

COMPENSATION EFFECT IN SOLID-STATE REACTIONS.
THERMOLYSIS OF ONE SUBSTANCE UNDER DIFFERING
EXPERIMENTAL CONDITIONS

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The compensation effect ($\lg Z = aE + b$) appearing at the thermolysis of one substance under different experimental conditions is discussed. The compensation effect of one and the same substance has no other physical meaning except the simple confirmation of the analytical relationship between $\lg Z$ and E that follows from the Arrhenius equation, and of the impossibility to determine Z from any independent experiment. Values of the coefficient a can not be the measure of the ruptured bond strength.

Interest in the so-called compensation effect ($\lg Z = aE + b$) has recently again been growing. Due to various circumstances, this interest was connected with the development of non-isothermal kinetic methods for the study of solid-state reactions, and part of the experimental data were obtained for coordination compounds.

The possibility of an apparent compensation effect arising when a spontaneous and a catalytic reaction take place simultaneously in a homogeneous medium has been indicated in the literature [1]. We already pointed out that in non-isothermal kinetics the relationship $\lg Z = aE + b$ is a consequence following from the Arrhenius equation [2, 3]. Later, Garn came to the same conclusion [4]. The coefficients a and b depend solely on the temperature range of the reaction and on the rate constant (k):

$$a = \frac{1}{2.3RT}; \quad b = \lg k.$$

In non-isothermal kinetics, the compensation effect is observed both at the thermolysis of one substance under varying experimental conditions (varying size of sample, rate of temperature rise, pressure of the gaseous reactions products) [5–7] and at the thermolysis of different substances similar in structure, under identical experimental conditions [8, 9].

In the present paper we will deal only with the compensation effect appearing at the thermolysis of one substance under different experimental conditions. Also, we shall not consider the cases where the compensation effect was observed at the thermolysis of specially processed samples of the same substance (differently aged samples, samples subjected to mechanical actions etc.), since in these cases the change in the kinetic parameters may be connected with a change in the mecha-

nism of the thermolysis process owing to changes in structural defects, and we do not wish to extend our study to such cases.

Two different viewpoints exist as to the causes of the compensation effect. Garn regards the appearance of the compensation effect (and consequently, the illogical inconstancy of the kinetic constants in the thermolysis process of one and the same substance) as the confirmation of the opinion that the Arrhenius equation cannot, on principle, be applied to describe solid-state reactions [4]. Zsakó et al. assume that the value of the parameter a characterizes the strength of the bond being split when the gaseous product is being formed [5].

In our opinion, the relationship $\lg Z = aE + b$ is observed for one and the same substance at varying experimental conditions only because the value Z is not determined by some independent experiment, but by calculation, using the Arrhenius equation, from which this relationship is derived [2, 3]. Therefore any change in the calculated value E_a is accompanied by a corresponding change in the value Z , and the range in which the compensation effect $\lg Z = aE + b$ appears is determined solely by the value of the error in the determination of E_a . In fact, Zsakó et al. calculated E_a and $\lg Z$ from 15 dissociation curves of CaCO_3 found in the literature and obtained the relationship $\log Z = 0.195 E - 1.86$. The essential point was that the value of E_a varied within the limits of 26 to 377 kcal/mole, and that of Z within the limits of $10^2 - 10^{69}$. For the dissociation of CaCO_3 ($\Delta H = 40$ kcal/mole) E_a values between 150 and 377 kcal/mole and Z values between 10^{25} and 10^{69} are definitely erroneous and have no physical meaning. None the less, they lie on the straight line defined by $a = 0.195$ and $b = -1.86$ [6].

The inconstancy of the kinetic constants observed by Garn is only due to the fact that any error in the determination of E_a leads to a corresponding error in the calculated value Z , in fact in agreement with the equation $\lg Z = aE + b$, where $a = \frac{1}{2.3 RT}$ and $b = \log k$. If the value of E_a would always be exactly and reproducibly determined, then, of course, the calculated value Z would also be reproduced.

The irreproducibility of E_a may be due to various circumstances. The major reason, from our viewpoint, is that the greatest part of experimental data obtained under non-isothermal conditions is processed using the simplest equation (taken over from homogeneous kinetics)

$$\frac{d\alpha}{dt} = Z(1 - \alpha)^n \exp\left(\frac{-E}{RT}\right)$$

The formal order of reaction n is determined either for the total kinetic curve or for a major part of it. The values of n in the papers included in our survey were as follows: 0; 1/3; 1/2; 2/3; 1.0 [5, 6]. For solid-state reactions, these values indicate evaporation ($n = 0$), the reaction on the interface of two phases in a one-dimensional space ($n = 1/3$), the interface reaction in a two-dimensional space ("contracting cylinder", $n = 1/2$), the interface reaction in a three-dimensional

space ("contracting sphere", $n = 2/3$), and random nucleus formation (one nucleus for one particle, $n = 1.0$). It is easy to see that, for instance, a change in the size of the sample within the range of 25 to 100 mg, or in the rate of heating within the range of 5 to 15 °/min [5] cannot effect such an essential change in the reaction mechanism. This signifies that the kinetic curve can only *formally* be described completely by an equation utilizing the function $f(\alpha) = (1 - \alpha)^n$. General considerations lead to the result that the kinetic curve of the process $A_s \rightarrow B_s + C_g$ cannot be described by one single equation, since in the beginning of the process the slowest, rate-controlling stage is nucleus formation, followed, in the main part of the process, by nucleus growth in the bulk of the sample or by an interface reaction as rate-controlling step, and finally the rate of reaction will be controlled by gas diffusion through the layer of the solid product B_s . When experimental conditions (size of sample, shape of crucible, rate of heating, pressure of the gas) vary, the proportions between these three processes, and consequently the shape of the kinetic curve will change. This is confirmed by using the kinetic equation applied in the cited papers at $n = 1.0$. It is unrealistic to assume that the total thermolysis process $A_s \rightarrow B_s + C_g$ will proceed along the mechanism of random nucleus formation. The determined formal order of reaction equal to one cannot refer to the totality of the process.

In our earlier work we have demonstrated that in studies on the reversible dehydration of EDTA complexes, utilizing a gas flowing reactor, the shape of gas evolution curves depends on the flow rate of the inert gas and on the heating rate. Consequently, the formal order of reaction calculated by using the total curve (method of Horowitz and Metzger) changes between 0.3 and 2.0 [3].

The formal description of the process leads to the loss of physical meaning in the analysis of solid-state reaction mechanisms, to the inconstancy of kinetic constants and to the appearance of the compensation effect in the thermolysis of one and the same substance. The only way out of this is to utilize kinetic equations for the analysis of experimental kinetic curves which will describe the realistic topochemical processes (nucleation, nucleus growth, diffusion, displacement of the interface), and to select those equations that will describe the different stages of the process with the greatest probability.

We used the program TA IB developed by J. Sestak and F. Skvara for computing kinetic parameters by the integral method. In this program, the experimental data DTA, DTG and TG are being analyzed on linearity of the function $\lg g(\alpha)$ vs. $1/T$ for 13 kinetic equations. The computation is carried out separately for three conversion ranges: (i) $0.08 \leq \alpha \leq 0.30$; (ii) $0.30 \leq \alpha \leq 0.80$; (iii) $0.80 \leq \alpha \leq 0.95$. The results of the most probable mechanisms are printed out. Then a logical analysis of the results is necessary, taking into consideration the linearity range of the function $\lg g(\alpha)$ vs. $1/T$, the values of standard deviation of $\lg g(\alpha)$ in these ranges, the sense of the mechanism and the realisticness of the E_a and Z values [10–12].

By way of example, we report data on the thermolysis of clathrates. A gas flowing reactor with controlled flow rate of inert gas through a sample of 10 mg in

an ampoule with a porous bottom was used. The kinetic curves were recorded by a conductometric detector.

In the thermolysis process of the clathrate thiourea- CCl_4 (3 : 1), within the conversion range $\alpha = 0.08 - 0.30$, at helium flow rates of 20–40 cm^3/min , the most probable mechanism appears to be diffusion according to the equation Komatsu-Emura ($E_a = 29.4 - 31.4$ kcal/mole). The computation corresponding to interface displacement yields much higher values of the standard deviation (Table 1). But

Table 1
Thermolysis of the clathrate thiourea- CCl_4 (3 : 1)

W_{He} cm^3/min	Diffusion equation of Komatsu-Emura		Equation of the contracting cylinder		Equation of the contracting sphere	
	E_a , kcal/mole	(st. dev.)	E_a , kcal/mole	(st. dev.)	E_a , kcal/mole	(st. dev.)
20	31.4	(0.04)	21.6	(0.13)	23.2	(0.20)
40	29.4	(0.04)	—	—	22.7	(0.08)
60	—	—	28.5	(0.09)	29.9	(0.26)
80	—	—	34.0	(0.10)	34.2	(0.10)
100	—	—	28.0	(0.07)	30.0	(0.06)

The standard deviations listed in the Table refer to $\lg g(\alpha)$ in that range of linearity of the function $\lg g(\alpha)$ vs. $1/T$ where the error in the E_a value (determined by means of the listed kinetic equation) is within $\pm 10\%$.

at helium flow rates as high as 60–100 cm^3/min , the diffusion equation cannot describe the kinetics of the process ($\lg g(\alpha)$ vs. $1/T$ is non-linear), while the equations of interface displacement yield minimum standard deviations for $\lg g(\alpha)$ in the linearity range. $E_a = 31 \pm 3$ kcal/mole, and the variation of ± 3 kcal/mole arises only from reproducibility. The appearance of the “contracting cylinder” equation is presumably due to the channel-like structure of the thiourea clathrate, where the decomposition of the structure accompanied by gas evolution proceeds on the surface of the channels.

In Fig. 1, the observed compensation effect in the thermolysis of the clathrate hydroquinone- CH_3CN (3 : 1) in the kinetic range corresponding to the equation “contracting sphere” is presented. At different helium flow rates the reproducibility of the activation energy value is $\pm 10\%$. Since it is impossible to determine Z by means of an independent experiment, the values E_a and $\lg Z$ are related, within experimental error limits ($E_a = 35 \pm 4$ kcal/mole and $\lg Z = 20.5 \pm 2.5$) by the compensation relationship, since a is always equal to $\frac{1}{2.3RT}$ and b to $\log k$. This

demonstrates that a correct analysis of the experimental data, separating the kinetic stage and eliminating the effect of diffusion, will lead to constancy of the kinetic constants (within the reproducibility error of E_a , that is $\pm 10\%$). Obviously one must presume that the compensation effect of one and the same substance has no other physical meaning except the confirmation of the analytical relationship

between $\lg Z$ and E_a that follows from the Arrhenius equation, and of the impossibility to determine Z from an independent experiment. The constantness and reproducibility of E_a naturally result in the constantness and reproducibility of Z .

Another important point should still be mentioned. Zsákó's opinion is that the stronger the bond that has to be ruptured to form the gaseous reaction product, the smaller the coefficient a [5]. In Fig. 2 the compensation relationships for several substances are presented. The figure clearly shows that, at $b = \text{const}$ and $\log Z = \text{const}$, the smaller the value of a , the higher the value of E_a $\left(a = \frac{\log Z - b}{E_a} \right)$ at $b = \text{const}$. Therefore Zsákó's formulation simply means that the stronger the

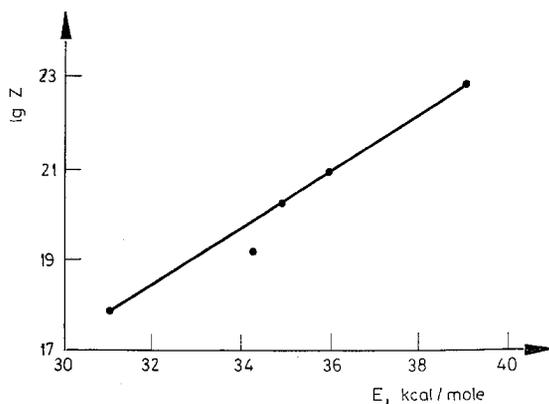


Fig. 1. Compensation effect in the range of reproducibility values of E_a for the thermolysis of the clathrate hydroquinone- CH_3CN (3 : 1)

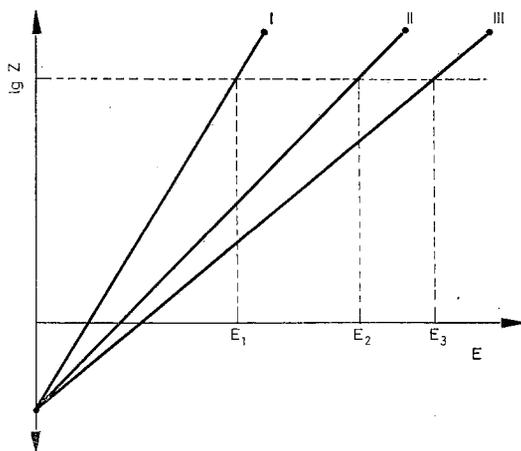


Fig. 2. Compensation effect for three different compounds; if $b = \text{const}$. and $\log Z = \text{const}$. then $a_1 > a_2 > a_3$ and $E_1 < E_2 < E_3$

bond to be ruptured, the higher the activation energy. This viewpoint is not novel in the literature. However, it is known that thermodynamic and kinetic lability may not correlate with one another. In addition, Pearson demonstrated that for coordination compounds, higher sterical density around the central atom increases the value of E_a in bond formation and reduces the value of E_a in bond rupture, owing to the readiness to distortion in the course of transition into an intermediate product [13]. In the case of solid-state ligand substitution processes of the type



studied by Zsakó, if the dissociative reaction mechanism proceeds, the experimental data will yield E_a referring to the rupture of the amine ligand bond (intermediate product with a reduced coordination number). If, however, the associative mechanism takes place, the E_a value calculated from experimental data will be that corresponding to anation and the formation of a new bond with the entering ligand X (intermediate product with an increased coordination number). In the case of the associative mechanism, the kinetic parameters of the process do not necessarily correlate with the characteristics of the ruptured bond.

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Резюме — Рассмотрен компенсационный эффект ($\lg Z = aE + b$), наблюдаемый экспериментально при изменении условий термолита одного вещества. Компенсационный эффект для одного и того же вещества не имеет другого физического смысла, кроме констатации аналитической зависимости между $\lg Z$ и E (вытекающей из уравнения Аррениуса) и невозможности определения величины Z из независимого эксперимента. Величина коэффициента a не может служить мерой силы разрываемой связи.