

KINETIC ANALYSIS OF A SEQUENCE OF TWO CONSECUTIVE REACTIONS FROM THERMOGRAVIMETRIC DATA UNDER NON-ISOTHERMAL CONDITIONS. I. CALCULATED THERMOGRAMS

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ABSTRACT

This paper suggests a method of drawing the thermogram of a sequence of two consecutive, partially overlapping processes of a given order, run under non-isothermal conditions.

INTRODUCTION

The existence of overlapping processes is confirmed by everyday experience in thermogravimetric kinetic analysis. The corresponding derivative of the thermogram (DTG) is generally different in shape to that given by simple (unique) processes. The latter shows a peak corresponding to a single turning-point. If a sequence of consecutive reactions is treated as a unique process the kinetic parameters obtained are false.

The aim of this paper is to investigate a sequence of two reactions in order to determine how such processes could be separated and characterized correctly by kinetic analysis under non-isothermal conditions. The case of two parallel first-order reactions has already been studied [1]. This procedure can easily be generalized to any order. If we denote the conversion of the i -th reaction by α_i , the rate of the reaction will be

$$\frac{d\alpha_i}{dt} = k_i(1 - \alpha)^{n_i}$$

where k_i = the rate constant of the i -th reaction, n_i = the order of the reaction, α represents the total conversion $\alpha = \sum \alpha_i$, and t = time. The total rate will be

$$\frac{d\alpha}{dt} = \sum \frac{d\alpha_i}{dt} = \sum k_i(1 - \alpha)^{n_i} \quad (1)$$

This rate equation allows the evaluation of kinetic parameters by the least-squares method, comparing the experimental values of $d\alpha/dT$ to those calcu-

lated using eqn. (1). The case of two consecutive first-order reactions was investigated by Heide et al. [2], making certain simplifying assumptions.

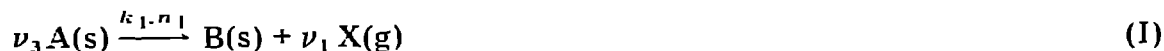
When trying to generalize the method to reactions of orders other than one, we face integrals which cannot be solved in analytic form. Furthermore, if instead of the function $f(\alpha) = (1 - \alpha)^n$, corresponding to the framework of the reaction order model, we use a conversion function given by

$$f(\alpha) = \alpha^n(1 - \alpha)^n$$

even the rate equation of the first process leads to a Tchebishev-type integral, which is seldom solvable.

THE CONSIDERED SYSTEM OF REACTIONS: THE METHOD OF SOLVING THE KINETIC DIFFERENTIAL EQUATIONS

If we consider the sequence



where $\alpha_1, \alpha_2 =$ conversions, $k_1, k_2 =$ rate constants, and $n_1, n_2 =$ reaction orders obtained from the thermogravimetric curve, we can find the total amount of gas evolved ($X(g)$ and $Y(g)$).

The system of kinetic differential equations is then

$$\begin{cases} \frac{d\alpha_1}{dt} = k_1(1 - \alpha_1)^{n_1} \\ \frac{d\alpha_2}{dt} = k_2(\alpha_1 - \alpha_2)^{n_2} \end{cases} \quad (2)$$

where

$$\alpha_1 = \frac{m_{X,t}}{m_{X,\infty}} \quad (3)$$

$$\alpha_2 = \frac{m_{Y,t}}{m_{Y,\infty}} \quad (4)$$

$m_{X,t}$ = the weight of X evolved at time t ; $m_{Y,t}$ = the weight of Y evolved at time t ; $m_{X,\infty}$ = the total amount of X; $m_{Y,\infty}$ = the total amount of Y.

The total conversion, α , will be given by

$$\alpha = \frac{m_{X,t} + m_{Y,t}}{m_{X,\infty} + m_{Y,\infty}} \quad (5)$$

Equations (3) and (4) may be written in the form

$$m_{X,t} = \alpha_1 m_{X,\infty} \quad (3a)$$

$$m_{Y,t} = \alpha_2 m_{Y,\infty} \quad (4a)$$

$$m_{X,\infty} = M_X \times \frac{\nu_1}{\nu_3} \times n_A \quad (6)$$

$$m_{Y,\infty} = M_Y \times \frac{\nu_2}{\nu_3} \times n_A \quad (7)$$

where n_A is the number of moles of A, and M_X and M_Y are the molecular weights of X and Y respectively.

Introducing eqns. (3a, 4a, 6 and 7) in Eqn. (5), one obtains

$$\alpha = \frac{\alpha_1 M_X \nu_1 + \alpha_2 M_Y \nu_2}{\nu_1 M_X + \nu_2 M_Y}$$

Determining α_1 , α_2 and knowing ν_1 , ν_2 , M_X and M_Y we may construct the α - T curve.

In order to solve the system (2) a numerical method [3] was applied, starting with a modified Euler-method and continuing with a predictor-corrector method.

PARTICULAR CASES

For $\nu_1 = 1$, $\nu_2 = 0$, reactions (I) and (II) become



The treatment of the thermogravimetric data as a unique process leads to the kinetic parameters of the reaction (Ia), unmodified by the reaction (IIa) as long as

$$\frac{\partial f_1(\alpha_1)}{\partial \alpha_2} = 0$$

namely

$$\frac{\partial \alpha_1}{\partial \alpha_2} = 0$$

From the point of view of the evaluation of the kinetic parameters of reaction (I), the general case reduces to that stated above, assuming we can measure separately the amount of one of the gases evolved.

For $\nu_1 = 0$ and $\nu_2 = 1$, the sequence of reactions reduces to



The total amount of gas is the amount of Y. The kinetic parameters determined are influenced by reaction (Ib). If the first reaction (Ib) is the slower, the kinetic parameters refer to this step and the amount of B(s) is constant throughout the reaction $d\alpha_1/dt = 0$; α_1 is known as the steady-state conversion. The kinetic parameters refer to reaction (IIb) if this step is slower.

DISCUSSION

The TG curves obtained are presented below, along with the values chosen for the kinetic parameters ($E_1, A_1, n_1, E_2, A_2, n_2$) where

$$k_1 = A_1 e^{-E_1/RT}$$

$$k_2 = A_2 e^{-E_2/RT}$$

and $n_1, n_2 =$ reaction orders; $A_1, A_2 =$ pre-exponential factors; $E_1, E_2 =$ activation energies; $T =$ temperature (K).

The derivative shown in Fig. 1 displays two peaks corresponding to the maximum development of each of the unique processes. Separation occurs because of the differences in A and because reaction (II) is connected to reaction (I).

The same separation is shown in Fig. 2 as in Fig. 1. This is due to the difference in the reaction orders. The reaction rate curve is asymmetric with two different maximum values.

Although we expected to get the same results in Fig. 3 as in Fig. 2, the only difference between reactions (I) and (II) lying in the reaction order, reaction (I) is very slow owing to its order ($n_1 = 4$) and the corresponding peak in the DTG curve disappears (Fig. 3).

A difference of 2 kcal mole⁻¹ in the activation energies is sufficient to produce two separate peaks although the pre-exponential factors tend to reduce the distance between these peaks (Fig. 4).

In the case of equal activation energies and pre-exponential factors, with values of the reaction orders characteristic of processes occurring in non-isothermal conditions and in a region of transition between kinetically and diffusionally-controlled reactions, the DTG curve no longer has two peaks, but one very large one. (This does not correspond to a single turning-point but to a region) (Fig. 5).

With the values shown in Fig. 6, reaction (II) is rapid and the "steady

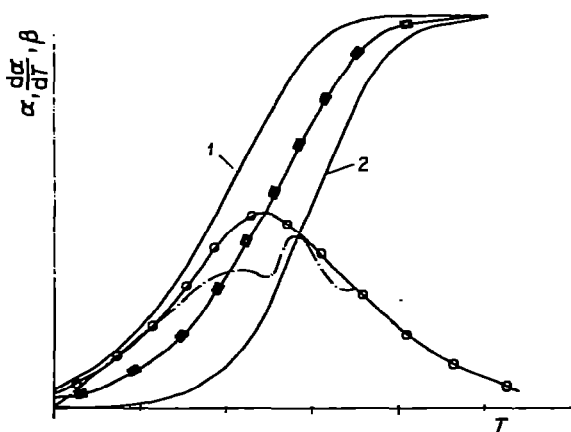


Fig. 1. $E_1 = 22$ kcal mole⁻¹, $A_1 = 2 \times 10^9$ s⁻¹, $n_1 = 1$; $E_2 = 22$ kcal mole⁻¹, $A_2 = 1 \times 10^9$ s⁻¹, $n_2 = 1$. ■, $\alpha(T)$; 1, $\alpha_1(T)$; 2, $\alpha_2(T)$; ●, $\alpha_1 - \alpha_2 = \beta = \beta(T)$; - · - · - ·, $d\alpha/dT = f(T)$ (the scale is much larger for $d\alpha/dT$).

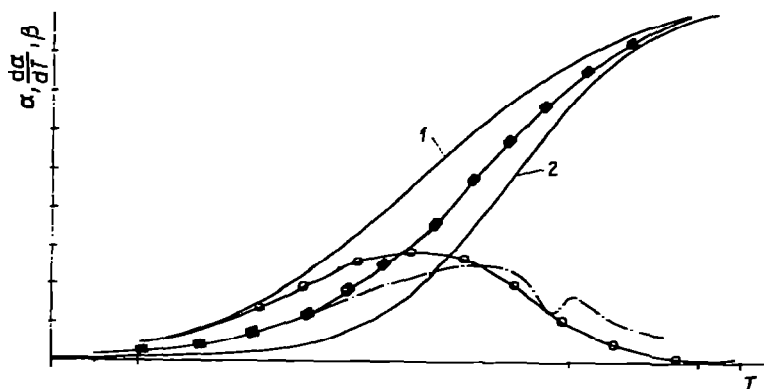


Fig. 2. $E_1 = 20 \text{ kcal mole}^{-1}$, $A_1 = 1 \times 10^7 \text{ s}^{-1}$, $n_1 = 2$; $E_2 = 20 \text{ kcal mole}^{-1}$, $A_2 = 1 \times 10^7 \text{ s}^{-1}$, $n_2 = 1$. For key, see Fig. 1.

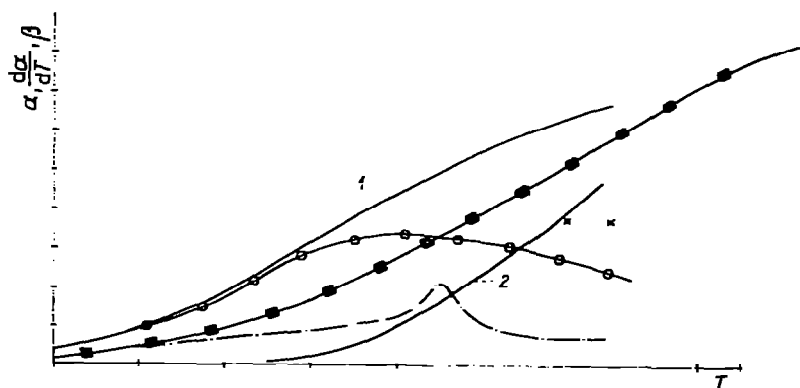


Fig. 3. $E_1 = 20 \text{ kcal mole}^{-1}$, $A_1 = 1 \times 10^7 \text{ s}^{-1}$, $n_1 = 4$; $E_2 = 20 \text{ kcal mole}^{-1}$, $A_2 = 1 \times 10^7 \text{ s}^{-1}$, $n_2 = 2$. For key, see Fig. 1.

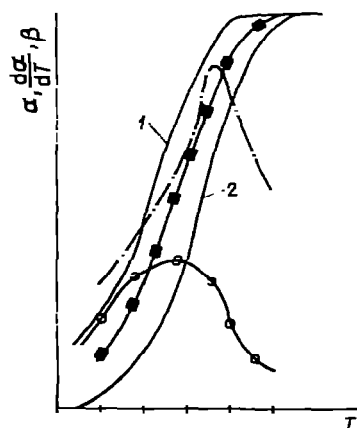
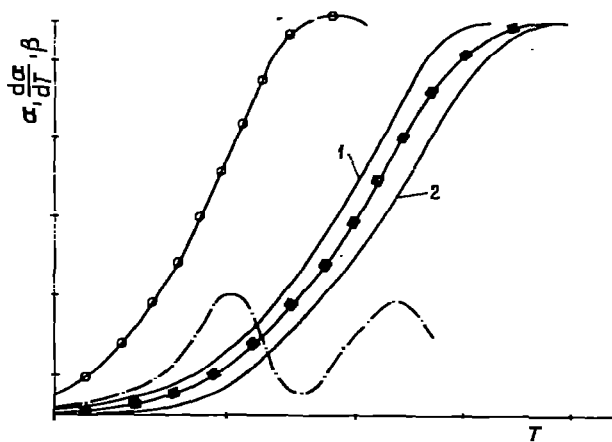


Fig. 4. $E_1 = 24 \text{ kcal mole}^{-1}$, $A_1 = 1.2 \times 10^9 \text{ s}^{-1}$, $n_1 = 1$; $E_2 = 22 \text{ kcal mole}^{-1}$, $A_2 = 1 \times 10^9 \text{ s}^{-7}$, $n_2 = 1$. To simplify the picture one β unit equals 10 α units. For key, see Fig. 1.

Fig. 5. $E_1 = 22 \text{ kcal mole}^{-1}$, $A_1 = 1 \times 10^{10} \text{ s}^{-1}$, $n_1 = 0.6$; $E_2 = 22 \text{ kcal mole}^{-1}$, $A_2 = 1 \times 10^{10} \text{ s}^{-1}$, $n_2 = 0.9$. For key, see Fig. 1.

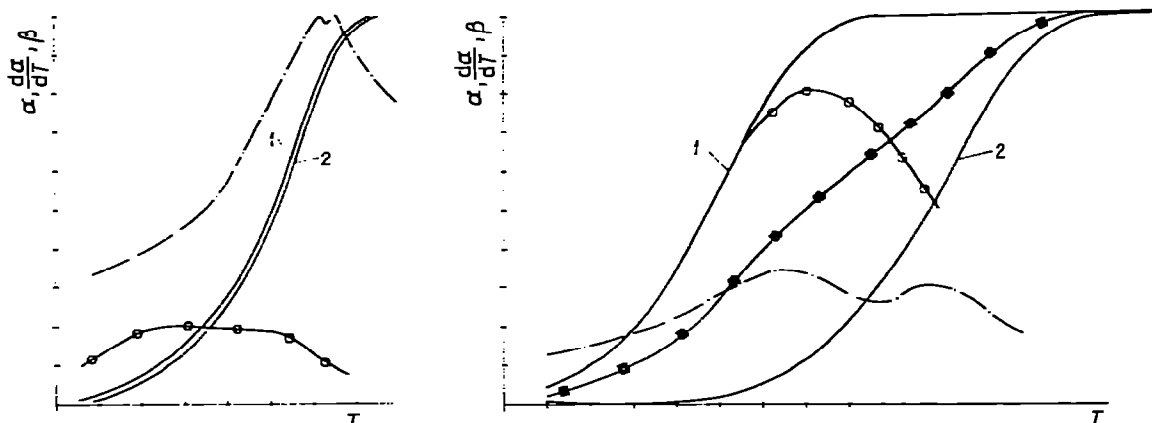


Fig. 6. $E_1 = 20 \text{ kcal mole}^{-1}$, $A_1 = 1 \times 10^8 \text{ s}^{-1}$, $n_2 = 0.2$; $E_2 = 20 \text{ kcal mole}^{-1}$, $A_2 = 1 \times 10^9 \text{ s}^{-1}$, $n_2 = 0.6$. As in Fig. 4, one β unit equals 10 α units. The $\alpha(T)$ curve is missing because $\alpha_2 < \alpha < \alpha_1$. For key, see Fig. 1.

Fig. 7. $E_1 = 22 \text{ kcal mole}^{-1}$, $A_1 = 2 \times 10^9 \text{ s}^{-1}$, $n_1 = 1$; $E_2 = 24 \text{ kcal mole}^{-1}$, $A_2 = 1.2 \times 10^9 \text{ s}^{-1}$, $n_2 = 1$. For key, see Fig. 1.

state" is reached practically as soon as reaction (I) begins. The TG curve is similar to any of the $\alpha-T$ curves obtained in unique processes, and there is only one peak in the DTG curve.

In the case shown in Fig. 7, the starting points of the two TG curves corresponding to α_1 and α_2 are well separated. It could be concluded that the processes could be treated separately, but the minimum of the DTG curve occurs only when $\alpha_2 > 0.3$, so that there would be a major error in the evaluation of the kinetic parameters of reaction (II) if this treatment were in fact carried out.

CONCLUSIONS

The results presented above show that the TG curve is especially influenced by the activation energies. The activation energy determines the starting point of the reaction. Starting points can provide information on the values of the activation energies.

Differences of more than 2 kcal mole^{-1} between the activation energies of the two processes lead to a total separation of the processes. Pre-exponential factors could compensate for this effect only if $A_2/A_1 > 10^2$, for $E_2 - E_1 = 1 \text{ kcal mole}^{-1}$.

The influence of reaction orders lying in a narrow range especially for values between 0 and 1, is not as large as that of activation energies, but is greater than that of the pre-exponential factors.

Generally the rate of reaction (II) is 1/100 of the rate of reaction (I) at a degree of conversion $\alpha_1 \sim \alpha > 0.4$. This means that the region $0.1 < \alpha < 0.3$ could give approximate values for the kinetic parameters of reaction (I). On drawing the calculated TG curve corresponding to these parameters and

comparing it to the real curve, two situations may occur: (1) the final point ($\alpha = 1$) of the two curves is different; (2) the two curves reach the value ($\alpha = 1$) at the same temperature. The former case obviously shows the existence of a complex process and suggests that the evaluation of the kinetic "parameters" should be done by a method "fitting" the calculated and experimental curves. The latter case is typical for either a unique process or for a sequence of hardly separable consecutive reactions. The method of calculation of the TG curves is easily generalized, in the case of more than two reactions, to

$$\alpha = \frac{\sum \alpha_i \nu_i M_i}{\sum \nu_i M_i}$$

Other conversion functions could also be taken into account, such as a function depending on all the products present

$$f_i(\alpha) = f(\alpha_1, \alpha_2, \dots, \alpha_n)$$

The curves presented above were obtained by a program run on a FELIX computer. The program starts calculating conversion at points separated by a 10°C step. Depending on the number of iterations necessary to obtain the desired precision, the step could be cut automatically down to 0.5°C.

On the basis of the kinetic analysis described here, a method of evaluating kinetic parameters has been elaborated and tested on the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This method will be presented in a future paper.

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