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CONSEQUENCES OF HOLBA–ŠESTÁK EQUATION

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It was proved on the basis of Holba–Šesták equation (1972) that the one is very interesting point of view to define the relative rate of reaction/process. Thereby, the assumption about interconnection between three-parametric equation and thermodynamic condition determined by equilibrium conversion degree in given temperature, is strengthened. Further considerations, still based on analysis of the inequality, made possible proposition of thesis about maximal rate of reaction/process in dynamic conditions in relation to modified van't Hoff's isobar (equation).

Keywords: *dynamic conditions, Holba–Šesták equation, modified van't Hoff's isobar, reaction rate, relative rate of reaction/process, three-parametric equation*

Introduction

Surveying ICTAC Kinetic Project (1996) achievements published in series of publications [1–5], as well as interesting reviews concerned discussed subject [6], it comes to mind that thermodynamic analysis of phenomena connected with thermal degradation of even simple chemical compounds is discreetly passed over in all investigations.

Thermodynamic analysis appears relatively rarely in publications and it generally refers to determination of relation between equilibrium conversion degree (α_{eq}) and/or average enthalpy of thermal dissociation (ΔH). Paulik, Paulik and Erdey in their work [7] present thermal dissociation of $CaCO_3$ towards temperature over (and below) equilibrium conversion degree, what is explained as thermal decomposition process of chemical compound determined by double gas diffusion equilibrium, which exists between interior of the sample, furnace atmosphere and the environment. In other words, it is determined by experimental conditions such as: sample holder, layer thickness, packing of the sample and its dimensions and the ventilation of furnace (Fig. 1 in [7]).

In similar way, although for different conditions, mentioned thermal dissociation of $CaCO_3$ is presented in [8] (Fig. 1 in [8]) or others (Figs 4 and 5 in [9]).

Mentioned considerations [7–9] may be expressed in the following way: equilibrium conversion degree has properties of the function of the state. Its changes are defined by total differential:

$$\mathrm{d}\boldsymbol{\alpha}_{\mathbf{eq}}=\left(\frac{\partial\alpha_{eq}}{\partial T}\right)_{p}\mathrm{d}T+\left(\frac{\partial\alpha_{eq}}{\partial p}\right)_{T}\mathrm{d}p \qquad (1)$$

In case of constant pressure (p) modified form of van't Hoff's isobar is applied [10–17, 18 (p. 210)]:

$$\ln\alpha_{eq}=\frac{\Delta H}{\nu R}\left(\frac{1}{T_{eq}}-\frac{1}{T}\right) \quad p=\text{const.} \qquad (2)$$

In variable pressure conditions in constant temperature (T) one may use van Laar and Planck's isotherm [19]. In the end, according to [9], the following relationship is obtained:

$$\boldsymbol{\alpha}_{\mathbf{eq}}=\alpha_{eq}\frac{p^{\mathbf{o}}}{p} \text{ for } p^{ø}>p\geq\alpha_{eq}p^{ø}$$
$$\text{and } 0\leq\alpha_{eq}\leq 1,\ T=\text{const.} \qquad (3)$$

Little changes of pressure caused by very fast removal of gaseous products induce equilibrium shift from α_{eq} to $\boldsymbol{\alpha}_{\mathbf{eq}}=\alpha_{eq}(T, p)$. Formation of the 'second' equilibrium line according to work [7] may be interpreted this way.

Practical aspect of discussed question was analysed in work [20], especially on Fig. 3 (in [20]), which presents TG curves shift according to method of gaseous products reception. This occurrence is interpreted by Gibbs energy variations induced by simplex of actual pressure to equilibrium pressure.

It should be noted that equilibrium conversion degree is sometimes used in kinetic equations [10, 12, 18 (pp. 145 and 210), 21, 22 (p. 172)] what leads to the formula [23]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha)\left[1-\left(\frac{\alpha}{\alpha_{eq}}\right)^{\nu}\right] \qquad (4)$$

where simplex (α/α_{eq}) is henceforth omitted.

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The aim of the work

The aim of the work is to show that analysis of thermal dissociation in dynamic conditions (linear increase of temperature in time) is natural consequence of function of the state ($d\alpha_{eq}/dT$) transformation into kinetic form strongly dependent on method of gaseous products removal.

The postulate is reached as a consequence of analysis of the universal non-isothermal equation proposed by Šesták *et al.* [18 (pp. 144–5), 21, 22 (p. 172), 24]. Modified rate of a process in dynamic conditions (passing over isothermal conditions) is defined:

$$\frac{d\xi}{dt}=\frac{\frac{d\alpha}{dt}-\alpha q\frac{d\ln\alpha_{eq}}{dT}}{\alpha_{eq}} \qquad (5)$$

Left or right hand side of the Eq. (5) is equal to the classic product $k(T)f(\alpha)$. Equation (5), is called by author of this work as Holba–Šesták equation (H–S). The quoted H–S equation was originally proposed to the kinetic analysis of non-stoichiometric and thus dissociating systems of solid is wider application towards its use in the pressure dependent decompositions. The H–S equation is starting point for further considerations.

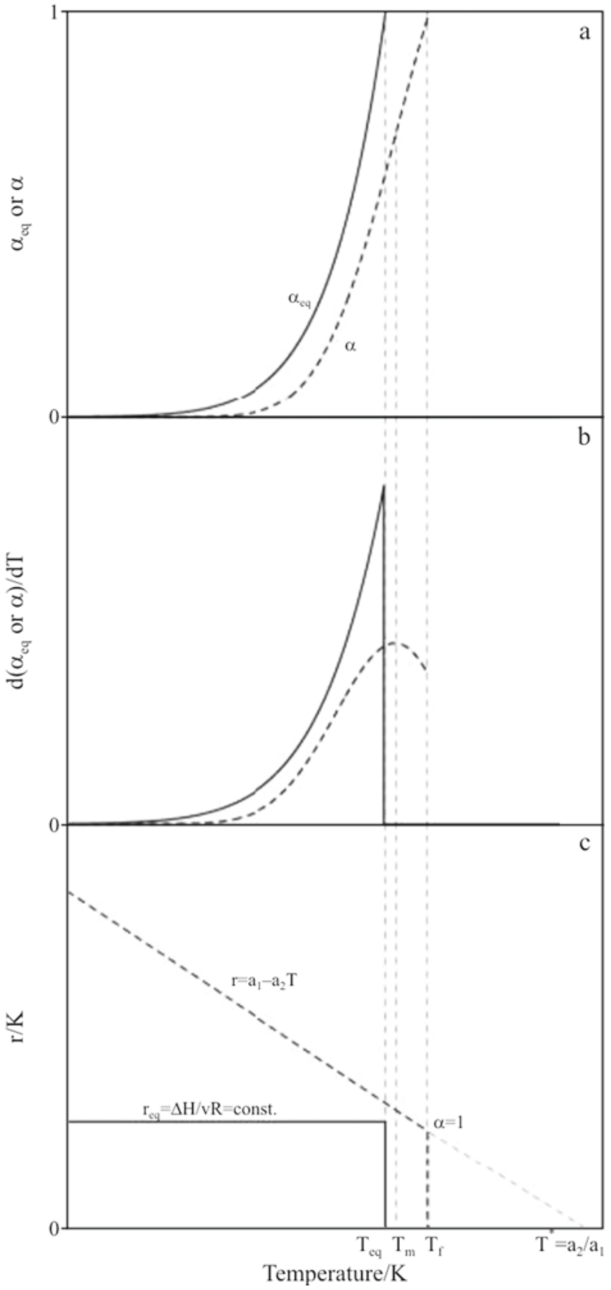

Fig. 1 Temperature relationships of a – equilibrium conversion degree and conversion degree for dynamic conditions, b – derivatives towards conversion degree temperatures (acc. to a), c – relative rate of reaction/process

Consequences of Eq. (5)

According to the canons of kinetic analysis, for condition $d\xi/dt\geq0$ one obtains:

$$\frac{d\alpha}{dt}-\alpha q\frac{d\ln\alpha_{eq}}{sT}\geq0 \qquad (6)$$

what implies inequality:

$$\frac{d\alpha}{dT}\geq\alpha\frac{d\ln\alpha_{eq}}{dT} \quad p\text{=const.} \qquad (7)$$

It may be presented as the left hand side – kinetic one ($d\ln\alpha/dT$), and the right hand side – thermodynamic one ($d\ln\alpha_{eq}/dT$), that is:

$$\frac{d\ln\alpha}{dT}\geq\frac{d\ln\alpha_{eq}}{dT} \qquad (8)$$

Transformation I

Multiplying both sides of inequality (8) (or (7)) by T^2 one obtains:

$$\frac{d\ln\alpha}{dT}T^2\geq\frac{d\ln\alpha_{eq}}{dT}T^2 \qquad (9)$$

For temperature $T\leq T_{eq}$ the left hand side of inequality (9) is the relative rate of reaction/process (introduced in previous work [25] $r=(d\ln\alpha/dT)T^2$). Differentiating Eq. (2) and introducing the result instead the right hand side of (9) one obtains:

$$r\geq\frac{\Delta H}{\nu R} \quad \text{but} \quad r_{eq}=\frac{\Delta H}{\nu R}=\text{const.} \qquad (10)$$

For r_{eq} Eq. (10) is other form of modified van't Hoff's isobar.

While for temperature $T>T_{\mathrm{eq}}$ in inequality (9) the right hand side is 0, because $\alpha_{\mathrm{eq}}=1$, that is $(\mathrm{d}\ln\alpha_{\mathrm{eq}}/\mathrm{d}T)=0$, thus value of the relative rate of reaction/process varies in range:

$$0\le r<\Delta H/vR \tag{11}$$

It is easy to show that inequalities (8), (9) and (11) satisfy linear equation:

$$r=a_1-a_2T \tag{12}$$

which is presented on Fig. 1c. Figure 1 presents situation, when $T_{\mathrm{eq}}<T_{\mathrm{m}}$ (compare with Fig. 5 in [26]).

It should be noticed that the analysis strengthens legitimacy of three-parametric equation proposed in [17]:

$$\ln\alpha=\mathrm{a}_0-a_1/T-a_2\ln T \tag{13}$$

and used in [9, 26–34].

Equation (13) may be presented in other form, assuming:

$$T=T_{\mathrm{f}},\ \text{when } \alpha=1 \tag{14}$$

By elimination of absolute term (a_0), three-parametric Eq. (13) reduces itself to two-parametric of type (2) with additional term containing coefficient a_2. The coefficient is a measure of both intensity of the reaction/process and the distance from equilibrium line:

$$\ln\alpha=a_1\left(\frac{1}{T_{\mathrm{f}}}-\frac{1}{T}\right)-a_2\ln\frac{T}{T_{\mathrm{f}}} \tag{15}$$

Equation (15) is linear relationship without absolute term (i.e. of type: $y=a_1x_1+a_2x_2$).

In his book [18] Šesták classified Eq. (13) to the category of equation–van't Hoff's isobar, broadening the meaning of Eq. (2). Thus, factor $[a_2\ln(T/T_{\mathrm{f}})]$ informs about reduction of strength of van't Hoff's equation in version (2).

Introducing conception of the universal non-isothermal equation, even in version (5), the idea appears that in dynamic conditions thermodynamic barrier is some 'threshold point'. In these conditions results of investigations are evaluated as well descriptively as by generating mass integrals presented in [35].

As a result of interconnection of Eqs (5) and (8), as well as the next ones, one may assume strong relationship between: three-parametric Eq. (13) or (15), as well as (12), and thermodynamic analysis of the phenomenon [25].

Mentioned considerations may be presented in simpler way starting from inequality (18) and using three-parametric Eq. (13) or (15). Left hand side of inequality (8) is presented as:

$$\frac{\mathrm{d}\ln\alpha}{\mathrm{d}T}=\frac{a_1}{T^2}-\frac{a_2}{T} \tag{16}$$

while right hand side (from Eq. (2)):

$$\frac{\mathrm{d}\ln\alpha_{\mathrm{eq}}}{\mathrm{d}T}=\frac{\Delta H}{vRT^2} \tag{17}$$

Comparing Eq. (16) with (17) and multiplying by T^2 one obtains relations (10) and (12) and:

$$a_1-a_2T\ge\frac{\Delta H}{vR} \tag{18}$$

$$r\ge r_{\mathrm{eq}} \tag{19}$$

According to the inequality (7) and notation (19), the relative rate of reaction/process is assessed to the level of $\Delta H/vR=r_{\mathrm{eq}}$.

Transformation II

According to the carried out considerations and Fig. 1b, as well as for temperature of maximal reaction rate (T_{m}) satisfying both possibilities $T_{\mathrm{m}}\gtrless T_{\mathrm{eq}}$, follows the inequality:

$$r_{\mathrm{eq}}\ge r_{\mathrm{m}} \tag{20}$$

Left hand side of inequality (20) is constant ($r_{\mathrm{eq}}=\Delta H/vR$=const., Eq. (10)).

For the right hand side, for Eq. (12) and condition $\mathrm{d}^2\alpha/\mathrm{d}T^2=0$ and after transformations, one obtains (Appendix I):

$$r_{\mathrm{m}}=a_1/\sqrt{1+a_2} \tag{21}$$

At last the inequality is obtained:

$$\Delta H\ge vRa_1/\sqrt{1+a_2} \tag{22}$$

In relationship (22), for $a_2=0$ – equilibrium state ($a_1=\Delta H/vR$ [25]), one obtains identity:

$$\Delta H=vRa_1=vR\frac{\Delta H}{vR},\ T_{\mathrm{m}}=T_{\mathrm{eq}}$$

The right hand side of Eq. (20), according to classic methods, is presented in Appendix II.

Continuing interpretation of inequality (20) one may propose a thesis that rate of reaction/process in temperature T_{m} cannot be higher than maximal gradient ($\mathrm{d}\alpha_{\mathrm{eq}}/\mathrm{d}T$) in temperature T_{eq}. Hence, there's adopted inequality as hypothesis other than Eq. (20), which is proved by *ex post* deduction. Postulated inequality is expressed in the following way:

$$\left(\frac{\mathrm{d}\alpha_{\mathrm{eq}}}{\mathrm{d}T}\right)_{\mathrm{T=T_{eq}}}\ge\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\mathrm{T=T_m}} \tag{23}$$

Left hand side is expressed according to Eq. (17) for $\alpha_{\mathrm{eq}}=1$, $T=T_{\mathrm{eq}}$:

$$\left(\frac{\mathrm{d}\alpha_{\mathrm{eq}}}{\mathrm{d}T}\right)_{T=T_{\mathrm{eq}}}=\frac{\Delta H}{vRT_{\mathrm{eq}}^2}$$

Inequality (23) may be expressed in the following way using concept of relative rate:

$$r_{\mathrm{eq}}\geq r_{\mathrm{m}}\alpha_{\mathrm{m}}\left(\frac{T_{\mathrm{eq}}}{T_{\mathrm{m}}}\right)^2 \qquad (24)$$

Conversion degree (α_m) in temperature T_m is known from [23, 36]:

$$\alpha_{\mathrm{m}}=1-n^{(1-n)^{-1}} \text{ for } n>0 \text{ but } n\neq 1 \qquad (25)$$

$$\alpha_\mathrm{m}=1-\mathrm{e}^{-1}=0.6321 \text{ for } n=1$$

where n is a reaction order and generally equals: $0<n\leq 3$.

For condition p=const., $0\leq\alpha/\alpha_\mathrm{eq}\leq 1$, thus $T_\mathrm{m}>T_\mathrm{eq}$ (Fig. 1a), in other words expression

$$\left[\alpha_{\mathrm{m}}\left(\frac{T_{\mathrm{eq}}}{T_{\mathrm{m}}}\right)^2\right]$$

is always lower than 1, thereby inequality (20) is satisfied.

Returning to inequality (23) one may compare left hand side of Eq. (17) and right one according to Eq. (I-11) (Appendix I):

$$\frac{\alpha_{\mathrm{eq}}}{T_{\mathrm{eq}}^2}\frac{\Delta H}{vR}\geq\frac{\alpha_{\mathrm{m}}}{T_{\mathrm{m}}^2}\frac{a_1}{\sqrt{1+a_2}} \qquad (26)$$

Taking similar values of ratios: $\alpha_\mathrm{eq}/T_\mathrm{eq}^2=1/T_\mathrm{eq}^2$ (and $\alpha_\mathrm{m}/T_\mathrm{m}^2\cong 1/T_\mathrm{m}^2$) one again obtains inequality (22).

Summary and verification of relationships

Transformation I (commentary)

Starting from H–S equation (5) one obtains definition of concept of the relative rate of reaction/process. For relations defined in strict chemical categories (pure individual compounds), Eq. (5) is valid for level described by inequality (19). For lower values one observes deviation between estimation of T_f from linear relationship (12) and final real temperature of reaction/process (Fig. 1c – also Fig. 1 in [25]):

$$0=a_1-a_2T^*, \text{ for the most part:}$$
$$T_\mathrm{f}<a_1/a_2, \text{ because } T^*=a_1/a_2,\ a_2\neq 0 \qquad (27)$$

Some possibility of minimization the effect is direct using of three-parametric equation in form (15), i.e. containing two estimated parameters and temperature T_f satisfying condition $\alpha=1$. Further analyses connected with condition (27) in Eq. (15) are included in next paper.

Transformation II (commentary)

Inequality (20) crosses beyond scope of defining according to H–S equation (5), but it is natural consequence of linear relationship (12) observation, while straight-line crosses level $r_\mathrm{eq}=\Delta H/vR$. But the inequality suggested more important one Eq. (23). It means that in temperature T_eq one observes variation ($\mathrm{d}\alpha_\mathrm{eq}/\mathrm{d}T$) within range [23]:

$$0\leq\frac{\mathrm{d}\alpha_{\mathrm{eq}}}{\mathrm{d}T}\leq\frac{\Delta H}{vRT_{\mathrm{eq}}^2}\alpha_{\mathrm{eq}} \qquad (28)$$

and maximal value is $\mathrm{d}\alpha_\mathrm{eq}/\mathrm{d}T=\Delta H/vRT_\mathrm{eq}^2$, because $\alpha_\mathrm{eq}=1$ for $T=T_\mathrm{eq}$.

Thus, inequality (23) means that in dynamic conditions maximal rate of reaction/process in temperature T_m is always lower (equal) than maximal value according to inequality (28).

For relationships given in work [35] for thermal decomposition of $\mathrm{CaCO_3}$ it was assumed that ΔH=176 kJ mol^{-1}, T_eq=1157.4 K, v=1, that is:

$$\ln\alpha_\mathrm{eq}=18.290-21169.11/T \qquad (29)$$

according to the formula (28) the maximal value:

$$(\mathrm{d}\alpha_{\mathrm{eq}}/\mathrm{d}T)_{T=T_{\mathrm{eq}}}=0.0158\ \mathrm{K}^{-1}$$

According to literature data (Table 1 in [37]) one obtains interval for $(\mathrm{d}\alpha/\mathrm{d}T)_{T=T_\mathrm{m}}=0.01412\ \mathrm{K}^{-1}$ (q=10 K min^{-1}) and 0.011726 K^{-1} (q=50 K min^{-1}).

In spite of the fact that the data concerns $\mathrm{CaCO_3}$ samples, one may consider this example as very good exemplification of validity of inequality (23).

Continuation of this paper [54] is connected with similar analysis of reference substance analyzed in series of works ($\mathrm{CaCO_3}$) [1–5].

Conclusions

1. The H–S equation (5) used in the paper formally can be written as:

$$\mathrm{d}\xi/\mathrm{d}t=k(T)f(\alpha) \qquad (30)$$

In that case, left hand side of the equation has to satisfy condition: $\mathrm{d}\xi/\mathrm{d}t>0$ according to inequality (6). This condition is justified by relative rate of reaction/process introduced in paper [25]:

$$r=-\mathrm{d}\ln\alpha/\mathrm{d}(1/T) \qquad (31)$$

and analogical quantity for equilibrium conversion degree according to [9]:

$$r_\mathrm{eq}=-\mathrm{d}\ln\alpha_\mathrm{eq}/\mathrm{d}(1/T)=\Delta H/vR=\text{const.} \qquad (32)$$

Equation (32) is differential form of modified van’t Hoff’s isobar (2).

In turn, from definition (31) and Eq. (12), the three-parameter Eq. (13) can be obtained and reduced to two-parameter form with experimentally assigned temperature T_f for $\alpha=1$ (15).

These considerations interchangeable indicate requirement of allowing equilibrium relations and comparing in dynamic conditions reaction/process rate with derivative $d\alpha_{eq}/dT$. The H–S equation also suggests successive conclusion, which idea derives from inequality (20).

2. Further considerations on H–S equation (5), in maybe a bit conjectural way, would lead to establishment of inequality (23). One may descriptively assume that in dynamic conditions maximal rate of reaction/process in temperature T_m is lower (or equal) than maximal value:

$$d\alpha_{eq}/dT \text{ in temperature } T_{eq} \qquad (33)$$

Quantity (33) of thermodynamic character strictly connected with equilibrium state, expressed by equilibrium conversion degree, suggests that realistic values $(d\alpha/dT)_{T=T_m}$ satisfy inequality (23).

Appendix I

Linear Eq. (12) in form:

$$\frac{d\alpha}{\alpha dT}T^2=a_1-a_2T \qquad (I\text{-}1)$$

may be presented as:

$$\frac{d}{dT}\left(\frac{d\alpha}{dT}\frac{T^2}{\alpha}\right)+a_2=0 \qquad (I\text{-}2)$$

For condition: $d^2\alpha/dT^2=0$ and notation $(d\alpha/dT)_{T=T_m}=x$ one obtains quadratic equation:

$$\left(\frac{T_m}{\alpha_m}\right)^2x^2-2\frac{T_m}{\alpha_m}x-a_2=0 \qquad (I\text{-}3)$$

From two possible solutions:

$$x=\frac{\alpha_m}{T_m}(1\pm\sqrt{1+a_2}) \qquad (I\text{-}4)$$

one is taken:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=\frac{\alpha_m}{T_m}(1+\sqrt{1+a_2}) \qquad (I\text{-}5)$$

Both sides are multiplied by ratio (T_m^2/α_m) and next one obtains one of two possibilities:

$$r_m=T_m(1+\sqrt{1+a_2}) \qquad (I\text{-}6)$$

For sameness of both temperatures T_f and T_m one directly uses the formula (5) from work [25] $T_f=T_m$:

$$T_m=\frac{a_1}{a_2}[1-(1+a_2)^{-1/2}] \qquad (I\text{-}7)$$

Equation (I-7) may be expressed in form:

$$T_m=\frac{a_1}{1+a_2+\sqrt{1+a_2}} \qquad (I\text{-}8)$$

In both Eqs (I-7) and (I-8) T_m has to be lower than T_f ($T_m<T_f$).

As a result of connection of two Eqs (I-6) and (I-7), one obtains second possibility expressed by formula (21). Introducing (I-7) or (I-8) into (I-5), one obtains:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=\alpha_m\frac{2(1+a_2)+(2+a_2)\sqrt{1+a_2}}{a_1} \qquad (I\text{-}9)$$

It remains one more very interesting possibility of Eq. (I-5) transformation, presenting it in form:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=\frac{\alpha_m}{T_m^2}T_m(1+\sqrt{1+a_2}) \qquad (I\text{-}10)$$

and substituting T_m with (I-7) or (I-8) one obtains:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=\frac{\alpha_m}{T_m^2}\frac{a_1}{\sqrt{1+a_2}} \qquad (I\text{-}11)$$

One may notice that formula (I-11) is extended form of Eq. (21), with which discussion about $a_2=0$ is connected.

Appendix II

Right hand side of inequality (20) may be written in form:

$$r_m=\left(\frac{d\alpha}{dT}\right)_{T=T_m}\frac{T_m^2}{\alpha_m} \qquad (II\text{-}1)$$

Derivative in Eq. (II-1) is equal in classic method to:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=\frac{k_m f(\alpha_m)}{q} \qquad (II\text{-}2)$$

Next, according to the Kissinger law [23]:

$$k_m=\frac{qE}{RT_m^2} \qquad (II\text{-}3)$$

Connecting Eqs (II-2) and (II-3) with (II-1) one obtains:

$$r_m=\frac{E}{R}\frac{f(\alpha_m)}{\alpha_m} \qquad (II\text{-}4)$$

After writing down formula (20) on the left hand side and after rearrangement one obtains:

$$\Delta H \geq vE\frac{f(\alpha_{\mathrm{m}})}{\alpha_{\mathrm{m}}} \qquad \text{(II-5)}$$

According to the postulate $E \geq \Delta H$ [17] and using relationship (II-5) one obtains double inequality

$$\frac{\alpha_{\mathrm{m}}}{f(\alpha_{\mathrm{m}})v} \geq \frac{E}{\Delta H} \geq 1 \qquad \text{(II-6)}$$

Left hand side of the equation can be expressed by relations (25), what is the voice in debate on relations between activation energy (E) and average enthalpy of endothermic reactions (ΔH) described in papers [38, 39] or directly on appropriate selecion of $f(\alpha)$ [40]. In inequality (II-5 and 6) both stoichiometric coefficient v and ΔH ($\Delta_r H$ is in- dependent on temperature and pressure) are related with reaction chemism, but $f(\alpha)$ is selected and E is estimated. The last is a minimum of energy resulted from definition of activation energy, so the second limitation ($\alpha_{\mathrm{m}}/f(\alpha_{\mathrm{m}})v$) has an informative or opinion meaning. In order to appropriate estimation of E one can recommend procedure of its averaging proposed in paper [33] (Eq. (6) in [33]). The method can be verified by simulated data. For example in paper [40] it was assumed that E=100 kJ mol^{-1} – for models D2, D3, D4, A2, A3 and A4, and calculated activation energy was E=98.94 kJ mol^{-1} (acc. to [33]). In the latest works (2007–2008) using isoconversional methods for various heating rates (q) is observed, which are linked to authors (in alphabetical order): Akahira, Budrugeac, Flynn, Friedmann, Kissinger, Ozawa, Segal, Sunose, Wall [41–53].

Hence, left hand side of inequality (II-6) loses its meaning.

Nomenclature

a_0, a_1, a_2	coefficients of three-parametric equation acc. to Eq. (13)
E	activation energy, J mol^{-1}
$f(\alpha)$	function symbol of the argument α
ΔH	enthalpy, J mol^{-1}
$k(T)$	reaction rate constant, min^{-1}
n	reaction order
p	pressure, Pa
q	heating rate, K min^{-1}
r	relative rate of reaction/process, K
R	gas constant, R=8.314 J mol^{-1} K^{-1}
t	time, min
T	temperature, K
α	conversion degree, $0 \leq \alpha \leq 1$
α_{eq}	equilibrium conversion degree, $0 \leq \alpha_{\mathrm{eq}} \leq 1$, p=const
$\boldsymbol{\alpha}_{\mathbf{eq}}$	equilibrium conversion degree, $0 \leq \boldsymbol{\alpha}_{\mathbf{eq}} \leq 1$, T, p=var
ξ	universal non-isothermal conversion degree, acc. to Eq. (5), $0 \leq \xi \leq 1$ [5]
ν	stoichiometric coefficients

Subscripts

eq	equilibrium state
f	final state, α=1
m	point of the maximal rate reaction/process
r	reaction

Superscripts

ø	standard state, $p^{ø} \cong 0.1$ MPa
*	final state acc. to condition (27)

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