# ON THE APPARENT COMPENSATION EFFECT FOUND FOR TWO CONSECUTIVE REACTIONS

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## Abstract

A critical analysis of the use of an overall single rate reaction equation instead of the true rate equation corresponding to a complex process consisting in two consecutive reactions is presented. In accordance with this approximation, often used in the kinetic analysis of the system in which several reactions take place, the overall process is described by the apparent activation parameters (the apparent activation energy, $E_{ap}$, and the apparent pre-exponential factor, $A_{ap}$) and the apparent conversion function.

The theoretical isotherms ($\alpha=\alpha(t)$, where $\alpha$ is the conversion degree and $t$ is the time) have been simulated for a system in which two consecutive reactions occur. In this case, the apparent activation parameters depends on: (a) the considered range of the temperature; (b) the temperature, for a given conversion degree. It is shown that the apparent activation parameters are corrrelated by the compensation effect relationship:

$$\ln A_{ap}=\alpha^*+\beta^* E_{ap}$$

where $\alpha^*$ and $\beta^*$ are the parameters of the linear regression.

The possibility of using the apparent kinetic parameters to predict the isotherms $\alpha=\alpha(t)$ for temperatures lower than those for which these parameters were evaluated, is discussed.

**Keywords:** apparent compensation effect, consecutive reactions, isothermal kinetics

## Introduction

The kinetic investigations of solid-gas decompositions enable to prove the following relation between the pre-exponential factor, $A$ and the activation energy, $E$:

$$\ln A=\alpha^*+\beta^* E \qquad (1)$$

where $\alpha^*$ and $\beta^*$ are constant coefficients [1–19].

Relationship (1) reflects a compensation effect (CE) between the exponential and pre-exponential factors in the Arrhenius equation.

In some recent papers [17, 18], Vyazovkin and Linert classify the compensation effect in two main types, namely false and true. For non-isothermal decomposition of solids, one considers three kinds of false CE [18] due to the change of (1) reaction model; (2) conversion and (3) heating rate. Garn [1] and Vyazovkin and Linert [17] have shown that the ture CE is associated with modification of a reagent or an environment for a series of closely related reactions. Analyzing the accelerated thermal degradation of the polymeric materials, Audouin and Verdu [20] showed that the overall rate cannot be expressed by a single term or, generally, near to a transition between two temperature domains corresponding to different predominating mechanism of themal degradation, a pseudo-compensation effect can be observed.

In this paper, a theoretical kinetic model for an isothermal decomposition in solid-gas system, which actually consists in two consecutive reactions, will be considered. A critical analysis of the use of an overall rate single reaction instead of the true rate equation will be presented. The apparent activation parameters will be evaluated. It will show that these parameters are correlated by the relationship (1). The possibility of using the apparent kinetic parameters to predict the isotherms $\alpha=\alpha(t)$ for temperatures lower than those for which these parameters were evaluated ($\alpha$ is the conversion degree and $t$ is the time) will be discussed.

## Kinetic model

Let us consider that the solid compound $A$ undergoes two consecutive decompositions:

$$A(s) \xrightarrow{k_1} B(s)+v_1 G_1(g) \tag{I}$$

$$B(s) \xrightarrow{k_2} C(s)+v_2 G_2(g) \tag{II}$$
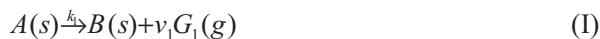
where $B$ and $C$ are solid products and $G_1$ and $G_2$ are gaseous products.

The rate constants, $k_1$ and $k_2$, can be expressed by Arrhenius equation:

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \tag{2}$$

where $i=1$ for the reaction I and $i=2$ for the reaction II.

Both consecutive reactions are characterized by a value of the reaction order which equals one. The following values of the activation parameters are going to be considered: $E_1=58.5$ kJ mol$^{-1}$; $A_1=9 \cdot 10^2$ s$^{-1}$; $E_2=125.4$ kJ mol$^{-1}$; $A_2=5 \cdot 10^8$ s$^{-1}$.

The system of kinetic differential equations is then [21]:

$$\frac{d\alpha_1}{dt} = k_1(1-\alpha_1)$$

$$\frac{d\alpha_2}{dt} = k_2(\alpha_1 - \alpha_2) \tag{3}$$

where $\alpha_1$ and $\alpha_2$ are the degree of conversion for reactions I and II respectively.

The particular case $v_1M_1=v_2M_2$, where $M_i$ is the molecular mass of the gaseous product $G_i$, and for which the total degree of conversion, $\alpha$, is given by: $\alpha=(\alpha_1+\alpha_2)/2$ is going to be considered.

Under such conditions, the integration of system (3) leads to:

$$\alpha=1-\left[\frac{1}{2}+\frac{k_2}{2(k_2-k_1)}\right]e^{-k_1t}+\frac{k_1}{2(k_2-k_1)}e^{-k_2t} \tag{4}$$

Now, we are going to analyze the consequences of the use, instead of real kinetic Eq. (3), the following one:

$$\frac{d\alpha}{dt}=k_{ap}f(\alpha) \tag{5}$$

where $f(\alpha)$ is the apparent differential conversion function and $k_{ap}$ is given by:

$$k_{ap}=A_{ap}\exp\left(-\frac{E_{ap}}{RT}\right) \tag{6}$$

where $A_{ap}$ and $E_{ap}$ are the apparent activation parameters.

Such an approximation of the true kinetic equation is often used when complex chemical reactions with unknown mechanism, like thermal and/or thermooxidative degradations of polymers, are kinetically analyzed.

## Dependence of the apparent activation parameters on the degree of conversion and temperature

For the temperature range 200–350°C, a step of 10°C and the previously mentioned values of the activation parameters, the isotherms $\alpha=\alpha(t)$ and the values of $d\alpha/dt$ were calculated. For the evaluation of the apparent activation parameters an isoconversional method based on the relation:

$$\ln\frac{d\alpha}{dt}=\ln A_{ap}f(\alpha)-\frac{E_{ap}}{RT} \tag{7}$$

which results directly from the relationships (5) and (6), was applied.

For $\alpha=$const., $E_{ap}$ and $A_{ap}f(\alpha)$ can be obtained from the slope and respectively the intercept of the straight lines $\ln d\alpha/dt$ vs. $(1/T)$. The obtained values of $A_{ap}f(\alpha)$ and $E_{ap}$ depend on the degree of conversion as well as on the temperature range in which the straight lines $\ln d\alpha/dt$ vs. $(1/T)$ were recorded, as is shown in Table 1.

For a given value of the conversion degree, from the derivative of the curve $\ln d\alpha/dt$ vs. $(1/T)$, the dependence $E_{ap}=E_{ap}(T)$ was obtained. Also, from the values of $E_{ap}$ and $\ln d\alpha/dt$ for a given temperature, $\alpha=\ln A_{ap}f(\alpha)$ was evaluated. For each value of the degree of conversion, a certain dependence of $E_{ap}$ on $T$ was obtained. It was equally observed that, for all the values of the degree of conversion, a linear dependence of $\alpha=\ln A_{ap}f(\alpha)$ vs. $E_{ap}$ exists. In other words, the existence of the compensation effect, as expressed by rela-

tion (1), is confirmed. Figure 1 shows how the compensation effect is verified or $\alpha=0.50$. Table 2 shows the values of the compensation parameters for $0.10 \leq \alpha \leq 0.90$, corresponding the the change of the apparent activation parameters with temperature.

**Table 1** The values of $E_{ap}$ and $\ln A_{ap}f(\alpha)$ obtained from the straight lines $\ln d\alpha/dt$ *vs.* $(1/T)$, recorded for various temperature ranges

| $\alpha$ | $\Delta T/$ °C | $\ln A_{ap}f(\alpha)$ | $E_{ap}/$ kJ mol$^{-1}$ | $r$ |
|---|---|---|---|---|
| 0.20 | 200–240 | 6.2133 | 60.9 | 0.99997 |
| | 240–280 | 7.1802 | 65.0 | 0.99989 |
| | 280–320 | 8.4987 | 71.0 | 0.99993 |
| | 200–350 | 7.5933 | 66.6 | 0.99928 |
| 0.50 | 200–240 | 15.5748 | 106.3 | 0.99997 |
| | 240–280 | 14.2778 | 100.8 | 0.99994 |
| | 280–320 | 12.6036 | 93.1 | 0.99990 |
| | 200–350 | 13.6706 | 98.4 | 0.99930 |
| 0.75 | 200–240 | 18.6894 | 125.6 | 1.00000 |
| | 240–280 | 19.6421 | 129.7 | 0.99999 |
| | 280–320 | 15.9844 | 112.7 | 0.99926 |
| | 200–350 | 17.4922 | 120.4 | 0.99867 |

$r$ is the correlation coefficient of the linear regression $\ln d\alpha/dt$ *vs.* $(1/T)$

**Table 2** The compensation effect parameters corresponding to the change of the activation parameters with temperature

| $\alpha$ | $\alpha^*-\ln f(\alpha)$ | $\beta^*/$ mol kJ$^{-1}$ | $r$ |
|---|---|---|---|
| 0.10 | −6.522 | 0.213 | 0.99966 |
| 0.20 | −7.282 | 0.222 | 0.99926 |
| 0.30 | −7.825 | 0.226 | 0.99978 |
| 0.40 | −8.912 | 0.236 | 0.99939 |
| 0.50 | −7.461 | 0.216 | 0.99948 |
| 0.60 | −7.767 | 0.217 | 0.99968 |
| 0.70 | −7.284 | 0.209 | 0.99977 |
| 0.80 | −7.341 | 0.206 | 0.99994 |
| 0.90 | −7.826 | 0.204 | 0.99996 |

$r$ is the correlation coefficient of the linear regression $\ln A_{ap}f(\alpha)$ *vs.* $E_{ap}$

In order to prove the dependence of the activation parameters on the degree of conversion, the temperature range 280–320°C was considered and the straight lines $\ln d\alpha/dt$ *vs.* $(1/T)$ were recorded. It was shown that at the change of $\alpha$ from 0.05 to 0.95, $E_{ap}$ increases from 61.5 to 122 kJ mol$^{-1}$, and for $0.05 \leq \alpha \leq 0.50$, $E_{ap}$ exhibits the following dependence on $\alpha$:

$$E_{ap}=E_0+E_1\ln(1-\alpha) \tag{8}$$

with $E_0$=57.762 kJ mol$^{-1}$, $E_1$= – 49.312 kJ mol$^{-1}$ and $r$=0.99894 (Fig. 2).

As relation (8) grounds a kinetic model which is going to be discussed in the next paragraph, in the following we shall concentrate on the range 0.05≤α≤0.50. In order to evaluate the pre-exponential factor, the expressions for the differential con-
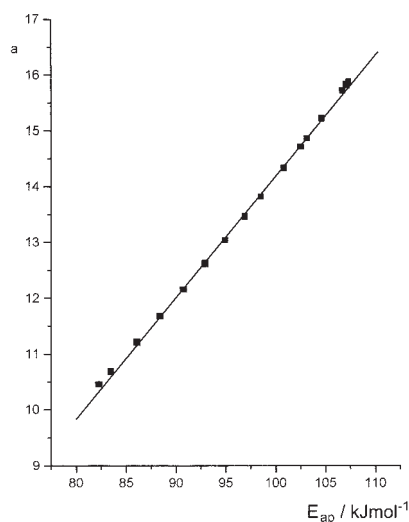


**Fig. 1** Checking the existence of the compensation effect for the dependence of the apparent activation parameters on the temperature. α=0.50; α=ln $A_{ap}$/(α)
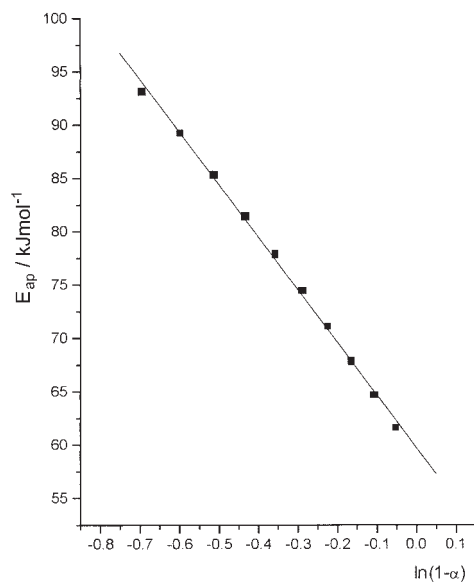


**Fig. 2** The linear dependence $E_{ap}$ $vs$. ln(1–α)

version function given in Table 3 will be considered. We will suppose that the most probable differential conversion function that describes the overall process is that corresponding to the closest to unity correlation coefficient of the straight line $\ln A_{ap}=\alpha^*+\beta^* E_{ap}$ (CE relationship). The method to find the conversion function was suggested by Tanaka and Koga [22]. As shown in Fig. 3, the models $D_1$, $D_2$ and $B_1$ do not verify the compensation effect relation. This relation is verified (Table 3, Fig. 3).

**Table 3** The considered kinetic models

| Model | Code | $f(\alpha)$ |
|---|---|---|
| Reaction order | R0.5 | $(1-\alpha)^{0.5}$ |
| | R1.0 | $1-\alpha$ |
| | R1.5 | $(1-\alpha)^{1.5}$ |
| | R2.0 | $(1-\alpha)^{2.0}$ |
| | R2.2 | $(1-\alpha)^{2.2}$ |
| | R2.3 | $(1-\alpha)^{2.3}$ |
| | R2.5 | $(1-\alpha)^{2.5}$ |
| Diffusion mechanism, one dimensional | $D_1$ | $\alpha^{-1}$ |
| Diffusion mechanism, two dimensional | $D_2$ | $[-\ln(1-\alpha)]^{-1}$ |
| Sigmoidal $\alpha$-time curves – Prout-Tompkins | $B_1$ | $\alpha(1-\alpha)$ |

For the reaction order models with a maximum correlation coefficient for the model R1.0. Thus for $f(\alpha)=1-\alpha$, the values of the compensation parameters are: $\alpha^*= -6.039$; $\beta^*=0.208$ mol kJ$^{-1}$. It is worth mentioning that for the temperature range 200–240°C,
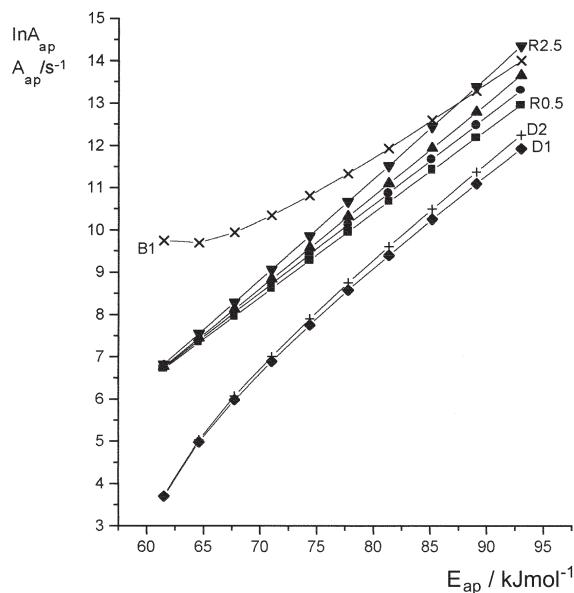


**Fig. 3** The curves $\ln A_{ap}$ *vs.* $E_{ap}$ for various forms of $f(\alpha)$

the differential conversion function $f(\alpha)$, found by the same procedure, corresponds to the model R2.2.

## Prediction of the isotherms $\alpha(t)$ using the compensation effect parameters and the dependence $E=E(\alpha)$

We suppose that the kinetic parameters were determined using the previously discussed method, the isotherms $\alpha=\alpha(t)$ recorded in the temperature range 280–320°C being known. Now the problem is to predict the isotherms $\alpha=\alpha(t)$ at the temperatures lower than 280°C, the parameters $\alpha^*$, $\beta^*$, $E_0$, $E_1$ being known. In order to accomplish this task, we suggest a simple kinetic model based on relations (1), (5), (6) and (8) which lead to:

$$\frac{d\alpha}{dt}=A_0\,(1-\alpha)^n\,f(\alpha) \tag{9}$$

where:

$$n=\beta^* E_1-\frac{E_1}{RT} \tag{10}$$

and

$$A_0=\exp\left(\alpha^*+\beta^* E_0-\frac{E_0}{RT}\right) \tag{11}$$

For the particular case $f(\alpha)=1-\alpha$, relation (9) takes the form:

$$\frac{d\alpha}{dt}=A_0\,(1-\alpha)^{n+1} \tag{12}$$

which shows that the overall process is described apparently by the reaction order model (the reaction order=$(n+1)$). But, according to Eq. (10) $n$ depends on temperature, thus violating the hypotheses, which ground the reaction order model.

Through integration of Eq. (12) for $n\neq0$, one obtains:

$$t=\frac{(1-\alpha)^{-n}-1}{nA_0} \tag{13}$$

Using the values of the compensation effect parameters, $\alpha^*$ and $\beta^*$, as well as the values $E_0$ and $E_1$, obtained from the true isotherms recorded for 280°C$\leq T\leq$320°C, the values of $n$ and $A_0$ for 230, 240, 250, 260 and 270°C were calculated. Introducing them in the relation (12), the values of $t$ for $0.05\leq\alpha\leq0.50$ and each previously mentioned temperature were calculated. As shown in Table 4, the deviation of the calculated values of $t$ with respect to the exact ones (which check Eq. (4)) increases with the decrease of temperature. It turns out that, for the considered case, the approximation of the true kinetic equation with an overall kinetic equation can be used for the

prediction of the isotherms for temperatures lower with maximum 50°C with respect to minimum temperature of the range in which the kinetic parameters were evaluated.

**Table 4** The relative errors of $t$ calculated by help of Eq. (13)

| $\alpha$ | 230°C | 240°C | 250°C | 260°C | 270°C |
|---|---|---|---|---|---|
| | | | e% | | |
| 0.10 | 6.80 | 5.18 | 3.75 | 2.50 | 1.45 |
| 0.20 | 10.18 | 7.39 | 5.06 | 3.17 | 1.66 |
| 0.30 | 12.68 | 8.87 | 5.78 | 3.40 | 1.64 |
| 0.40 | 12.81 | 8.52 | 5.26 | 2.92 | 1.30 |
| 0.50 | 6.18 | 4.00 | 2.43 | 1.36 | 0.58 |

## Conclusions

For a sequence of two first order successive reactions the isotherms $\alpha = \alpha(t)$ were simulated. The use of an overall single rate equation instead of the true rate equation was critically analyzed.

It was shown that the apparent activation parameters depend on the degree of conversion, the temperature range in which they were evaluated, and temperature for a given degree of conversion.

It was equally shown that the apparent activation parameters are correlated through the compensation effect relation.

A model for the prediction of the isotherms $\alpha = \alpha(t)$, using the apparent kinetic parameters, was suggested.

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