13}	41.842	10^{13}	–	41.885	–
3.0	10^{13}	62.763	10^{13}	–	62.827	–
3.0	10^{13}	83.684	10^{13}	–	83.769	–
3.0	10^{13}	104.605	10^{13}	–	104.712	–
3.0	10^{13}	125.526	10^{13}	–	125.654	–
3.0	10^{13}	146.447	10^{13}	–	146.596	–
3.0	10^{13}	167.368	10^{13}	–	167.538	–
3.0	10^{5}	83.684	10^{5}	–	83.583	–
3.0	10^{8}	83.684	10^{8}	–	83.731	–
3.0	10^{10}	83.684	10^{10}	–	83.763	–
3.0	10^{15}	83.684	10^{15}	–	83.765	–

Appendix A

Numerical evaluation of the peak temperatures of the first and second DTPD curves.

Peak temperatures of the first DTPD curve can be obtained by solving the equation

$$f(X) = 2\frac{\mathrm{d}I}{\mathrm{d}X} + X\frac{\mathrm{d}^2 I}{\mathrm{d}X^2} = 0 \tag{31}$$

Eq. (31) has been solved by Newton–McAuley method [5]. This method requires the derivative of $f(X)$ which is given by

$$\frac{\mathrm{d}f}{\mathrm{d}X} = X\frac{\mathrm{d}^3 I}{\mathrm{d}X^3} + 3\frac{\mathrm{d}^2 I}{\mathrm{d}X^2} \tag{32}$$

where for n=1

$$\frac{\mathrm{d}I}{\mathrm{d}X} = I\left(\frac{\mathrm{d}F}{\mathrm{d}X} - 1\right) \tag{33}$$

$$\frac{\mathrm{d}^2 I}{\mathrm{d}X^2} - \frac{\mathrm{d}I}{\mathrm{d}X}\left(\frac{\mathrm{d}F}{\mathrm{d}X} - 1\right) + I\frac{\mathrm{d}^2 F}{\mathrm{d}X^2} \tag{34}$$

$$\frac{\mathrm{d}^3 I}{\mathrm{d}X^3} = \frac{\mathrm{d}^2 I}{\mathrm{d}X^2}\left(\frac{\mathrm{d}F}{\mathrm{d}X} - 1\right) + 2\frac{\mathrm{d}I}{\mathrm{d}X}\frac{\mathrm{d}^2 F}{\mathrm{d}^2 X} + I\frac{\mathrm{d}^3 F}{\mathrm{d}X^3} \tag{35}$$

and for $n \neq 1$

$$\frac{\mathrm{d}I}{\mathrm{d}X} = -I + \frac{\mathrm{d}G}{\mathrm{d}X}\exp(X_m - X) \tag{36}$$

$$\frac{\mathrm{d}^2 I}{\mathrm{d}X^2} - -2\frac{\mathrm{d}I}{\mathrm{d}X} - I + \frac{\mathrm{d}^2 G}{\mathrm{d}X^2}\exp(X_m - X) \tag{37}$$

$$\frac{\mathrm{d}^3 I}{\mathrm{d}X^3} = -I - 3\frac{\mathrm{d}I}{\mathrm{d}X} - 3\frac{\mathrm{d}^2 I}{\mathrm{d}X^2} + \exp(X_m - X)\frac{\mathrm{d}^3 G}{\mathrm{d}X^3} \tag{38}$$

Similarly the peak temperatures of the second DTPD curve can be obtained by solving the equation

$$g(X) = X^2\frac{\mathrm{d}^3 I}{\mathrm{d}X^3} + 6X\frac{\mathrm{d}^2 I}{\mathrm{d}X^2} + 6\frac{\mathrm{d}I}{\mathrm{d}X} = 0 \tag{39}$$

The first derivative of $g(X)$ which is also required for the computation in Newton–McAuley method is given

Table 5
Comparison of the values of the activation energy and pre-exponential factor for second DTPD curves using present sets of formulas with those of Hu et al.

n	Input A (s^{-1})	Values E (kJ)	A (s^{-1})	Calculated	Values E (kJ)	
			Present	Hu et al.	Present	Hu et al.
0.7	10^{13}	41.842	10^{13}	–	41.869	–
0.7	10^{13}	62.763	10^{13}	–	62.803	–
0.7	10^{13}	83.684	10^{13}	–	83.738	–
0.7	10^{13}	104.605	10^{13}	–	104.672	–
0.7	10^{13}	125.526	10^{13}	–	125.605	–
0.7	10^{13}	146.447	10^{13}	–	146.540	–
0.7	10^{13}	167.368	10^{13}	–	167.474	–
0.7	10^{5}	83.684	10^{5}	–	83.636	–
0.7	10^{8}	83.684	10^{8}	–	83.722	–
0.7	10^{10}	83.684	10^{10}	–	83.737	–
0.7	10^{15}	83.684	10^{15}	–	83.733	–
1.0	10^{13}	41.842	10^{13}	6.71×10^{13}	41.873	43.150
1.0	10^{13}	62.763	10^{13}	7.41×10^{13}	62.809	64.789
1.0	10^{13}	83.684	10^{13}	7.41×10^{13}	83.745	86.330
1.0	10^{13}	104.605	10^{13}	7.44×10^{13}	104.681	107.946
1.0	10^{13}	125.526	10^{13}	7.31×10^{13}	125.617	129.482
1.0	10^{13}	146.447	10^{13}	7.48×10^{13}	146.553	151.332
1.0	10^{13}	167.368	10^{13}	7.48×10^{13}	167.489	172.728
1.0	10^{5}	83.684	10^{5}	7.26×10^{5}	83.630	88.747
1.0	10^{8}	83.684	10^{8}	7.37×10^{8}	83.727	87.521
1.0	10^{10}	83.684	10^{10}	7.10×10^{10}	83.743	86.826
1.0	10^{15}	83.684	10^{15}	7.52×10^{15}	83.739	86.157

by

$$\frac{\mathrm{d}g}{\mathrm{d}X} = x^2\frac{\mathrm{d}^4I}{\mathrm{d}X^4} + 8X\frac{\mathrm{d}^3I}{\mathrm{d}X^3} + 12\frac{\mathrm{d}^2I}{\mathrm{d}X^2} \tag{40}$$

where for n=1

$$\frac{\mathrm{d}^4I}{\mathrm{d}X^4} = \frac{\mathrm{d}^3I}{\mathrm{d}X^3}\left(\frac{\mathrm{d}F}{\mathrm{d}X} - 1\right) + 3\frac{\mathrm{d}^2I}{\mathrm{d}X^2}\frac{\mathrm{d}^2F}{\mathrm{d}X^2} + 3\frac{\mathrm{d}I}{\mathrm{d}X}\frac{\mathrm{d}^3F}{\mathrm{d}X^3} + I\frac{\mathrm{d}^4F}{\mathrm{d}X^4} \tag{41}$$

and for $n \neq 1$

$$\frac{\mathrm{d}^4I}{\mathrm{d}X^4} = -I - 4\frac{\mathrm{d}I}{\mathrm{d}X} - 6\frac{\mathrm{d}^2I}{\mathrm{d}X^2} - 4\frac{\mathrm{d}^3I}{\mathrm{d}X^3} + \exp(X_m - X)\frac{\mathrm{d}^4G}{\mathrm{d}X^4} \tag{42}$$

with

$$\frac{\mathrm{d}^3G}{\mathrm{d}X^3} = -\frac{n}{n-1}\left[T_1\frac{\mathrm{d}D}{\mathrm{d}X} + T_2\frac{\mathrm{d}^2D}{\mathrm{d}X^2} + T_3\frac{\mathrm{d}^3D}{\mathrm{d}X^3}\right] \tag{43}$$

where

$$T_1 = \frac{1}{D}\frac{\mathrm{d}^2G}{\mathrm{d}X^2} - \frac{2}{D^2}\frac{\mathrm{d}D}{\mathrm{d}X}\frac{\mathrm{d}G}{\mathrm{d}X} + \frac{2G}{\mathrm{d}^3}\left(\frac{\mathrm{d}D}{\mathrm{d}X}\right)^2 - \frac{G}{D^2}\frac{\mathrm{d}^2D}{\mathrm{d}X^2} \tag{44}$$

$$T_2 = 2\left[\frac{1}{D}\frac{\mathrm{d}G}{\mathrm{d}X} - \frac{G}{D^2}\frac{\mathrm{d}D}{\mathrm{d}X}\right] \tag{45}$$

$$T_3 = \frac{G}{D} \tag{46}$$

Again

$$\frac{\mathrm{d}^4G}{\mathrm{d}X^4} = -\frac{n}{n-1}\left[T_3\frac{\mathrm{d}^4D}{\mathrm{d}X^4} + T_4\frac{\mathrm{d}^3D}{\mathrm{d}X^3} + T_5\frac{\mathrm{d}^2D}{\mathrm{d}X^2} + T_6\frac{\mathrm{d}D}{\mathrm{d}X}\right] \tag{47}$$

with

$$T_4 = \frac{3}{D}\frac{\mathrm{d}G}{\mathrm{d}X} - \frac{3G}{D^2}\frac{\mathrm{d}D}{\mathrm{d}X} \tag{48}$$

$$T_5 = \frac{3}{D}\frac{\mathrm{d}^2G}{\mathrm{d}X^2} - \frac{6}{D^2}\frac{\mathrm{d}D}{\mathrm{d}X}\frac{\mathrm{d}G}{\mathrm{d}X} + \left[\frac{6}{D^3}\left(\frac{\mathrm{d}D}{\mathrm{d}X}\right)^2 - \frac{3}{D^2}\frac{\mathrm{d}^2D}{\mathrm{d}X^2}\right]G \tag{49}$$

Table 6
Comparison of the values of the activation energy and pre-exponential factor for second DTPD curves using present sets of formulas with those of Hu et al.

n	Input A (s^{-1})	Values E (kJ)	A (s^{-1})	Calculated	Values E (kJ)	
			Present	Hu et al.	Present	Hu et al.
1.5	10^{13}	41.842	10^{13}	–	41.861	–
1.5	10^{13}	62.763	10^{13}	–	62.791	–
1.5	10^{13}	83.684	10^{13}	–	86.721	–
1.5	10^{13}	104.605	10^{13}	–	104.651	–
1.5	10^{13}	125.526	10^{13}	–	125.581	–
1.5	10^{13}	146.447	10^{13}	–	146.511	–
1.5	10^{13}	167.368	10^{13}	–	167.441	–
1.5	10^{5}	83.684	10^{5}	–	83.659	–
1.5	10^{8}	83.684	10^{8}	–	83.714	–
1.5	10^{10}	83.684	10^{10}	–	83.722	–
1.5	10^{15}	83.684	10^{15}	–	83.717	–
2.0	10^{13}	41.842	10^{13}	4.75×10^{14}	41.871	44.005
2.0	10^{13}	62.763	10^{13}	4.65×10^{14}	62.805	65.944
2.0	10^{13}	83.684	10^{13}	4.75×10^{14}	83.740	87.823
2.0	10^{13}	104.605	10^{13}	4.85×10^{14}	104.673	109.862
2.0	10^{13}	125.526	10^{13}	4.64×10^{14}	125.607	131.585
2.0	10^{13}	146.447	10^{13}	4.65×10^{14}	146.541	153.577
2.0	10^{13}	167.368	10^{13}	4.75×10^{14}	167.475	175.607
2.0	10^{5}	83.684	10^{5}	5.52×10^{6}	83.646	92.291
2.0	10^{8}	83.684	10^{8}	5.29×10^{9}	83.728	90.037
2.0	10^{10}	83.684	10^{10}	5.05×10^{11}	83.741	88.927
2.0	10^{15}	83.684	10^{15}	4.65×10^{16}	83.733	87.433

Table 7
Comparison of the values of the activation energy and pre-exponential factor for second DTPD curves using present sets of formulas with those of Hu et al.

n	Input A (s^{-1})	Values E (kJ)	A (s^{-1})	Calculated	Values E (kJ)	
			Present	Hu et al.	Present	Hu et al.
2.5	10^{13}	41.842	10^{13}	–	41.875	–
2.5	10^{13}	62.763	10^{13}	–	62.811	–
2.5	10^{13}	83.684	10^{13}	–	83.747	–
2.5	10^{13}	104.605	10^{13}	–	104.682	–
2.5	10^{13}	125.526	10^{13}	–	125.625	–
2.5	10^{13}	146.447	10^{13}	–	146.560	–
2.5	10^{13}	167.368	10^{13}	–	167.495	–
2.5	10^{5}	83.684	10^{5}	–	83.757	–
2.5	10^{8}	83.684	10^{8}	–	83.801	–
2.5	10^{10}	83.684	10^{10}	–	83.786	–
2.5	10^{15}	83.684	10^{15}	–	83.725	–
3.0	10^{13}	41.842	10^{13}	–	41.902	–
3.0	10^{13}	62.763	10^{13}	–	62.850	–
3.0	10^{13}	83.684	10^{13}	–	83.797	–
3.0	10^{13}	104.605	10^{13}	–	104.744	–
3.0	10^{13}	125.526	10^{13}	–	125.590	–
3.0	10^{13}	146.447	10^{13}	–	146.635	–
3.0	10^{13}	167.368	10^{13}	–	167.579	–
3.0	10^{5}	83.684	10^{5}	–	83.833	–
3.0	10^{8}	83.684	10^{8}	–	83.935	–
3.0	10^{10}	83.684	10^{10}	–	83.833	–
3.0	10^{15}	83.684	10^{15}	–	83.755	–

$$T_6 = \left[\frac{6}{D^3}\frac{\mathrm{d}D}{\mathrm{d}X}\frac{\mathrm{d}^2D}{\mathrm{d}X^2} - \frac{6}{D^4}\left(\frac{\mathrm{d}D}{\mathrm{d}X}\right)^3 - \frac{1}{D^2}\frac{\mathrm{d}^3D}{\mathrm{d}X^3}\right]G + \left[\frac{6}{D^3}\left(\frac{\mathrm{d}D}{\mathrm{d}X}\right)^2 - \frac{3}{D^2}\frac{\mathrm{d}^2D}{\mathrm{d}X^2}\right]\frac{\mathrm{d}G}{\mathrm{d}X} - \frac{3}{D^2}\frac{\mathrm{d}D}{\mathrm{d}X}\frac{\mathrm{d}^2G}{\mathrm{d}X^2} + \frac{1}{D}\frac{\mathrm{d}^3G}{\mathrm{d}X^3} \tag{50}$$

where

$$\frac{\mathrm{d}^3D}{\mathrm{d}X^3} = -\frac{n-1}{n}\frac{\mathrm{d}^3F}{\mathrm{d}X^3} \tag{51}$$

$$\frac{\mathrm{d}^4D}{\mathrm{d}X^4} = -\frac{n-1}{n}\frac{\mathrm{d}^4F}{\mathrm{d}X^4} \tag{52}$$

$$\frac{\mathrm{d}^3F}{\mathrm{d}X^3} = -\frac{\mathrm{d}^2F}{\mathrm{d}X^2}\left(1 + \frac{2}{X}\right) + \frac{2}{X^2}\frac{\mathrm{d}F}{\mathrm{d}X} \tag{53}$$

$$\frac{\mathrm{d}^4F}{\mathrm{d}X^4} = -\frac{\mathrm{d}^3F}{\mathrm{d}X^3}\left(1 + \frac{2}{X}\right) + \frac{4}{X^2}\frac{\mathrm{d}^2F}{\mathrm{d}X^2} - \frac{4}{X^3}\frac{\mathrm{d}F}{\mathrm{d}X} \tag{54}$$

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