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CRITICAL INVESTIGATION OF METHODS FOR KINETIC ANALYSIS OF THERMOANALYTICAL DATA

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The methods of Freeman and Carroll (I), Coats and Redfern (II), Sharp and Wentworth (III) and the present author (IV) are applied to five theoretical thermoanalytical data calculated for assumed kinetic parameters at various heating rates. These are a first-order reaction, a second-order reaction, two cases of random scission in main chains of polymers, and a system of two parallel competitive first-order reactions. Although methods I, II and III cannot be applied to the latter three cases, when one does apply them to these cases, nearly straight relations are observed and false unreal kinetic parameters are obtained. For the two cases of random scission in the main chains of polymers, the author's method gives correct kinetic parameters. For the last case, the increase of the apparent activation energy with increasing conversion implies that even method IV cannot be applied. The reason for these results and methods for avoiding false unreal results are discussed.

Since Freeman and Carroll [1] set forth a method of kinetic analysis of thermoanalytical data in 1958, various methods have been proposed [2]. However, most of them are based on the kinetic equation of an n-th-order reaction. As the present author has pointed out [3, 4], the methods involve the dangerous tendency to study (unjustifiably) processes of great variety within the limited framework of the particular specialized formulae, which leads to false unreal results.

In this paper, some typical methods are applied to a few theoretical thermoanalytical curves calculated for assumed kinetic parameters, and it is clearly demonstrated that some methods lead to false unreal results. These results are discussed; the effect of the heating rate on the results is elucidated, and in order to avoid false results, the importance of measurement at different heating rates is postulated.

Method of obtaining theoretically calculated curves

Five cases of thermoanalytical curves are calculated:

1. A first-order reaction in which

$$A = 10^{14}\ \mathrm{sec}^{-1}$$

and

$$\Delta E = 60\ \mathrm{kcal/mole}$$

where A and ΔE are the pre-exponential factor and the activation energy, respectively.

2. A second-order reaction in which

$$A = 10^{16}\ \text{sec}^{-1}$$

and

$$\Delta E = 40\ \text{kcal/mole}$$

3. Thermogravimetric curves (TG) or curves of evolved gas analysis (EGA) for random scission in main chains of polymers in which

$$A = 10^{12}\ \text{sec}^{-1}$$

$$\Delta E = 40\ \text{kcal/mole}$$

and

$$L = 4$$

where L is the lowest degree of polymerization of the oligomer remaining unvolatilized. When we study the random scission in the main chains of polymers by differential scanning calorimetry (DSC) or other methods for observing the scission directly, the curve obtained is of the first-order [5], because the scission follows a first-order reaction, but the scission occurs at random points in the main chains.

4. TG or EGA curves of random scission in the main chains of polymers, in which

$$A = 10^{18}\ \text{sec}^{-1}$$

$$\Delta E = 60\ \text{kcal/mole}$$

and

$$L = 2$$

5. A parallel competitive reaction system in which the reacting species react by two alternative mechanisms, the parameters of which are

$$A_1 = 2 \times 10^{11}\ \text{sec}^{-1}$$

$$\Delta E_1 = 40\ \text{kcal/mole}$$

$$A_2 = 10^{19}\ \text{sec}^{-1}$$

$$\Delta E_2 = 60\ \text{kcal/mole}$$

and both reaction orders are unity.

The method of theoretically calculating thermoanalytical curves of n-th-order reactions and random scission in the main chains of polymers is described elsewhere [3]. The thermoanalytical curve of parallel competitive reactions is calculated on the basis of the following equation:

$$\frac{dC}{dt} = A_1 \exp\left(-\frac{\Delta E_1}{RT}\right) g_1(C) + A_2 \exp\left(-\frac{\Delta E_2}{RT}\right) g_2(C) \qquad (1)$$

where C, t, R, T and $g(C)$ are the conversion, the time, the gas constant, the temperature and a function of the conversion depending on the mechanism, respectively, and the subscript denotes one of two competitive reactions.

For $g_1(C) = g_2(C) = (1 - C)$, i.e. a first-order reaction:

$$\frac{dC}{dt} = A_1 \exp\left(-\frac{\Delta E_1}{RT}\right)(1 - C) + A_2 \exp\left(-\frac{\Delta E_2}{RT}\right)(1 - C) \tag{2}$$

By integration:

$$\int_0^C \frac{dC}{(1 - C)} = A_1 \int_0^t \exp\left(-\frac{\Delta E_1}{RT}\right) dt + A_2 \int_0^t \exp\left(-\frac{\Delta E_2}{RT}\right) dt \tag{3}$$

Introducing the reduced time, θ [3, 4]:

$$-\ln(1 - C) = A_1\theta_1 + A_2\theta_2 \tag{4}$$

When the temperature is raised at a constant rate, a:

$$-\ln(1 - C) = \frac{A_1 \Delta E_1}{aR} p\left(\frac{\Delta E_1}{RT}\right) + \frac{A_2 \Delta E_2}{aR} p\left(\frac{\Delta E_2}{RT}\right) \tag{5}$$

where p is the p-function defined by Doyle [6].

For these five cases, the conversions and the rates of conversion are calculated at every 2°C for heating rates of 0.25, 0.5, 1.0, 2.5, 5.0 and 10.0°C/min, and those for the parallel competitive reactions are reproduced in Fig. 1. Although the two parallel competitive unit reactions have different activation energies, the thermoanalytical curves in Fig. 1 are similar to the curves of simple reactions drawn elsewhere [3]. The other curves are also similar to the curves drawn elsewhere [3].

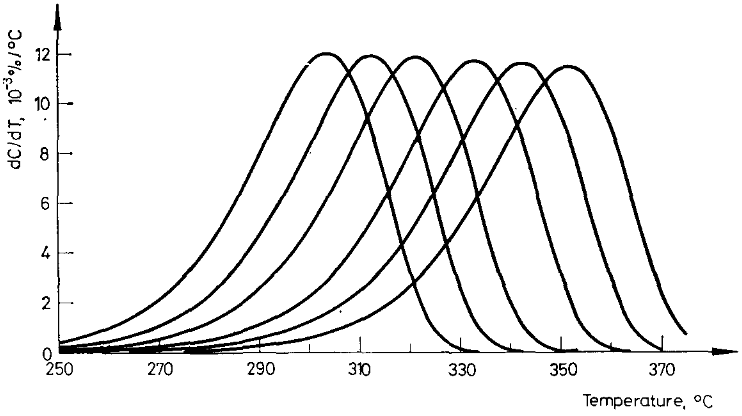

Fig. 1. Calculated thermoanalytical curves for parallel competitive reactions (case (5)) obtained at heating rates of 0.25, 0.5, 1.0, 2.5, 5.0 and 10°/min (from left to right)

Results and discussion

Among the various methods for kinetic analysis of thermoanalytical curves, four typical methods are applied to the theoretical curves; they are the methods of Freeman and Carroll [1], Coats and Redfern [7], Sharp and Wentworth [8] and the present author [9].

In the method of Freeman and Carroll, the following linear relation is utilized:

$$\frac{\Delta \log dC/dt}{\Delta \log (1-C)} = n - \frac{\Delta E}{2.303R} \Delta \left(\frac{1}{T}\right) \Big/ \Delta \log (1 - \mathrm{C}) \tag{6}$$

where n is the order of reaction and Δ represents the difference between two points of a thermoanalytical curve. The left side is plotted against $\Delta(1/T)/\Delta \log(1 - \mathrm{C})$.

The method of Coats and Redfern utilizes the following equations; for $n = 1$:

$$\log\left\{-\frac{\ln(1-C)}{T^2}\right\} = \log\frac{AR}{a\Delta E} - \frac{\Delta E}{2.303RT} \tag{7}$$

where a is the heating rate; and for $n \neq 1$:

$$\log\left\{\frac{1-(1-C)^{1-n}}{T^2(1-n)}\right\} = \log\frac{AR}{a\Delta E} - \frac{\Delta E}{2.303RT} \tag{8}$$

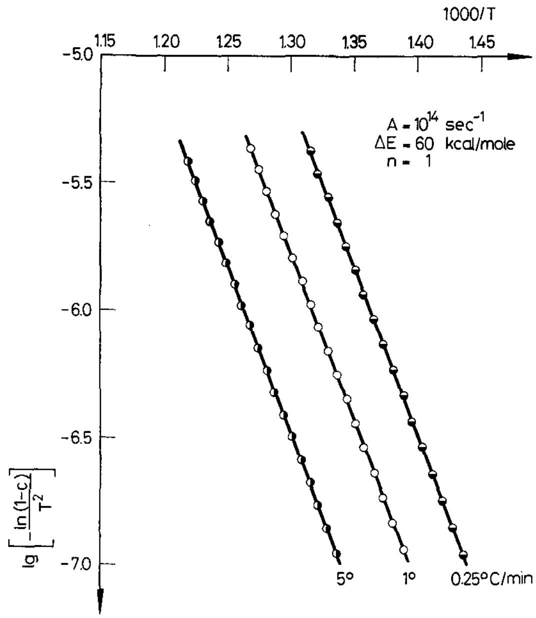

Fig. 2. Plots of first-order reaction (case (1)) by the method of Coats and Redfern. First-order reaction is assumed

In Eqs (7) and (8), the terms of higher order are neglected. The left side is plotted against the reciprocal absolute temperature, assuming the order of reaction, and the activation energy is estimated from the slope of the linear plot obtained for the correct value of n.

In the method of Sharp and Wentworth, the reaction rate constant is estimated at some points of a thermoanalytical curve. For instance, assuming the order of reaction, the reaction rate constant is estimated by dividing dC/dt by $(1 - C)^n$. If the order of reaction assumed is correct, the linear Arrhenius plot is obtained, and the activation energy and pre-exponential factor are estimated from the slope and intercept of the linear plot.

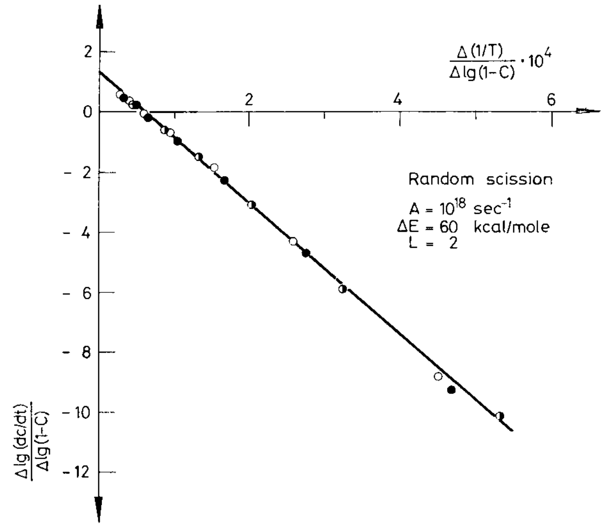

Fig. 3. Plots of random scission in the main chains of polymers (case (3)) by the method of Freeman and Carroll. Heating rates: ○: 0.25°/min, ●: 1.0°/min, ◑: 10.0°/min

The present author's method utilizes the following approximate relation; for a given conversion:

$$\log a + 0.4567\ \Delta E/RT = \text{constant} \qquad (9)$$

Plotting log a against the reciprocal absolute temperature for a given conversion, one can estimate the activation energy. By using the activation energy estimated and the thermoanalytical curves obtained at different heating rates, an experimental master curve is drawn, and compared with the theoretical curves. The mechanism and pre-exponential factor are elucidated from this comparison. This method has general applicability and can be applied to all thermoanalytical curves consisting of a single unit process.

First, the methods are applied to the curve of a first-order reaction. Examples of the results obtained by the method of Coats and Redfern for three heating rates are reproduced in Fig. 2. Naturally, very smooth linear plots are obtained. The kinetic parameters obtained by the methods are tabulated in Table 1. It is interesting to note that the pre-exponential factors obtained by the method of Coats and Redfern, neglecting the terms of higher order, are very close to the true value. This fact suggests that the method of Coats and Redfern can be utilized to estimate the pre-exponential factor. The activation energy estimated by the method proposed by the present author is less accurate than those obtained by the other methods, presumably because the temperature at which the conversion reaches

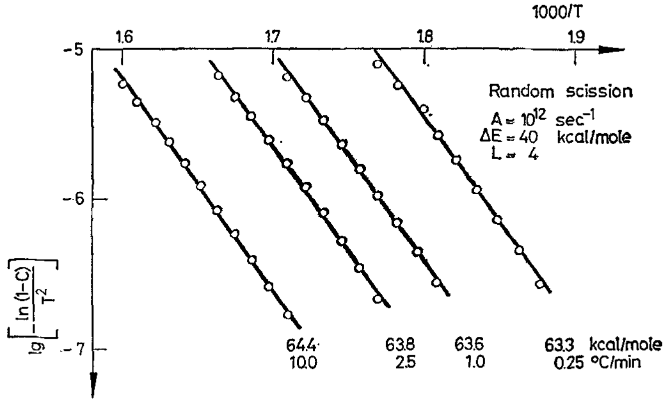

Fig. 4. Plots of random scission in the main chains of polymers (case (3)) by the method of Coats and Redfern, assuming first-order reaction

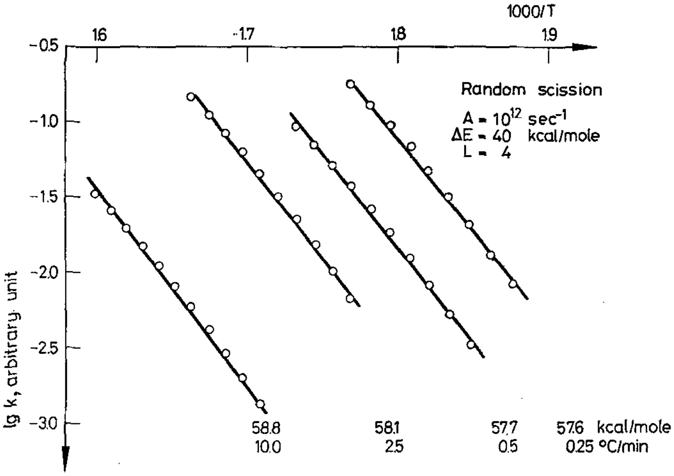

Fig. 5. Plots of random scission in the main chains of polymers (case (3)) by the method of Sharp and Wentworth, assuming first-order reaction

Table 1

Kinetic parameters estimated for case (1)

Heating rate °C/min	Freeman – Carroll		Coats – Redfern		Sharp – Wentworth		Conversion %	Ozawa		
	ΔE	n	ΔE	$\log A$	ΔE	$\log A$		ΔE	$\log A$	n
							5	59.74	13.97	1
0.25	60.0	1.00	60.0	13.97	60.0	14.00	10	59.77	13.96	
							15	59.80	13.96	
							20	59.82	13.96	
0.5	60.0	1.00	60.0	13.95	60.0	14.00	25	59.83	13.96	
							30	59.85	13.96	
							35	59.86	13.97	
1.0	60.0	1.00	60.0	13.96	60.0	14.00	40	59.88	13.96	
							45	59.88	13.96	
							50	59.90	13.97	
2.5	60.0	1.00	60.0	13.96	60.0	14.00	55	59.91	13.96	
							60	59.92	13.97	
							65	59.93	13.96	
5.0	60.0	1.00	60.0	13.96	60.0	14.00	70	59.94	13.96	
							75	59.94	13.97	
							80	59.96	13.97	
10.0	60.0	1.00	60.0	13.96	60.0	14.00	85	59.97	13.97	
							90	59.99	13.97	
							95	60.01	13.96	
Average	60.0	1.00	60.0	13.96	60.0	14.00		59.89 ±0.07	13.96 ±0.004	

* The dimensions of the activation energy and the pre-exponential factor are kcal/mole and sec^{-1}, respectively, and the range with the average is the standard deviation.

a given value of every 5% is obtained approximately by linear interpolation between two adjacent conversions calculated at every 2°, and the activation energy listed in Table 1 is the average of those estimated at every 5% conversion, while the calculated accurate conversion and/or the calculated accurate rate of conversion

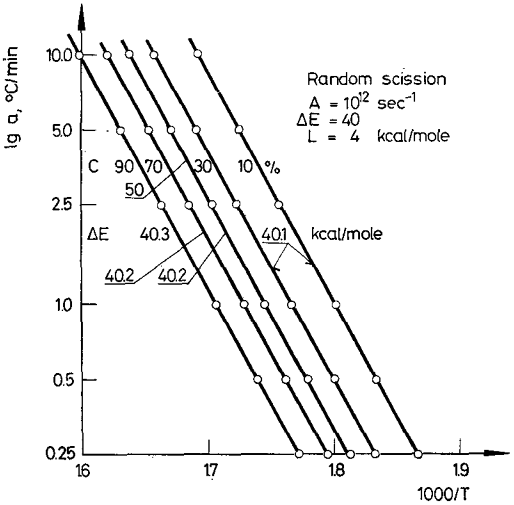

Fig. 6. Plots of random scission in the main chains of polymers (case (3)) by the method of the present author

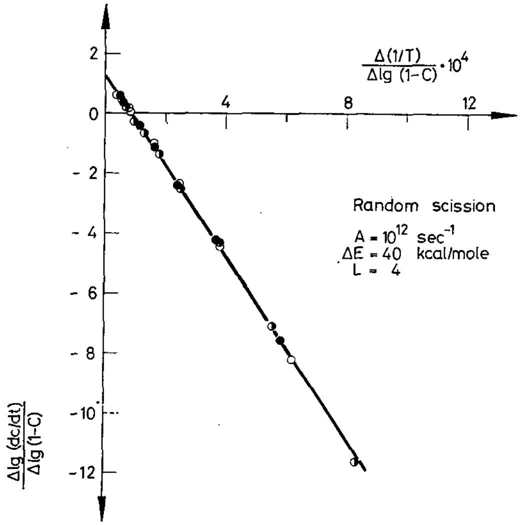

Fig. 7. Plots of random scission in the main chains of polymers (case(4)) by the method of Freeman and Carroll. Heating rates: ○: 0.25°/min, ●: 1.0°/min, ◑: 10.0°/min

itself is used in the other methods. Furthermore, the activation energy obtained tends to become larger with the increase of the conversion, presumably because of the accuracy of linear approximation of the logarithm of the *p*-function [6], but the difference between the conversion of 5 % and that of 95 % is less than 0.5 %. The kinetic parameters estimated by all methods are very accurate, taking into account experimental errors existing in the actual measurement. The results obtained by applying the methods to the curves of a second-order reaction are similar to the results of the first-order reaction, and are tabulated in Table 2.

On the other hand, the results obtained by applying the methods to the other types of reaction are quite different. The plots obtained for the third case, random scission in the main chains of polymers, are shown in Figs 3, 4, 5 and 6. For the methods of Coats and Redfern (Fig. 4) and Sharp and Wentworth (Fig. 5),

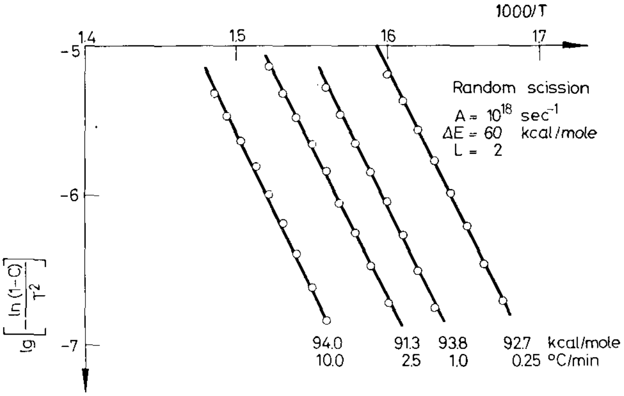

Fig. 8. Plots of random scission in the main chains of polymers (case (4)) by the method of Coats and Redfern, assuming first-order reaction

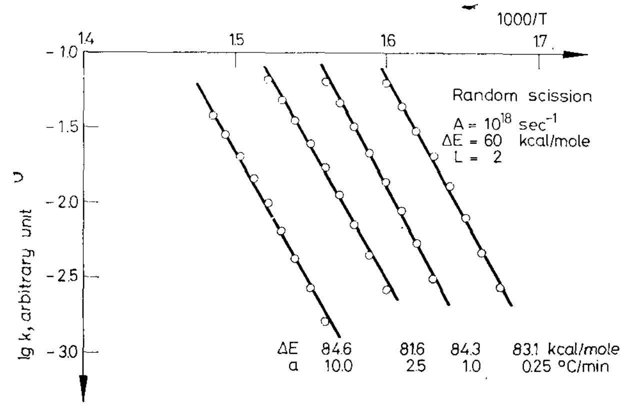

Fig. 9. Plots of random scission in the main chains of polymers (case (4)) by the method of Sharp and Wentworth, assuming first-order reaction

Table 2

Kinetic parameters estimated for case (2)

Heating rate °C/min	Freeman – Carroll		Coats – Redfern		Sharp – Wentworth		Conversion %	Ozawa		
	ΔE	n	ΔE	log A	ΔE	log A		ΔE	log A	n
							5	39.66	15.89	2
0.25	40.0	2.00	40.0	15.97	40.0	16.00	10	39.68	15.89	
							15	39.71	15.89	
							20	39.73	15.89	
0.5	40.0	2.00	40.0	15.97	40.0	16.01	25	39.73	15.89	
							30	39.75	15.89	
							35	39.76	15.89	
1.0	40.0	2.00	40.0	15.96	40.0	16.01	40	39.77	15.89	
							45	39.78	15.89	
							50	39.79	15.89	
2.5	40.0	2.00	40.0	15.96	40.0	16.00	55	39.79	15.89	
							60	39.80	15.89	
							65	39.81	15.89	
5.0	40.0	2.00	40.0	15.96	40.0	16.01	70	39.83	15.90	
							75	39.83	15.90	
							80	39.86	15.90	
10.0	40.0	2.00	40.0	15.97	40.1	16.02	85	39.86	15.89	
							90	39.89	15.89	
							95	39.92	15.90	
Average	40.0	2.00	40.0	15.965 ±0.005	40.0 ±0.05	16.01 ±0.005		39.79 ±0.02	15.89 ±0.004	

* The dimensions of the activation energy and the pre-exponential factor are kcal/mole and sec^{-1}, respectively, and the range with the average is the standard deviation.

a first-order reaction is assumed. For the other heating rates, similar, almost linear plots are also obtained. As is clear from Figs 3, 4 and 5, the plots are slightly curved. Despite this, plots actually obtained in analysis of experimental data of the random scission in the main chains of polymers tend to be recognized as straight lines, taking into account the experimental errors. The kinetic parameters obtained by the least squares approximation of these slightly curved plots are tabulated in Table 3, and when one applies the methods of Coats and Redfern and of Sharp and Wentworth, a first-order reaction is deduced. The estimated parameters are quite different from the true values. False and unreal values are also derived by applying the method of Freeman and Carroll. It is interesting to note that there are also differences between the parameters obtained at different heating rates and also between those obtained with the different methods. In contrast, the kinetic parameters estimated by the present author's method are very accurate.

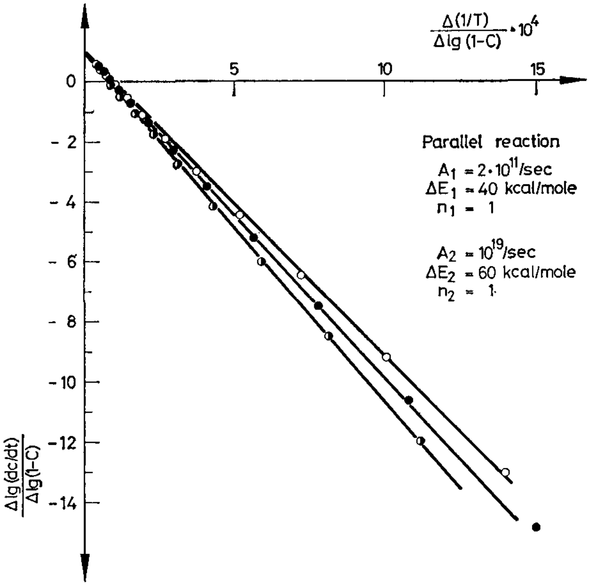

Fig. 10. Plots of parallel competitive reactions (case (5)) by the method of Freeman and Carroll. Heating rates: ○: 0.25°/min, ●: 1.0°/min, ◑: 10.0°/min

The situations are quite similar in the fourth case; the plots are shown in Figs 7, 8 and 9, and the parameters obtained are listed in Table 4. In this case, the first-order reaction is also assumed when the methods of Coats and Redfern and of Sharp and Wentworth are applied.

The plots for the fifth case, the parallel competitive reactions, are shown in Figs 10, 11, 12 and 13. For the methods of Coats and Redfern and of Sharp and

Table 3

Kinetic parameters estimated for case (3)

Heating rate °C/min	Freeman–Carroll		Coats–Redfern		Sharp–Wentworth		Conversion %	Ozawa		
	ΔE	n	ΔE	log A	ΔE	log A		ΔE	log A	mechanism
							5	40.07	12.22	random scission in main chain of polymers $L = 3$
0.25	69.0	1.29	63.3	21.52	57.6	19.25	10	40.11	12.22	
							15	40.13	12.22	
							20	40.13	12.22	
0.5	69.7	1.30	63.3	21.38	57.7	19.17	25	40.13	12.22	
							30	40.14	12.21	
							35	40.16	12.22	
1.0	68.8	1.29	63.6	21.30	57.8	19.11	40	40.16	12.22	
							45	40.16	12.22	
							50	40.17	12.21	
2.5	69.6	1.31	63.8	21.16	58.1	19.04	55	40.18	12.22	
							60	40.18	12.21	
							65	40.20	12.22	
5.0	70.9	1.35	64.5	21.26	59.0	19.22	70	40.19	12.22	
							75	40.20	12.22	
							80	40.21	12.22	
10.0	70.4	1.34	64.4	21.03	58.8	19.02	85	40.22	12.22	
							90	40.26	12.21	
							95	40.23	12.22	
Average	69.7 ±0.8	1.31 ±0.03	63.8 ±0.5	21.28 ±0.17	58.2 ±0.6	19.14 ±0.09		40.17 ±0.05	12.22 ±0.003	

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* The dimensions of the activation energy and the pre-exponential factor are kcal/mole and $\sec^{-1}$, respectively, and the range with the average is the standard deviation.

Table 4

Kinetic parameters estimated for case (4)

Heating rate °C/min	Freeman—Carroll		Coats—Redfern		Sharp—Wentworth		Conversion %	Oz wa		
	ΔE	n	ΔE	log A	ΔE	log A		ΔE	log A	mechanism
							5	59.37	17.79	random scission in main chain of polymers L = 2
0.25	102.7	1.35	92.7	29.51	83.1	26.10	10	59.32	17.79	
							15	59.39	17.78	
							20	59.40	17.78	
0.5	102.8	1.36	93.1	29.51	83.6	26.16	25	59.40	17.78	
							30	59.38	17.78	
							35	59.38	17.78	
1.0	103.3	1.38	93.8	29.59	84.3	26.36	40	59.40	17.79	
							45	59.41	17.78	
							50	59.41	17.78	
2.5	101.8	1.32	91.3	28.49	81.5	25.18	55	59.42	17.79	
							60	59.42	17.79	
							65	59.43	17.79	
5.0	102.9	1.35	92.5	28.79	82.9	25.56	70	59.44	17.79	
							75	59.45	17.78	
							80	59.42	17.79	
10.0	104.0	1.39	94.0	29.13	84.6	26.02	85	59.44	17.79	
							90	59.44	17.79	
							95	59.49	17.79	
Average	102.9 ±0.7	1.36 ±0.02	92.9 ±1.0	29.17 ±0.46	83.3 ±1.2	25.89 ±0.43		59.41 ±0.05	17.79 ±0.004	

*The dimensions of the activation energy and the pre-expontential factor are kcal/mole and sec^{-1}, respectively, and the range with the average is the standard deviation.

Wentworth, a first-order reaction is again assumed. The results obtained, except for those of the present author's method, are quite similar to the results obtained for random scission in the main chains of polymers; all plots are similarly slightly curved and the estimated kinetic parameters in Table 5 are naturally unreal and false ones. As to the plots by the present author's method, straight lines can also be drawn. However, the activation energy estimated increases from 46.7 kcal/mole at a conversion of 5% to 53.5 kcal/mole at a conversion of 95%. This implies that the process is not a simple one governed by a single activation energy, and that it consists of multiple unit processes. Thus, the method cannot be applied to the process.

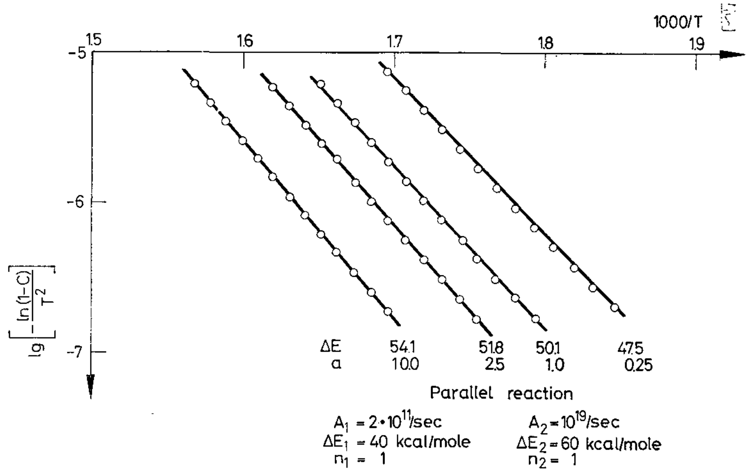

Fig. 11. Plots of parallel competitive reactions (case (5)) by the method of Coats and Redfern, assuming first-order reaction

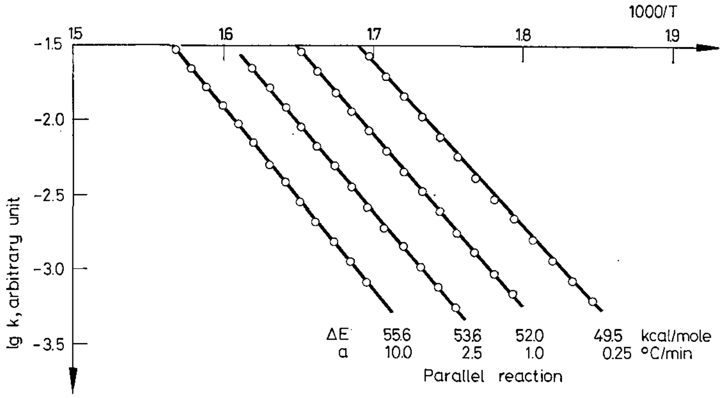

Fig. 12. Plots of parallel competitive reactions (case (5)) by the method of Sharp and Wentworth, assuming first-order reaction

Table 5

Kinetic parameters estimated for case (5)

Heating rate °C/min	Freeman—Carroll		Coats—Redfern		Sharp—Wentworth		Conversion %	Ozawa
	ΔE	n	ΔE	log A	ΔE	log A		ΔE
							5	46.7
0.25	46.0	0.86	47.6	18.06	49.5	11.97	10	48.0
							15	48.8
							20	49.3
0.5	47.3	0.86	48.9	18.58	50.8	13.10	25	49.8
							30	50.1
							35	50.5
1.0	48.6	0.86	50.1	19.02	52.0	14.13	40	50.8
							45	51.0
							50	51.3
2.5	50.5	0.88	51.8	19.67	53.6	15.51	55	51.5
							60	51.7
							65	52.0
5.0	52.0	0.90	53.1	20.15	54.7	16.54	70	52.2
							75	52.4
							80	52.6
10.0	53.1	0.91	54.1	20.54	55.6	17.45	85	52.9
							90	53.1
							95	53.5
Average	49.6 ±2.7	0.88 ±0.02	50.9 ±2.7	19.34 ±0.91	52.7 ±2.4	14.78 ±2.10		51.0 ±1.1

* The dimensions of the activation energy and the pre-exponential factors are kcal/mole and $\sec^{-1}$, respectively, and the range with the average is the standard deviation.

As clearly demonstrated above, the methods based on particular specialized formulae tend to lead to false unreal results. These methods are based on linear relationships such as Eqs (6), (7) and (8), and derivation of the linear relationships is made logically. However, it is not proved that the converse is always true, i.e. if linear relations are observed, it does not follow that the process is necessarily the one based on the fundamental equation of the n-th-order reaction. On the contrary, for some cases other than the n-th-order reaction, it is clearly demonstrated that the linear relations hold approximately.

We must now discuss some methods of avoiding false unreal kinetic parameters such as those in Tables 3, 4 and 5. In these Tables, the apparent false parameters depend on the heating rate. This fact suggests that one of the methods of avoiding false parameters is to observe a process at different heating rates. If the kinetic parameters estimated by analysing the curves at different heating rates coincide with each other, the kinetic parameters are not false. There is also a difference between the false parameters obtained by the different methods; another way, therefore, is to utilize more than two methods, and if the kinetic parameters estimated by the different methods coincide with each other, the kinetic parameters are not false. However, the third and most desirable way is to utilize a method based on a more general fundamental kinetic equation, such as the present author's method. The experimental master curve should be drawn by using the data from different heating rates. This experimental master curve should be either one which can be compared with the fundamental kinetic equation directly, or one corresponding to an isothermal curve. In the present author's method, the experimental master curve corresponds to the isothermal curve, since the reduced time is proportional to the actual time in the isothermal measurement. Furthermore, it is also desirable to observe the process by different types of thermal analysis.

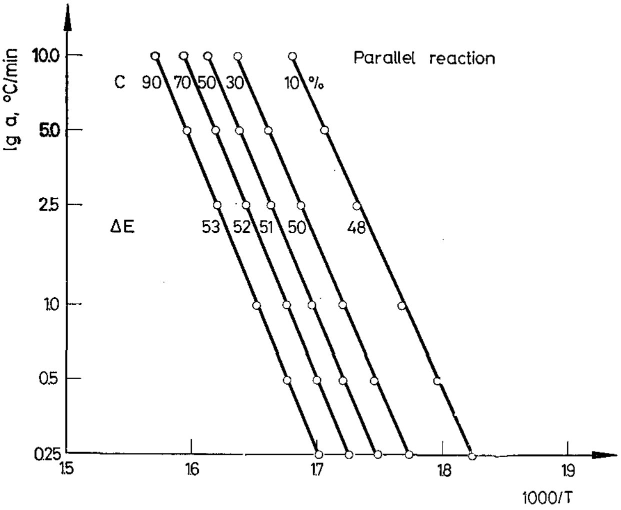

Fig. 13. Plots of parallel competitive reactions (case (5)) by the present author's method

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RÉSUMÉ — On a appliqué les méthodes de Freeman et Carroll (I), Coats et Redfern (II), Sharp et Wentworth (III) ainsi que celle de l'auteur de cette publication (IV) à cinq données thermoanalytiques théoriques calculées pour des paramètres cinétiques supposés, à diverses vitesses de chauffage. Il s'agit d'une réaction du premier ordre, une réaction du second ordre, deux cas de scission au hasard dans les chaînes principales de polymères et une réaction compétitive parallèle consistant en deux réactions du premier ordre.

Bien que les méthodes (I), (II) et (III) ne s'appliquent pas dans ces trois derniers cas, on les a néanmoins utilisées. On a alors observé des corrélations quasi linéaires et obtenu des paramètres cinétiques irréels. Pour les deux cas de scission au hasard des chaînes principales des polymères, la méthode développée par l'auteur donne des paramètres cinétiques corrects. Quant au dernier cas, l'augmentation de l'énergie d'activation apparente avec l'accroissement du taux de conversion signifie que la méthode (IV) ne peut pas être appliquée. On discute les raisons de ces résultats et les méthodes pour éviter les erreurs.

ZUSAMMENFASSUNG — Die Freemann—Carroll'sche (I), Coats—Redfern'sche (II), Sharp—Wentworth'sche (III) Methode, sowie die des Verfassers (IV) wurde auf fünf theoretische thermoanalytische Daten angewandt und für angenommene kinetische Parameter bei verschiedenen Aufheizgeschwindigkeiten berechnet. Es handelte sich hierbei um eine Reaktion erster Ordnung, eine von zweiter Ordnung, um zwei Fälle von Hauptkettenaufriß von Polymeren und um ein System aus zwei wetteifernden Reaktionen erster Ordnung. Die Methoden I, II, III können für die letzten drei Fälle nicht angewandt werden, zieht man sie dennoch heran, so erhält man unreale, falsche kinetische Parameter. Für den Kettenaufriß gibt des Verfassers Verfahren exakte kinetische Parameter. Für den letzten Fall spricht die Zunahme der scheinbaren Aktivierungsenergie mit steigender Konversion dafür, daß auch die IV. Methode nicht gebraucht werden kann. Die Begründung der Beobachtungen und die Vermeidung unrealer Parameter werden besprochen.

Резюме — Методы Фримена и Кэрролла (I), Коутся и Редферна (II), Шарпа и Вентсворса (III), а также метод, предложенный автором, (IV), были использованы для вычисления пяти теоретических термоаналитических данных для предполагаемых кинетических параметров при различной скорости нагревания. Это были реакции первого порядка, второго порядка, два случая произвольного расщепления главной цепи полимеров и параллельно протекающая конкурентная реакция, состоящая в свою очередь из двух реакций первого порядка. Методы I, II и III не применимы к последним трем случаям. Однако, в случае их использования наблюдались почти прямые зависимости, но при этом были получены ошибочные, нереальные кинетические параметры. Предложенный же автором метод в двух случаях произвольного расщепления главной цепи полимеров дает корректные кинетические параметры. Для последнего случая увеличение кажущейся энергии активации с увеличением конверсии означет, что метоы IV не может быть при этом использован. Обсуждены причины таких результатов и методы устранения этих нереальных результатов.