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THE EFFECT OF HEATING RATE UPON THE COUPLING OF COMPLEX REACTIONS. I. INDEPENDENT AND COMPETITIVE REACTIONS *

JOSEPH H. FLYNN

Polymer Science and Standards Division, National Bureau of Standards, Washington, D.C. 20234 (U.S A.)

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ABSTRACT

Theoretical curves of the rate of conversion vs. temperature at constant heating rate for first-order reactions with activation energies of 80, 160, 240 and 320 kJ mole^{-1} are compared over a range of heating rates from 10^{-9} to 10^5 K s^{-1} for independent and competitive reactions. Independent reactions with different activation energies may be separated from one another by either increasing or decreasing the rate of heating. The spectrum of derivative peaks for two competing reactions at various heating rates has a dispersion effect in the region of change from low to high activation energy reactions. The practical range of heating rates in thermal analytical experiments and the application of these model cases to the understanding of the kinetics of complex systems at high and low temperatures are discussed.

INTRODUCTION

The processes which are measured during a thermal analytical experiment occur within and/or at the surface of a condensed phase where often both the physical and chemical compositions of the interacting species are changing with respect to time. Therefore the kinetics of these processes may involve a complex interplay of competing reactions and it is not surprising that they can seldom be depicted adequately by simple kinetic models. Some of the problems in modeling the kinetics for these intractable multiphase systems have been discussed elsewhere [1—3].

New methods for analyzing thermal analytical data in which entire kinetic spectra, obtained from experiments performed at heating rates from 6 degrees per minute to 9 degrees per day, are compared have been applied to the investigation of the degradation of several polymers [4,5]. These techniques, when used over a wide range of heating rates and under different atmospheres, have the potential for separating competing reactions and allowing inferences as to their kinetic coupling.

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From these experiments, a shift of twin or multiple derivative peaks with respect to one another or a change of characteristics of a single peak may be observed at different heating rates. Comparison of these shifts with those calculated for model cases should give an insight into the mode of kinetic coupling of competing processes.

THE KINETIC MODELS AND THEIR CALCULATION

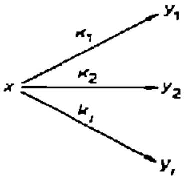
Theoretical values for the two most amenable models, independent reactions and competitive reactions, are calculated for a wide range of heating rates in this paper. These models have been discussed previously but for a much more limited range of heating rates [1,6—8]. The detailed analysis of these two models will be useful for interpreting thermal analytical kinetic data and formulating reaction mechanisms. A better understanding of high temperature reactions in flames and explosions will result from the calculations at very fast heating rates. On the other hand, the calculations at very slow heating rates will serve as useful models for the prediction of dominant or rate-limiting processes at low temperatures in the extrapolation from accelerated aging experiments to service lifetime prediction.

The two cases are represented in eqns. (1) and (2).

Case I. Independent reactions

$$x_1 \xrightarrow{k_1} y_1, x_2 \xrightarrow{k_2} y_2, \ldots, x_i \xrightarrow{k_i} y_i \qquad (1)$$

Case II. Competitive reactions



where x_i represents the concentration of reactant, y_i the concentration of product. and the k_i's are the respective rate constants.

We will use a reduced reaction coordinate, α, the extent or fraction of reaction , instead of concentration, weight, etc. It is related to the concentration by the equation, $\alpha = (x_0 - x)/(x_0 - x_f)$ where the subscripts 0 and f refer to the values at the beginning and end of the reaction of interest. The reduced reaction rate, $d\alpha/dt$, will not be used formally in the discussion. At any constant heating rate, β, the derivative of α with respect to temperature, $d\alpha/dT$, is linearly proportional to $d\alpha/dt$, i.e. $d\alpha/dT = \beta^{-1}\, d\alpha/dt$. $d\alpha/dT$ is used in the derivative plots in this paper and referred to as the "rate of reaction". This is a practical convenience since values of $d\alpha/dt$ at widely differing heating rates could not be compared on the same coordinate scale.

All of the models in this paper assume first-order kinetics, i.e. rate proportional to the first power of the reactant concentration. First-order kinetics were selected here so that derivative peaks would be more or less symmetrical about the maximum value. The functional form of the dependence of the extent of reaction upon the rate of reaction, f(α), affects mainly the shape of the rate curve and not its time—temperature positioning. Reactions of orders less than unity cause catastrophic falling off of the high-temperature side of the derivative peak while orders greater than one cause a skewness of the high-temperature tail [6]. However, since the purpose of this paper is to model changes in the rate with respect to temperature, $d\alpha/dT$, at different rates of heating, the form of f(α) is unimportant.

One-to-one stoichiometry is assumed for all reactions; thus, areas under derivative peaks of all independent reactions are equal. The inclusion of varied stoichiometric ratios would increase the size of this paper without greatly extending its usefulness as each experimental case will have its own unique stoichiometry.

The temperature dependence of the rate constants is modeled by the Arrhenius equation

$$k_i = A_i \exp(-E_i/RT) \tag{3}$$

where R is the gas constant, T the temperature, and the pre-exponential factor, A_i, and the activation energy, E_i, are assumed to be independent of temperature.

Therefore, the rate equations for the independent reactions are

$$\frac{d\alpha_i}{dT} = \beta^{-1}\frac{d\alpha_i}{dt} = A_i\beta^{-1}(1-\alpha_i)\exp(-E_i/RT) \tag{4}$$

and, for two competitive reactions

$$\frac{d\alpha}{dT} = \beta^{-1}(1-\alpha)[A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT)] \tag{5}$$

Values for α vs. T were calculated from the integral forms of eqns. (4) and (5), viz.

$$1-\alpha_i = \exp[-(A_iE_i/\beta R)\,p(E_i/RT)] \tag{6}$$

for each independent reaction, and for the two competing reactions

$$1-\alpha = \exp[-(A_1E_1/\beta R)\,p(E_1/RT) - (A_2E_2/\beta R)\,p(E_2/RT)] \tag{7}$$

where $p(E_i/RT) = \int_{E_i/RT}^{\infty} x^{-2}\exp(-x)dx$. It is assumed that the initial temperature is low enough so that its integration may be neglected [6]. The tables of Vallet [9], extended to cover a range of E/RT from 1 to 100, were used for most of these calculations while some utilized a continued fraction solution [10] for the function, $E_2(z) = \int_1^{\infty} t^{-2}\exp(-zt)dt$, since $p(z) = z^{-1}E_2(z)$. The values for the derivative curves were obtained by substituting values of α, calculated from eqns. (6) and (7), into eqns. (4) and (5).

The values of the parameters E, A and β used in these calculations are summarized in Table 1. The values for the pre-exponential factor, A, were selected so that, in each case, at a heating rate of 10^{-1} degrees per second, the maximum of the derivative curve ($d\alpha/dT$ vs. T) would occur at a temperature of 600 K (326.8°C). Since A appears in ratio with the heating rate, β, in eqns. (4)—(7), a change in the former parameter primarily shifts the curves

TABLE 1

Values of activation energy (E), pre-exponential factor (A), and heating rate (β) used in calculations

Reaction	E (kJ mole^{-1})	A (s^{-1})
I	80	2.439×10^{4}
II	160	4.457×10^{11}
III	240	6.104×10^{18}
IV	320	7.422×10^{25}

$\beta = 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, 1, 10, 10^{2}, 10^{3}$ and 10^{4} K s^{-1}.

along the temperature axis. The peak breadth will be proportional to the corresponding value of E/RT. Thus the four A values and eleven β values used in these calculations include a large family of $A\beta^{-1}$ ratios with which to fit the experimental data of interest.

The activation energy, E, has been assigned four values which range from 80 kJ mole^{-1} (~19 kcal mole^{-1}) to 320 kJ mole^{-1} (~76.4 kcal mole^{-1}). This range encompasses a large portion of the values found in thermal analytical experiments.

CALCULATED RESULTS AND THEIR DISCUSSION

Before discussion of the calculated results, it is of interest to look at the practical range of heating rates which can be utilized in thermal analysis. Table 2 lists the time to scan 300 degrees for heating rates from 10^{-6} to 10^{4} degrees per second.

At the fast end of the scale, 10^{-1} degrees per second (6 degrees per minute) is probably an upper limit if meaningful kinetic data are to be obtained

TABLE 2

Time required to scan 300 degrees at different heating rates

Heating rate (K s^{-1})	Time to scan 300 degrees	
10^{4}	0.03 s	
10^{3}	0.3 s	
10^{2}	3 s	
10	30 s	
1 (60 deg min^{-1})	5 min	
10^{-1} (6 deg min^{-1})	50 min	Practical range for thermal analysis kinetics
10^{-2} (0 6 deg min^{-1})	8.33 h	
10^{-3} (3.6 deg h^{-1})	3.47 days	
10^{-4} (8.6 deg day^{-1})	34.7 days	
10^{-5} (0 86 deg day^{-1})	347 days	
10^{-6}	9.51 years	

from a typical thermal analytical apparatus. Even at this heating rate, thermal flow into the sample or sensors may be slow enough to perturb measurement. For example, at 10^{-1} degrees per second, a thermal resistance with a time constant of 10 s will be equivalent to 2.5% of the maximum reaction rate. Apparatus can be specially designed to permit accurate kinetic measurement at somewhat faster heating rates. However, for a sample, on one hand, to be small enough and so intimately coupled with a heat source as to allow rapid thermal equilibration while, on the other hand, being large enough to allow quantitative property measurement at well-characterized heating rates, involves contrary problems in experimental design.

At the slow end of the heating rate spectrum, the limitations are temporal rather than experimental. Table 2 indicates that a 300 degree scan takes about a month at 10^{-4} degrees per second (~9 degrees per day). A similar scan at 10^{-5} degrees per second (~1 degree per day) would consume approximately one year's time. Any slower heating rate would tax the patience of even the most dedicated experimenter. However, there are several ways in which the time span may be reduced somewhat. Curves tend to become sharper at slower rates so the three hundred degree span may be truncated. If only initial reaction rates are of interest, the range may be shortened even more. Also, it has been pointed out that a parabolic heating rate, i.e. $\mathrm{d}T/\mathrm{d}t = aT^2$, greatly facilitates integration of the temperature integral [6]. It will also, for the same initial rate, cut the experimental time in half. However, this advantage may be only apparent as the heating rate in the higher temperature region is accelerated.

In the succeeding examples, the heating rate range extends well beyond the capabilities of a single instrument. This is done to demonstrate a wide variety of cases of competing reaction kinetics. As was previously noted, A was arbitrarily assigned to match all curves at a heating rate, β, of 10^{-1} degrees per second. The values in the ratio, $A\beta^{-1}$, may be selected to fit an experimental system of interest.

Independent reactions

The maximum rates of reaction, $(\mathrm{d}\alpha/\mathrm{d}T)_{\max}$, for the four cases in Table 2 of first-order reactions with activation energies of 80, 160, 240 and 320 kJ mole^{-1} are shown as a function of the logarithm of the heating rate in Fig. 1 for heating rates from 10^{-9} to 10^{5} degrees per second. Figure 2 is a plot of the temperatures at the maximum rates of reaction for the same conditions. The maximum rate of reaction increases in amplitude with increasing activation energy, i.e. the $\mathrm{d}\alpha/\mathrm{d}T$ vs. T peaks become more sharp. The amplitude decreases and the peaks become broader as the heating rate is increased. As the breadth of the derivative peaks is proportional to E/RT, its value changes dramatically for the extreme examples shown in Fig. 2. For reaction I (80 kJ mole^{-1}) at 10^{5} degrees per second, the peak half-width is 857 degrees as the curves approach a continuum as the heating rate becomes very fast. For reaction IV (E = 320 kJ mole^{-1}) at 10^{-9} degrees per second, the half-width is only 13.7 degrees as the peaks approach a delta function for zero heating rate (the isothermal case). The temperature at the maximum rate shifts to

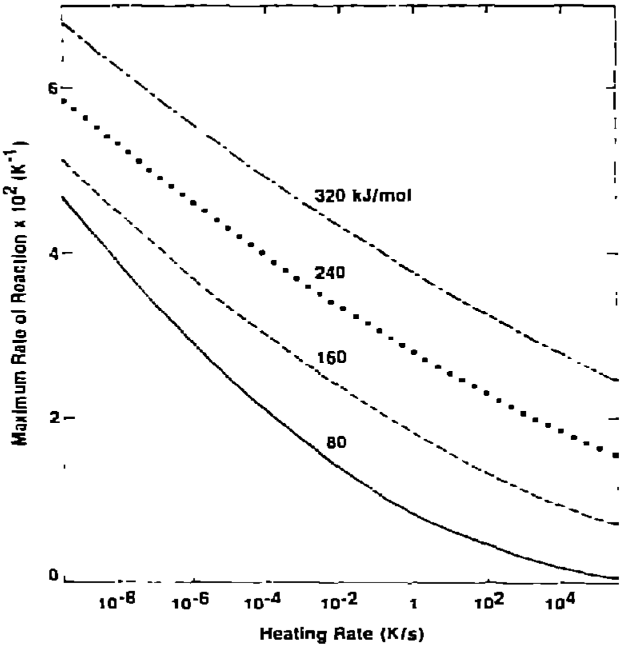


Fig. 1. Maximum rates of reaction vs. logarithm heating rate for first-order reactions at four activation energies. ———, 80 kJ mole^{-1}; - - - - - -, 160 kJ mole^{-1}; · · · · · ·, 240 kJ mole^{-1}; · — · — ·, 320 kJ mole^{-1}.

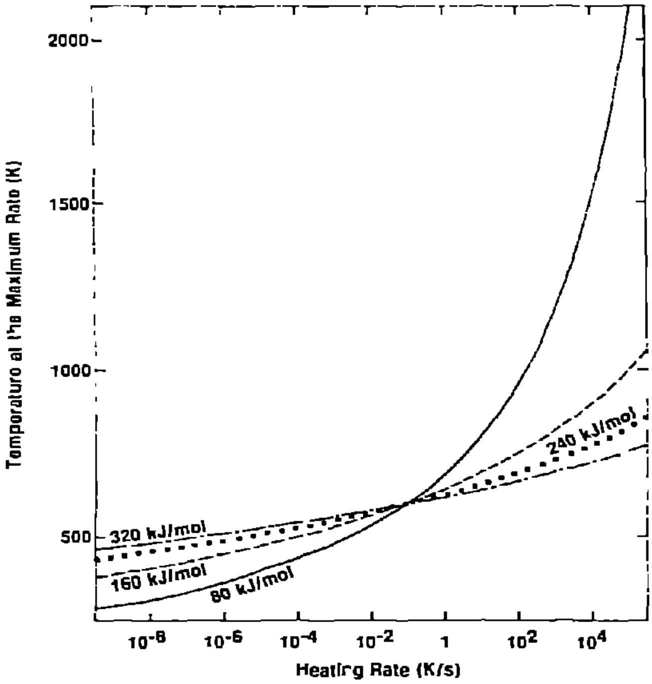


Fig. 2. Temperature at the maximum rate vs. logarithm heating rate for first-order reactions at four activation energies. ———, 80 kJ mole^{-1}; - - - - - -, 160 kJ mole^{-1}; · · · · ·, 240 kJ mole^{-1}; · — · — ·, 320 kJ mole^{-1}.

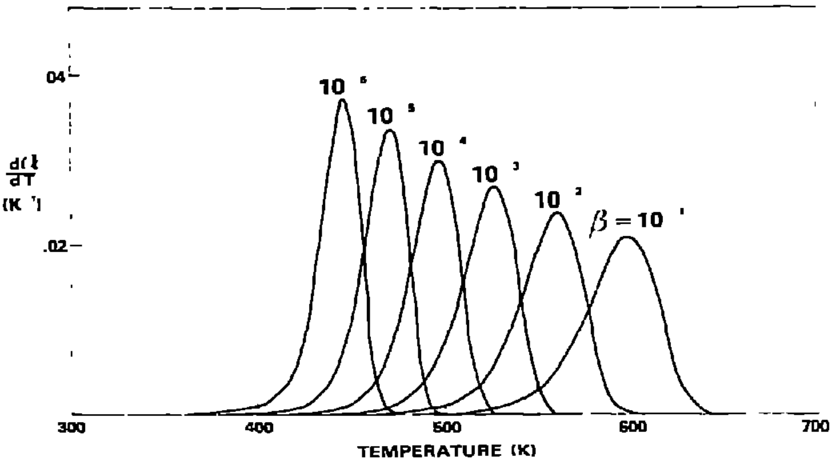


Fig. 3. $d\alpha/dT$ vs. temperature for a first-order reaction at heating rates of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} K s^{-1}. E = 160 kJ mole^{-1}, A = 4.457 × 10^{11} s^{-1}.

higher values at faster heating rates and to lower values at slower rates as indicated in Fig. 2. The size of the temperature shift varies inversely with the activation energy. This shift is quite dramatic for reactions with low activation energies. For reaction I, E = 80 kJ mole^{-1}, the maximum shifts from 600 K at 10^{-1} degrees per second to below room temperature at 10^{-9} degrees per second and to above 2000 K at 10^{5} degrees per second.

These shifts are illustrated for reaction II, E = 160 kJ mole^{-1}, in Fig. 3 for heating rates of 10^{-1}—10^{-6} degrees per second. During the 10^{-5} decrease in heating rate, the peaks sharpen as their amplitude doubles and the temperature at the maximum shifts from 600 to 430 K.

A similar family of curves for heating rates of 10^{-1}—10^{4} degrees per second is shown in Fig. 4 for the same reaction. The amplitude decreases by a factor of one-half and the temperature at the maximum rate shifts from 600 to 900 K as a result of the 10^{5} increase in heating rate.

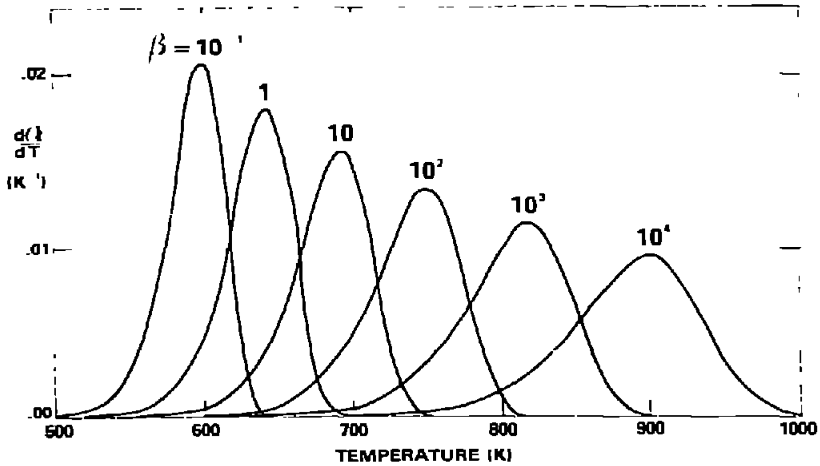


Fig. 4. $d\alpha/dT$ vs. temperature for a first-order reaction at heating rates of 10^{-1}, 1, 10, 10^{2}, 10^{3} and 10^{4} K s^{-1}. E = 160 kJ mole^{-1}; A = 4.457 × 10^{11} s^{-1}.

Simultaneous independent reactions

The first case of complex reaction kinetics taken up involves two independent, first-order reactions with widely differing activation energies of 80 and 320 kJ mole^{-1}, respectively. The curves for $d\alpha/dT$ as a function of temperature are plotted in Fig. 5 for heating rates of 10^{-1}—10^{-6} degrees per second. At a heating rate of 10^{-1} degrees per second, the maxima of the broad, low activation energy curve and the sharp, high E, curve coincide at 600 K. However, a hundred-fold decrease in heating rate to 10^{-3} degrees per second brings about almost complete separation of the two reactions due to the dramatic shift of the low E reaction to lower temperature. At a heating rate of 10^{-6} degrees per second, the low energy reaction has shifted to near room temperature. Reactions involving diffusion of material through a solid matrix often have low energies of activation. Therefore, they will occur at a comparatively more rapid rate at slow heating rates and low temperatures than will competitive high activation energy processes.

A similar family of curves is shown in Fig. 6 for heating rates of 10^{-1}—10^{4} degrees per second. As before, the 80 and 320 kJ mole^{-1} curves which have the maxima of their rate curves matched at 10^{-1} degrees per second are well separated by an increase in heating rate to 10 degrees per second. Although the peaks broaden with increasing temperature resulting in increasing overlap of their tails, the peak maxima separations on the temperature scale are even greater than for the converse reactions at slow heating rates and low temperatures. Thus, at least in theory, separation of competing reactions can be attained by increasing the heating rate as well as by decreasing it.

There is a large shift of the low activation energy peak to higher temperatures as the heating rate is increased to very fast values. The peak also becomes quite diffuse and, in this case, is almost a continuum at 10^{4} degrees per second. This agrees with the intuitive feeling that, at very high temperatures, the activation enthalpy becomes much less of a factor; rather, entropically favorable reactions will gain in importance. That is, the probability of energy localizing in a particular bond-splitting vibrational mode will be the criterion for reaction.

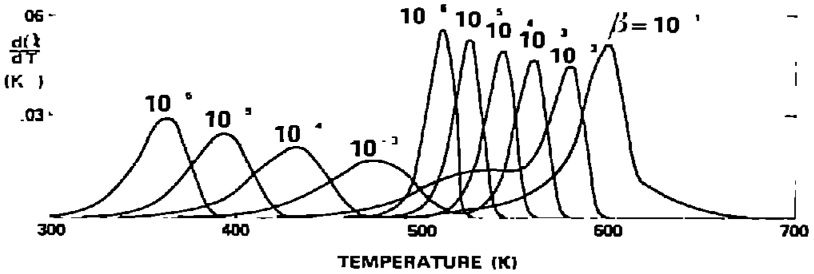


Fig. 5. $d\alpha/dT$ vs. temperature for two independent first-order reactions at heating rates of 10^{-1}—10^{-6} K s^{-1}. $E_1 = 80$ kJ mole^{-1}, $A_1 = 2.439 \times 10^4\ s^{-1}$; $E_4 = 320$ kJ mole^{-1}, $A_4 = 7.422 \times 10^{25}\ s^{-1}$.

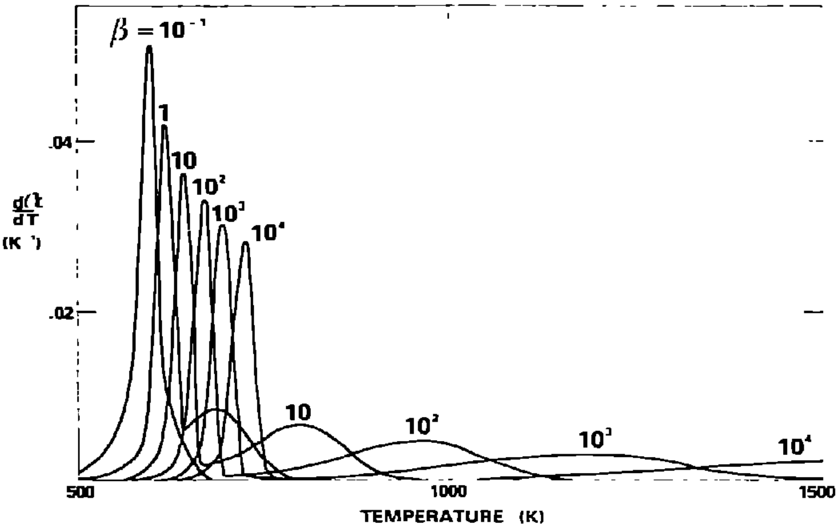


Fig. 6. $d\alpha/dT$ vs. temperature for two independent first-order reactions at heating rates of 10^{-1}—10^4 K s^{-1}. Parameters as in Fig. 5.

However, theoretical models for reaction kinetics on which the Arrhenius equation is based make the assumption that only a statistically small portion of the reacting systems have a sufficiently large energy to pass over a barrier in reaction coordinate space so that the reaction can proceed. Therefore, in the above case of the 80 kJ $mole^{-1}$ reaction at fast heating rate where $E/RT < 10$ and a large fraction of the systems have the energy to jump the barrier, the Arrhenius model is no longer valid and the highly diffuse rate curves can not be given literal significance.

The separation of reactions achieved by heating rate change in the above case is quite dramatic. However, it is probably quite rare that such large differences in activation energy are found in reactions occurring in the same temperature range as alternatives to one another. A less extreme case is illustrated in Fig. 7 where the rate for two independent first-order reactions of

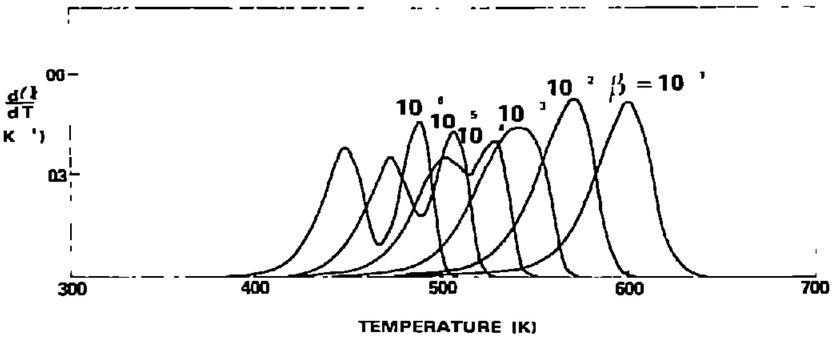


Fig. 7. $d\alpha/dT$ vs. temperature for two independent first-order reactions at heating rates of 10^{-1}—10^{-6} K s^{-1}. E_2 = 160 kJ $mole^{-1}$, $A_2 = 4.457 \times 10^{11}$ s^{-1}; E_3 = 240 kJ $mole^{-1}$, A_3 = 6 104 × 10^{18} s^{-1}.

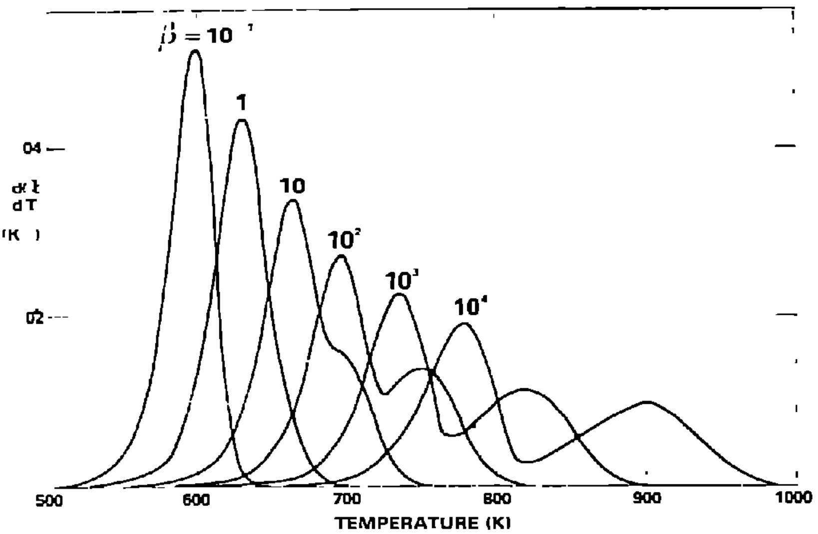


Fig. 8. $d\alpha/dT$ vs. temperature for two independent first-order reactions at heating rates of 10^{-1}—10^{4} K s^{-1}. Parameters as in Fig. 7.

160 and 240 kJ mole^{-1} respective activation energies are plotted as a function of temperature for heating rates from 10^{-1} to 10^{-6} degrees per second. Figure 8 contains a similar family of curves for heating rates from 10^{-1} to 10^{4} degrees per second. The separation achieved by changing the heating rate from 10^{-1} degrees per second in either direction is discouragingly poorer than in the 80—320 kJ mole^{-1} case and still incomplete after a $10^{\pm 5}$ change. However, it is probably rare that two independent reactions will have identical Arrhenius parameters. Therefore, some sort of partial separation of the peaks should be present initially and their separation should be enhanced by a heating rate shift. Should a whole spectrum of overlapping reaction rate peaks shift intact with a large heating rate change, then average or "global"

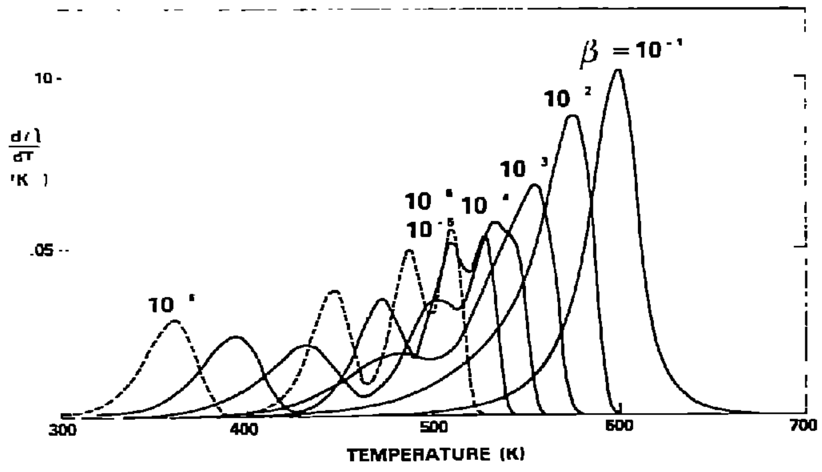


Fig. 9. $d\alpha/dT$ vs. temperature for four independent first-order reactions at heating rates of 10^{-1}—10^{-6} K s^{-1}. Parameters as in Figs. 5 and 7. ———, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} K s^{-1}; - - - - - -, 10^{-6} K s^{-1}.

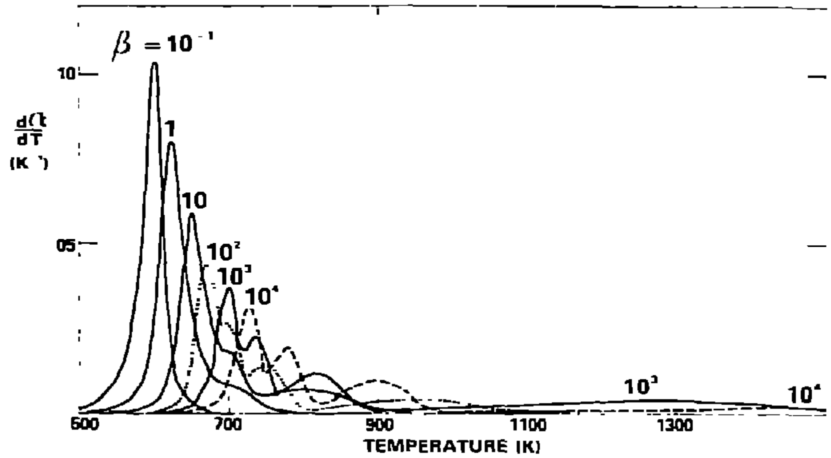


Fig. 10. $d\alpha/dT$ vs temperature for four independent first-order reactions at heating rates of 10^{-1}—10^4 K s^{-1}. Parameters as in Figs 5 and 7. ———, 10^{-1}, 1, 10 K s^{-1}; - - - - - -, 10^2 K s^{-1}, ———, 10^3 K s^{-1}; — — —, 10^4 K s^{-1}.

Arrhenius parameters may be calculated without complication.

Figures 9 and 10 are $d\alpha/dT$ vs. T curves for heating rate ranges of 10^{-1}—10^{-6} and 10^{-1}—10^4 degrees per second, respectively, for the case of four independent reactions with activation energies of 80, 160, 240 and 320 kJ mole^{-1}. As in the previous cases, the maximum rates are matched at 600 K for $\beta = 10^{-1}$ degrees per second. Four separate reactions are discernible in both figures after a $1000^{\pm 1}$-fold change in heating rate to 10^{-4} and 10^2 degrees per second. By 10^{-6} and 10^4, only the 240 and 320 peaks are not well-resolved from one another. Again, although the peaks are less sharp at the faster heating rates, their separation is better than at correspondingly slower heating rates since the temperature shifts of their maxima are so much greater.

Competitive reactions

The second model case illustrated in this paper was expressed by eqn. (2) in which two first-order reactions are vying with each other for the same material. An example of this case is shown in Fig. 11 for two reactions with activation energies of 80 and 320 kJ mole^{-1}. At slow heating rates (10^{-5}—10^{-3}) and correspondingly low temperatures, the low activation energy reaction with its low broad peaks dominates. On the other hand, at fast heating rates (10—10^4) and high temperatures, the high activation energy reaction with tall, sharp peaks takes over. In the region of intermediate heating rates (10^{-2}—1) where the two processes are in even competition, the amplitudes of the derivative curves go through a minimum. The dispersion effect obtained here by varying the heating rate closely resembles the similar dispersion effect observed in the comparison of derivative curves obtained by varying the frequency of a forcing variable in relaxational processes. In each case, the amplitude minimum marks the region in which a change in the mechanism of the measured process takes place.

If competing reactions have smaller differences between their activation energies, the shift shown in Fig. 11 will occur over a wider range and the peak amplitude change will be proportionally smaller.

SUMMARY AND DISCUSSION

An unexpected fact concerning independent reactions was that, not only can low activation energy and high activation energy processes be separated from one another by shifting to slower heating rates and lower temperatures, but conversely, they can be separated equally well by shifting to faster heating rates and higher temperatures as the maxima of the rates of the low energy reactions are quite sensitive to heating rate change. Thus, low E reactions are favored at slow β and low T, while high E reactions are favored at fast β and high T.

Similarly, for the case of two reactions in relatively even competition, the low activation energy reaction will dominate the kinetics at slow rates and low temperatures while the high activation energy reactions will take over at fast rates and high temperatures.

However, one cannot generalize from the results of these two simplest cases of complex reaction kinetics. The obvious continuation of this work is an investigation of model cases of successive reactions of the type

$$A \xrightarrow{k_1} B \xrightarrow{k_2} \dots \xrightarrow{k_i} X \qquad (8)$$

again, over a wide range of heating rates. The reactions dominating the kinetics here will be the reverse of the previous cases of competing reactions. In this case, for a series of reactions, the overall reaction kinetics will be affected only by the rate constants of the slowest reaction in the sequence and the rate constants of those reactions preceding it. Thus, at sufficiently

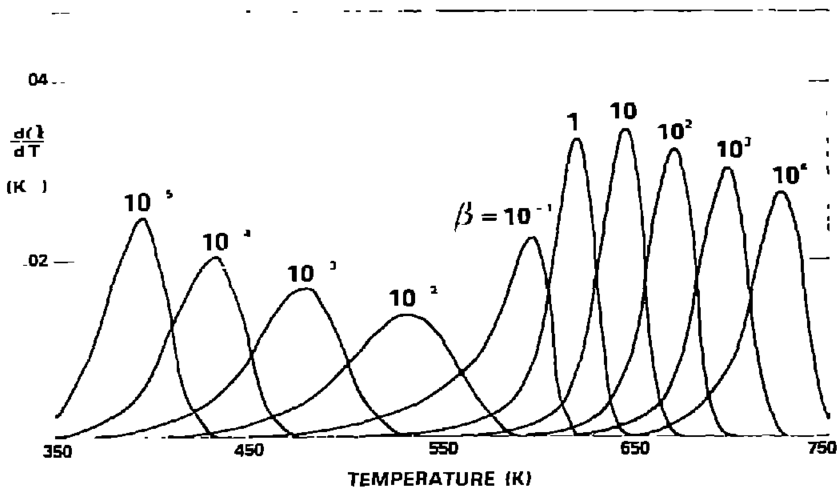


Fig. 11. dα/dT vs. temperature for two competitive first-order reactions at heating rates of 10^{-5}—10^4 K s^{-1}. Parameters as in Fig 5.

slow heating rates and low temperatures, a high activation energy reaction in the sequence will tend to be rate-limiting. On the other hand, at high temperatures and fast heating rates, a low E reaction may become the slow step of the process.

The case of eqn. (8) and the even more mathematically complex case in eqn. (9)

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \ldots \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \mathrm{X} \qquad (9)$$

involving reversible reactions, may model the reversible dehydration and decarboxylation reactions which can occur in thermal analysis experiments. Several of these cases have been calculated over a range of reaction parameters [11] but not as a function of heating rate.

Polymer degradation reactions are being investigated by thermogravimetry over a heating rate range from 10^{-1} to 10^{-4} degrees per second in inert atmosphere, in air, and in the presence of water vapor [4,5]. At 10^{-4} degrees per second, the reactions take place at temperatures over one hundred degrees below those of the usual thermal analytical experiment. Therefore the temperature extrapolation for service lifetime prediction is greatly lessened. From an analysis of the kinetic interplay under different atmospheres at different heating rates and a comparison of them with cases of model reaction kinetics, an assessment can be made as to which one, or combination of, thermal, hydrolytic or oxidative reactions will probably be the primary agent for deterioration of properties at service conditions.

The interpretation of these and similar kinetic data will be facilitated when the results from many other model cases of complex reaction kinetics become available.

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