Journal of Thermal Analysis, Vol. 31 (1986) 1253–1262

KINETIC ANALYSIS OF COMPLEX REACTIONS

*R. K. Agrawal**

ADVANCED ENERGY AND MATERIALS RESEARCH
5500 BEATTY DRIVE, UNIT NO. J305 IRVIN, PA 15642, U.S.A.

(Received November 4, 1985; in revised form February 10, 1986)

TG and DSC techniques have been extensively used to study complex solid state reactions. For complex reactions (constituting of all exothermic or all endothermic one step first order individual reactions), it has been shown that the results of TG and DSC instruments may not be identical. This is because the TG instrument is incapable of correctly recording the true effective reaction rate of complex reactions (if the reaction rate is not proportional to the total amount of reactants). This may happen when the reaction rates of the individual reactions in the composite reaction mixture are significantly different. In this communication it has also been suggested that the Friedman analysis of obtaining activation energy (E) may be inapplicable for complex or composite reaction due to the fact that, there may be no unique effective constant conversion at various heating rates.

During the past years, some groundbreaking research has been conducted in understanding the thermal behaviour of some complex reactions [1–5]. Flynn [1, 4] and Ozawa [3] have discussed the effect of heating rate on the effective reaction for competitive as well as for mutually independent reaction models. For the competitive reaction, Flynn [4] reported that low activation energy reaction dominated the kinetics at low heating rates and low temperature. The high activation energy (E) reaction was found to be dominating at fast heating rates and high temperatures. For mutually independent reactions, Flynn [4] found that low E and high E reactions can be separated from one another by either increasing or decreasing the heating rates.

The studies of Ozawa [2, 3] was limited to consideration of two independent reactions, while that of Flynn [4] to four independent reactions. The recent study of Elder [5] was directed to understanding the effective nature of a set of ten independent reactions for both, the competitive and the mutually independent reaction models. Elder [5] reported that the effective competitive reaction occured at a significantly lower temperature than that of independent individual reactions

---

* Communications should be addressed to the author. Development Engineering and Analysis, KRW Energy Systems Inc., P.O. Box 334, Madison, PA 15663, U.S.A.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

over the entire extent of the reaction. The effective mutually independent reaction was assumed to represent the sum of the individual reactions. For a set of first order individual reactions, the competitive reaction always exhibited a first order reaction. In contrast the effective mutually independent reaction exhibited a pseudo n^{th} order reaction. The value of n was found to depend on the reaction mixture concentration and on the rates of individual reactions.

Elder [5] also found that the activation energy of the mutually independent reaction was comparable to those of the individual reactions. Recent results of Agrawal [6] confirm this finding. However, this viewpoint is in direct conflict with the popular belief in coal pyrolysis literature [7, 8] which implies that a set of independent first order reactions can be approximated by a single first order mutually independent reaction model having a lower activation energy than any of the reactions in the set. Coal scientists routinely quote the findings of Juntgen and van Heek [7] and Anthony and Howard [8] to have mathematically demonstrated this viewpoint. However, it has been recently shown by Elder [5] that the published results of Juntgen and van Heek [7] are not consistent with their reported findings. An independent study of Agrawal [6] has questioned the validity of Anthony and Howard's [8] results.

The previous mentioned papers [1–6] were limited to studying combination of first order one step reactions. Some progress has also been made in understanding the nature of consecutive and reversible complex reactions [9].

In recent years there has been an extensive use of thermogravimetric (TG) and differential scanning calorimetric (DSC) techniques to understand the nature of complex solid state reactions. The kinetic parameters estimated from TG analysis are based on weight loss, where as in the case of DSC, the kinetic parameters are based on the change in enthalpy of the reaction. Since a large number of reactions occur with a change in enthalpy, at least theoretically, the principles of DSC can be used to study most of the reactions. Some reactions occur with a change in enthalpy but not necessarily with a change in weight. In such a case the results of DSC and TG will be different. This is primarily because the TG device is not capable of measuring such isogravimetric reactions. If a reaction occurs with both, a change in weight and a change in enthalpy, then the kinetic parameters derived from TG and DSC should be identical. However, the TG and DSC results are not always in agreement due to influence of some experimental factors. To minimize the experimental factors efforts have been directed towards simultaneous TG and DSC measurement of the reaction.

In case of composite reactions, where more than one reaction occurs simultaneously, the overall or the effective reaction rate can be estimated from the algebraic sum of the individual reactions. If we assume that the results of TG and DSC techniques for the individual reactions are identical and that all the individual reactions have the same sign for the heat of reaction (i.e. all the individual reactions are exothermic or all endothermic), then the results for the composite reaction from the TG and DSC devices is generally accepted to yield comparable results. If some of these individual reactions are endothermic and some exothermic with comparable magnitudes of the heats of reaction, then they may nullify the signals of each other resulting in a difference in TG and DSC results.

In this paper the nature of composite reaction resulting from four individual reactions having the same sign of the heat of reaction is discussed. In case of the competitive reaction model the simulated results of TG and DSC studies yielded identical results. For the mutually independent reaction which exhibits multiple peaks, it was found that the results of TG and DSC studies need not be identical. Some reasons for the differences in the results of TG and DSC studies of multiple peaked complex reactions are discussed. Comparison of simulated results for the competitive and the mutually independent reactions based on one step first order individual reactions are made. Some arguments against the use of Friedman's method [10] for composite reactions are also presented.

Kinetic analysis

A mutually independent set of reaction may be visualized as:

$$a_1 \xrightarrow{k_1} b_1$$

$$a_2 \xrightarrow{k_2} b_2$$

$$\vdots$$

$$a_i \xrightarrow{k_i} b_i$$

where a_i represents the amount of the ith species in the reacting mixture, b_i the amount of product of the ith species, and k_i's are their respective rate constants. The temperature dependence of the rate constant is modeled by the Arrhenius equation

$$k_i = A_i \exp(-E_i/RT) \tag{1}$$

The rate equation for a first order independent raction is

$$\frac{\mathrm{d}\alpha_i}{\mathrm{d}t} = -k_i\alpha_i \tag{2}$$

α_i represents the fraction of the reactant and is related to the concentration by the relation $\alpha_i = (a_i - a_{i\infty})/(a_i^0 - a_{i\infty})$. a_i^0 represents the initial amount of a_i and $a_{i\infty}$ represents the value at the end of the reaction. It can be seen that α_i varies from 1 to 0 as the reaction proceeds to completion. If the temperature of the system is linearily increased Eq. (2) can be rewritten as:

$$\frac{d\alpha_i}{dT} = \frac{1}{\beta}\frac{d\alpha_i}{dt} = -\frac{A_i}{\beta}\alpha_i \exp(-E_i/RT) \tag{3}$$

where $\beta = dT/dt$, represents the heating rate. $d\alpha_i/dT$ may be refered to as the temperature derivative or to as the nonisothermal reaction rate or simply to as the reaction rate. The integrated from of Eq (3) is [1]

$$-\ln \alpha_i = \frac{A_i E_i}{\beta R} p(x_i) \tag{4}$$

where $x_i = -E/RT$ and $p(x_i)$ is the temperature integral represented by the equation:

$$p(x_i) = -\frac{e^{x_i}}{x_i} + \int_{-\infty}^{x_i} \left[\frac{e^{x_i}}{x_i}\right] dx_i \tag{5}$$

Several approximations of the $p(x)$ function are available in the literature. Flynn's [11] results indicate that his tables yields reasonable values of the $p(x)$ function. Consequently, the tables of Flynn [11] were used for calculating the $p(x)$ function. Once the temperature integral $p(x)$ is evaluated, α_i can be obtained by Eq. (4). The temperature derivative can finally be obtained by substituting the value of α_i in Eq. (3). The reaction rate for the effective multiple independent reaction is obtained by summing the individual reaction rates, i.e.,

$$\frac{d\alpha}{dT} = \Sigma g_i \frac{d\alpha_i}{dT} \tag{6}$$

where $\alpha = \Sigma g_i \alpha_i$ = total fraction of the reactants or the effective sum of conversion of the reactants. g_i is the weight factor and $\Sigma g_i = 1$. g_i enables the calculation of the contribution of each individual reaction to the effective reaction. α varies from 1 to 0 as the reaction proceeds to completion. Using the relation expressed in Eq. (3), Eq. (6) may be rewritten as

$$\frac{d\alpha}{dT} = -\Sigma g_i \frac{A_i}{\beta}\alpha_i \exp(-E_i/RT) \tag{7}$$

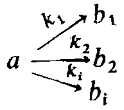
The DSC signal for the effective mutually independent reaction model (assuming all individual reactions have the same sign of the heat of reaction) will record the rate expressed by Eq. (7). Consequently in this study we assume the results obtained from Eq. (7) to be those of a DSC device.

Now if the reaction is being recorded by a TG device, the instrument would record the reaction rate which is proportional to the net effective conversion, α. The equation may be mathematically represented as

$$\frac{d\alpha}{dT} = f(\alpha, T) = -\frac{A'}{\beta}\alpha^n \exp(-E'/RT) \tag{8}$$

Here A' and E' are pseudo Arrhenius parameters of the effective mutually independent reaction used to describe the temperature dependence of the effective reaction rate constant. n is the effective order of reaction. The term pseudo is used to explain the effective reaction because the net reaction rate, $d\alpha/dT$, may not be truely proportional to α. This may happen if some of the reactants in the reaction mixture do not react or react at a very different rate compared to the average reaction rate. Depending on the nature of the individual reactions, A' and E' in this case may be functions of temperature and/or concentration. It may also be mentioned that there is no known relationship between the effective pseudo Arrhenius parameters, A' and E', and the individual Arrhenius parameters A_i and E_i. In our study the results obtained from Eq. (8) are assumed to be the rate determined by a TG device.

A competitive reaction model may be visualized as



The rate expression for the competitive reaction is

$$\frac{d\alpha}{dT} = -\frac{A}{\beta}\alpha \exp(-E/RT) \tag{9}$$

where $\alpha = (a-a_\infty)/(a^0-a_\infty)$, and a^0 is the initial concentration of a and a_∞ is the final (or equilibrium) value of a. The Arrhenius parameters of the effective competitive reaction are related to those of the individual reaction by the relation

$$A \exp(-E/RT) = \Sigma A_i \exp(-E_i/RT) \tag{10}$$

The fraction of reactant, α, at any time, t, is obtained by integrating Eq. (9):

$$-\ln \alpha = \sum \frac{A_i E_i}{\beta R} p(x_i) \tag{11}$$

The temperature derivatives of the effective competitive reaction can then be calculated by substituting the value of α in Eq. (9).

Results and discussion

To demonstrate some potential differences in the results from TG Eq. (8) and DSC Eq. (7) studies, we consider the consequences of a set of four independent one step, first order reactions with the following Arrhenius parameters: $A_1 = 2.4\times10^4$ s^{-1}, $E_1 = 19.1$ kcal/mol; $A_2 = 4.5\times10^{11}$ s^{-1}, $E_2 = 38.2$ kcal/mol; $A_3 = 6.1\times10^{18}$ s^{-1}, $E_3 = 57.4$ kcal/mol; and $A_4 = 7.4\times10^{25}$ s^{-1}, $E_4 = 76.5$ kcal/mol. These values have been chosen since some theoretical behaviour of rate of conversion versus temperature for these parameters are available in the literature [4]. It is further assumed that all the individual reactions have the same sign of the heat of reaction.

In order to simplify calculations the value of the heating rate β is assumed as 1 K/s. The advantage of assuming $\beta = 1$ K/s not only simplifies the calculations, but also limits the reaction range of the competitive reaction to 525–625 K. This is important since all the individual reaction rates are comparable within this temperature range. If however β is changed significantly then, the results of Flynn [4] indicate that we may not be studying the effective nature of all four reactions but, of only those which may be dominating the reaction. Since our aim is to study the composite reaction of all four individual reactions, a heating rate of 1 K/s provides us with an opportunity to do so.

The values of α_i for the individual reactions obtained using the tables of Flynn [11] for $p(x)$ are shown in Fig. 1. An increase in the heating rate, β, will not significantly influence the nature of these curves but will primarily shift the curves to higher temperatures along the temperature axis and will also increase the temperature range of the reaction. A decrease in β will have an identical opposite effect.

The temperature derivatives of the individual reactions calculated using Eq. (3) are described in Fig. 2 as a function of temperature. It may be mentioned that the temperature derivatives described in Fig. 2 are more informative and sensitive than the nonisothermal conversion of the reactant shown in Fig. 1. Hence a comparison of the temperature derivative curves should bring out more differences than the nonisothermal conversion curve. Consequently the use of the temperature derivative rather than the nonisothermal conversion should be emphasized. Figure 2 shows that the reaction 1 occurs over a broad temperature range compared to reactions 2, 3 and 4. Reactions 2, 3 and 4 overlap and occur in a narrower temperature range. These results are in good agreement with those of Flynn [4].

Figure 3 summarizes the effective reaction rates of competitive (curve 1) and mutually independent (curves 2 and 3) reaction models. The competitive reaction in this case could be represented by a first order reaction with the Arrhenius parameters $A = 5.6\times10^{10}$ s^{-1} and $E = 57.8$ kcal/mol. A comparison of the rates

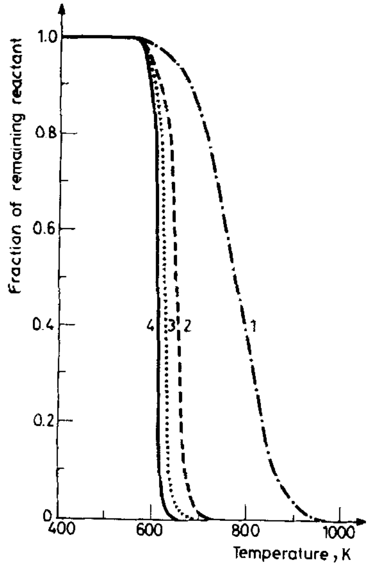


Fig. 1 Fraction of remaining amount of individual reactants *vs.* temperature at $\beta = 1$ K/s

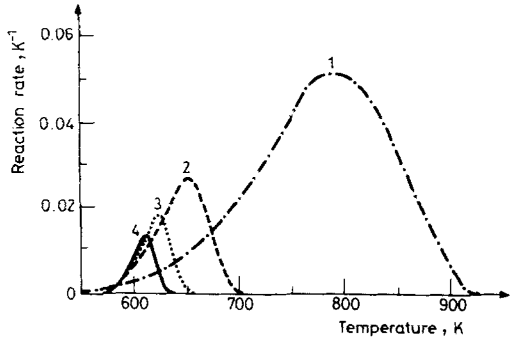


Fig. 2 Nonisothermal reaction rates $(d\alpha/dT)$ *vs.* temperature for individual reactions

of competitive reaction (curve 1, Fig. 3) and those of the individual reactions (Fig. 2) indicates that although all four reactions occur in this temperature range, the competitive reaction is dominated by reactions 2, 3 and 4. This may also be concluded from the fact that the value of the effective E is the average of the E_i' of reactions 2, 3 and 4.

As discussed earlier, results of Flynn [4] suggests that by varying the heating rates the effective nature of the competitive reaction can be changed. In such a case the effective Arrhenius parameters of the competitive reaction will change and may reflect the average value of the dominating ractions. If the individual reactions are

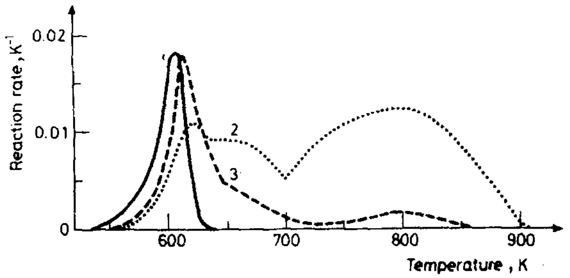


Fig. 3 Nonisothermal reaction rates ($d\alpha/dT$) of the effective competitive and the effective mutually independent reactions. Curve 1 represents the competitive reaction; Curve 2 represents the rate of multiple reaction calculated from Eq. (7) for a reaction mixture where $g_1 = g_2 = g_3 = g_4 = 0.25$ (simulated DSC signal); Curve 3 represents the rate of multiple reaction calculated from the slope of a plot of α *vs.* temperature (simulated TG signal)

very competitive as represented by this set, then it is possible that E becomes a function of the heating rate. Hence in studying complex reactions where the rates of individual reactions are unknown, methods which involve multiple heating rates such as those of Friedman [10] and the isoconversion method [11] may be inapplicable. This may be a possible explanation to Elder's [5] finding than, the E obtained by the Friedman's method changed with the extent of reaction.

Curve 2 in Fig. 3 represents the rate for the multiple reaction calculated from Eq. (7) for a reaction mixture where $g_1 = g_2 = g_3 = g_4 = 0.25$ (simulated DSC signal). Curve 3 in Fig. 3 represents the reaction rate for the same reaction mixture but calculated from the slope of a plot of α versus temperature as suggested by Eq. (8) (simulated TG signal). Initially the TG signal exhibits a more rapid rate than the DSC signal, primarily due to the compounding effect of reactions 3 and 4. The latter part of the TG signal is more sluggish in response. The effective mutually independent reaction represented by curves 2 and 3 of Fig. 3 exhibit multiple peaks indicating the dominance of individual reactions in various temperature ranges. Therefore the effective reaction exhibits multiple Arrhenius parameters which are functions of temperature and or conversion.

If the rate of reaction is proportional to the amount of the reactant mixture then curves 2 and 3 of Fig. 3 will yield identical results. Since not all of the reactants in the reaction mixture are reacting over the entire temperature range (see Fig. 2), the rapid rate in the initial period and the sluggish rate in the later period represented by curve 3 indicates that, at least in this case the assumption in Eq. (8) does not strictly hold. Hence in this case the results of TG may be flawed. However, if the effective reaction rate is proportional to the total amount of reactants as assumed in Eq. (8), then the results of TG and DSC instruments should be identical.

In case of mutually independent reaction we may argue that the results for a constant effective conversion, α, at various heating rates may not be unique. This is because though we can obtain a constant value for the sum of the individual conversions, α, at various heating rates, the individual conversions, α_i's, can vary due to competition of individual reactions. Since there may be no unique conversion of all individual reactions to yield an identical effective conversion at various heating rates, Friedman's method of obtaining E may yield meaningless results. If we are able to measure the conversion of individual reactions, then perhaps the Friedman's method may yield useful results. It may be suggested that Friedman's method to obtain E may be applicable only to one step simple reactions where there is unique effective conversion. Finally it may be mentioned that, in actual experimentation increasing the heating rates increases the magnitude of the temperature gradients across the sample [12]. Therefore the confidence in the measured reaction temperature decreases with increasing heating rates. Since an accurate estimate of the reaction temperature is prerequisite for reliable results, low weightage should be given to results from multiple heating rate studies.

Conclusions

Summarizing, we can conclude that curve 2 of Fig. 3 represents the "true" rate which can be measured by a DSC or a differential thermal analysis (DTA) instrument which measure the kinetics based on change in enthalpy of a reaction. Curve 3 of Fig. 3 represents the apparent rate which may be observed by a TG or a differential thermogravimetric (DTG) devices, which are capable of measuring the change in the mass of reactants undergoing a phase change decomposition reaction. Since the change in enthalpy of the reaction represents a "truer" measure of the reaction rate, the results from DTA/DSC may be of more value than those obtained by using TG/DTG devices. However, if the effective rate of reaction is proportional to the total amount of the reactants (Eq. (8)), then the results obtained from DTA/DSC and TG/DTG instruments should be identical. Hence it can be concluded that the results of TG and DSC for complex reactions (constituting of individual reactions with the same sign of heat of reactions) may not be identical, not only due to differences in experimental errors but, also due to kinetic differences in their governing principles and their measuring techniques. Therefore the simultaneous use of TG and DSC should prove valuable in understanding complex solid state reactions.

In case of composite reactions there may be no unique overall conversion of the individual reactions to yield an identical value of the effective conversion at various heating rates. In such a case methods which involve multiple heating rates such as those of Friedman [10] and the isoconversion method [11] may be inapplicable. Also in experimentation changes in heating rates influences the temperature gradient across the sample and the measure of the sample temperature. Therefore low weightage should be given to the value of E which results from multiple heating rate studies in case of complex reactions.

* * *

The author would like to thank the reviewer for his comments.

References

1 J. H. Flynn and L. A. Wall, J. Research NBS, 70A (1966) 487.
2 T. Ozawa, J. Thermal Anal., 7 (1975) 601.
3 T. Ozawa, J. Thermal Anal., 9 (1976) 217.
4 J. H. Flynn, Thermochimica Acta, 37 (1980) 225.
5 J. P. Elder, J. Thermal Anal., 29 (1984) 1327.
6 R. K. Agrawal, manuscript in preparation.
7 H. Juntgen and K. H. van Heek, Fort. der Chemischen Forsch., 13 (1970) 601.
8 D. B. Anthony and J. B. Howard, AIChE J., 22 (1976) 625.
9 K. Heide, G. Kluge, W. Reprich and H. Hobert, Thermal Analysis, Vol. I, Proc. IV ICTA, Budapest, 1 (1974) 123.
10 H. L. Friedman, J. Polymer Sci., 6C (1965) 183.
11 J. H. Flynn, J. Thermal Anal., 27 (1983) 95.
12 A. Blazek, Thermal Analysis, Translation Ed. J. F. Tyson, Van Nostrand, NY, 1972.

Zusammenfassung — TG- und DSC-Techniken wurden in großem Umfang zur Untersuchung komplexer Festkörperreaktionen herangezogen. Für (alle exotherme oder alle endotherme individuelle Einschritt-Reaktionen erster Ordnung in sich einschließende) komplexe Reaktionen wurde gezeigt, daß die Ergebnisse von TG- und DSC-Geräten nicht notwendigerweise identisch sind, weil das TG-Gerät die wahre effektive Reaktionsgeschwindigkeit komplexer Reaktionen nicht korrekt zu registrieren imstande ist (wenn die Reaktionsgeschwindigkeit nicht proportional der Gesamtmenge der Reaktanten ist). Dies kann der Fall sein, wenn die Reaktionsgeschwindigkeiten der individuellen Reaktionen im Reaktionsgemisch signifikant unterschiedlich sind. In der vorliegenden Publikation wird auch darauf hingewiesen, daß die Friedman-Analyse zur Ermittlung der Aktivierungsenergie (E) bei komplexen Reaktionen nicht unbedingt anwendbar ist, da die Konversion von der Aufheizgeschwindigkeit abhängig sein kann.

Резюме — Методы ТГ и ДСК были широко использованы для изучения твердотельных реакций. Показано, что для сложных реакций, состоящих из всех экзотермических или эндотермических одноступенчатых реакций первого порядка, результаты ТГ и ДСК измерений могут быть не идентичными. Причиной этого является то, что ТГ аппаратура не позволяет точно определять истинную эффективную скорость сложных реакций, если скорость реакции не пропорциональна общему количеству реагирующих веществ. Это происходит в том случае, когда скорости отдельных реакций в сложной смеси реакций значительно отличаются. В статье также предположено, что в случае сложных реакций анализ Фридмена для определения энергии активации E неприменим. Это обусловлено тем, что в таких реакциях нет единственной эффективной константы превращения при различных скоростях нагрева.