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ANALYSIS OF IRREVERSIBLE COMPLEX CHEMICAL REACTIONS AND SOME OBSERVATIONS ON THEIR OVERALL ACTIVATION ENERGY

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ABSTRACT

The nature of the overall reaction and its activation energy are investigated for both competitive and multiple reactions resulting from a one-step, irreversible, first-order reaction. For the competitive reaction model, the overall reaction is a function of the rates of the individual reactions in the reaction mixture. The rate constant of the competitive reaction in most cases can be represented satisfactorily by the Arrhenius equation. If the ratios of the individual reaction rates vary significantly with temperature, then the activation energy of the competitive reaction may vary with temperature and becomes a function of the activation energy of the most dominating reaction. The nature of the multiple reaction is a strong function of the individual reaction rates and the initial composition of the reaction mixture. It is demonstrated that a set of independent first-order reactions cannot be approximated by a single first-order multiple reaction having a lower activation energy than any of the reactions in the set. Possible reasons for previously reported "low" activation energies observed in coal and biomass pyrolysis studies are briefly discussed.

INTRODUCTION

Many industrial processes involve complex cracking and decomposition reactions of heterogeneous materials such as crude oil, oil shale, coal, biomass, etc. In order to model such reactions it is popularly assumed that these heterogeneous materials can be approximated by a continuous mixture in which the components are distinguished by a continuous variable [1–6]. Since it is impossible to have a knowledge of each individual reacting species, it is commonly assumed that these heterogeneous reacting species can be divided into several groups or lumps. These lumps are then treated as an entity. The problem which is then encountered is the structural depen-

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dence of the overall reaction on these lumps and their influence in the construction of a consistent network of reaction pathways for the reaction mixture.

In their theory of reactions in continuous mixtures, Aris and Gavalas [1] suggest that different lumping rules might be required for various reaction networks and they discuss the problem of fitting the parameters of such models to experimental data. Working with these theories, Aris [2] proposed that for various parallel first-order reactions the rate expression describing the aggregate need not be first order. In fact, the functional form of the overall reaction is reported to depend on the initial distribution of the reactants in the feed. In cases where detailed kinetics of the underlying reactions are unknown, Hutchinson and Luss [4,5] have proposed a method for evaluating the upper and lower bounds on the conversion of a mixture. This permits the estimation of the uncertainty about the exact concentration of a reacting mixture from the knowledge of the initial reaction rate of the lumps. For reactions with a wide spread of activation energies, Golikeri and Luss [7] have reported a "non-Arrhenius" behavior of the overall rate constant. In this paper it is shown that the non-Arrhenius behavior of the overall rate constant is due to the difference in the values of the individual rate constants. Luss and coworkers [4,5,7–9] have also reported some studies on the pitfalls and magnitude of errors involved in the use of empirical rate expressions for grouping many independent or consecutive reactions. Unfortunately due to various mathematical approximations and assumptions, and due to a large number of parameters involved, these models have found little use in the interpretation of experimental data.

In a parallel approach, coal researchers have developed a multiple reaction model (similar to the grouped reaction mixtures previously discussed) to explain the thermal decomposition reactions of coal [10–14]. This model assumes that the decomposition of coal consists of a large number of independent chemical reactions representing the rupture of various bonds within the coal macromolecule. It is further assumed that the evolution of each class of volatile species can be lumped together and can be modeled using a multiple independent parallel first-order reaction model. The initial distribution of each species is obtained from the ultimate yield of these species. This theory has been extensively used in interpreting non-isothermal coal pyrolysis data. The lack of success in correlating some data has led to theories which assume that species can be formed numerous independent pathways which are dependent on the decomposition temperature. This sophistication unfortunately requires additional parameters, thus guaranteeing a good fit.

The apparent success of the multiple reaction model is believed to be due to its ability to explain the "low" value of activation energy (E) observed in coal pyrolysis studies [12]. However, most of the "low" values of E reported in the literature are not derived from the multiple reaction model. Therefore, the use of this argument to justify the application of the multiple reaction model is not convincing, especially since the theoretical findings of Golikeri and Luss [7] suggest that the E value of a multiple reaction is bounded by the maximal and minimal values of the individual activation energies E_i.

In a recent paper Reuther et al. [15] claim to have experimentally demonstrated that "low" apparent global activation energy results from the multiple reaction model. The value of E for combustion was calculated as the slope of a plot of burning velocity vs. inverse temperature, based on the assumption of Kaskan [16]. Since burning velocity is a function of the total amount of gases (which consists of both combustible reactants and non-combustible inert gases), a better assumption may be that the slope of a plot of burning velocity vs. inverse temperature is the heat of reaction of the gaseous mixture [17]. With these arguments the results of Reuther et al. [15] become an experimental artifact due to their disregard of the inert gases present in the reaction mixture [17].

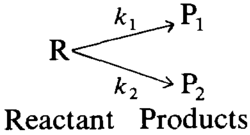
When comparing results or proposing theories, quoting the value of activation energy rather than the rate constant is inappropriate and sometimes even misleading. This is because the rate constant is of interest in the prediction of the rates of reaction rather than E. Further, due to the compensation effect (linear relation between ln A and E, see Agrawal [18] for more details), numerous values of E will fit the data. For example, a reaction with a rate constant of 0.015 min^{-1} at 300 °C can be reasonably well represented by an Arrhenius equation where E can be either 20 kcal mol^{-1} or 60 kcal mol^{-1} in the narrow temperature region around 300 °C. Owing to the compensation effect, both E values will fit the data provided the rates are equal at 300 °C (i.e. provided the value of A for the reaction with $E = 20$ kcal mol^{-1} is 6.8×10^5 min^{-1} and the value of A for the reaction with $E = 60$ kcal mol^{-1} is 1.1×10^{21} min^{-1}). Thus the E values which fit the data differ significantly and therefore the significance of E is lost. Hence it is not sufficient to report the value of E derived from the experimental data. Instead the reaction rates should be compared for more meaningful analysis. Furthermore, an estimate of the product yield cannot be made from the knowledge of E. Therefore investigators should report both A and E, and comparison of the rate constant rather than E should be made. Hence it is not surprising that, despite numerous studies, the true nature of irreversible complex reactions and their overall E values remain elusive.

The first section of this paper briefly reviews and summarizes the nature of classical homogeneous parallel and competitive reactions. The second section focuses on the nature of overall multiple reactions (multiple independent reactions or grouped reactions or continuous reacting mixtures) resulting from first-order irreversible independent reactions. The second section is further subdivided into two subsections, the isothermal and the non-isothermal reaction analysis. Comparison of results from non-isothermal studies for the individual, competitive and the overall multiple reactions are made and discussed. To demonstrate various viewpoints, three individual sets of first-order Arrhenius parameters have been chosen. As the first example a set of Arrhenius parameters for non-overlapping individual reactions is considered. The second example deals with a set of Arrhenius parameters of overlapping individual reactions and the third example deals with extremely competitive individual reactions.

If the rates of individual reactions are not comparable over the temperature range studied, then they are classified as non-overlapping reactions. If the rates of individual reactions are fairly comparable over the temperature range studied, then they are classified as overlapping reactions. If the rates of individual reactions are comparable in a narrow temperature range but are not comparable over a broader temperature range, then they are classified as competitive individual reactions. The overlapping and the competitive individual reactions may exhibit an isokinetic temperature (the temperature at which all the individual reaction rates are equal; for further details on isokinetic temperature and compensation effect see Agrawal [18,19] and Galwey [20]). Non-overlapping reactions may not exhibit an isokinetic temperature. In this study, it has been found that the overall reaction is a function of the rates of the individual reactions for the competitive reaction model. The nature of the overall multiple reaction model has been found to depend strongly on the individual reaction rates and the initial composition of the reaction mixture.

PARALLEL AND COMPETITIVE REACTIONS

Consider a reaction in which the reactant decomposes via two parallel/competing homogeneous first-order irreversible reactions



The rate expressions for this reaction scheme are

$$\frac{dR}{dt} = -(k_1 + k_2)R = -kR \tag{1}$$

$$\frac{dP_1}{dt} = k_1 R \tag{2}$$

and

$$\frac{dP_2}{dt} = k_2 R \tag{3}$$

where k is the overall reaction rate constant $(= \Sigma k_i)$ of R. Here the decomposition of R is an overall reaction and the formation of products P_i are individual reactions. These rate expressions can be integrated subject to their respective boundary conditions. At time $t = 0$, no conversion of the reactant R would have taken place and hence, $R = R^0$ and the products $P_1 = P_2 = 0$. Integrating eqns. (1)–(3) we have

$$R = R^0 \exp(-kt) \tag{4}$$

$$P_1 = (k_1/k) R^0 [1 - \exp(-kt)] \tag{5}$$

$$P_2 = (k_2/k) R^0 [1 - \exp(-kt)] \tag{6}$$

Assuming an Arrhenius dependence of the rate constants, the ratio of eqns. (5) and (6) is

$$P_1/P_2 = k_1/k_2 = (A_1/A_2)\exp\left[-(E_1 - E_2)/R_g T\right] \tag{7}$$

where A_1 and A_2 are pre-exponential factors for the reactions 1 and 2, respectively, T is the absolute temperature and R_g is the gas constant. The notation R_g is used for the gas constant to avoid confusion with R, which in this paper represents the amount of reactant present at time t. Equation (7) implies that $P_1 : P_2 = k_1 : k_2$, i.e. the ratio of the products is constant, independent of time and the initial concentration of the reactant. If the ratios of the product yields or the ultimate product yields are independent of temperature, then the products are formed via parallel reactions. This implies $E_1 = E_2$. Hence for parallel reactions, eqn. (7) reduces to

$$P_1/P_2 = k_1/k_2 = A_1/A_2 \tag{8}$$

The above discussions imply that the activation energy E for the overall reaction, in the case of parallel independent reactions, is the same as the E values for the individual reactions (i.e. $E = E_1 = E_2$). Although only a two reaction scheme is discussed here, this can be easily generalized.

In the case of competing reactions the ultimate product yields are a function of temperature. If $E_1 > E_2$, then the reaction leading to P_1 is more temperature sensitive than the reaction leading to P_2. High temperatures will favor reaction 1 and low temperatures will favor reaction 2. The temperature at which the rates are equal is referred to as the isokinetic temperature (T_{iso}) [18–20]. Above T_{iso}, P_1 is favored and below T_{iso}, P_2 is favored. At very high temperatures ($T \gg T_{iso}$) reaction 1 is very dominant and reaction 2 is almost negligible. Depending on experimental conditions, the rates of individual reactions may result in a change in the value of the overall reaction rate constant, k, reflecting a change in the value of E for the overall reaction.

If a reactant decomposes via homogeneous reactions, then the overall degradation rate constant for the reactant R is equal to the sum of the rate constants for the formation of individual species i, i.e.

$$k = \Sigma k_i \tag{9}$$

This equation can be visualized from eqn. (1) and is a well-established fact in the literature [21,22]. Assuming an Arrhenius temperature dependence of the rate constants, eqn. (9) can be rewritten as

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

Example 1. As the first example the Arrhenius set proposed by Anthony and Howard [10] for four hypothetical independent first-order reactions having $A_i = 2 \times 10^{10}$ s^{-1} and E_i values of 47, 50, 53 and 56 kcal mol^{-1} have been chosen. Assuming a homogeneous reaction, solving for A and E for the overall reaction using eqn. (10), we obtain $A = 3.7 \times 10^{10}$ s^{-1} and $E = 47.7$ kcal mol^{-1} over the temperature range 800–1100 K. A comparison of the rate constants suggests that the overall reaction is dominated by the reaction with $E_1 = 47$ kcal mol^{-1}. This reaction contributes to over 75% of the overall reaction. The other reactions with $E_2 = 50$, $E_3 = 53$ and $E_4 = 56$ kcal mol^{-1} contribute to less than 19, 5 and 1% of the overall reaction, respectively. Hence the E value for the overall reaction appears to represent most closely the E_i of the most dominating reaction. Since the rates of individual reactions are not comparable, the Arrhenius parameters used by Anthony and Howard [10] do not represent overlapping reactions.

Example 2. In order to consider mutually overlapping reactions the experimentally derived Arrhenius parameters for lignite pyrolysis from Agrawal [23] will be discussed as example 2. The Arrhenius parameters obtained by Agrawal for lignite pyrolysis are: $A_1 = 39.1$ s^{-1}, $E_1 = 17.0$ kcal mol^{-1}; $A_2 = 9.26$ s^{-1}, $E_2 = 12.7$ kcal mol^{-1}; and $A_3 = 7.73$ s^{-1}, $E_3 = 14.5$ kcal mol^{-1}. Here, reactions 1, 2 and 3 represent the reactions for the formation of tars, chars and gases, respectively. The overall Arrhenius parameters obtained using eqn. (10) are $A = 40.7$ s^{-1} and $E = 14.4$ kcal mol^{-1} over the temperature range 800–1900 K. Hence, in the case of comparable competitive overlapping reactions the overall reaction can be represented by a single set of Arrhenius parameters whose overall E value represents the average of the E_i values.

Example 3. Finally, in order to include an extreme case, we consider the following parameters for the individual reactions: $A_1 = 2.4 \times 10^4$ s^{-1}, $E_1 =$ 19.1 kcal mol^{-1}; $A_2 = 4.5 \times 10^{11}$ s^{-1}, $E_2 = 38.2$ kcal mol^{-1}; $A_3 = 6.1 \times 10^{18}$ s^{-1}, $E_3 = 57.4$ kcal mol^{-1}; and $A_4 = 7.4 \times 10^{25}$ s^{-1}, $E_4 = 76.5$ kcal mol^{-1}. These values have been chosen since data on the theoretical behavior of rate of conversion vs. temperature using these parameters are available in the literature [24]. Using eqn. (10), these four individual reactions can be represented with an overall reaction with the Arrhenius parameters $A = 5.0 \times 10^{18}$ s^{-1} and $E = 55.9$ kcal mol^{-1} over the temperature range 525–625 K. This temperature range was chosen since all reactions were equally dominating in this range. Hence, in this case, the E value for the overall reaction is about equal to the average of the E_i values, when the individual reaction rates are comparable.

If the reaction rates are comparable, then eqn. (10) can represent the overall E value, independent of temperature. However, if the individual E_i values vary significantly, as in the case of Flynn's data [24], eqn. (10) will yield the overall E value as a function of temperature. This is primarily because, depending on the temperature, an individual reaction may dominate the entire overall reaction. For example, at temperatures below 500 K, the reaction with $E_1 = 19.1$ kcal mol^{-1} contributes to over 92% of the overall reaction. At temperatures above 650 K, the reaction with $E_4 = 76.5$ kcal mol^{-1} contributes to over 92% of the overall reaction. Therefore, at temperatures below 500 K the overall reaction exhibits an E value close to 19 kcal mol^{-1}, and at temperatures above 650 K the overall reaction exhibits an E value close to 76 kcal mol^{-1}. Hence, in the case of extremely competitive reactions, the overall rate constant cannot be represented over a broad temperature range by an Arrhenius-type equation whose A and E values are independent of the reaction temperature. Instead, the overall reaction reflects an activation energy whose value is a function of the activation energy of the dominant individual reaction in the particular temperature range. Therefore, if individual reaction rates vary significantly, the overall rate behaves in a "non-Arrhenius" manner.

Recapitulating the nature of overall competitive reactions, it is found that the overall E value reflects the average of the E_i values if the individual reaction rates are comparable. If the rates of individual reactions are significantly different, then the overall E value reflects the value of E_i of the most dominating reaction or reactions. Therefore, non-Arrhenius behavior of the overall rate constant is due to the difference in the magnitudes of the individual rate constants. These results for competitive reactions are consistent with some experimental observations available in the literature [23,25–28].

MULTIPLE INDEPENDENT REACTIONS

Multiple independent reactions may be represented as

$$R_1 \xrightarrow{k_1} P_1$$

$$R_2 \xrightarrow{k_2} P_2$$

$$\vdots$$

$$R_i \xrightarrow{k_i} P_i$$

where R_i represents the fraction of the i-th species in the reacting mixture and P_i represents the amount of the i-th species. The k_i values are the respective rate constants. The rate equation for a multiple independent reaction is

$$\frac{dR_i}{dt} = -k_i R_i \tag{11}$$

and the temperature dependence of the rate constant, k_i, is modeled by the Arrhenius equation. It is generally assumed that the overall reaction can be represented as

$$\frac{dR}{dt} = -\Sigma k_i R_i = -kR \tag{12}$$

where $R = \Sigma R_i$ = total amount of individual species, and k is the reaction rate for the overall reaction. The earlier theories [1–12] fail to discuss the nature of possible errors involved by introducing the identity represented in eqn. (12). Equation 12 implies that the rate of overall reaction is proportional to the total amount of individual reacting species present in the reaction mixture. This assumption holds as long as the reaction rates and the activation energies of the individual reacting species are comparable. In cases where some species present in the reacting mixture do not react or react at a very different rate compared with the average reaction rate, then the overall rate of reaction is no longer proportional to the total amount of species present in the reaction mixture and eqn. (12) is no longer valid. If the individual reactions are simple, one-step, irreversible, first-order reactions and the overall reaction is not sporadic, then, the overall multiple reaction may be classified into three categories: (a) multiple-overlapping reaction (where individual reaction rates and their activation energies are comparable over the temperature range studied); (b) multiple-non-overlapping reaction (where individual reaction rates are not comparable); and (c) multiple-mixed reaction (a combination of overlapping and non-overlapping individual reactions). The mechanisms of these reactions may be studied either by the conventional isothermal technique or by the non-isothermal technique where the reaction temperature is increased with time.

Isothermal studies

In the case of multiple-overlapping reactions the conditions for eqn. (12) are likely to be fulfilled. Hence a plot of ln R vs. time will be linear as shown in Fig. 1. The slope of this line will be equal to the overall rate constant k and the overall E value calculated from a plot of ln k versus $1/T$ will be observed to be the average of the individual E_i values. The Arrhenius parameters in example 2, representing overlapping reactions, yield results consistent with this statement.

In the case of multiple-non-overlapping reactions, if the number of lumps is small and the reaction rates of the lumps are significantly different, then a

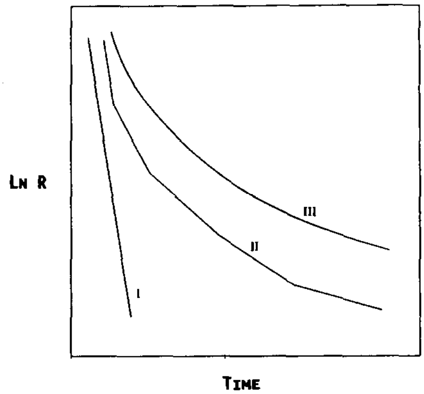


Fig. 1. A plot of ln R vs. time. Trend I is for multiple-overlapping reactions, trend II for multiple-non-overlapping reactions and trend III for some multiple-mixed reactions.

plot of ln R vs. time may yield linear segments with varying slopes, shown as trend II in Fig. 1. This behavior implies that the assumption made in eqn. (12) is not satisfied, since the overall reaction rate is not proportional to the total amount of the reaction mixture. If the overall reaction shows trend II in Fig. 1 then one can, in fact, obtain the initial concentration of the individual lumps in the reaction mixture. The slopes of the individual segments are proportional to the rate constant of the individual reaction dominating the linear segment. Hence, knowing the initial concentration and the reaction rates of the individual lumps, one can easily model and predict the nature of the overall reaction. The Arrhenius set used in example 1 suggests that the average reaction time for reaction 1 is about 13 s at 900 K compared with average reaction times of 70, 370 and 1990 s for reactions 2, 3 and 4, respectively. Hence, if an isothermal analysis is carried out, the overall reaction may exhibit 4 linear segments in a plot of ln R vs. time as discussed earlier. Each segment will then correspond to a particular individual reaction which dominates the reaction at that time. Since an individual reaction can dominate the entire reaction, depending on the reaction time, the physical significance of the overall reaction in the case of non-overlapping reactions could be misleading, since there may be no unique overall reaction.

In some cases of multiple-mixed reactions where the number of individual reactions is large, a plot of ln R vs. time may not be linear. This non-linear behavior is observed since the rate of the overall reaction is not proportional to the sum of the individual reacting species. If this is true then the overall reaction order may display a pseudo *n*th order (trend III shown in Fig. 1). In such a case the overall reaction may be treated as an *n*th order reaction and the overall characteristics of the reaction mixture may then be satisfactorily predicted even though a knowledge of the initial lump composition and individual reaction rates may be lacking. The reader should be cautioned that these arguments may not hold true in some cases of complex reactions.

These arguments regarding *n*th order reactions are of importance in pyrolysis studies of coal, biomass, oil shale, etc., where one of the products is the solid char which remains behind in the pyrolyzing sample. In such a case the rate of decomposition of the unpyrolyzed material is not proportional to the weight of the residue, but to the amount of the unpyrolyzed material in the residue. Since in the solid residue it is not possible to estimate the amount of char and the amount of unpyrolyzed material, one must normalize the weight of the residue (w) to the original (w^0) and the final (w_∞) residue weights as $N_w = (w - w_\infty)/(w^0 - w_\infty)$. The normalized weight, N_w, can then be treated as equivalent to the amount of reactant, in order to obtain meaningful results [27]. If the chars are not accounted for in the residue then the reaction rate will no longer be proportional to the amount of residue and hence the reaction may display *n*th order characteristics.

Non-isothermal studies

Non-isothermal experiments generally involve heating the reactants at a constant rate. If the temperature of a first-order system is linearly increased, eqn. (11) can be rewritten as

$$\frac{\mathrm{dR}_i}{\mathrm{d}T} = \frac{1}{\beta}\frac{\mathrm{dR}_i}{\mathrm{d}t} = -\frac{A_i}{\beta}\mathrm{R}_i \exp(-E_i/R_g T) \tag{13}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$, represents the heating rate. $\mathrm{dR}_i/\mathrm{d}T$ is the temperature derivative of the extent of non-isothermal conversion. The integrated form of eqn. (13) is

$$-\ln \mathrm{R}_i = \frac{A_i}{\beta} p(x_i) \tag{14}$$

where $x = E/R_g T$ and $p(x)$ is the temperature integral represented by the equation [29]

$$p(x_i) = \int_0^T \exp(-E_i/R_g T)\,\mathrm{d}T$$
$$= \frac{R_g T^2}{E_i}\left[\frac{1 - 2(R_g T/E_i)}{1 - 5(R_g T/E_i)^2}\right]\exp(-E_i/R_g T) \tag{15}$$

This equation, proposed by Agrawal [29], deviates from the exact value by less than 0.1% for $E/R_g T$ values greater than 7. Therefore in this study, eqn. (15) has been used to evaluate the temperature integral. Once the temperature integral is evaluated, R_i can be obtained using eqn. (14). The temperature derivative can finally be obtained by substituting R_i in eqn.

(13). The temperature derivatives and the conversion for the overall multiple reaction is obtained by the relation

$$\frac{\mathrm{dR}}{\mathrm{d}T} = \Sigma g_i \frac{\mathrm{dR}_i}{\mathrm{d}T} \tag{16a}$$

and

$$\mathrm{R} = \Sigma g_i \mathrm{R}_i \tag{16b}$$

where g_i is the weight factor and $\Sigma g_i = 1$. The use of g_i enables the calculation of the contribution of each individual reaction to the overall reaction. A similar method can be used to estimate the overall reaction for the competitive reaction. For a competitive reaction the amount of the reactant R can be written as

$$-\ln \mathrm{R} = \Sigma \frac{A_i}{\beta} p(x_i) \tag{17}$$

Alternatively, for a competitive reaction R can also be estimated from the relation

$$\mathrm{R} = \Pi \mathrm{R}_i \tag{18a}$$

The temperature derivative for the competitive reaction can then be calculated from the equation

$$\mathrm{dR}/\mathrm{d}T = -(\mathrm{R}/\beta)\left[\Sigma A_i \exp(-E_i/R_{\mathrm{g}}T)\right] \tag{18b}$$

The results from eqns. (1) and (18b) should be identical. Hence results obtained from eqns. (4), (17) and (18a) will be identical. In the following, results for individual, competitive and multiple reactions are discussed using the three previous sets of Arrhenius parameters.

Example 1. As the first example the set of Arrhenius parameters used by Anthony and Howard [10] is discussed. In order to simplify calculations the value of heating rate β is assumed to be 1 K s^{-1}. The R_i values for the four individual reactions obtained by using the equation proposed by Agrawal [29] are shown in Fig. 2. An increase in the heating rate 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 the heating rate will have a similar effect in the opposite direction. For an excellent discussion of the effect of heating rate on chemical reactions the interested reader is referred to Flynn [24].

The temperature derivatives of the four individual reactions calculated using eqn. (13) are shown in Fig. 3. For kinetic analysis, the temperature derivatives are more informative and sensitive than the non-isothermal conversion shown in Fig. 2. Hence a comparison of the temperature derivative curves should reveal more differences than comparison of the non-isothermal curves. Consequently, for kinetic analysis the use of the temperature

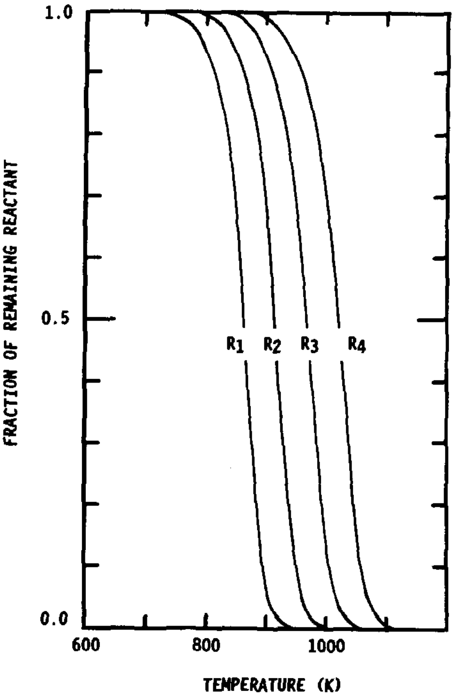


Fig. 2. Fraction of individual reactants remaining vs. temperature (heating rate = 1 K s^{-1}) in example 1. Notations: R_1, R_2, R_3 and R_4 stand for individual reactions 1, 2, 3 and 4, respectively.

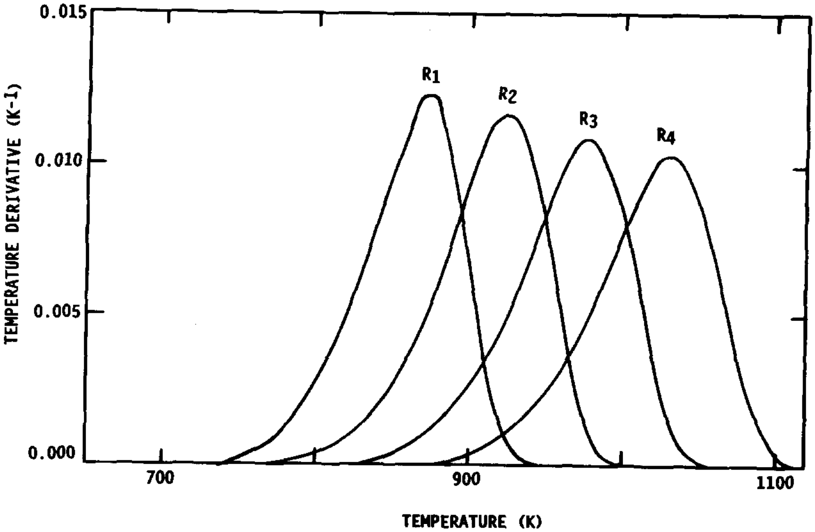


Fig. 3. Temperature derivatives (dR/dT) vs. temperature (heating rate = 1 K s^{-1}) for individual reactions in example 1 (see Fig. 2 for notations).

derivative rather than the non-isothermal conversion should be emphasized. Figure 3 indicates that reaction R_1 is nearly complete at about 920 K when reaction R_4 just begins. Therefore, this set of Arrhenius parameters represent non-overlapping reactions as previously discussed.

Figure 4 summarizes conversion as a function of temperature for the multiple as well as for the competitive reaction. The results for the individual reactions are also shown by broken lines. Curve CR represents the conversion for the competitive reaction. Curve CR was obtained using eqn. (18a). Equations (17) and (18b) yielded identical results. From Fig. 4, it can be concluded that the competitive reactions occur at lower temperatures than any of the individual reactions. The multiple reaction curve MX1 represents the conversion of a reaction mixture containing 70% R_1 and 10% each of R_2, R_3 and R_4. Since the majority of the reactant in MX1 is R_1, the initial portion of the MX1 curve resembles the R_1 curve. After the reaction R_1 is nearly complete, the curve MX1 resembles the average of the reactions R_2, R_3 and R_4. The multiple reaction curve MX2 represents the conversion of a reaction mixture containing equal amounts of R_1, R_2, R_3 and R_4. Since

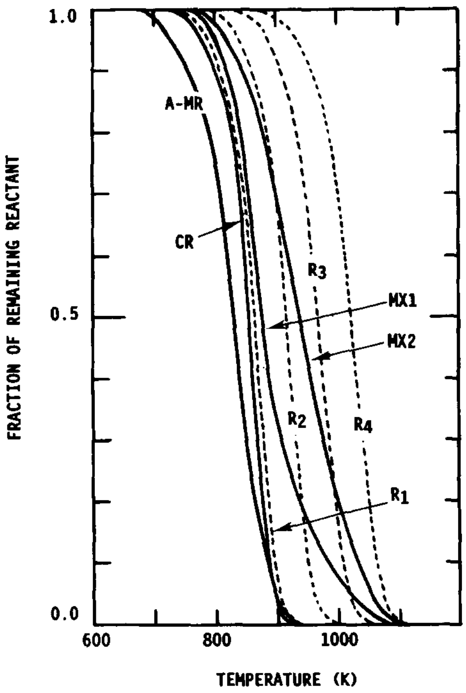


Fig. 4. Fraction of reactant remaining as a function of temperature (heating rate = 1 K s^{-1}) in example 1. Notations: CR = competitive reaction; MX1 = multiple reaction containing 70% R_1 and 10% each of R_2, R_3 and R_4; MX2 = multiple reaction containing equal amounts of R_1, R_2, R_3 and R_4; A-MR = multiple reaction proposed by Anthony and Howard [10]. The broken lines represent individual reactions shown in Fig. 2 and the solid lines represent competitive and multiple reactions.

MX2 represents the average of all four reactions, it therefore behaves in an average manner. The multiple reactions, MX1 and MX2 occur within the temperature range of the individual reaction and occur over the entire temperature range. The behavior of MX1 and MX2 are significantly different and no generalization regarding the nature of the overall multiple reaction can be made. The nature of the overall multiple reaction is a strong function of the initial composition of the reaction mixture and the reaction rates of the individual reactions in the mixture. Earlier, Anthony and Howard [10] reported that the multiple reaction for this Arrhenius set could be approximated by a single first-order reaction with $A = 1.6 \times 10^6$ s^{-1} and $E = 30.3$ kcal mol^{-1}. Curve A-MR represents the results for the Arrhenius set proposed by Anthony and Howard [10]. Clearly, A-MR does not occur within the temperature range and instead occurs at a significantly lower temperature than any individual reaction. Therefore curve A-MR does not represent the overall multiple reaction for this set of Arrhenius parameters.

The temperature derivatives for the competitive and multiple reactions are shown in Fig. 5. The competitive reaction shows a first-order behavior and exhibits Arrhenius parameters of $A = 3.7 \times 10^{10}$ s^{-1} and $E = 47.7$ kcal mol^{-1}. This result for the Arrhenius parameters is in good agreement with the results discussed in the isothermal section for the competitive reaction. The solid curves for MX1 and MX2 in Fig. 5 represent the temperature derivatives for the multiple reaction calculated from eqn. (16a). The broken lines are the results obtained for MX1 and MX2 from the slopes of the

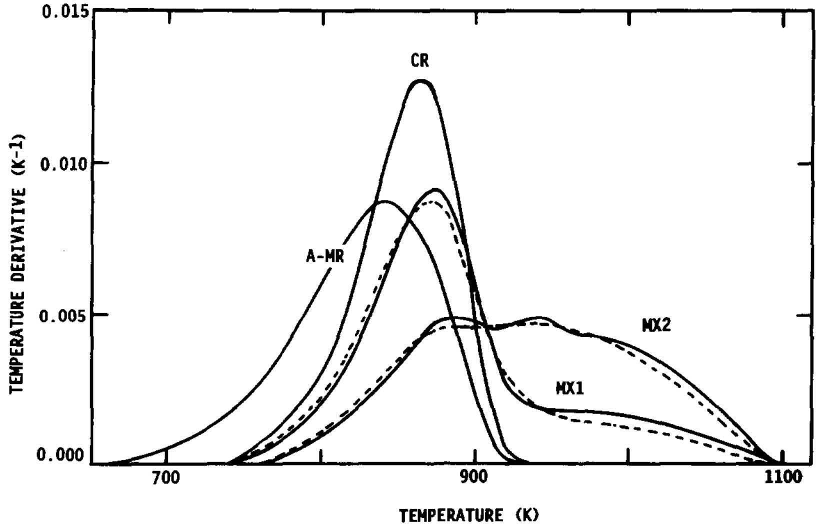


Fig. 5. Temperature derivatives of competitive and multiple reactions in example 1 vs. temperature (heating rate = 1 K s^{-1}) (see Fig. 4 for notations). Broken lines for MX1 and MX2 represent simulated DTG signals and solid lines for MX1 and MX2 represent simulated DSC signals.

curves MX1 and MX2 in Fig. 4. As discussed earlier by Agrawal [30], the solid lines for MX1 and MX2 represent the results from differential thermal analysis (DTA) or differential scanning calorimetry (DSC) which measure the change in enthalpy of a reaction. The broken lines represent the apparent rate which is observed by thermogravimetric (TG) or differential thermogravimetric (DTG) devices which are capable of measuring the change in the mass of reactants undergoing a phase change decomposition reaction. Therefore for the purpose of discussion, the solid lines will be referred to as simulated DSC signals and the broken line as simulated DTG signals. For discussion of assumptions and details of this theory, the reader is referred to Agrawal [30].

Figure 5 indicates, that, when compared with the simulated DSC signal, the simulated DTG signal is smoother and the peak is broader. In addition the DTG curve is shifted to a lower temperature. If the temperature derivative is proportional to the amount of the reactant mixture (eqn. (12)), both DSC and DTG results would be identical. Since not all of the reactants in the reaction mixture are reacting over the entire temperature range (see Fig. 3), the sluggish behavior of the DTG signal indicates that in this case the assumption in eqn. (12) does not strictly apply. Therefore, if the assumption underlying eqn. (12) is not satisfied, DSC and DTG results will not be identical. The multiple reaction could not be represented by a single set of Arrhenius parameters. Curve MX1 in Fig. 5 indicates a higher reaction order, whereas curve MX2 in Fig. 5 indicates multiple peaks. For the case of non-overlapping reactions undergoing a non-isothermal reaction in which the temperature is linearly increased, it appears that E for the multiple reaction shifts from E_i of the individual reaction dominating the low temperature region to E_i of the individual reaction dominating the high temperature region. The results of MX1 and MX2 also suggest that the E value of the multiple reaction for this set of Arrhenius parameters is a function of the initial composition of the reaction mixture. The multiple reactions occur in the temperature range covered by the individual reactions. Curve A-MR, representing the Arrhenius set for the multiple reaction proposed by Anthony and Howard [10] occurs at a lower temperature. The lack of agreement of curves A-MR, MX1 and MX2 imply that the multiple reaction could not be approximated by the Arrhenius set proposed by Anthony and Howard [10]. Further, these results question the theories which state that a set of independent reactions having high values of E can be represented by a multiple reaction with a lower value of E, independent of the initial composition of the reaction mixture.

Example 2. The simulated results using the Arrhenius parameters of Agrawal [23], for overlapping reactions, are shown in Fig. 6 for a heating rate of 1 K s^{-1}. For individual reactions, R_1, R_2 and R_3 are shown in Fig. 6 by broken lines. MX1 represents the overall multiple reaction for a mixture containing 70% R_1 and 15% each of R_2 and R_3. MX2 represents a mixture containing 70% R_1 and 15% each of R_2 and R_3. MX2 represents a mixture containing equal amounts of R_1, R_2 and R_3. CR represents the competitive reaction. Again, the multiple reaction is bounded by the temperature range of the individual reactions and the competitive reaction occurs at a lower temperature than any of the individual reactions. The temperature derivatives shown in Fig. 7 also indicate that the individual reactions occur in an overlapping temperature range. Since the values of the activation energies and the rate constants are comparable, this set of Arrhenius parameters represents an overlapping reaction. The results for the temperature derivatives of the competitive reaction and the multiple reaction are given in Fig. 8. The competitive reaction occurs in a lower temperature range and can be represented by a single Arrhenius set of $A = 41.0\ \mathrm{s}^{-1}$ and $E = 14.8$ kcal mol^{-1}. These values are in good agreement with the parameters obtained earlier using eqn. (1). The smoothness of curves MX1 and MX2 suggests that in this case the overall multiple reaction can be fairly well approximated by a single set of Arrhenius parameters. However, the gradual asymptotic approach to the abscissa by the tail of the temperature derivatives suggests a

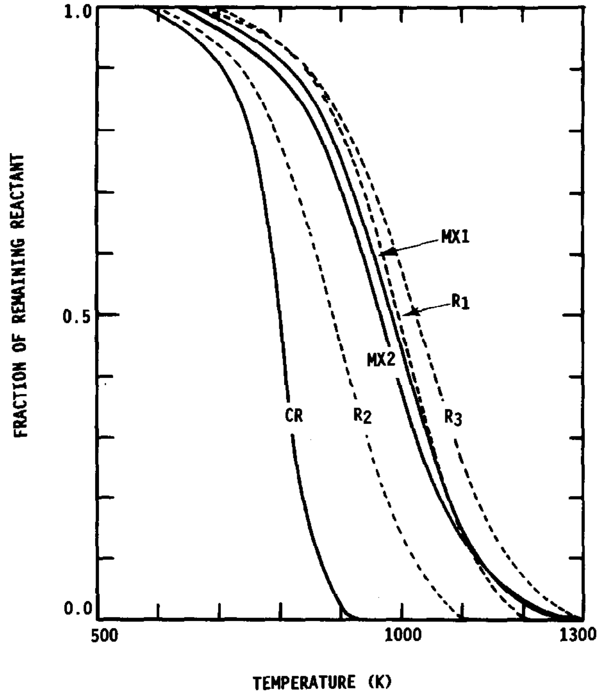


Fig. 6. Fraction of reactant remaining vs. temperature (heating rate = 1 K s^{-1}) in example 2. Notations: R_1, R_2 and R_3 stand for individual reactions 1, 2 and 3, respectively; CR = competitive reaction; MX1 = multiple reaction containing 70% R_1 and 15% each of R_2 and R_3; MX2 = multiple reaction containing equal amounts of R_1, R_2 and R_3.

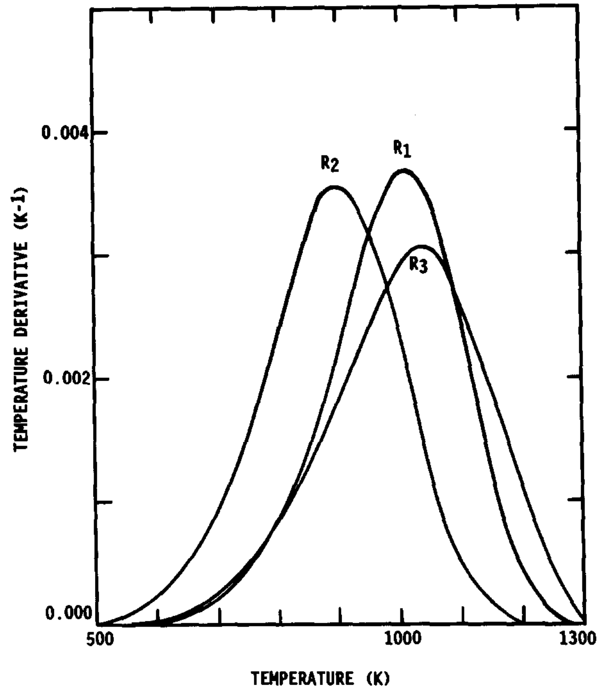


Fig. 7. Temperature derivatives (dR/dT) vs. temperature (heating rate = 1 K s^{-1}) for individual reactions in example 2 (see Fig. 6 for notations).

reaction order greater than unity. The overall E value for the multiple reaction was found to depend on the composition of the reaction mixture. A comparison of the temperature derivatives of the individual reactions shown in Fig. 7 and the multiple reaction (curves MX1 and MX2 in Fig. 8) suggests that the overall E value closely represents the value of E_i of the most dominating reaction. For the case of overlapping reactions, no difference in the simulated DSC and DTG curves was observed. This implies that the assumption in eqn. (12) is satisfied in the case of overlapping reactions.

Example 3. Figures 9–11 summarize the results for the set of Arrhenius parameters used by Flynn [24]. This set represents a mixture of overlapping and non-overlapping reactions. Previously, Agrawal [30] also studied this set of reactions using the tables of Flynn [31]. It is now believed that the tables of Flynn [31] are not accurate enough at low E/RT values and high conversions. Therefore, the results of Agrawal [30] for low E/RT values are in error. Although most of the findings of that paper are not influenced by this error, the results of Agrawal [30] have been updated in this paper.

Figure 9 summarizes the results for the fraction of remaining reactant for the independent reactions R_1, R_2, R_3 and R_4; for the competitive reaction, CR and for the overall multiple reactions MX1 and MX2. MX1 represents

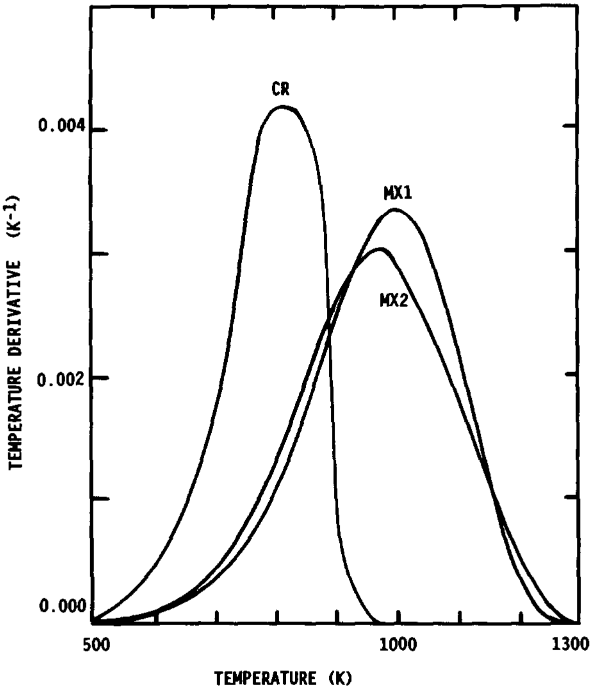


Fig. 8. Temperature derivatives of competitive and multiple reactions in example 2 vs. temperature (heating rate = 1 K s^{-1}) (see Fig. 6 for notations).

equal amounts of R_1, R_2, R_3 and R_4 and MX2 represents a mixture of 70% R_1 and 10% each of R_2, R_3 and R_4. Figure 10 summarizes the results for the temperature derivatives of the individual reactions. Figure 10 shows that reaction R_1 occurs over a broader temperature range than reactions R_2, R_3 and R_4. Reactions R_2, R_3 and R_4 overlap and occur in a narrow temperature range. Therefore this set of Arrhenius parameters represents a combination of overlapping and non-overlapping reactions. Figure 11 summarizes the results of the competitive reaction (CR) and the overall multiple reactions (MX1 and MX2). The competitive reactions could be fairly well approximated by a single set of Arrhenius parameters $A = 5.2 \times 10^{18}$ s^{-1} and $E = 55.9$ kcal mol^{-1}. The solid lines for curves MX1 and MX2 represent the results from simulated DSC signals and the broken lines represent the DTG signals. Differences between the two signals occur since the assumption in eqn. (12) does not hold for this set of reactions. Initially the DTG signal exhibits a more rapid rate and leads the DSC signal. This effect is believed to be due to the compounding effects of reactions R_3 and R_4. After the signal peaks, the DTG signal becomes sluggish and smooth. The DSC signal appears to be more sensitive and picks up minor changes in the reaction. Therefore, in a simultaneous analyzer, if the individual reactions are not overlapping, the DSC and DTG instruments will record

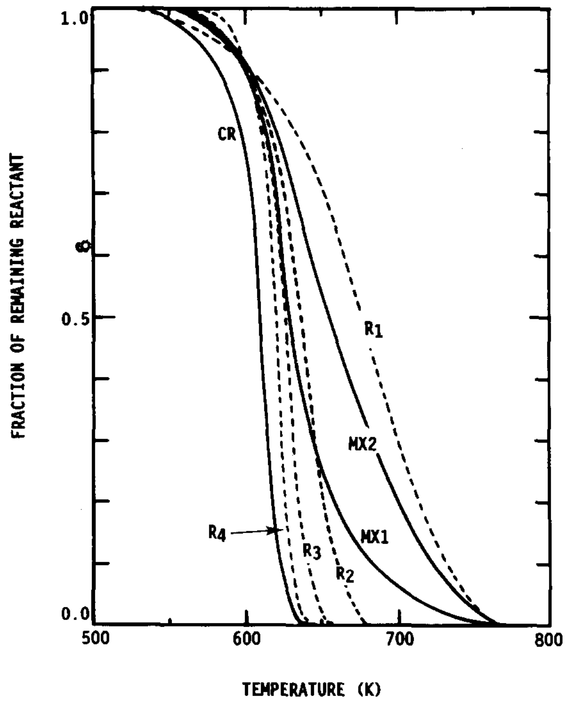


Fig. 9. Fraction of reactant remaining vs. temperature (heating rate = 1 K s^{-1}) in example 3. Notations: R_1, R_2, R_3 and R_4 stand for individual reactions 1, 2, 3 and 4, respectively; CR = competitive reaction; MX1 = multiple reaction containing equal amounts of R_1, R_2, R_3 and R_4; MX2 = multiple reaction containing 70% R_1 and 10% each of R_2, R_3 and R_4.

differences and will prove valuable in the understanding of the complex solid state reactions [30]. Both MX1 and MX2 could not be modeled by a single set of Arrhenius parameters. Instead the reaction exhibits a range of E values which is dependent on the E_i value of the dominating individual reaction.

DISCUSSION AND CONCLUSIONS

In the first part of this paper, it was seen that if the rates of individual reactions and their E_i values are comparable, then the overall reaction for a competitive reaction model exhibits an E value which is an average of the E_i values of the individual reactions and a rate which is an average of these reactions. In the case where the E_i values of individual reactions in the reaction mixture are identical, then it is difficult to distinguish the nature of the overall reaction, i.e. it is not possible to differentiate between a single homogeneous reaction and a parallel competitive reaction. However, if the rates of individual reactions and their E_i values are significantly different, then both the overall reaction for the competitive reaction model and its E value become a function of the dominating individual reaction.

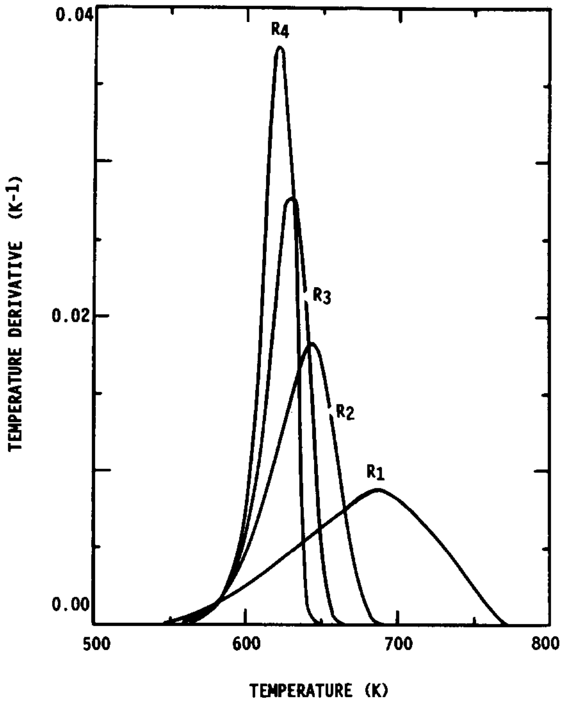


Fig. 10. Temperature derivatives (dR/dT) vs. temperature (heating rate = 1 K s^{-1}) for individual reactions in example 3 (see Fig. 9 for notations).

In the case of isothermal studies of multiple reactions, the nature of the overall reaction will depend on how rigorously the assumptions made in formulating eqn. (12) are satisfied. If the individual reactions are overlapping eqn. (12) are satisfied. If the individual reactions are overlapping, then the overall reaction appears to be a single first-order reaction and E will be the average of the individual E_i values. If the rates of individual reactions are significantly different then there may be no unique overall reaction. Hence the overall reaction may exhibit non-Arrhenius behavior. If the number of individual reactions is large and some of their rates are comparable and overlap, then the overall reaction may exhibit nth order behavior. In some isothermal studies a plot of ln R vs. time may be helpful in determining the nature of the complex reaction.

In studying non-isothermal kinetics, a problem commonly encountered is that of finding a suitable solution of eqn. (13) to estimate the "best value" of A and E. The literature [29–31] contains many discussions on this problem. The major hurdle hindering the understanding of multiple reactions is the justification of the assumptions in eqn. (12). If the rates of individual reactions are extremely competitive, the overall reaction for the competitive as well as for the multiple reaction model becomes a function of temperature. For the competitive reaction the rate constant can be repre-

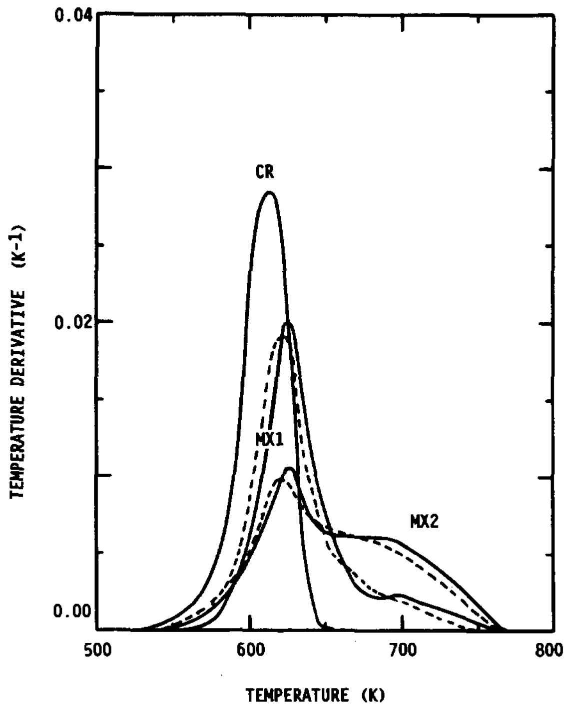


Fig. 11. Temperature derivatives of competitive and multiple reactions in example 3 vs. temperature (heating rate = 1 K s^{-1}) (see Fig. 9 for notations). Broken lines for MX1 and MX2 represent simulated DTG signals and solid lines for MX1 and MX2 represent simulated DSC signals.

sented reasonably well by an Arrhenius equation only within the narrow vicinity of the isokinetic temperature. Beyond this range the overall reaction exhibits non-Arrhenius behavior and becomes a function of temperature. The overall reaction reflects a trend which is a strong function of the most dominating individual reaction. Depending on how rigorously eqn. (12) is satisfied, the multiple reaction may or may not exhibit a unique reaction. The value of E for the overall multiple reaction in all cases depends on the individual rates and also the initial composition of the reaction mixture. In this study it was found that, for some cases, the multiple reaction can exhibit different behavior depending on the measurement technique.

Further, the temperature range in which the overall multiple reaction occurs is bounded by the temperature range in which the individual reactions occur (eqn. (16b)) and it occurs over the entire temperature range. The competitive reaction occurs in a lower temperature range than that of the individual reactions (eqn. (18a)). In addition, the assumption underlying eqn. (12) does not hold for non-overlapping reactions. Therefore if a knowledge of individual reactions is available, then the governing rate mechanisms (i.e. competitive vs. multiple) for complex systems such as coal, biomass, oil shale, etc. can be evaluated.

Contrary to statements in the coal pyrolysis literature it has been shown that a set of parallel, independent, first-order reactions cannot be approximated by a single first-order Arrhenius equation having a lower E value than any of the reactions of the set. Recently, Elder [32] examined the Arrhenius parameters suggested by Hanbaba (quoted by Juntgen and van Heek [13]) and concluded that the parameters used for the multiple reaction did not agree with the reported data. Earlier, Hanbaba had suggested that a set of eight reactions with E_i values of 48–62 kcal mol^{-1} with $\Delta E = 2$ kcal mol^{-1} and a fixed A value of 10^{15} min^{-1} could be approximated by an overall first-order reaction with an A value of 10^4 min^{-1} and $E = 20$ kcal mol^{-1}. For an equal initial composition of the individual reactants, Elder reported that the overall multiple reaction exhibited multiple peaks and, therefore, he concluded that there was no unique overall reaction. However, for a skewed distribution, where the initial composition of the reactants were 4, 8, 10, 16, 20, 24, 12 and 6%, Elder reported that the overall multiple reaction matched the curves reported by Hanbaba. However, the multiple reaction exhibited an order of 0.9 with an E value of 44.1 kcal mol^{-1} and $A = 2.3 \times 10^{12}$ min^{-1}. This does not match with the values reported by Hanbaba. As Hanbaba used an inaccurate approximation to evaluate the temperature integral [29], his results are believed to be erroneous. The findings of the present study and that of Elder are in accord with the earlier studies of Golikeri and Luss [7]. Golikeri and Luss [7] concluded that the overall E value is bounded by the E_i values and that it is a function of the initial reaction mixture. However, these results are in direct conflict with the results of Juntgen and van Heek [13] and Anthony and Howard [10]. Since these results are of importance in understanding mechanisms of various complex reactions, researchers must carefully weigh the arguments presented.

The past success of multiple reactions in modeling experimental data of non-isothermal coal pyrolysis is believed to be due to their ability to explain the "low" observed value of E. Numerous papers have appeared in the coal pyrolysis literature suggesting that a "low" apparent E value is probably due to the overlapping of multiple independent first-order reactions [10–13]. The conclusion of a "low" E value for coal pyrolysis is based on a comparison with the bond energies of C–C and C–H linkages. This comparison is difficult to visualize, especially since there is little theoretical significance for E values obtained from heterogeneous solid state reactions. While the energy barrier for a solid state reaction may be related to the calculated value of E, the true relation will not be clear until a better understanding of a "mole of solid" and its significance (especially in the case of three-dimensional solids such as coal and biomass) can be attained. It is clear that a better understanding of the derived value of E from solid state reactions is needed.

It should be noted that the situation for coal and biomass is complicated by the presence of ash which may catalyze the degradation reaction, therefore resulting in a lower observed E value [23,33].

At high temperatures the pyrolysis reactions in coal and biomass are a combination of numerous endothermic elementary reactions. If the magnitude of the activation energy of the elementary reactions is comparable with the endothermicity of the reaction, then this may result in a lower value of E. The extreme endothermic nature of a reaction may sometimes result in negative temperature coefficients, i.e. the reaction rate decreases with temperature [22,34,35]. Further, steric hindrances can also result in a lowering of the E value of the degradation reactions. These arguments clearly indicate that it is difficult to identify the degradation mechanism to a diffusion-controlled process due to the "low" E value. Therefore it is difficult to speculate on the nature of the reaction based on the E value.

SUMMARY

(i) No generalization regarding the behavior of the multiple reaction can be made. The nature of the multiple reaction is a function of the composition of the reaction mixture and the rates and activation energies of individual reactions in the mixture.

(ii) The overall order of a multiple reaction resulting from a mixture of first-order reactions need not be first order. Depending on the nature of the individual reactions it may exhibit a higher order or even consecutive reactions.

(iii) The temperature range and the "activation energy" of the multiple reaction is bounded by those of the individual reactions.

(iv) A set of independent first-order reactions cannot be approximated by a single first-order multiple reaction having a lower activation energy than any of the reactions in the set.

(v) The competitive reaction reflects the average of the E_i values of the individual reactions and occurs at a lower temperature than any of the individual reactions.

(vi) When comparing results, it is more appropriate to compare the rates of reaction rather than the activation energies.

(vii) If the reaction rate is not proportional to the total amount of reactant (i.e. eqn. (12) is not satisfied), then the DSC and DTG results will be different.

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