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Note

REMARKS ON THE RELATIONSHIP BETWEEN ISOTHERMAL AND NON-ISOTHERMAL KINETIC RESULTS. A NEW METHOD FOR THE KINETIC ANALYSIS OF ISOTHERMAL DATA

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It is well known that the kinetic analysis of chemical reactions from non-isothermal experiments has usually been carried out [1] by means of the fundamental equation

$$\frac{d\alpha}{dt} = A \exp(-E/RT)\, f(\alpha) \tag{1}$$

where α is the conversion at time t,f(α) is a function depending on the actual reaction mechanism, A is the pre-exponential of Arrhenius, E is the activation energy, and the other parameters have their usual meaning.

However, the validity of eqn. (1) was criticised by McCallum and Tanner [2] who considered that since α is a function of both temperature and time

$$\alpha = \alpha(T, t) \tag{2}$$

the total differential is given by the following constitutive equation

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \left(\frac{\partial\alpha}{\partial T}\right)_t \left(\frac{\partial T}{\partial t}\right)_\alpha \tag{3}$$

From eqn. (3) they concluded that only when $(\partial T/\partial t)_\alpha = 0$ (i.e., under isothermal conditions) can we write

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_T \tag{4}$$

Norwisz [3] and Dutta and Ryan [4] have recently evaluated the function $(\partial\alpha/\partial T)_t$ under isothermal conditions and derived the following expression for the reaction rate under a linear heating programme (i.e., when $(\partial T/\partial t) = \beta$)

$$\frac{d\alpha}{dt} = A \exp(-E/RT)\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right] f(\alpha) \tag{5}$$

where T_0 is the initial temperature.

Koch and Stilkerieg [5] have carried out a comparative study of the applicability of eqns. (1) and (4) by evaluating non-isothermal data from more than 90 homogeneous reactions, and they have observed that only the kinetic parameters calculated from eqn. (1) show very good agreement with those determined from isothermal runs. Therefore, these authors have concluded that eqn. (5) seems to be utterly unfounded, but have not reported any theoretical support to their finding.

The scope of the present paper is, firstly, to show why eqn. (5) does not work, and secondly, to explore the applicability of the mathematical expression of $(\partial\alpha/\partial T)_t$, deduced by Norwisz [3], in order to calculate kinetic parameters from isothermal data.

THEORETICAL

Relationship between isothermal and non-isothermal differential kinetic equations

It is well known that the rate of a chemical reaction under isothermal conditions can usually be described by the equation

$$\frac{d\alpha}{dt} = f(\alpha)\, g(T) \qquad (6)$$

g(T) being expressed by the Arrhenius law

$$g(T) = k = A \exp(-E/RT) \qquad (7)$$

and k being the constant rate at a particular value of T.

By integrating eqn. (6) under isothermal conditions, Norwisz [3] has obtained the following expression

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(T) \int_0^t dt = g(T)\, t \qquad (8)$$

By introducing the designation

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \qquad (9)$$

and defining the function h(α) as the antifunction of g(α) he obtains

$$\alpha = h[g(T)\, t] \qquad (10)$$

Differentiation of expression (10) with respect to T leads to

$$\left(\frac{\partial\alpha}{\partial T}\right)_t = \frac{AE}{RT^2} \exp(-E/RT)\, f(\alpha)\, t \qquad (11)$$

Taking into account that under a linear heating programme

$$T = T_0 + \beta t \qquad (12)$$

relationship (5) can be obtained from eqns. (3), (4), (7), (11) and (12).

However, we must point out that eqn. (8) cannot be used for describing non-isothermal experiments. The reason is that under these conditions the temperature is a function of time. Thus, these two variables cannot be separated in order to ingrate eqn. (6). In other words, under non-isothermal conditions, instead of eqn. (8), we should write

$$g(\alpha) = \int_0^t g(T)\, dt \tag{13}$$

Therefore, bearing in mind that h(α) is the antifunction of g(α), we obtain from eqn. (13)

$$\alpha = h\left[\int_0^t g(T)\, dt\right] \tag{14}$$

and deriving eqn. (14) with respect to time

$$\frac{d\alpha}{dt} = h'\left[\int_0^t g(T)\, dt\right] g(T) \tag{15}$$

On the other hand, as function (14) is continuous and monotonous in all the α range, the following relationship applies

$$h'(\alpha) = \frac{1}{g'(\alpha)} \tag{16}$$

which, taking into account that $g'(\alpha) = 1/f(\alpha)$, becomes

$$h'(\alpha) = f(\alpha) \tag{17}$$

By substituting eqns. (7) and (17) into eqn. (15), we obtain eqn. (1).

In summary, we can conclude that eqn. (1), instead of eqn. (5), is the one describing the differential kinetic data obtained under non-isothermal conditions, whatever the mathematical function relating temperature and time.

A new method for analysing isothermal data of chemical reactions

The previous considerations permit us to conclude that eqn. (11) cannot be used for performing the kinetic analysis of non-isothermal data, although it must be fulfilled by isothermal results.

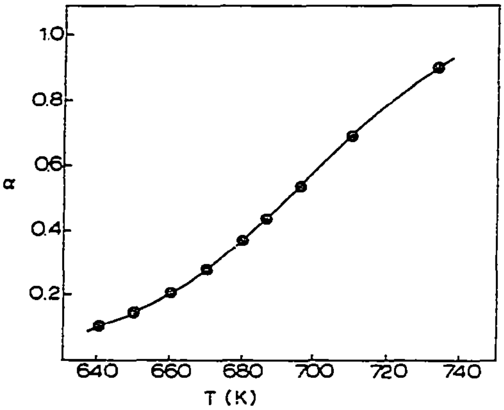
By integrating eqn. (11) at constant time, we obtain

$$\frac{1}{t_c} g(\alpha)\, t_c = A \exp(-E/RT) \tag{18}$$

which after rearranging in logarithmic form becomes

$$\ln\left[\frac{1}{t_c} g(\alpha)_{t_c}\right] = \ln A - \frac{E}{RT} \tag{19}$$

Therefore, α values would be taken at a time t_c from a set of isothermal runs and represented in agreement with eqn. (19), once the reaction mechanism is known. The plot of $\ln[1/t_c)\ g(\alpha)_{t_c}]$ vs. $1/T$ gives a straight line whose slope and intercept give the activation energy and the pre-expo-



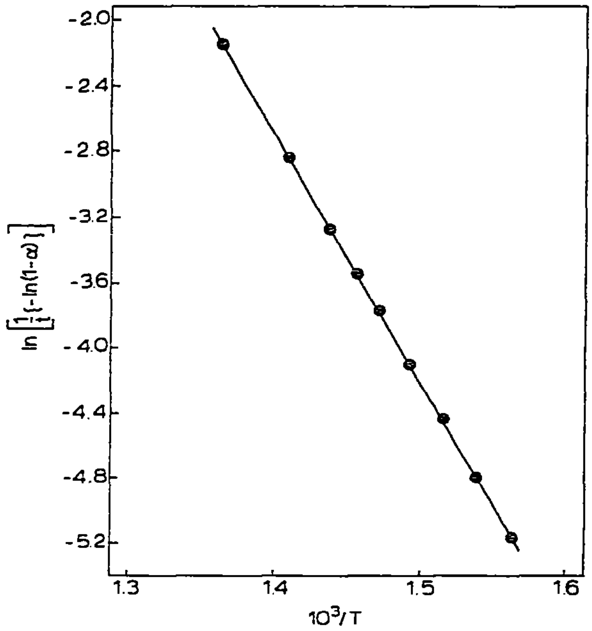


Fig. 1. Values of α at a time $t_c = 20$ min as a function of the temperature of the corresponding isothermal runs.

Fig. 2. Plot of the data in Fig. 1, according to eqn. (19). $E = 30$ kcal mole^{-1}; $A = 9.98 \times 10^7$ min^{-1}; $r = -1.0000$.

nential factor of Arrhenius, respectively.

In order to test the applicability of eqn. (19) we have calculated a series of isothermal curves by assuming first order kinetics (i.e., $g(\alpha) = -\ln(1 - \alpha)$] and the following kinetic parameters: $E = 30$ kcal mole^{-1}, $A = 10^8$ min^{-1}. Accordingly, the values of the rate constant obtained from eqn. (7) at a number of temperatures, ranging from 640 to 740 K, have been substituted into eqn. (8) in order to obtain the values of α as a function of time. The values of α taken from these isothermal curves at a time $t_c = 20$ min are shown in Fig. 1 against the corresponding temperatures.

From the data in Fig. 1 the plot in Fig. 2 can be drawn. The kinetic parameters obtained from this Fig. ($E = 30$ kcal mole^{-1} and $A = 9.98 \times 10^7$ min^{-1}) agree very well with those previously assumed for constructing the isotherms.

The above results demonstrate rather clearly that eqn. (19) supplies a good procedure for a rapid determination of the kinetic parameters, once the reaction mechanism has been settled from the analysis of a single α—t isothermal curve. This method avoids the rather cumbersome calculation of the rate constant from each isotherm involved in the conventional methods.

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