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Some theoretical considerations on the degree of conversion, α_{max}, for various heating programs

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Abstract

This paper introduces $\alpha_{t,max}$ and $\alpha_{T,max}$ for the values of the degree of conversion corresponding to maximum values of $d\alpha/dt$ and $d\alpha/dT$ respectively. It is shown that for constant heating rate $\alpha_{t,max} = \alpha_{T,max}$ and that in the general case $\alpha_{t,max} \neq \alpha_{T,max}$. For a heating rate of the form βT^a, $\alpha_{t,max} \simeq \alpha_{T,max}$.

INTRODUCTION

In nonisothermal kinetics physical and chemical changes are followed while temperature changes in time [1–3]. Thus

$$T = \theta(t) \tag{1}$$

or

$$t = \phi(T) \tag{2}$$

Relationships (1) and (2) actually define the same heating program, T and t being independent variables.

The heating rate is defined as dT/dt and is given by

$$\frac{dT}{dt} = \theta'(t) \tag{3}$$

or

$$\frac{dT}{dt} = \frac{1}{\phi'(T)} = h(T) \tag{4}$$

Relationships (3) and (4) show that a variable heating rate can be expressed either as a function of t or as a function of T.

Starting from the classical isothermal kinetic equation

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{5}$$

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where I is constant and with the classical conditions

$$A = \text{constant} \tag{6}$$

$$E = \text{constant} \tag{7}$$

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{8}$$

$$n = \text{constant} \qquad m = \text{constant} \qquad p = \text{constant} \tag{9}$$

the form (8) of $f(\alpha)$ being suggested by Šesták and Berggren [4], considering eqn. (5) as a postulated primary isothermal differential kinetic equation (p-PIDKE) and applying to it the classical nonisothermal change (CNC) using eqn. (3) or (4) [2,3], the following nonisothermal differential kinetic equations are obtained:

$$\frac{d\alpha}{dt} = A f(\alpha) \exp\left(-\frac{E}{R\theta(t)}\right) \tag{10}$$

$$\frac{d\alpha}{dT} = \frac{A}{h(T)} f(\alpha) \exp\left(-\frac{E}{RT}\right) \tag{11}$$

As T and t are dependent variables, eqns. (10) and (11) are equivalent.

THE CONCEPT OF α_{max}

The α_{max} value corresponds to the maximum reaction rate. As in nonisothermal conditions two variables (namely t and T) should be considered and one has to introduce the following values of α_{max}: $\alpha_{t,max}$ as a solution of the equation

$$\left(\frac{d^2\alpha}{dt^2}\right)_{max} = 0 \tag{12}$$

and $\alpha_{T,max}$ as a solution of the equation

$$\left(\frac{d^2\alpha}{dT^2}\right)_{max} = 0 \tag{13}$$

Attempts will be made to answer the question as to whether $\alpha_{t,max}$ equals $\alpha_{T,max}$ or not, and of the eventual conditions for such an equality, which may arise, through the following considerations.

From the obvious relationship

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} \tag{14}$$

and taking into account eqn. (4) one obtains

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} h(T) \tag{15}$$

From eqn. (15) through differentiation and division by $\mathrm{d}t$ one obtains successively

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\mathrm{d}t = \frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}h(T)\ \mathrm{d}T + \frac{\mathrm{d}}{\mathrm{d}T}h'(T)\ \mathrm{d}T \tag{16}$$

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} = \frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}h^2(T) + \frac{\mathrm{d}}{\mathrm{d}T}h'(T)h(T) \tag{17}$$

From eqn. (17) for

$$h'(T) = 0 \tag{18}$$

or

$$h(T) = \beta = \text{constant} \tag{19}$$

one obtains

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} = \frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}\beta^2 \tag{20}$$

In this case relationships (12) and (13) are equivalent, thus

$$\alpha_{t,\max} = \alpha_{T,\max} = \alpha_{\max} \tag{21}$$

For the general case when

$$h'(T) \neq 0 \tag{22}$$

eqns. (12) and (13) cannot be simultaneously fulfilled due to the term $(\mathrm{d}\alpha/\mathrm{d}T)h'(T)h(T)$, thus

$$\alpha_{t,\max} \neq \alpha_{T,\max} \tag{23}$$

EQUATIONS TO EVALUATE $\alpha_{t,\max}$ AND $\alpha_{T,\max}$

As T and t are dependent variables any of them can be used in subsequent calculations. Taking into account that it is easy to pass from one variable to the other, the variable T will be used in the following.

The derivative of relationship (11) with respect to T is

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2} = -\frac{A}{h^2(T)}h'(T)f(\alpha)\exp\left(-\frac{E}{RT}\right) + \frac{A}{h(T)}f'(\alpha)\exp\left(-\frac{E}{RT}\right)\frac{\mathrm{d}\alpha}{\mathrm{d}T}$$
$$+\frac{A}{h(T)}f(\alpha)\exp\left(-\frac{E}{RT}\right)\frac{E}{RT^2} \tag{24}$$

Taking into account eqn. (11), eqn. (24) turns into

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2} = \frac{\mathrm{d}\alpha}{\mathrm{d}T}\left(\frac{A}{h(T)}f'(\alpha)\exp\left(-\frac{E}{RT}\right) + \frac{E}{RT^2} - \frac{h'(T)}{h(T)}\right) \tag{25}$$

By introducing this last result in eqn. (17) we obtain

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2} = \frac{\mathrm{d}\alpha}{\mathrm{d}T}\left(Ah(T)f'(\alpha)\exp\left(-\frac{E}{RT}\right) + \frac{E}{RT^2}h^2(T)\right) \tag{26}$$

Equation (25) taking into account condition (13) leads to

$$Af'(\alpha_{T,\max})\exp\left(-\frac{E}{RT_{\max}}\right) + \frac{E}{RT_{\max}^2}h(T_{\max}) - h'(T_{\max}) = 0 \tag{27}$$

where $T_{\max}$ in the temperature for which condition (13) is valid.

Correspondingly eqn. (26) with condition (12) leads to

$$Af'(\alpha_{t,\max})\exp\left(-\frac{E}{RT^*}\right) + \frac{E}{RT^{*2}}h(T^*) = 0 \tag{28}$$

where temperature T^* for which $\alpha = \alpha_{t,\max}$ is given by

$$T^* = \theta(t_{\max}) \tag{29}$$

Besides relationships (27) and (28) derived from relationships (12) and (13) the integral relationships obtained from (10) and (11) will be considered. Thus

$$g(\alpha_{t,\max}) = A\int_0^{t_{\max}}\exp\left(-\frac{E}{R\theta(t)}\right)\mathrm{d}t \tag{30}$$

$$g(\alpha_{T,\max}) = A\int_{T_0\sim 0}^{T_{\max}}\frac{\exp\left(-\frac{E}{RT}\right)}{h(T)}\mathrm{d}T \tag{31}$$

$$g(\alpha) = \int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} \tag{32}$$

$$T_0 = \theta(t=0) \tag{33}$$

Applying in relationship (30) the variable change $t \to T$ one obtains

$$g(\alpha_{t,\max}) = A\int_{T_0\sim 0}^{T^*}\frac{\exp\left(-\frac{E}{RT}\right)}{h(T)}\mathrm{d}T \tag{34}$$

Using the second average theorem in eqns. (31) and (32) [5,6] one can write

$$g(\alpha_{T,\max}) = \frac{A}{h(T_1)}\int_0^{T_{\max}}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{35}$$

$$g(\alpha_{t,\max}) = \frac{A}{h(T_2)}\int_0^{T^*}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{36}$$

where $T_1 \in (0, T_{\max})$ and $T_2 \in (0, T^*)$. The values of T_1 and T_2 depend upon the form of $h(T)$.

Taking into account the approximation [7]

$$\int_0^T \exp\left(-\frac{E}{RT}\right) \mathrm{d}T \cong \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right) Q\left(\frac{E}{RT}\right) \tag{37}$$

from eqns. (35) and (36) one obtains

$$g(\alpha_{T,\max}) = \frac{A}{h(T_1)} \frac{RT_{\max}^2}{E} \exp\left(-\frac{E}{RT_{\max}}\right) Q\left(\frac{E}{RT_{\max}}\right) \tag{38}$$

$$g(\alpha_{t,\max}) = \frac{A}{h(T_2)} \frac{RT^{*2}}{E} \exp\left(-\frac{E}{RT^*}\right) Q\left(\frac{E}{RT^*}\right) \tag{39}$$

From relationships (27) and (28) taking into account eqns. (38) and (39) it follows that

$$\frac{g(\alpha_{T,\max}) f'(\alpha_{T,\max})}{Q\left(\frac{E}{RT_{\max}}\right)} + \frac{h(T_{\max})}{h(T_1)} - \frac{h'(T_{\max})}{h(T_1)} \frac{RT_{\max}^2}{E} = 0 \tag{40}$$

$$\frac{g(\alpha_{t,\max}) f'(\alpha_{t,\max})}{Q\left(\frac{E}{RT^*}\right)} + \frac{h(T^*)}{h(T_2)} = 0 \tag{41}$$

For the condition (19) eqns. (40) and (41) turn into

$$g(\alpha_{\max}) f'(\alpha_{max}) = -Q\left(\frac{E}{RT_{\max}}\right) \tag{42}$$

a relationship which was also obtained by other authors [8].

In another paper [9] the values $\alpha_{\max}$ for various functions $f(\alpha)$ have been determined. It is beyond the scope of this work to calculate $\alpha_{\max}$ for various forms of $f(\alpha)$. The first utilization of conditions (12) and (13) in nonisothermal kinetics with constant heating rate is due to Kissinger [10].

As relationships (40) and (41) contain $h(T_1)$ and $h(T_2)$, these cannot be used to evaluate $\alpha_{T,\max}$ and $\alpha_{t,\max}$.

Nevertheless without demonstration one has to admit intuitively the following:

(1) If

$$\frac{h(T_{\max})}{h(T_1)} \gg \frac{h'(T_{\max})}{h(T_1)} \frac{RT_{\max}^2}{E} \tag{43}$$

then

$$T_1 \simeq T_2 \tag{44}$$

$$T_{\max} \simeq T^* \tag{45}$$

Thus

$$\alpha_{T,\max} \simeq \alpha_{t,\max} \tag{46}$$

(2) There is an infinity of heating programs $h(T)$ which fulfil condition (43) and

$$\frac{h(T_{\max})}{h(T_1)} \simeq 1 \tag{47}$$

$$\frac{h(T^*)}{h(T_1)} \simeq 1 \tag{48}$$

Thus $\alpha_{T,\max} \simeq \alpha_{t,\max}$ equals approximately, the $\alpha_{\max}$ value given by eqn. (42).

APPLICATIONS FOR $h(T) = \beta T^a$

In the general heating program given by

$$h(T) = \beta T^a \tag{49}$$

where β and a are constants, the $a = 0$ value corresponds to the linear program, the $a = 1$ value to the exponential one and $a = 2$ value to the hyperbolic program.

Relationships (31) and (34), taking into account eqn. (49), turn into

$$g(\alpha_{T,\max}) = A \int_0^{T_{\max}} \frac{\exp\left(-\frac{E}{RT}\right)}{\beta T^a} \mathrm{d}T \tag{50}$$

$$g(\alpha_{t,\max}) = A \int_0^{T^*} \frac{\exp\left(-\frac{E}{RT}\right)}{\beta T^a} \mathrm{d}T \tag{51}$$

In these cases there is no need to introduce the temperatures T_1 and T_2 as the integrals from eqns. (50) and (51) can be calculated with good precision [7]. Thus

$$\int_0^T y^r \exp\left(-\frac{E}{Ry}\right) \mathrm{d}y \cong \frac{R}{E} T^{r+2} \exp\left(-\frac{E}{RT}\right) Q_r\left(\frac{E}{RT}\right) \tag{52}$$

where if

$$\frac{E}{RT} = x \tag{53}$$

$Q_r(r)$ is given by [7]

$$Q_r(x) = \frac{x+1}{x+3+r} \tag{54}$$

or more precisely

$$Q_r(x) = \frac{x^2 + x(4+r)}{x^2 + r(6+2r) + (r+3)(r+2)} \tag{55}$$

Using these approximations one obtains

$$h(T_1) = h(T_2) = 1 \tag{56}$$

and relationships (35) and (36) turn into

$$g(\alpha_{T,\max}) = \frac{A}{\beta}\frac{RT_{\max}^{2-a}}{E}\exp\left(-\frac{E}{RT_{\max}}\right)Q_{-a}\left(\frac{E}{RT_{\max}}\right) \tag{57}$$

$$g(\alpha_{t,\max}) = \frac{A}{\beta}\frac{RT^{*2-a}}{E}\exp\left(-\frac{E}{RT^*}\right)Q_{-a}\left(\frac{E}{RT^*}\right) \tag{58}$$

Taking into account eqn. (48), relationships (27) and (28) can be written as

$$Af'(\alpha_{T,\max})\exp\left(-\frac{E}{RT_{\max}}\right) + \frac{E}{RT_{\max}^2}\beta T_{\max}^a - a\beta T_{\max}^{a-1} = 0 \tag{59}$$

$$Af'(\alpha_{t,\max})\exp\left(-\frac{E}{RT^*}\right) + \frac{E}{RT^{*2}}\beta T^{*a} = 0 \tag{60}$$

From relationships (59) and (60) taking into account eqns. (57) and (58) one obtains

$$g(\alpha_{T,\max})f'(\alpha_{T,\max}) = Q_{-a}(x_{\max})\left(-1 + \frac{a}{x_{\max}}\right) \tag{61}$$

where

$$x_{\max} = \frac{E}{RT_{\max}} \tag{62}$$

and

$$g(\alpha_{t,\max})f'(\alpha_{t,\max}) = -Q_{-a}(x^*) \tag{63}$$

where

$$x^* = \frac{E}{RT^*} \tag{64}$$

Taking into account that in most cases $x \simeq 20$–30 and that $Q_r(x)$ is a function with a very slow variation, one can conclude that the solutions of eqns. (61) and (63) are approximately equal; that is

$$x_{T,\max} \simeq x_{t,\max} \tag{65}$$

as

$$-1 + \frac{a}{x} \simeq -1 \tag{66}$$

As previously stated we do not intend to calculate various values for $\alpha_{\max}$. Nevertheless we shall exemplify the use of relationships (61) and (53) for

$$f(\alpha) = 1 - \alpha \tag{67}$$

TABLE 1

Values of $\alpha_{T,\max}$ calculated for various values of a and $x_{\max}$

a	$x_{\max}$				
	10	20	30	40	50
0	0.571	0.599	0.609	0.615	0.618
1	0.562	0.586	0.608	0.614	0.617
2	0.551	0.593	0.607	0.613	0.617

TABLE 2

Values of $\alpha_{t,\max}$ calculated for various values of a and x^*

a	x^*				
	10	20	30	40	50
0	0.571	0.599	0.609	0.615	0.618
1	0.600	0.615	0.620	0.623	0.625
2	0.632	0.632	0.632	0.632	0.632

using $a = 0, 1, 2$ and various values of $x_{\max}$ and x^*. For $Q_r(x)$ the approximation (54) will be used. The results are listed in Tables 1 and 2.

The data given in Tables 1 and 2 show the validity of relationship (65) the value of $\alpha_{\max}$ being close to 0.60 mainly for $x \simeq 20$–30. One has to note that there are not significant changes of $\alpha_{T,\max}$ and $\alpha_{t,\max}$ with a; thus these values are invariants at the heating programs given by eqn. (49).

CONCLUSIONS

(1) The maximum degrees of conversion $\alpha_{t,\max}$ and $\alpha_{T,\max}$ have been introduced.

(2) For variable heating rates $\alpha_{t,\max} \neq \alpha_{T,\max}$

(3) For constant heating rate $\alpha_{t,\max} = \alpha_{T,\max}$

(4) For heating rates of the form βT^a, $\alpha_{t,\max} \simeq \alpha_{T,\max}$.

The quasicommon value of $\alpha_{t,\max}$ and $\alpha_{T,\max}$ does not depend practically on a.

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