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# ON A NEW KINETIC CLASSIFICATION OF THE SOLID–GAS THERMAL DECOMPOSITION REACTIONS WHICH OCCUR IN NON-ISOTHERMAL CONDITIONS

E. URBANOVICI

*Research Institute for Electrotechnics, Sfîntu Gheorghe Branch, Str. Jozsef Attila, Nr. 9, Sfîntu Gheorghe, Judeţul Covasna (Romania)*

E. SEGAL

*Department of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Technology, Polytechnic Institute of Bucharest, Bulevardul Republicii 13, Bucharest (Romania)*

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## ABSTRACT

An analysis of the change in the non-isothermal reaction rate with heating rate presented in a previous paper allowed a classification criterion for the thermal decompositions which occur in non-isothermal conditions to be proposed and a kinetic classification of these reactions to be suggested. This paper attempts to explain the changes in the non-isothermal reaction rate with heating and, thus, to define the above-mentioned criterion and classification.

## INTRODUCTION

The classical non-isothermal rate equation is [1]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} f(\alpha)\, \mathrm{e}^{-E/RT} \tag{1}$$

the heating rate $\beta$ being considered constant, with

$$A = \text{const.} \tag{2}$$

$$E = \text{const.} \tag{3}$$

and

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{4}$$

according to Šesták and Berggren [2] where

$$n = \text{const.}; \qquad m = \text{const.}; \qquad p = \text{const.} \tag{5}$$

For variable kinetic parameters, the equation [1]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A(\alpha)}{\beta} f^{\star}(\alpha)\, \mathrm{e}^{-E(\alpha)/RT} \tag{6}$$

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with

$$f^{\star}(\alpha)=f(\alpha,\ n(\alpha),\ m(\alpha),\ p(\alpha)) \tag{7}$$

should be used instead of eqn. (1)

In a previous paper [3], two types of change in the non-isothermal reaction rate with heating rate were demonstrated. For the dehydration of calcium oxalate with $\alpha$ constant

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}(\beta)\downarrow \text{ as } \beta\uparrow \tag{8}$$

Correspondingly for the thermal decomposition of potassium permanganate with $\alpha$ constant

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}(\beta)\uparrow \text{ as } \beta\uparrow \tag{9}$$

In the following we shall try to explain the differences in eqns. (8) and (9) using the classical equation, eqn. (1), as well as the non-classical equation, eqn. (6).

## CLASSICAL CASE

Integrating eqn. (1), one obtains

$$g(\alpha)=\frac{A}{\beta}\int_{0}^{T}\mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{10}$$

or by solving approximately the integral from the right side of eqn. (10)

$$g(\alpha)=\frac{A}{\beta}\,\frac{RT^{2}}{E}\,\mathrm{e}^{-E/RT}Q\left(\frac{E}{RT}\right) \tag{11}$$

where

$$Q\left(\frac{E}{RT}\right)<1 \tag{12}$$

Let $\alpha$ be constant and let

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}(\beta)=\alpha^{\star}(\beta) \tag{13}$$

Taking the derivative of eqn. (1) with respect to $\beta$ for $\alpha$ being constant

$$\frac{\mathrm{d}\alpha^{\star}(\beta)}{\mathrm{d}\beta}=\frac{A}{\beta}f(\alpha)\,\mathrm{e}^{-E/RT}\left[-\frac{1}{\beta}+\frac{E}{RT^{2}}\,\frac{\mathrm{d}T}{\mathrm{d}\beta}\right] \tag{14}$$

where, for simplicity's sake, $T$ is written for $T(\beta)$.

From eqn. (10), taking the derivative with respect to $\beta$ we get [4]

$$g(\alpha)=A\,\mathrm{e}^{-E/RT}\frac{\mathrm{d}T}{\mathrm{d}\beta} \tag{15}$$

Equation (14) with $\mathrm{d}T/\mathrm{d}\beta$ given by eqn. (15) becomes

$$\frac{\mathrm{d}\alpha^\star(\beta)}{\mathrm{d}\beta} = \alpha^\star(\beta)\left[-\frac{1}{\beta} + \frac{E}{RT^2}\,\mathrm{e}^{E/RT}\frac{g(\alpha)}{A}\right] \tag{16}$$

Substituting the pre-exponential factor $A$ from eqn. (11) into eqn. (16)

$$\frac{\mathrm{d}\alpha^\star(\beta)}{\mathrm{d}\beta} = \frac{\alpha^\star(\beta)}{\beta}\left[Q\left(\frac{E}{RT}\right) - 1\right] \tag{17}$$

As $\alpha^\star(\beta)/\beta > 0$, taking into account relationship (12)

$$\frac{\mathrm{d}\alpha^\star(\beta)}{\mathrm{d}\beta} < 0 \tag{18}$$

According to inequality (18), the function $\alpha^\star(\beta)$ decreases when the heating rate $\beta$ increases, thus

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}(\beta)\downarrow \text{ as } \beta\uparrow \tag{19}$$

This result shows that a description of the decomposition in classical terms leads only to a decrease in the non-isothermal reaction rate with the heating rate (for $\alpha$ constant), as was demonstrated experimentally in the dehydration of calcium oxalate.

## NON-CLASSICAL CASE

For $\alpha$ constant, the derivative of eqn. (6) with respect to $\beta$ gives

$$\frac{\mathrm{d}\alpha^\star(\beta)}{\mathrm{d}\beta} = \alpha^\star(\beta)\left[-\frac{1}{\beta} + \frac{E(\alpha)}{RT^2}\frac{\mathrm{d}T}{\mathrm{d}\beta}\right] \tag{20}$$

In this case, $\mathrm{d}T/\mathrm{d}\beta$ cannot be evaluated as a function of the kinetic parameters.

Nevertheless, taking into account that for $\alpha$ constant [5]

$$\frac{1}{T} = a + b\ln\beta \qquad (a = \text{const.},\ b = \text{const.}) \tag{21}$$

and

$$\frac{\mathrm{d}T}{\mathrm{d}\beta} = -T^2\frac{b}{\beta} \tag{22}$$

Taking into account this result, eqn. (2) becomes

$$\frac{\mathrm{d}\alpha^\star(\beta)}{\mathrm{d}\beta} = \frac{\alpha^\star(\beta)}{\beta}\left[-1 - \frac{E(\alpha)b}{R}\right] \tag{23}$$

The sign of this expression cannot be predicted for the general case as the dependences of $b$ on the kinetic parameters are unknown. Assessing the dependences of $b$ on $A(\alpha)$, $f^\star(\alpha)$ and $E(\alpha)$ is a future project. For the time being, $b$ and $E(\alpha)$ will be determined from experimental data. The two following examples make use of experimental data given elsewhere [3].

*First example: the decomposition of potassium permanganate*

$\alpha = 0.45$

$E(\alpha = 0.45) = 33.87$ kcal mol$^{-1}$

$\beta_1 = 1.5$ K min$^{-1}$ and $\beta_2 = 3$ K min$^{-1}$

The system

$$\left.\begin{aligned} \frac{1}{514.0} &= a + b \ln 1.5 \\ \frac{1}{529.5} &= a + b \ln 3 \end{aligned}\right\} \tag{24}$$

leads to the following value for $b$

$$b = -8.2163 \times 10^{-5} \text{ K}^{-1} \tag{25}$$

For the expression $\mathrm{d}\alpha^{\star}(\beta)/\mathrm{d}\beta$, obviously

$$\frac{\mathrm{d}\alpha^{\star}(\beta)}{\mathrm{d}\beta} = 0.4004 \frac{\alpha^{\star}(\beta)}{\beta} > 0 \tag{26}$$

Thus for the decomposition of potassium permanganate

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \alpha^{\star}(\beta) \uparrow \text{ as } \beta \uparrow \tag{27}$$

in qualitative agreement with the experimental data.

*Second example: the dehydration of calcium oxalate*

$\alpha = 0.50$

$E = (\alpha = 0.50) = \dfrac{E(\alpha = 0.4583) + E(\alpha = 0.5417)}{2} = 23.03$ kcal mol$^{-1}$

$\beta_1 = 1$ K min$^{-1}$ and $\beta_2 = 5$ K min$^{-1}$

From the system

$$\left.\begin{aligned} \frac{1}{429.2} &= a + b \ln 1 \\ \frac{1}{449.2} &= a + b \ln 5 \end{aligned}\right\} \tag{28}$$

it follows that

$$b = -6.4455 \times 10^{-5} \text{ K}^{-1} \tag{29}$$

and

$$\frac{\mathrm{d}\alpha^{\star}(\beta)}{\mathrm{d}\beta} = -0.2530\frac{\alpha^{\star}(\beta)}{\beta} < 0 \tag{30}$$

Thus, in this case

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}(\beta) = \alpha^{\star}(\beta)\downarrow \text{ as } \beta\uparrow \tag{31}$$

in qualitative agreement with the experimental data.

## CONCLUSIONS

(1) For the change in $\mathrm{d}\alpha/\mathrm{d}T(\beta)$ with the heating rate, $\beta$, at $\alpha$ constant, the classical model predicts only the case $\mathrm{d}\alpha/\mathrm{d}T(\beta)\downarrow$ as $\beta\uparrow$.

(2) The non-classical model with variable kinetic parameters predicts the previous case as well as the case $[\mathrm{d}\alpha/\mathrm{d}T](\beta)\uparrow$ as $\beta\uparrow$.

(3) The decompositions in solid–gas systems which occur in non-isothermal conditions can be classified according to the changes in the non-isothermal reaction rate with the heating rate at $\alpha$ constant.

## REFERENCES

1 E. Urbanovici and E. Segal, Thermochim. Acta, 135 (1988) 193.
2 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
3 E. Urbanovici and E. Segal, Thermochim. Acta, 94 (1985) 399.
4 E. Urbanovici and E. Segal, Thermochim. Acta, 95 (1985) 273.
5 E. Urbanovici and E. Segal, Thermochim. Acta, in press.