A breath of fresh air

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Abstract

Certain processes by virtue of the nature of the reaction interface produce zero order kinetics. Numbered among these processes is evaporation. Instances of this kind of phenomena can be cited from the cosmetic and pharmacy industries. This phenomenon can be studied using thermal analysis. However, a general model for rising temperature, solid state kinetics can be used, which is much simpler than other advocated methods. The model is based on the existence of a reaction interface and the assumption that over a small range of temperatures (say $2^{\circ}C$) the interface area remains constant. The logical deductions from such a model are detailed in the present study. © 1999 Elsevier Science B.V. All rights reserved.

1. Preamble

Acknowledgments are provided to all those students who have taught me in my years at Salford and Toledo. They provide a breath of fresh air that enables me to go from one topic to another, and they keep me on a steady track and prevent my making too many blunders. The imaginative research of others with whom I have worked has played an important part in presenting my research. The early years spent at Exeter University — then the University College of the South West — found me under the influence of Dr. S.J. Gregg, whose creative research and fertile mind and love of the subject brought out the best in all his students. I have tried to live up to his ideal. The 27 years I spent at Salford brought me into contact with real problems that could be solved by a general extension of those principles laid down by Dr. Gregg and allowed excursions into the fields of coal chemistry, cement technology, glass manufacture, polymer science and the behavior of carbons. The 15 years at the University of Toledo has provided fresh topics and indicated fresh avenues of approach and provided new fields of industrial geology and pharmacy in which to pursue the subject. As evidence of this, I offer the following contribution to rates of reaction, where I hope the reader can detect a breath of fresh air.

2. Introduction

In certain cases of transition, a zero order process can be predicted as the kinetic mechanism with a high degree of certainty. This is based on a constant area of reaction interface existing throughout the reaction. In recent years, the work forthcoming from the group has been centered on drugs, ibuprofen can be cited as an example [1] or cosmetics, especially perfumes [2], where evaporation is the operating process. A typical evaporation process for ibuprofen subjected to simul-
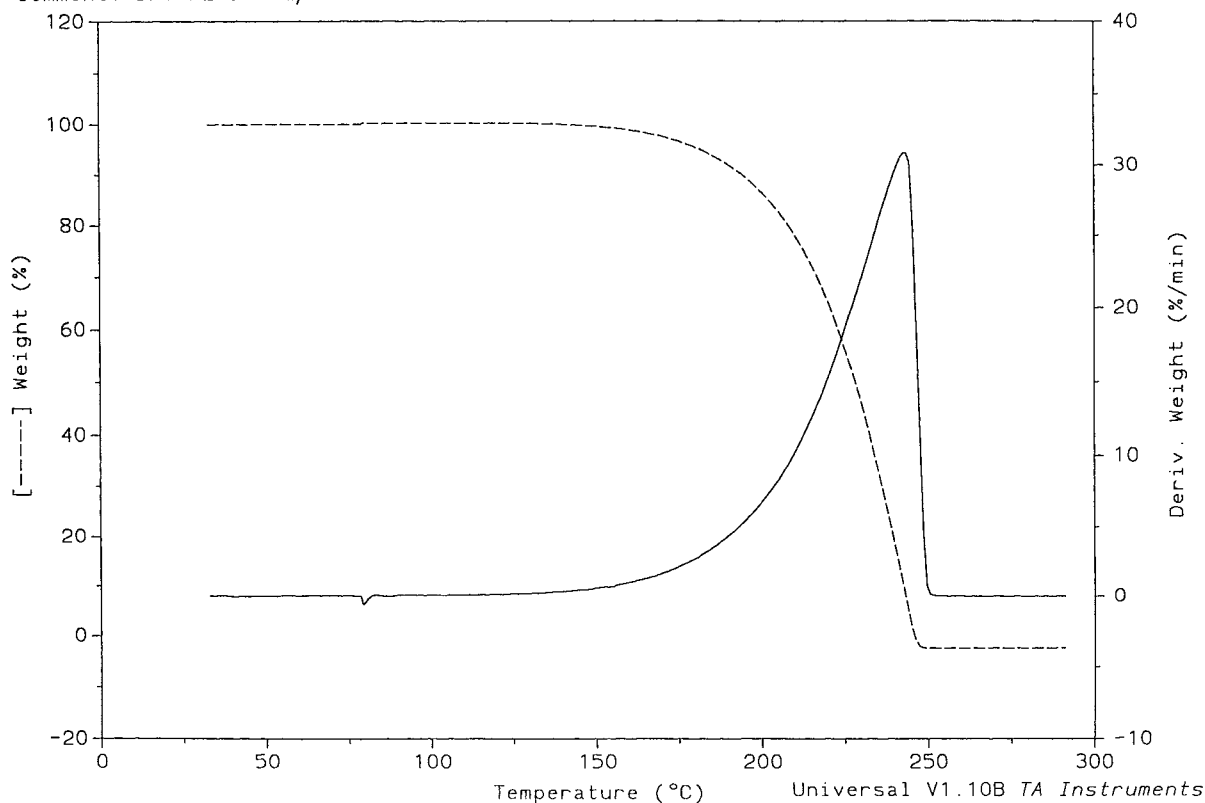
Universal V1.10B *TA Instruments*

Fig. 1. TG and DTG of ibuprofen heated in nitrogen at a nominal heating rate of 10°C/min using a simultaneous DTA/TG unit (TA Instruments 2960).

taneous TG/DTA studies is shown in Figs. 1–3. The TG and DTG data show an obvious loss in mass, which is then attributed to evaporation, a zero order process. More detail is seen on the DTG plot where there is a small perturbation at the melting point and characteristically shaped peak due to evaporation. The perturbation at the melting point is the subject of some speculation [3], but it always occurs at the melting point. The two processes of melting and evaporation can be seen on the DTA plot as endothermic processes. The second peak is as stated due to evaporation and should not be confused with the normal boiling point. Fig. 3 shows the small perturbation in the temperature–time plot due to the endothermic processes of melting and evaporation. This has given rise to a series

of papers on the possibility of using temperature–time plots to generate a DTA trace on the basis of a single crucible, single thermocouple signal [3,4]. Figs. 4–6 show a typical fragrance component trace. The process of evaporation can be clearly discerned in the TG plot (Fig. 4), the DTA signal (Fig. 5) and in the small perturbation shown on the time–temperature plots (Fig. 6). Evaporation of a fragrance represents a paradox. Logically, it is pollution of the atmosphere, but the entire basis of the perfume industry is to introduce the concept of a "breath of fresh air" brought about by the evaporation of the perfume under consideration.

It should not be thought that zero order kinetics is confined to liquid reaction interfaces. A flat crystal,
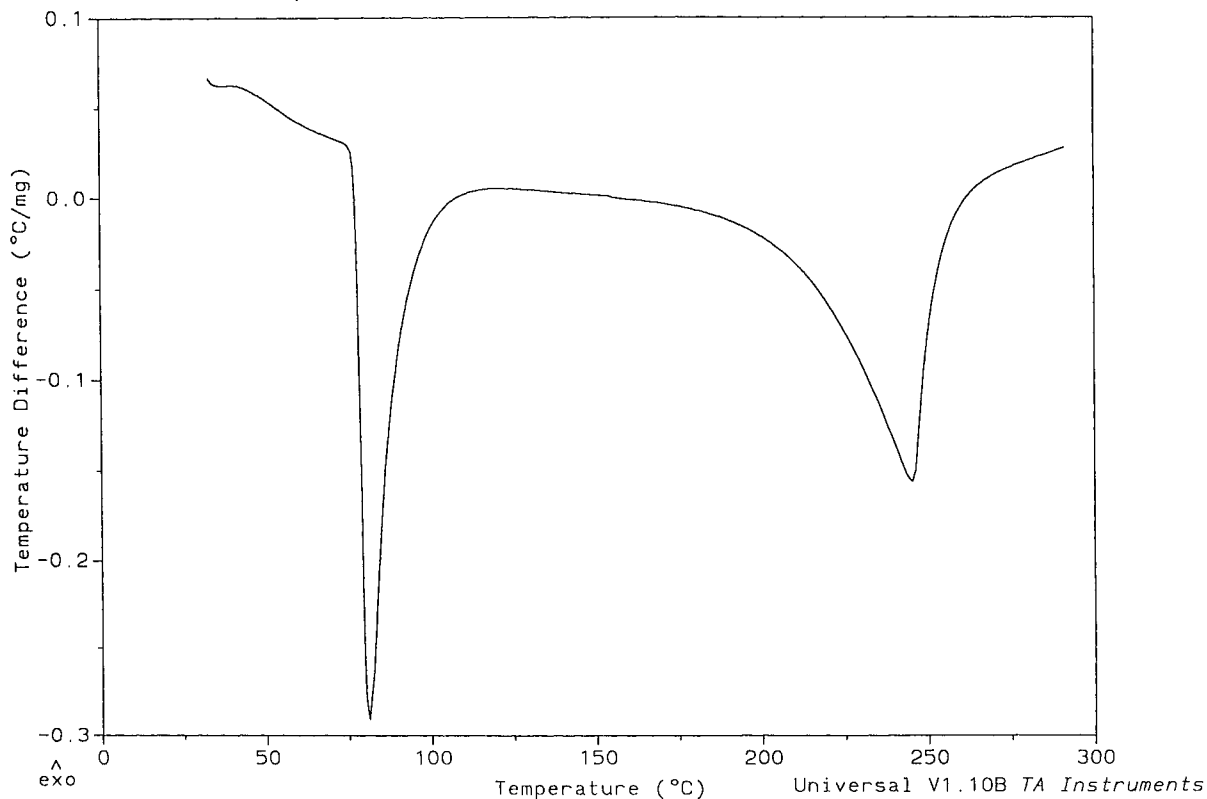
Fig. 2. DTA of ibuprofen heated in nitrogen at a nominal heating rate of 10°C/min using a simultaneous DTA/TG unit (TA Instruments 2960).

such as graphite, might be expected in air to progress through total gasification to CO and CO_2 via a zero order mechanism and over a large range of decomposition. This is true for many carbons [5,6]. Obviously at the beginning of the process of degradation and at the very end where the crystal finally breaks up into fragments this concept of zero order kinetics will not hold. In the present study, the concept of zero order kinetic processes associated with evaporation is outlined and the idea is then extended to a kinetic interpretation that can be generally applied to almost all solid state decompositions where the material is subjected to a programmed rising temperature regime.

3. Theory and application

3.1. Evaporation

In Figs. 1–4, the TG and DTG show a typical evaporation process. Application of models due to Dollimore et al. [7,8] show that these types of DTG plots are associated with a zero order process. If α the fraction decomposed, is defined by:

$$\alpha = \frac{(\%w_i - \%w_t)}{(\%w_i - \%w_f)}, \tag{1}$$

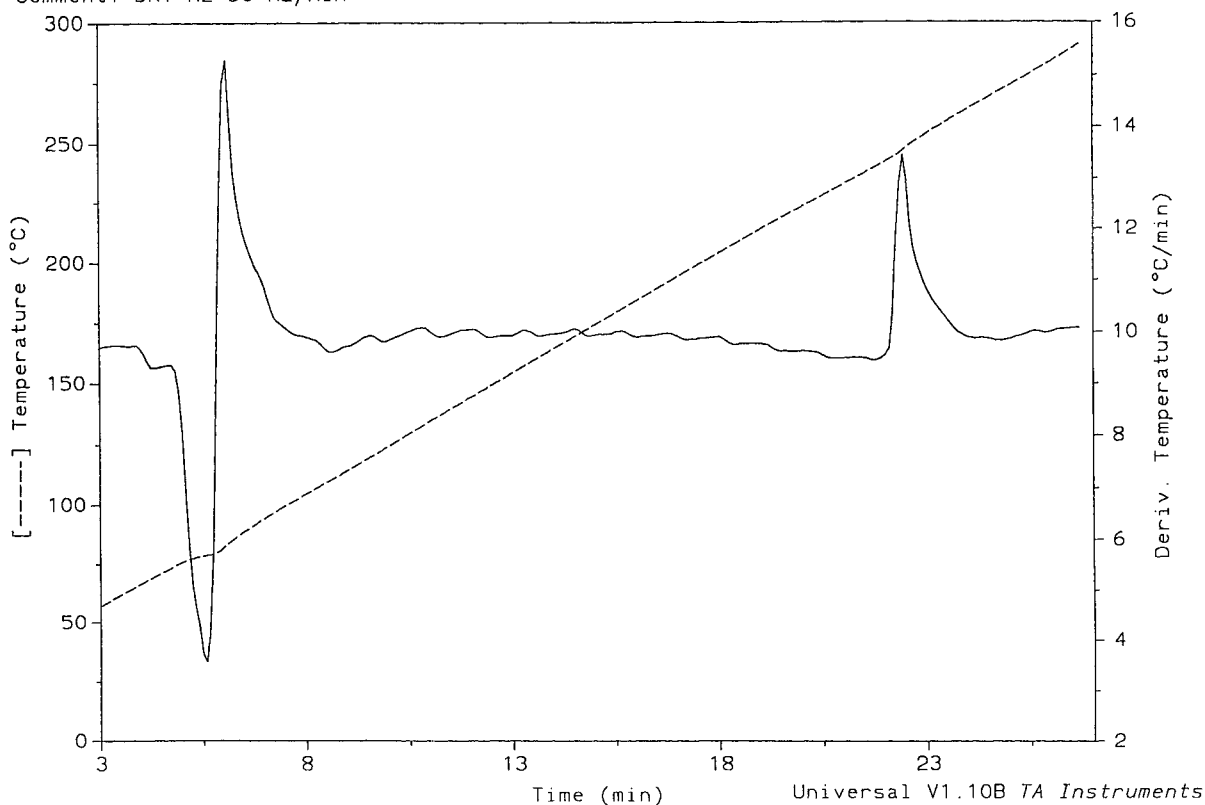where $\%w_i$ is the initial percentage weight, $\%w_f$ the

Fig. 3. The time–temperature plot and its first derivative for ibuprofen heated in nitrogen at a nominal heating rate of 10°C/min using a simultaneous DTA/TG unit (TA Instruments 2960).

final percentage weight and $\%w_t$ the percentage weight at time t, corresponding in a linear programmed temperature control to some temperature T_t. Then, plots of α versus temperature can be constructed (a typical plot is shown in Fig. 7). In evaporation, it should be noted that $\%w_f$ is zero. Now, at any given temperature the rate of evaporation (dα/dt) is given by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kF(\alpha) = k_T, \qquad (2)$$

for the function of α, $F(\alpha) = 1$ for zero order reactions and k_T is then the rate of evaporation at that tempera-

ture. The value of dα/dt at any temperature can be evaluated from rising temperature experiments:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T\beta} = \frac{\mathrm{d}\alpha}{\mathrm{d}t}, \qquad (3)$$

where β is the rate of heating (dT/dt). However, as most work stations will produce graphs of α versus time, superimposed upon a plot of temperature versus time, the value of dα/dt can be collected directly and such a process would take into account any local perturbations in dT/dt versus time [9].

For chemical processing operations, the data are best kept in terms of weight (in mg) designated as w_{mg}, plotted against temperature, if w_{mg} is divided by the
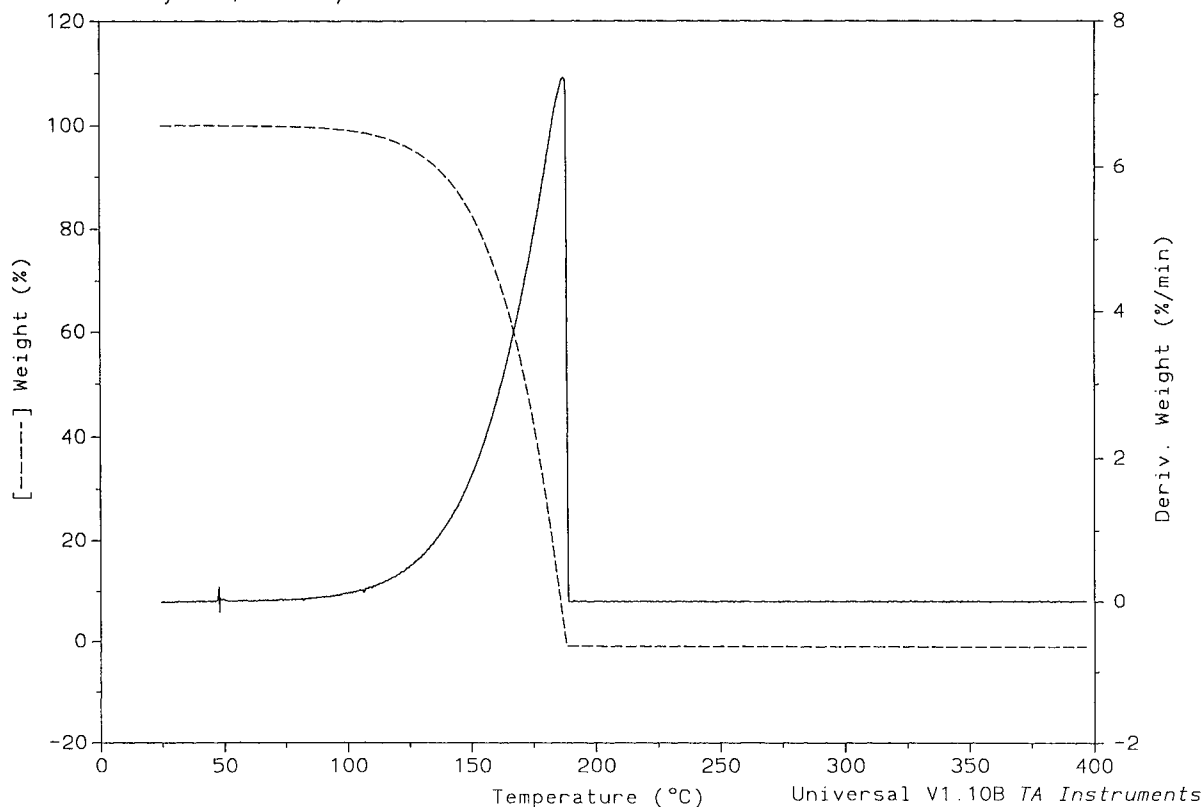
Fig. 4. TG and DTG plot of fragrance component heated in nitrogen at a nominal heating rate of 10°C/min using a simultaneous DTA/TG unit (TA Instruments 2960).

area of interface (*A*, the cross sectional area of the crucible) then:

$$\frac{1}{A}\frac{\mathrm{d}(w_{\mathrm{mg}})}{\mathrm{d}t} = \text{Coefficient of Evaporation} = k_{\mathrm{evap}}. \tag{4}$$

In this form, the data can be processed to be of use in chemical process technology. Reverting back to the terminology used in Eq. (2), the values of k_T at any temperature can be fitted to get Arrhenius equation:

$$\ln k_T = \ln A - \left(\frac{E_{\mathrm{act}}}{RT}\right). \tag{5}$$

A plot of $\ln k_T$ versus $1/T$ is linear (see Fig. 8) from which E_{act} (the energy of activation) and A (the pre-

exponential term) can be calculated. The experimental data shows small deviations at the high temperature end. The best straight line and the R^2 value are indicated on the graph.

These small deviations are systematic and not random. The deviation at the high temperature is due to the break up of the material at the end of the experiment from a system with a constant area of interface to one of altering area caused by there being insufficient material to maintain the constant area and the subsequent formation of liquid drops.

Typical values of E_{evap} and ΔH_{vap} are listed in Table 1. The ibuprofen value of E_{evap} differs from the Troutons estimate of ΔH_{vap} because the ibuprofen molecule exists as a dimer in the liquid state and dissociation to a monomer in the vapor state [1]. The

Sample: Benzophenone   TGA-DTA   File: D:\PAULINE\BENZOP.022
Size: 12.4682 mg   Operator: Pauline Phang
Method: 2°C/min to 400°C   Run Date: 23-Mar-98 13:50
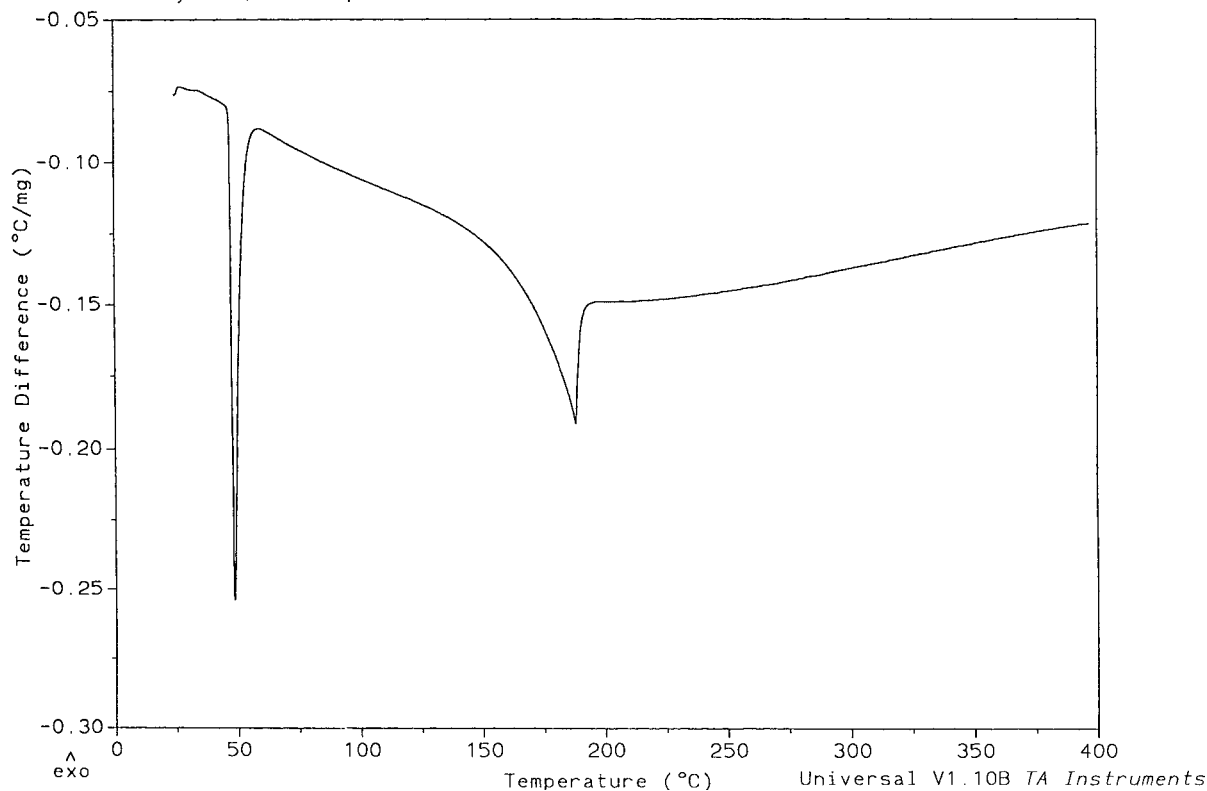Comment: Dry Air, 100 mL/min

Fig. 5. DTA of fragrance component heated in nitrogen at a nominal heating rate of 10°C/min using a simultaneous DTA/TG unit (TA Instruments 2960).

Table 1
Values of E_{act} for the evaporation process for various systems compared with latent heat of evaporation calculated by Trouton rule or modified Trouton rule

System	E_{act} (kJ mol^{-1})	ΔH_{evap} (kJ mol^{-1})
Methyl benzoate	47	40.1
Ibuprofen	42.7–46.1	88
Benzophenone	65.7	51.7
Cinnamic acid	68.5	50.4

other values listed in Table 1 suggest that the energy of activation approximates to the latent Heat of Evaporation. This is the general trend in many similar experiments carried out in the author's laboratory. A very simplified reaction coordinate diagram for an endothermic process is shown in Fig. 9. The calcula-

tion of the enthalpy of vaporisation (ΔH_{vap}) based on the Trouton rule [10,11] is the source of the ΔH_{evap} given in Table 1 and it can be seen that except where perturbations in the enthalpy are to be expected that $E_{evap} \approx \Delta H_{evap}$.

3.2. Kinetics of solid state change

The concept of zero order mechanism can also be applied very simply to rising temperature studies. It should be noted that the universal description used to describe such studies is "non-isothermal" — a more realistic term is simply "rising temperature" implying the study of a system under a regime of controlled temperature rise.
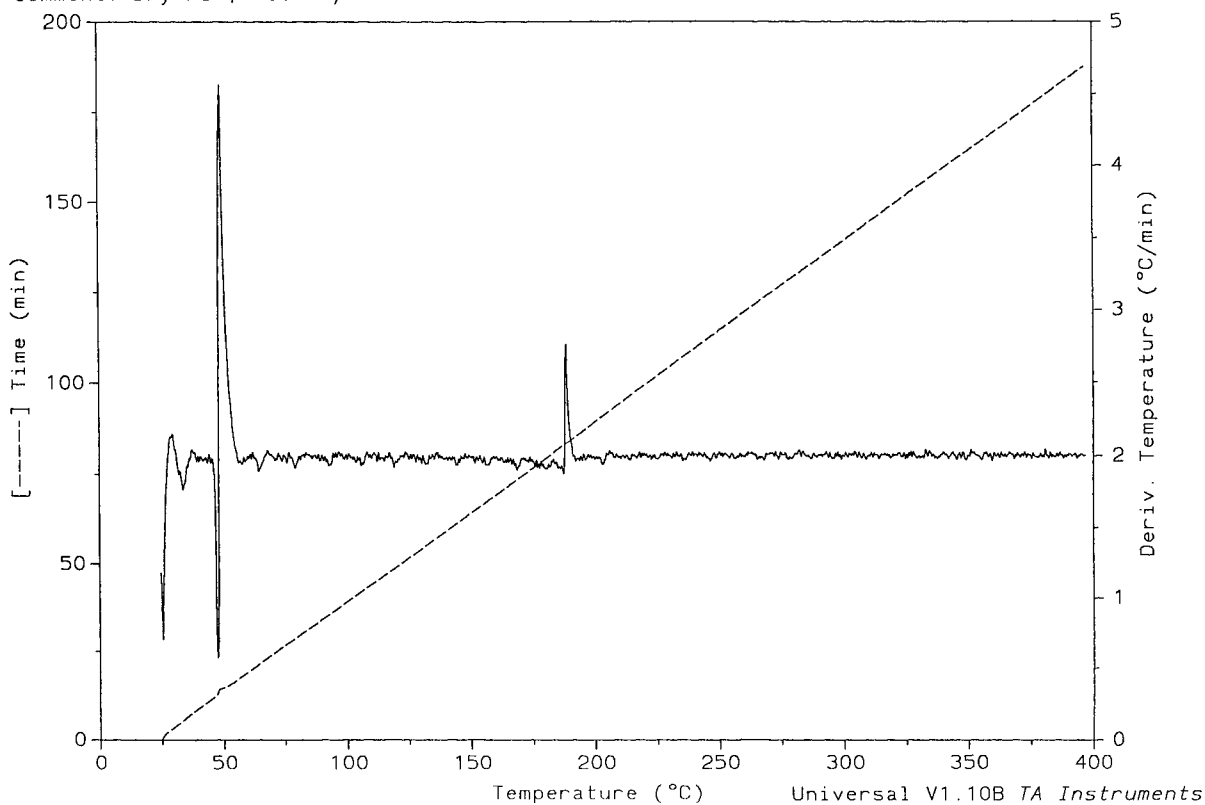
Fig. 6. The time–temperature plot and its first derivative of a fragrance component heated in nitrogen at a nominal heating rate of 10°C/min using a simultaneous DTA/TG unit (TA Instruments 2960).

The necessary assumptions for the application of a model based on zero kinetic order are:

1. The existence of a reaction interface.
2. The rate of reaction for unit area of interface is constant at any given temperature.
3. That for a small incremental change for temperature or time, the area of the reaction interface does not change, i.e. it is a zero order process.
4. The total area of the reaction interface over a prolonged temperature may or may not change depending on the overall mechanism.

It must be stressed that although this model allows for a geometrically based overall mechanism [12,13] for the small increment of temperature $\Delta T_{1,2}$ between temperatures T_1 and T_2, it is considered as a zero order process. However, in another small increment of temperature, T_{n+1} and T_{n+2}, the reaction is also zero order but is only conformable with the zero order process of T_1 and T_2 if the overall mechanism is also zero order. The model described is one of a few which apply directly to the rising temperature experiments; all previous models [14] were originally applied to isothermal experiments and then adapted to deal with rising temperature experimentation.

The description at any temperature T_{n-1} of a rising temperature reaction is then:

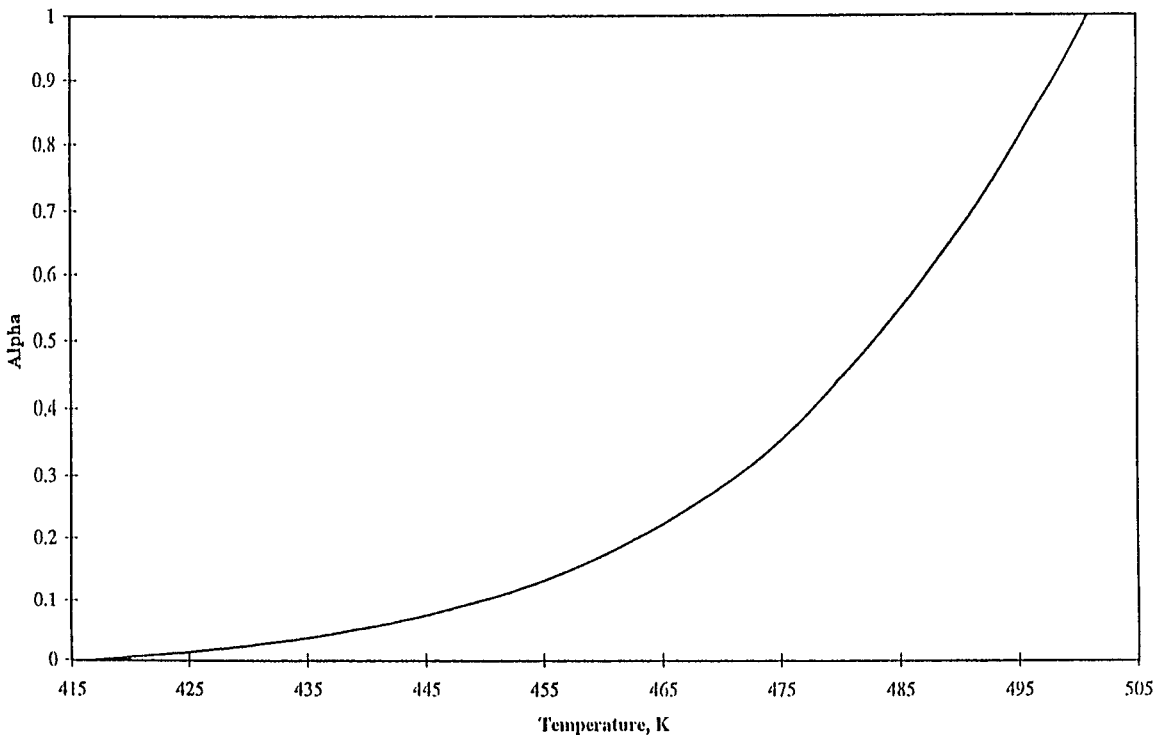$$\ln k_{T_{n-1}} = \ln A - \left(\frac{E_{\text{act}}}{R T_{n-1}} \right). \tag{6}$$

Fig. 7. Typical plot of α–T for the evaporation process.

Then at temperature T_{n+1}:

$$\ln k_{T_{n+1}} = \ln A - \left(\frac{E_{\text{act}}}{RT_{n+1}}\right). \tag{7}$$

Based on the assumptions already noted, it follows that:

$$\ln\left(\frac{k_{T_{n-1}}}{k_{T_{n+1}}}\right) = -\frac{E_{\text{act}}}{RT_{n-1}} + \frac{E_{\text{act}}}{RT_{n+1}}$$
$$= \frac{E_{\text{act}}}{R(1/T_{n+1} - 1/T_{n-1})}.$$

The resultant relationship is then:

$$\ln\left(\frac{k_{T_{n-1}}}{k_{T_{n+1}}}\right) = -\frac{2E_{\text{act}}}{R(T_{n+1})(T_{n-1})}. \tag{8}$$

Writing

$$T_n^2 \cong (T_{n+1})(T_{n-1}), \tag{9}$$

gives

$$\ln\left(\frac{k_{T_{n-1}}}{k_{T_{n+1}}}\right) = -\frac{2E_{\text{act}}}{RT_n^2}. \tag{10}$$

This enables E_{act} to be calculated at any temperature over the entire decomposition range. The calculations are easy and need not be applied at every one degree intervals. The value for E_{act} is only going to be true for a temperature interval of 2 K for every T_n used in the calculation.

The question of what to infer if E_{act} is constant over the entire decomposition range or what to conclude if E_{act} varies over some of the α range needs addressing. The first case to consider is one where the reaction interface alters with increasing temperature (or with increasing values of α). Three cases can be considered:

1. The contracting surface model (designated usually as R2) where:

$$\left(\frac{\text{d}\alpha}{\text{d}t}\right)_T = (k_{\text{R2}})_T 2(1-\alpha)^{1/2}, \tag{11}$$
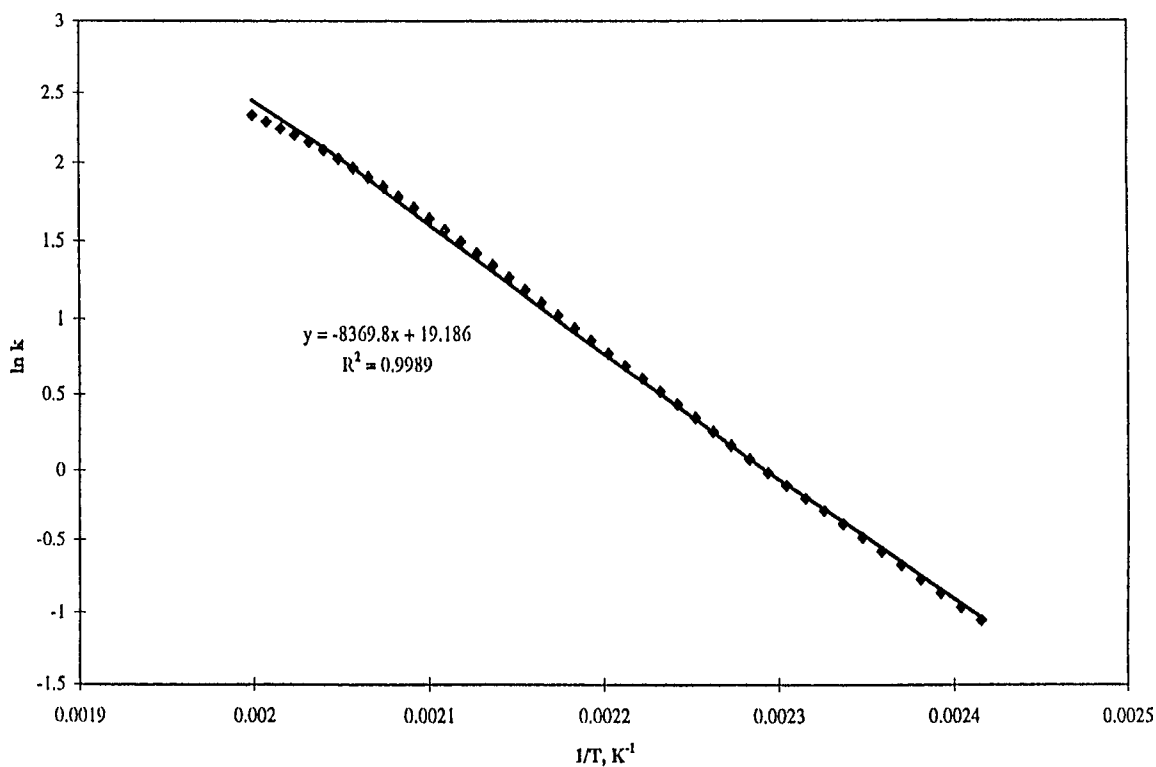
at a particular temperature.

Fig. 8. Typical plot of $\ln k_T$ versus $1/T$ used in the calculation of E_{evap} and A for the evaporation process.
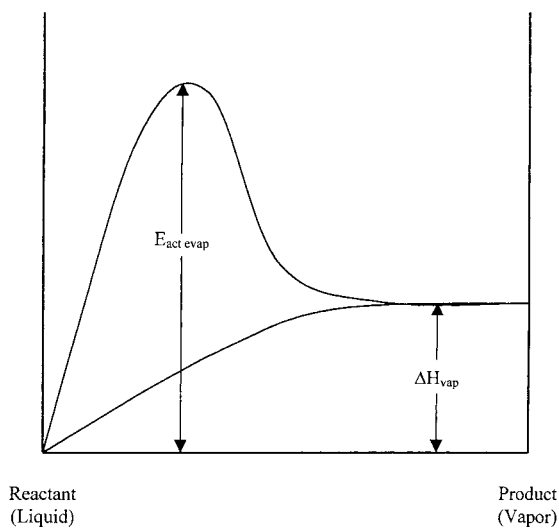

Fig. 9. Simplified reaction coordinate diagram for the process of evaporation.

2. The contracting sphere model (designated usually as R3) where:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_T = (k_{\text{R3}})_T 3(1-\alpha)^{2/3}. \tag{12}$$

3. A constant reaction interface area over the entire decomposition range when:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_T = k_0. \tag{13}$$

Alongside these three geometrical models, we may also consider a first order (designated F1) process shown in some geometrical approaches [15], under certain experimental conditions, when:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_T = k_{\text{F1}}(1-\alpha). \tag{14}$$

If at any small increment of time or temperature these geometrical models hold (or could be experi-

mentally derived over such a small increment) then rearrangement and substitution gives:

$$k_0 = k_{R2}2(1-\alpha)^{1/2}, \tag{15}$$

$$k_0 = k_{R3}3(1-\alpha)^{2/3}, \tag{16}$$

$$k_0 = k_{F1}(1-\alpha), \tag{17}$$

or in general:

$$k_0 = k_X f(1-\alpha), \tag{18}$$

where $f(1-\alpha)$ is some function $1-\alpha$ appertaining to the reaction rate for a specified geometrical model.

Then Eq. (10) can be rewritten:

$$\ln\left(\frac{k_{T_{n-1}}}{k_{T_{n+1}}}\right) = \ln\left(\frac{[k_0/f(1-\alpha)]_{T_{n-1}}}{[k_0/f(1-\alpha)]_{T_{n+1}}}\right) = -\frac{2E_{act}}{RT_n^2}, \tag{19}$$

where the subscript to the square bracket indicates values at T_{n-1} and T_{n+1}, respectively.

It can be argued that $f(1-\alpha)$ at T_{n-1} is not going to be very different from the value of $f(1-\alpha)$ at T_{n+1}. Writing

$$[f(1-\alpha)]_{T_{n-1}} = [f(1-\alpha)]_{T_{n+1}}, \tag{20}$$

leaves us with the original equation:

$$\ln\left(\frac{(k_0)_{T_{n-1}}}{(k_0)_{T_{n+1}}}\right) = -\frac{2E_{act}}{RT_n^2}, \tag{21}$$

and provides the necessary justification for considering the reaction interface to remain constant in area over a small increment of temperature.

A further implication of this argument is that a variation in the value of E calculated by this method would be due to a change in the chemical kinetic mechanism. This could imply a change in the interface model or a different chemical route for the process under consideration.

4. Conclusions

It is concluded that:

- A model especially applied to solid state rising temperature kinetic experiments is applicable on the basis of:

1. the existence of a reaction interface.

2. the rate of reaction per unit area of interface is constant at any given temperature.
3. that for a small incremental change of temperature or time the area of the reaction interface does not change.

- The use of mechanisms (F1, R1, R2, etc.) other than zero order to describe the change in E_{act} over the small incremental change in temperature is considered to have a negligible effect in the evaluation of E_{act}.
- The method is a simpler and speedier method of evaluating E_{act} over a range of temperatures or fractions decomposed than other methods.
- Any variation of E_{act} with temperature or fraction decomposed is related to a change in the chemical kinetic mechanism.
- Applied to liquid interface processes, such as evaporation, the zero order process is shown to be non-activated, and the energy of activation for the evaporation process approximates the latent heat of vaporisation.

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