

SOME DEMONSTRATIONS OF THE EFFECT OF THE HEATING RATE ON THERMOANALYTICAL CURVES

T. OZAWA

Electrotechnical Laboratory, Tanashi, Tokyo, Japan

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Thermoanalytical curves of two parallel competitive reaction systems and of two systems in which two mutually independent reactions occur concurrently are made by simulation, as well as isothermal curves of the systems. From these curves, an effect of heating rate is illustratively shown; one peak is observed in a derivative thermoanalytical curve at one heating rate, while a shoulder or two peaks appear in another derivative curve of the same reaction system at another heating rate. An advantage of thermal analysis over isothermal experiments, and its limitations, are discussed.

In a previous paper [1], the present author demonstrated an effect of the heating rate on thermoanalytical curves; i.e. a thermoanalytical curve of a single unit reaction shifts at a higher heating rate to a higher temperature range, the extent of the shift being proportional to the difference of the logarithms of the heating rates and inversely proportional to the activation energy. In other words, when the integral thermoanalytical curves are plotted against the reciprocal absolute temperature, the curves can be superposed on each other by lateral shift. This dependence is utilized for kinetic analysis of thermoanalytical data. Another dependence on the heating rate is shown in another paper [2], in which apparently false kinetic parameters obtained by injudicious application of a method for kinetic analysis are apparently dependent on the heating rate, and it is proposed to utilize this dependence to check the validity of the applied method.

Another effect of the heating rate is shown by simulation in the present report, where the natures of thermoanalytical curves of two competitive reaction systems and of two reaction systems consisting of mutually independent unit reactions change with the heating rate; at one heating rate a single peak is observed in a derivative thermoanalytical curve, while two peaks or one with a shoulder are obtained at another heating rate. This demonstrates the possibility of elucidating whether a system is one consisting of multiple unit reactions or not. An advantage of thermal analysis over isothermal experiments is also demonstrated by simulation, and is discussed later.

Method of simulation

Four cases of reaction systems are calculated:

1. A parallel competitive reaction system, in which one kind of reacting species reacts by two unit reaction mechanisms, is simulated. For this case, the following equation holds:

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

where C , t , A , ΔE , R , T and $g(C)$ are the conversion, the time, the pre-exponential factor, the activation energy, the gas constant, the absolute temperature and a function of the conversion depending on the reaction mechanism, respectively, and the subscript denotes each unit reaction mechanism. These kinetic parameters of the simulated system are as follows:

$$A_1 = 10^5 \text{ sec}^{-1}$$

$$\Delta E_1 = 20 \text{ kcal/mole}$$

$$g_1(C) = (1 - C)^2$$

$$A_2 = 3 \times 10^{27} \text{ sec}^{-1}$$

$$\Delta E_2 = 80 \text{ kcal/mole}$$

and

$$g_2(C) = (1 - C)^2$$

i.e., both unit reaction mechanisms are second-order.

Integrating Eq. (1), we get

$$\int \frac{dC}{(1 - C)^2} = A_1 \theta_1 + A_2 \theta_2 \quad (2)$$

where θ is the reduced time [1]. The reduced time can be calculated by using the p -function [3] at a given temperature and a given heating rate [2, 4]:

2. A similar parallel competitive reaction system, in which the pre-exponential factors and the activation energies are the same as above, but with both unit reaction mechanisms of third-order, is simulated.

3. The third simulated case is a system in which two mutually independent reactions occur simultaneously, and the overall changes of the unit reactions, e.g., the overall weight changes in thermogravimetry, the overall heats of reaction in differential scanning calorimetry, and the overall amounts of volatilized gas analysis, are equal to each other. The assumed kinetic parameters are as follows:

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

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

$$g_1(C_1) = (1 - C_1)$$

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

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

and

$$g_2(C_2) = (1 - C_2)$$

The kinetic equations in this case are

$$\begin{cases} \frac{dC_1}{dt} = A_1 \exp\left(-\frac{\Delta E_1}{RT}\right)(1 - C_1) \\ \frac{dC_2}{dt} = A_2 \exp\left(-\frac{\Delta E_2}{RT}\right)(1 - C_2) \end{cases} \quad (3)$$

and the quantity measured in the thermal analysis is $C_1 + C_2$ or $dC_1/dt + dC_2/dt$. The method of calculating thermoanalytical curves for each unit reaction is the same as for case (1) and has been described elsewhere [4].

4. The fourth case is the same as case (3), except for the kinetic parameters, which are

$$A_1 = 10^{13} \text{ sec}^{-1}$$

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

$$g_1(C_1) = (1 - C_1)$$

$$A_2 = 3 \times 10^{27} \text{ sec}^{-1}$$

$$\Delta E_2 = 80 \text{ kcal/mole}$$

and

$$g_2(C_2) = (1 - C_2)$$

Results and discussion

Derivative thermoanalytical curves for the four cases are given below, since the derivative curve shows the nature of the process more clearly than the integral curve does. The curves for case (1) are shown in Fig. 1. As clearly demonstrated, a derivative curve of a single peak is obtained at $10^\circ/\text{min}$, while a shoulder is observed in the curve at $1^\circ/\text{min}$. If one observes this system only at $10^\circ/\text{min}$, one tends to consider it as a simple reaction. When the same system is observed isothermally, the relations between the time, the conversion and the rate are the same as the normal relations of the second-order reaction, as is apparent from Eqs (1) and (2). Now, let us suppose cases in which only either one of the two unit reactions of the system occurs, i.e., either of the two terms on the right side of Eq. (1) is made to be zero. From comparison of these supposed cases with case (1), the nature of the isothermal experiment is made clear. In Table 1, conversions at a certain time in isothermal runs are compared at several temperatures. The first unit reaction is predominant in the low temperature range, and the second is predominant in the high temperature range. In the temperature range where the reac-

tion proceeds at a rate suitable to be measured experimentally, neither of the unit reactions becomes negligibly small. Hence, we can not observe these unit reactions separately by the isothermal experiment. If one observes case (1) isothermally, one can not find any difference in experimental results measured at a single tem-

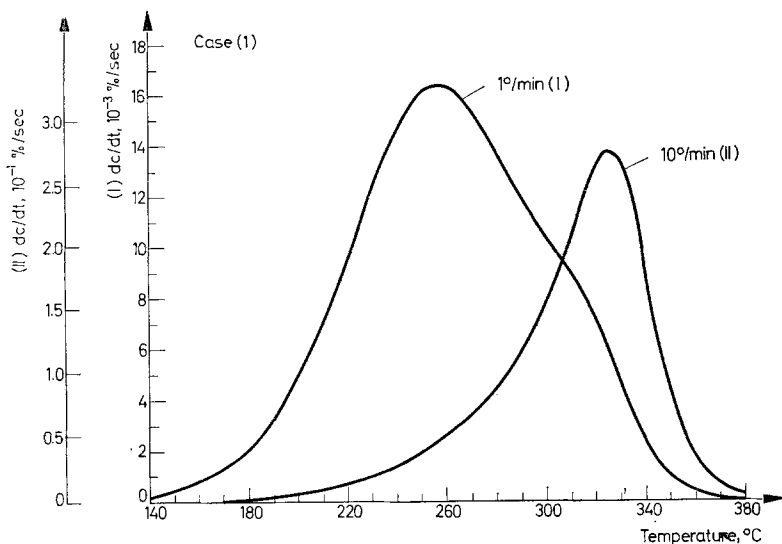


Fig. 1. Derivative thermoanalytical curves for case (1)

Table 1
Comparison of conversions in isothermal runs for case (1)

Temperature, °C	Time	Conversion overall %	Conversion* 1 %	Conversion* 2 %
200	48.1 h	90.9	90.9	6×10^{-3}
250	6.3 h	90.9	90.9	2.5
300	50.5 min	90.9	87.7	74.0
350	36.7 sec	90.9	26.2	90.6
400	0.3 sec	90.9	1.0	90.9

* Conversion 1 is for the case when only the first unit reaction proceeds, and conversion 2 is that when only the second unit reaction occurs.

perature from the normal second-order reaction, but the plots of the rate constants obtained from the isothermal measurements against the reciprocal absolute temperature are on the curved line, as seen in Fig. 2. This plot is the only difference of case (1) from the normal second-order reaction.

The thermoanalytical curves for case (2) are shown in Fig. 3. A more clear shoulder is again found at $1^\circ/\text{min}$, while only a single peak is seen at $10^\circ/\text{min}$. In thermoanalytical curves for a competitive reaction system in which the activation energies and the pre-exponential factors are the same as in cases (1) and (2), but with both reaction orders unity, only a single peak is observed, in spite of changing the heating rate from $0.25^\circ/\text{min}$ to $10^\circ/\text{min}$. Thus, as the reaction order increases, the shoulder becomes clear in the competitive reaction system. The comparison as in Table 1 is also made for case (2) and is shown in Table 2. The situation is quite similar to case (1).

Thermoanalytical curves for case (3) are reproduced in Fig. 4, where curves for each unit reaction are also shown; the curve for case (3) is the sum of them. In this case, a shoulder is found at high heating rate. This result suggests that a low heating rate is not always preferable to a high heating rate. Conversions of each unit reaction in isothermal runs are compared in Table 3. It is seen that it is difficult to observe either unit reaction separately in isothermal experiments; the

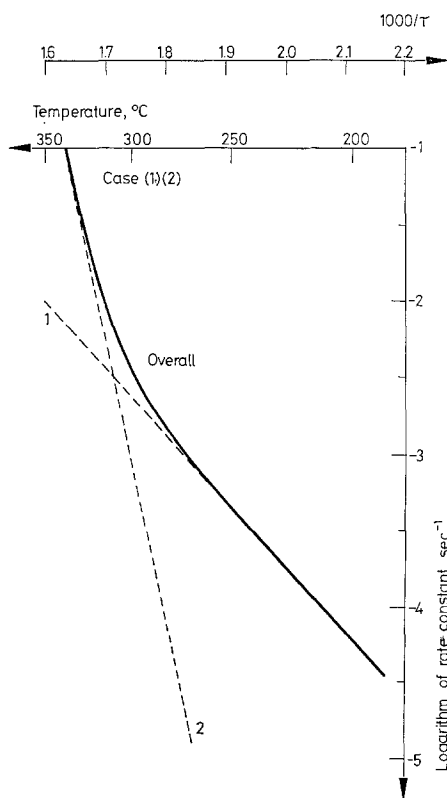


Fig. 2. Temperature-dependence of apparent overall rate constant and rate constants of unit reactions for cases (1) and (2)

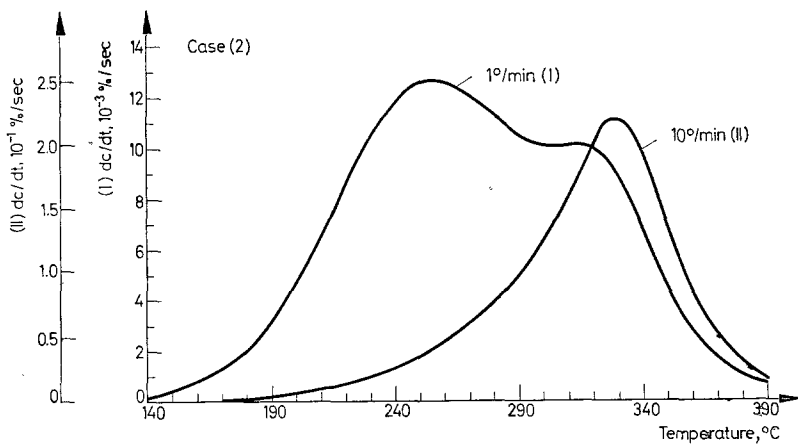


Fig. 3. Derivative thermoanalytical curves for case (2)

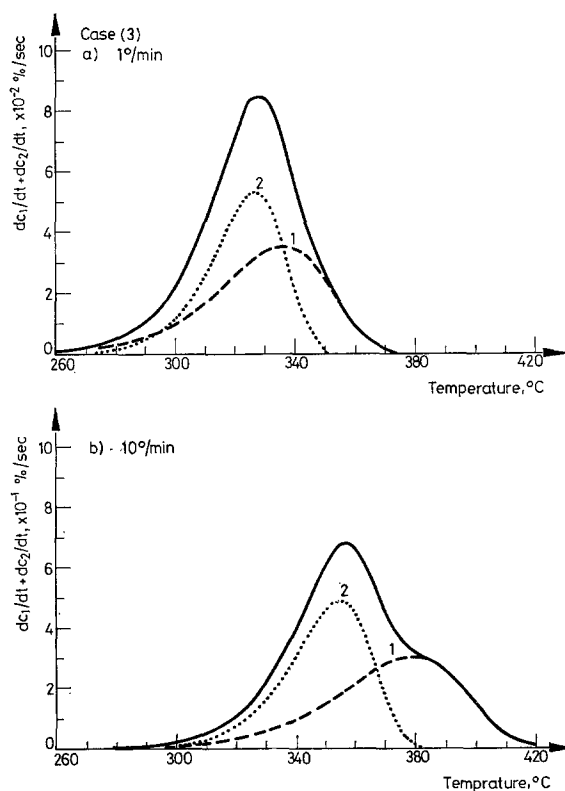


Fig. 4. Derivative thermoanalytical curves for case (3) and its unit reactions. Case (3) is the solid line, the first unit reaction is the chain line, and the second is the dotted line

situation is more clear than in cases (1) and (2), taking into account the smaller difference in the activation energies. However, the relation between the time and the conversion is very complicated and different from the first-order reaction.

Table 2
Comparison of conversions in isothermal runs for case (2)

Temperature °C	Time	Conversion overall %	Conversion* 1 %	Conversion* 2 %
200	48.1 h	78.2	78.2	6×10^{-3}
250	6.3 h	78.2	78.2	2.5
300	50.5 min	78.2	74.5	61.3
350	36.7 sec	78.2	23.5	77.8
400	0.3 sec	78.2	1.0	78.2

* Conversion 1 is for the case when only the first unit reaction proceeds, and conversion 2 is that when only the second unit reaction occurs.

Table 3
Comparison of conversions in isothermal runs for case (3)

Temperature °C	Time	Conversion 1 %	Conversion 2 %
200	2.2 year	99.0	12.5
250	13.7 day	99.0	63.8
300	9.7 h	98.0	99.0
350	8.5 min	61.4	99.0
400	14.0 sec	24.9	99.0
450	0.6 sec	9.7	99.0

Table 4
Comparison of conversions in isothermal runs for case (4)

Temperature °C	Time	Conversion 1 %	Conversion 2 %
200	15.9 day	99.0	0.05
250	6.6 h	99.0	2.7
300	13.7 min	99.0	53.8
350	17.5 sec	80.6	99.0
400	0.14 sec	13.8	99.0

For case (4), two peaks are observed in the thermoanalytical curve at $1^\circ/\text{min}$, but a shoulder or multiple peaks are not found in the curve at $10^\circ/\text{min}$, as is shown in Fig. 5. The results of the isothermal experiments are shown in Table 4, and are the same as those for case (3). A high order of reaction is preferable for separation in competitive reaction systems, but in reaction systems of mutually independent unit reactions, a low order of reaction is preferable for separation in contrast, because a derivative thermoanalytical curve of a reaction of low order is sharp, whereas that of one of high order is diffuse [5].

From these results, an advantage of thermal analysis over isothermal experiments is clearly demonstrated, i.e., for a reaction system in which multiple unit reactions proceed concurrently, thermal analysis is preferable to isothermal measurements, because the nature of the reaction system may be revealed by thermal analysis via the existence of shoulders or multiple peaks. The reason for the separation and coincidence of unit reactions in thermoanalytical curves due to the heating rate, such as seen above, is shown schematically in Fig. 6. The reciprocal

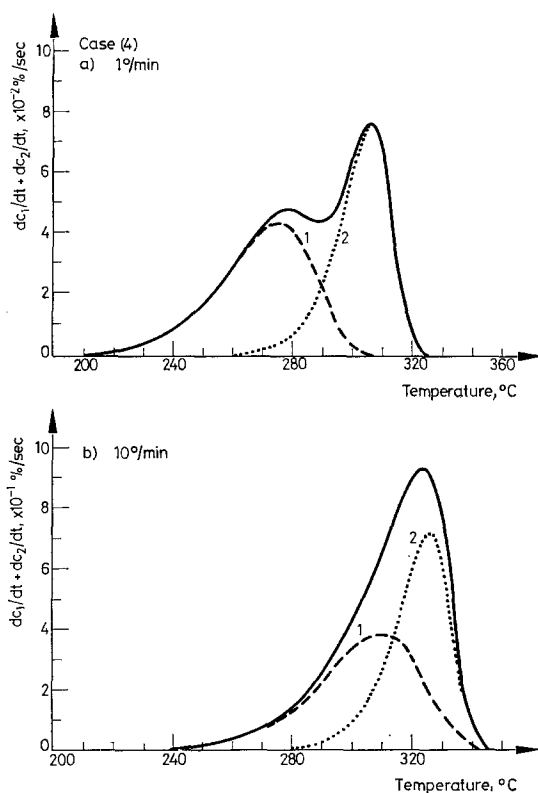


Fig. 5. Derivative thermoanalytical curves for case (4) and its unit reactions. Case (4) is the solid line, the first unit reaction is the chain line, and the second is the dotted line

absolute temperature at which the simple unit reaction proceeds to the peak or a given conversion in thermal analysis is in a linear relation with the logarithm of the heating rate, and the slope is inversely proportional to the activation energy [1, 4]. Therefore, the peak temperature of a unit reaction of low activation energy shifts farther than that of one of high activation energy. This difference in the shift is the cause of the change in the thermoanalytical curves due to the heating rate; in some cases of reaction systems consisting of multiple unit reactions, the temperature is scanned from low temperature, where one unit reaction is predominant over the others, to high temperature, where another unit reaction becomes predominant and the reacting species still remain, so that multiple peaks or shoulders can be observed.

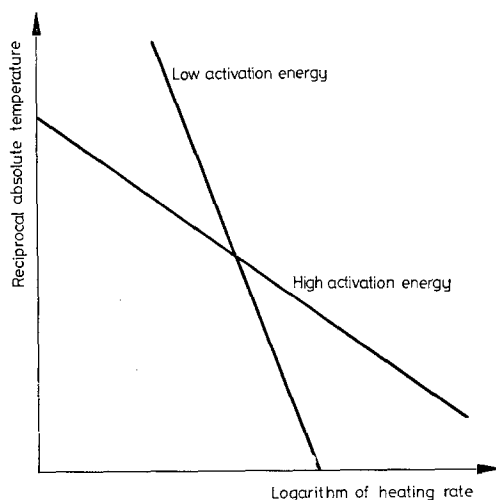


Fig. 6. Schematic diagram for explanation of separation and coincidence of peaks

In comparison with the fact that there is one peak in a derivative thermoanalytical curve, the reaction rate decreases monotonously in isothermal runs of most reactions, except random scission in main chains of polymers and autocatalytic reactions, and the rate constant is unchanged during the isothermal run, while it changes in thermal analysis, depending on the activation energy. As a result of these differences, the existence of multiple unit reactions is hardly revealed in isothermal experiments.

However, this advantage of thermal analysis is limited. As described above, for competitive reaction systems, separation occurs in a system with a high order of reaction and a large difference in the activation energies. For instance, in the case of a competitive reaction system in which

$$\begin{aligned}A_1 &= 4 \times 10^{12} \text{ sec}^{-1} \\ \Delta E_1 &= 40 \text{ kcal/mole} \\ A_2 &= 2 \times 10^{27} \text{ sec}^{-1} \\ \Delta E_2 &= 80 \text{ kcal/mole}\end{aligned}$$

and

$$g_1(C) = g_2(C) = (1 - C)^2 \text{ or } (1 - C)^3$$

neither a shoulder nor two peaks are detected at heating rates from 1°/min to 10°/min, but there is a single peak in the derivative curves obtained.

Therefore, in order to investigate such a reaction by thermal analysis, it is desirable to study it at several different heating rates. In fact, for some materials, such as high polymers, the thermoanalytical curves sometimes change with the heating rate. However, a single peak does not necessarily imply that the reaction under study is a simple reaction. Furthermore, the nature of the reaction can also be revealed from kinetic analysis by appropriate methods, as pointed out previously [2]. From this point of view, evolved gas analysis is a preferable tool to differential thermal analysis, differential scanning calorimetry, thermogravimetry and so on, because it provides information about the chemical composition of the volatilized products, as well as the rate of production of each component. For instance, the author has found that derivative thermogravimetric curves of decomposition of a polycarbonate in vacuum are curves of a single peak without a shoulder, but it is revealed by evolved gas analysis with a mass-spectrometer that some products are volatilized in the low temperature range of the thermogravimetric curve and others in the high temperature range. Thermofractography [6] also seems to be a powerful tool for checking the mechanism.

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RÉSUMÉ — On a simulé les courbes d'analyse thermique de deux systèmes parallèles de réactions compétitives et de deux systèmes dans lesquels deux réactions mutuellement indépendantes ont lieu de manière concurrente. On a établi de même les courbes de ces systèmes en chauffage isotherme. L'effet de la vitesse de chauffage a ainsi été mis en évidence. On observe un pic sur la courbe d'analyse thermique dérivée pour une certaine vitesse de chauffage tandis qu'avec le même système, mais pour une autre vitesse de chauffage, on obtient un épaulement ou deux pics. On discute les avantages de l'analyse thermique sur l'étude isotherme ainsi que ses limites.

ZUSAMMENFASSUNG — Die thermoanalytischen Kurven zweier paralleler kompetitiver Reaktionssysteme und zweier Systeme, in welchen zwei voneinander unabhängige Reaktionen gleichzeitig stattfinden, wurden simuliert, sowie die isothermen Kurven der Systeme ermittelt. Diese Kurven veranschaulichen die Wirkung der Aufheizungsgeschwindigkeit; ein Peak wird an der derivativen thermoanalytischen Kurve bei einer gegebenen Aufheizungsgeschwindigkeit beobachtet, während an einer anderen derivativen Kurve desselben Reaktionssystems bei einer anderen Aufheizungsgeschwindigkeit eine Schulter oder zwei Peaks vorliegen. Die Vorteile der Thermoanalyse gegenüber dem isothermen Experiment sowie ihre Grenzen werden erörtert.

Резюме — Методом моделирования были выполнены термоаналитические кривые двух параллельных конкурирующих реакционных систем и двух систем, в которых конкурентно протекают две взаимно независимые реакции, а также и их изотермические кривые. На примере этих кривых наглядно показано влияние скорости нагрева; один пик наблюдали на кривой ДТА при одной скорости нагрева, в то время как плечо или два пика проявляются на другой кривой той же самой реакционной системы, но при другой скорости нагрева. Обсуждено преимущество термического анализа над изотермическим, а также и недостатки.