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Note

THERMAL DESORPTION IN NON-ISOTHERMAL KINETICS

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Non-isothermal kinetics and thermal desorption are two chapters of physical chemistry which have been developed quite independently, in spite of their very close correlation. To illustrate this correlation, it is sufficient to point out that non-linear heating programmes introduced into thermal desorption by Hickmott and Ehrlich [1] in 1958 were used in non-isothermal kinetics only in 1970–1971 [2], although they were suggested by Flynn and Wall in 1966 [3].

A general kinetic treatment of thermal desorption was given by Smutek and co-workers [4]. The results obtained are easily transposed into non-isothermal kinetics. To do that, one has to change the fraction of the surface covered, θ, a typical variable for surface chemistry with variables used in chemical kinetics (extent of reaction or concentration for homogeneous kinetics and degree of conversion for heterogeneous kinetics). This is the first aim of this paper.

Secondly, the above mentioned treatment is based mainly on the "reaction order" model using for the reaction order, n, only the values $n = 1$, 2 and 3, which are significant in thermal desorption [5]. In spite of the criticism of the "reaction order" model in heterogeneous kinetics, some values of n which fulfil the condition $0 \leqslant n \leqslant 1$ have been proved to be significant. Among them, $n = 2/3$, which properly describes the "contracting sphere" model [6]. Thus, we should get general kinetic equations corresponding to all the values of the reaction order which describe heterogeneous, as well as homogeneous reactions. This is the second aim of this paper.

In order to solve the above mentioned problems, let us consider the decomposition of solids:

$$A(s) \rightarrow B(s) + C(g)$$

described in the framework of the "reaction order" model by the rate equation

$$r = (d\alpha/dt) = A\, e^{-E/RT}(1-\alpha)^n \tag{1}$$

where r stands for the reaction rate, A for the pre-exponential factor, E for the activation energy, α for the degree of conversion and n for the reaction order. Assuming a heating rate which depends on the temperature according to the relationship

$$\frac{dT}{dt} = a_x T^{2-x}$$

where $x = 0$, 1 and 2 for hyperbolic, exponential and linear programmes of heating respectively, through integration, from eqn. (1), one gets:

$$\left.\begin{array}{ll} \ln\dfrac{1}{1-\alpha} & (n=1) \\ \dfrac{1}{(n-1)}\left[\dfrac{1}{(1-\alpha)^{n-1}}-1\right] & (n\neq 1) \end{array}\right\} = \frac{AT^{x}}{a_x}\left[E_x\left(\frac{E}{RT}\right)-\left(\frac{T_0}{T}\right)^{x-1}E_x\left(\frac{E}{RT_0}\right)\right] \tag{2}$$

where

$$E_x(y)=\int_1^{\infty} v^{-x}\,\mathrm{e}^{-yv}\,\mathrm{d}v$$

and T_0 is the initial temperature of the system. Taking into account that

$$E_x\left(\frac{E}{RT_0}\right) \ll E_x\left(\frac{E}{RT}\right)$$

and

$$E_x(y) \simeq \frac{\mathrm{e}^{-y}}{y+x}$$

eqn. (2) becomes

$$\left.\begin{array}{ll} \ln\dfrac{1}{1-\alpha} & (n=1) \\ \dfrac{1}{(n-1)}\left[\dfrac{1}{(1-\alpha)^{n-1}}-1\right] & (n\neq 1) \end{array}\right\} = \frac{A}{a_x}\,\frac{\mathrm{e}^{-E/RT}}{(E/RT)}\,T^{x-1}\left(1+\frac{x}{(E/RT)}\right) \tag{3}$$

From the condition of maximum reaction rate, it turns out that

$$\frac{1}{(1-\alpha)_{\mathrm{m}}^{n-1}}=\frac{nA\,\mathrm{e}^{-E/RT_{\mathrm{m}}}}{a_x(E/RT_{\mathrm{m}})}\,T_{\mathrm{m}}^{x-1} \quad (n\neq 0) \tag{4}$$

where the subscript m refers to values corresponding to the maximum referred to above.

Equations (3) and (4) lead easily to

$$\frac{A}{a_x}\,\frac{\mathrm{e}^{-E/RT_{\mathrm{m}}}}{(E/RT_{\mathrm{m}})}\,T_{\mathrm{m}}^{x-1}=\frac{(E/RT_{\mathrm{m}})+x}{(E/RT_{\mathrm{m}})+nx} \quad (n\neq 0) \tag{5}$$

Taking into account eqns. (3) and (5), the remaining fraction of the volatile compound C for the maximum reaction rate, r_{m}, can be expressed by

$$\left.\begin{array}{ll} (1-\alpha)_{\mathrm{m}} \simeq \dfrac{1}{\mathrm{e}}\,\dfrac{(E/RT_{\mathrm{m}})+2x}{(E/RT_{\mathrm{m}})+x} & (n=1) \\ (1-\alpha)_{\mathrm{m}} = \left\{\dfrac{(E/RT_{\mathrm{m}})+nx}{n[(E/RT_{\mathrm{m}})+x]}\right\}^{1/(n-1)} & (n\neq 1),\ (n\neq 0) \end{array}\right\} \tag{6}$$

Equations (1), (5) and (6) allow the calculation of the maximum reaction rate as follows.

$$\left.\begin{aligned} r_m &\simeq \frac{1}{e} a_x T_m^{1-x} \frac{E}{RT_m} \frac{(E/RT_m)+2x}{(E/RT_m)+x} && (n=1) \\ r_m &= a_x T_m^{1-x} \frac{E}{RT_m} \frac{(E/RT_m)+x}{(E/RT_m)+nx} \left\{ \frac{(E/RT_m)+nx}{n[(E/RT_m)+x]} \right\}^{n/(n-1)} && (n \neq 1), (n \neq 0) \end{aligned}\right\} \tag{7}$$

It is to be noticed that eqns. (1)–(7) are valid not only for $n = 1, 2, 3$, but also for values of n less than unity, which might properly describe some cases of decomposition.

The solutions of eqns. (7) with respect to E are

$$\left.\begin{aligned} E &\simeq r_m \frac{RT_m^x}{a_x} \frac{(E/RT_m)+x}{(E/RT_m)+2x} e && (n=1) \\ E &= r_m \frac{RT_m^x}{a_x} \frac{(E/RT_m)+nx}{(E/RT_m)+x} \left\{ \frac{n[(E/RT_m)+x]}{(E/RT_m)+nx} \right\}^{n/(n-1)} && (n \neq 1), (n \neq 0) \end{aligned}\right\} \tag{8}$$

Equations (2)–(8) are valid for heterogeneous kinetics and were derived by changing the surface concentration, which proved to be useful in the kinetic investigation of thermal desorption [4] with the degree of conversion α.

As concerns eqn. (8) for $n \neq 1$ and $n \neq 0$, this is a general form of a similar equation used in non-isothermal kinetics which looks as follows

$$E \simeq RT_m^2 \left(\frac{d\alpha}{dT} \right)_m n^{n/(n-1)} \qquad (n > 0, \neq 1)$$

In order to check the validity of eqns. (8), we tried to evaluate the activation energy for the dehydration of calcium oxalate. For this reaction taking place in air at atmospheric pressure, the following data are considered: $T_m = 509$ K, $r_m = 1.75 \times 10^{-1}$ min^{-1}, $a_2 = 10$ K min^{-1}. Taking into account the value of the reaction order which, according to the literature data, is near unity, the first eqn. (8) was used. Firstly, considering only the factor $r_m(RT_m^2/a_2)e$, the value 24500 cal mole^{-1} was obtained. This value was used to calculate (E/RT_m) and then the value of the activation energy was recalculated, using the complete formula (8). Finally, the value $E = 22700$ cal mole^{-1} was obtained, in satisfactory agreement with the values reported in literature [8].

This is only one application of the results obtained in the kinetic investigation of thermal desorption in non-isothermal kinetics. In a later paper, some other applications will be presented.

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