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THE KINETIC COMPENSATION EFFECT

J. ZSAKÓ*

University of Constantine, Constantine, Algeria

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On the basis of theoretical TG curves it has been shown that the kinetic compensation effect observed in thermal decomposition reactions is not due to the special form of the Arrhenius equation. Formally, the validity of a linear kinetic compensation law implies the existence of a characteristic temperature at which the rate constants of all reactions have the same value, but this temperature can be higher or lower than the temperatures at which the decomposition takes place.

Thermal decomposition processes can be better characterized by means of the compensation parameters than by means of the common kinetic parameters or decomposition temperatures, since the shape and the position of the TG curves and the kinetic parameters derived can be very much influenced by procedural variables, but the compensation parameters are independent of them.

The kinetic compensation effect is completely real, but its formulation in terms of the Arrhenius equation is only formal and does not reveal the physical significance of the compensation parameters.

The concept of the "kinetic compensation effect" developed in catalysis studies originally [1] has been introduced in the study of the thermal decomposition of solids as well [2, 3]. This effect consists of a correlation between the "kinetic parameters" of the decomposition, viz. the increase of the "activation energy" is accompanied by the increase of the "pre-exponential factor". This means that if owing to the modification of procedural variables, or to the change of some substituents in a class of similar compounds, a variation of the activation energy E is observed, there will be a change also in the pre-exponential factor Z, which partially compensates for the effect of the activation energy change. This kinetic compensation effect takes frequently the form of a

$$\log Z = aE + b \tag{1}$$

type linear compensation law [2–8].

According to Garn [9, 10], the kinetic compensation effect is only an apparent

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* Permanent address: Faculty of Chemistry, University Babeş-Bolyai, Cluj-Napoca, Romania

effect and it is due to the form of the Arrhenius equation. As shown by this author, one can write the Arrhenius equation in the following form:

$$\log k = -\frac{E}{2.3\,RT} + \log Z \quad \text{or} \quad \log Z = \frac{E}{2.3\,RT} + \log k \tag{2}$$

This author presumes that if the thermal decomposition occurs practically in the same temperature range, log Z will be a linear function of E, i.e. the compensation parameter a is simply

$$a = \frac{1}{2.3\,RT_c} \tag{3}$$

Our results [3] are cited by him as being in agreement with the a parameter values obtained.

As shown in our earlier paper [11], deriving of kinetic parameters as activation energy E, pre-exponential factor Z and reaction order n, is a completely formal approach. One cannot assign the same physical significance to these magnitudes as in homogeneous kinetics. These parameters are some kind of variational parameters, allowing to describe the TG curves in terms of the homogeneous kinetics. In this respect Garn is completely right, since the physical significance of the parameters obtained is obscure and in this acception the kinetic compensation effect can be an apparent effect only. Kinetic parameters obtained cannot be utilized in proving decomposition mechanisms. This is completely true and it has been stated by us repeatedly, the most clearly in [11].

On the other hand, the linear variation of log Z with E is not so simple as presumed by Garn. It is true that if the thermal decomposition occurs in the same temperature range, the apparent rate constant k must have a certain finite value k_c in the same temperature range, consequently, in Eq. (2) T has nearly the same value and one observes the kinetic compensation effect with a given by (3) and

$$b = \log k_c \tag{4}$$

This can be the situation if procedural variables or the nature of the substituents in a certain class of co-ordination complexes modify only the slope of the TG curves and do not shift them along the temperature axis. But very frequently the working conditions can shift the TG curves, or the "decomposition temperature", even by hundreds of degrees. In these cases (see e.g. the thermal decomposition of $CaCO_3$ [4]) the validity of a linear compensation law is not so obvious, since a shift of the TG curve accompanied by a modification of the slope is obtained also if only one kinetic parameter (E or Z) is modified [12].

Results and discussion

In order to show what can express the "kinetic compensation effect", several theoretical TG curves have been calculated in the present paper by using the following formula [12]:

$$\log g(\alpha) = \log E + \log Z + \log p(x) - \log Rq \tag{5}$$

where $g(\alpha)$ stands for the conversion integral, $p(x)$ for the the exponential integral tabulated in [13], q for the heating rate, R for the gas constant. Calculations have been made by presuming an apparent reaction order $n = 2/3$, and a heating rate of

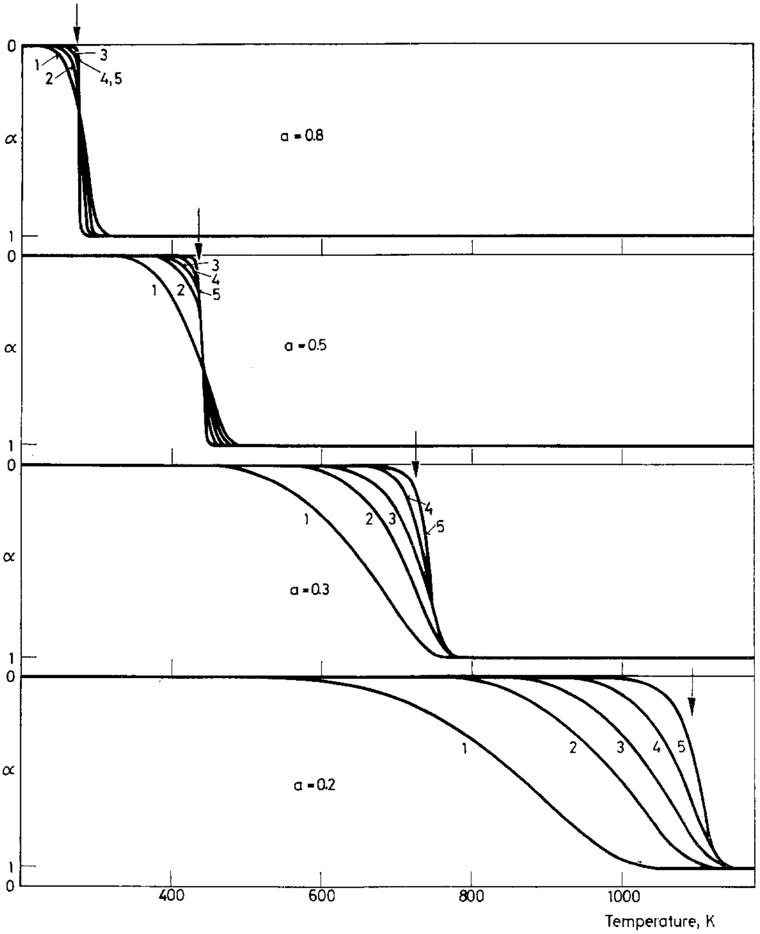

Fig. 1. Influence of the compensation parameter a upon the shape of the TG curves. $b = -3$. E (kcal/mole): 1 — 10; 2 — 20; 3 — 30; 4 — 50; 5 — 100

$q = 3°/\mathrm{min}$. In order to study the meaning of the compensation parameters a and b, one of them has been varied, while the other one has been maintained at a constant value. By using formula (1), log Z values have been calculated for the following apparent activation energy values: $E = 10$, 20, 30, 50 and 100 kcal/mole. Results are given in Table 1.

Theoretical TG curves, calculated by means of (5), by using tabulated $\log p(x)$ values, and corresponding to the kinetic parameters given in Table 1, are presented in Figs 1 and 2.

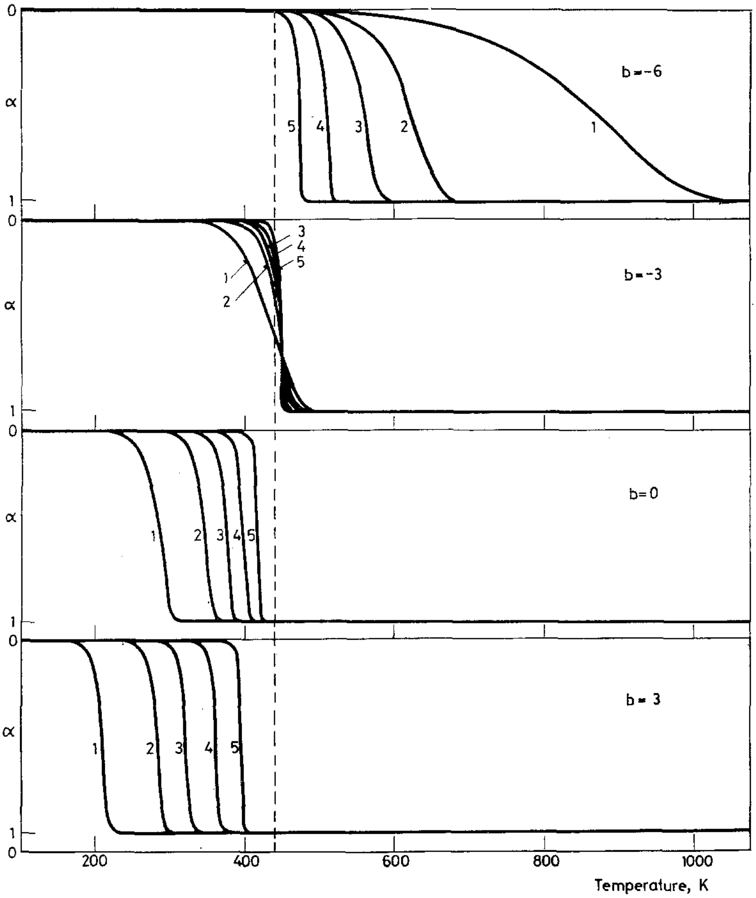

Fig. 2. Influence of the compensation parameter b upon the shape of the TG curves. $a = 0.5$. E (kcal/mole): 1 — 10; 2 — 20; 3 — 30; 4 — 50; 5 — 100

From these examples it is clear that a linear compensation law can express the shift of TG curves both to the higher or to the lower temperatures, with or without a simultaneous change in the slope, but it can express only a change in the slope.

At any rate, the validity of a linear kinetic compensation law implies formally the existence of a certain characteristic temperature T_c, given by (3), at which the rate constant of all processes has the same value k_c, given by (4). This charac-

Table 1

log Z values corresponding to different compensation parameters according to Eq. (1)

a	b	E, kcal/mole				
		10	20	30	50	100
0.8	−3	5	13	21	37	77
0.5	−3	2	7	12	22	47
0.3	−3	0	3	6	12	27
0.2	−3	−1	1	3	7	17
0.5	−6	−1	4	9	19	44
0.5	−3	2	7	12	22	47
0.5	0	5	10	15	25	50
0.5	3	8	13	18	28	53

teristic temperature is marked in Fig. 1 by means of arrows, in Fig. 2 by means of a dashed line. It is apparent that the characteristic temperature is never situated in the temperature range where the decomposition actually occurs. As seen from Fig. 2, if $b = -6$, practically no decomposition is observed at the characteristic temperature, but the decomposition is already completed at this temperature if $b = 0$ or $b = 3$.

Consequently, the existence of a kinetic compensation effect does not imply that all decomposition processes described by the same compensation law must occur in the same small temperature range, as presumed by Garn. On the other hand, the Arrhenius equation does not require the existence of a characteristic temperature for more than 2 TG curves, i.e. the kinetic compensation effect is not due to the form of the Arrhenius equation.

The "kinetic compensation effect" is something real, given by the experiment, but it is formulated "in terms of the Arrhenius equation", both if one states that "activation energy" and "pre-exponential factor" vary in parallel, according to (1), or if one presumes the existence of a "characteristic temperature" T_c at which the rate constant has a "characteristic" value k_c for all processes correlated by the same compensation law.

The most important thing is that the compensation parameters characterize a whole family of TG curves. If one tries to characterize them by means of an apparent activation energy E, apparent pre-exponential factor Z, decomposition temperature $T_{0.01}$, temperature of total decomposition $T_{0.99}$ or a decomposition interval ΔT, the values obtained can be rather different for each individual curve, but the compensation parameters a and b are the same for all of them.

In order to give a clear picture of the variety of "kinetic parameters", decomposition temperatures and decomposition temperature intervals, which are consistent with different "compensation parameters", several characteristics obtained by means of the theoretical TG curves presented in Figs 1 and 2 are given in Table 2. In this table T_c stands for the characteristic temperature given by (3).

By using the symbol T^E_α for the temperature at which the transformation degree is α in the case of the TG curve corresponding to the activation energy E, the magnitudes given in Table 2 can be defined as follows:

$$\begin{aligned} \Delta T_{0.01} &= T^{100}_{0.01} - T^{10}_{0.01} \\ \Delta T_{0.99} &= T^{100}_{0.99} - T^{10}_{0.99} \\ \Delta T^{10} &= T^{10}_{0.99} - T^{10}_{0.01} \\ \Delta T^{100} &= T^{100}_{0.99} - T^{100}_{0.01} \end{aligned}$$

Table 2

Characteristics of the TG curves given in Figures 1 and 2

a	b	T_c, K	$\Delta T_{0.01}$	$\Delta T_{0.99}$	ΔT^{100}	$\frac{\Delta T^{10}}{\Delta T^{100}}$
0.8	−3	273.16	36.7	−26.0	8.1	8.74
0.5	−3	437.06	98.0	−32.8	20.7	7.32
0.3	−3	728.44	239.8	−20.3	63.7	4.85
0.2	−3	1092.66	465.4	106.6	119.4	4.06
0.5	−6	437.06	−91.1	−552.4	23.4	20.71
0.5	−3	437.06	98.0	−32.8	20.7	7.32
0.5	0	437.06	171.3	118.9	18.4	3.85
0.5	3	437.06	204.3	180.4	16.5	2.45

As seen from Table 2, the decomposition temperature $T_{0.01}$ and the temperature of the completion of the reaction $T_{0.99}$ can be shifted by hundreds of degrees. The most important shift (for $a = 0.5$, $b = -6$) exceeds 500°. On the other hand, for $a = 0.5$ and $b = -3$, all decomposition reactions occur practically in the same temperature range, although E varies between 10 and 100 kcal/mole and Z varies between 10^2 and 10^{47}. The slope of the TG curves, and consequently the extent of the temperature interval of the decomposition can be sometimes practically the same (e.g. for $a = 0.5$, $b = 3$), but it can be completely different. Thus, for $a = 0.5$, $b = -6$ one obtains $\Delta T^{100} = 23.4°$, but $\Delta T^{10} = 484.6°$. It is obvious that in a family of TG curves, corresponding to the same compensation parameters, the shape and the position of the individual TG curves can be similar or fundamentally different. Meanwhile, the apparent activation energy and pre-exponential factor can vary in an extremely wide range, e.g. in the case of the thermal decomposition of $CaCO_3$ [4] activation energy values derived from TG curves vary between 26 and 377 kcal/mole, and the corresponding pre-exponential factor values between 10^2 and 10^{69}, but all curves obey the same linear compensation law and all the family of TG curves can be characterized by a single pair of a and b parameters.

This means that the compensation parameters a and b are better characteristics of a decomposition reaction than the other magnitudes. All of them are some parameters of unknown physical significance. The main difference between them is the following: the apparent kinetic parameters E, Z, n and the decomposition temperatures $T_{0.01}$, $T_{0.99}$, ΔT, characterize a single TG curve, all of them depend on procedural variables, but the compensation parameters a and b do not depend on these procedural variables and presumably they characterize the decomposition reaction itself.

The reality of the kinetic compensation effect does not mean, of course, that actually the variation of the frequency factor compensates for a variation in the activation energy. It means that the linear "kinetic compensation law" hides something real, that the "compensation parameters" do have a physical significance and it is worth to seek for this significance. On the other hand, it is obvious that the analysis of the TG curves cannot reveal this physical significance and other methods of investigation are needed for this purpose.

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Résumé — A l'aide de courbes TG théoriques, on montre que le soi-disant effet de compensation cinétique observé lors des réactions de décomposition thermique n'est pas dû à la forme spéciale de l'équation d'Arrhenius et qu'il n'est pas nécessaire que la décomposition thermique ait lieu dans le même intervalle de température pour qu'une loi de compensation cinétique linéaire soit valable. La validité d'une loi de compensation cinétique linéaire implique formellement l'existence d'une température caractéristique à laquelle les constantes de vitesse de toutes les réactions aient la même valeur, mais cette température peut être plus élevée ou plus faible que celle à laquelle la décomposition a lieu.

Les paramètres de compensation permettent de caractériser les processus de décomposition thermique de meilleure façon que les paramètres cinétiques habituels ou les températures de décomposition. En effet, la forme et la position des courbes TG et les paramètres cinétiques qui sont déduits de celles-ci peuvent être fortement influencés par les variables expérimentales. Au contraire, les paramètres de compensation sont indépendants des variables expérimentales.

L'effet de compensation cinétique est tout à fait réel mais sa description à l'aide de l'équation d'Arrhenius est simplement formelle et ne révèle pas la signification physique des paramètres de compensation.

ZUSAMMENFASSUNG — Am Beispiel theoretischer TG-Kurven wurde gezeigt, daß thermischen Zersetzungsreaktionen beobachtete, sogenannte kinetische Kompensationseffekt nicht der speziellen Form der Arrhenius-Gleichung zuzuschreiben ist und daß die Gültigkeit eines linearen kinetischen Kompensationsgesetzes die thermische Zersetzung in demselben Temperaturbereich nicht voraussetzt. Formal bedeutet die Gültigkeit eines kinetischen Kompensationsgesetzes die Existenz einer charakteristischen Temperatur, bei welcher die Geschwindigkeitskonstanten sämtlicher Reaktionen denselben Wert besitzen, doch kann diese Temperatur höher oder niedriger sein als diejenige, bei welcher die Zersetzung stattfindet.

Thermische Zersetzungsvorgänge können eher durch Kompensationsparameter charakterisiert werden, als durch gemeinsame kinetische Parameter oder Zersetzungstemperaturen, da die Form und Lage der TG-Kurven und der abgeleiteten kinetischen Parameter durch Prozeßvariablen stark beeinflußt werden können. Die Kompensationsparameter sind von diesen unabhängig.

Der kinetische Kompensationseffekt ist vollkommen real, doch ist seine Formulierung nach der Arrhenius-Gleichung bloß formal und enthüllt die physikalische Bedeutung der Kompensationsparameter nicht.

Резюме — Используя теоретические TG кривые, было показано, что, так называемый, кинетический компенсационный эффект, наблюдаемый в реакциях термического разложения, не обусловлен особой формой уравнения Аррениуса и что для соблюдения линейного кинетического компенсацинного закона нет необходимости проводить термическое разложение в том же самом температурном интервале. Формально, соблюдение закон линейной кинетической компенсации, означает существование характеристической температуры, при которой константы скорости всех реакций имеют то же самое значение, но эта температура может быть выше или ниже той температуры, при которой происходит разложение. Процессы термического разложения могут быть лучше охарактеризованы компенсационными параметрами, чем общими кинетическими параметрами или температурами разложения, так как вид и положение кривых TG и производных кинетических параметров, могут в значительной степени затрагиваться процедурными изменениями, в то время как компенсационные параметры независимы от них. Кинетический компенсационный эффект совершенно реальный, но формулировка его на основе уравнения Аррениуса является формальной и не раскрывает физического смысла компенсационных параметров.