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COMPENSATION EFFECT IN HETEROGENEOUS NON-ISOTHERMAL KINETICS

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Abstract

A number of 1145 sets of kinetic parameters derived in our earlier papers from TG curves have been worked up. The apparent activation energy and pre-exponential factor values have been found to obey a linear compensation law (isokinetic relation) if the thermal decomposition begins in the same temperature interval, irrespective of the nature of the chemical reaction. The isokinetic temperature T_i has been found to be very close to the mean value of the temperatures $T_{0.1}$ at which the conversion becomes equal to 0.1 and at T_i the rate constant has been found to be approximately equal to $10^{-3}s^{-1}$ in all $T_{0.1}$ intervals investigated. It is concluded that the kinetic compensation effect observed in heterogeneous non isothermal TG kinetics is not a true one.

Keywords: isokinetic relations, kinetic compensation effect, non-isothermal kinetics, thermal decomposition, thermogravimetry

Introduction

In the last 25 years we studied under dynamic temperature conditions, viz. by using a constant heating rate, the thermal decomposition of a great number of compounds. In the case of about 400 substances some portions of the TG curves have been used to derive kinetic parameters [1–35]. In these calculations the reaction rate defined by means of the conversion α has been presumed to obey the rate law

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

the rate constant k to obey the Arrhenius equation

$$k = A\exp\{-E/RT\} \tag{2}$$

and the conversion function to be of the form

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$$f(\alpha) = (1-\alpha)^n \tag{3}$$

By using a linear temperature program

$$T = T_o + qt \tag{4}$$

integration of Eq. (1), combined with Eqs (2)–(4) yields [36]

$$g(\alpha) = \frac{AE}{Rq} p(x) \tag{5}$$

where $g(\alpha)$ and $p(x)$ stand for

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{(1-\alpha)^n} \quad \text{and} \quad p(x) = \int_x^\infty \frac{e^{-x}}{x^2}\mathrm{d}x \quad \text{with} \quad x = \frac{E}{RT} \tag{6}$$

This integrated form (5) has been used to derive kinetic parameters n, E and A by means of different calculation techniques [1, 14, 15, 24, 37, 38].

Frequently, the TG curves used for deriving kinetic parameters have been recorded under different experimental conditions, viz. by using sample weights of 5, 25, 50, 75 and 100 mg and heating rates of 1, 2, 3, 5, 10, 15 and 20 K min^{-1}. The type of substances studied, their number and the number of sets of kinetic parameters derived are summarized in Table 1. In the case of the complex compounds only the composition of the inner co-ordination sphere is given, the external sphere anion/cation, as well as the crystal solvate molecules are neglected. The meaning of the symbols used in Table 1 is the following: DH_2 stands for α-dion-dioximes as dimethyl-, diphenyl-glyoxime, propyl-, cyclopentane-, cyclohexane-, cycloheptane-, cyclooctane-dion-dioxime; A and D for NH_3, H_2O, aniline (an), pyridine (py), Cl, Br, I, NCS, CN, NO_2, SO_3; en for ethylenediamine; E and G for en, an, py, Cl Br; L for Cl, Br, I, NCO, NCS, NCSe; M for py, an with $n=2$ or 4; ac for acetylacetone; Q for NO_2 or thiourea; R for NCS, NH_3 or an, X for Cl, Br or NCS; Y for Li, Na, K, Rb, Cs, NH_4, 1/2 (Mg, Ca, Sr, Ba, Zn).

In the case of the great majority of the substances, viz. with 352 compounds, TG curves have been recorded under a single experimental condition. With the remaining 28 compounds TG curves have been recorded under several different working conditions and in some cases also different calculation procedures have been used in deriving kinetic parameters. Thus, even 36 sets of kinetic parameters have been reported for the same decomposition reaction, by working up TG curves recorded under 12 different working conditions and by using 3 different calculation procedures [18].

Table 1 Type and number of substances studied and number of sets of kinetic parameters derived

Type*	Substances	Sets of kinetic parameters
$[Co(DH)_2AD]$	213	518
$[Co(en)_2EG]$	30	246
$[CoL_2M_n]$	38	181
$[Co(ac)_2(NO_2)Q]$	4	4
$[Cr(NCS)_4R_2]$	27	27
$[Cr(en)_3]$	8	10
$[PtX_6]$	37	80
$[ReCl_6]$	10	16
$Y_2S_2O_6$	11	18
$CaCO_3$	1	17
$Ca(COO)_2 \cdot H_2O$	1	28
Total	380	1145

*Meaning of symbols in text

The linear compensation law

As observed, in the case of substances of related structure, or with a given compound studied under different working conditions, the kinetic parameters derived from the TG curves, frequently obey a linear kinetic compensation law [7–13, 15–19, 22, 24–32, 39, 40]:

$$\lg A = aE + b \tag{7}$$

where the constants a and b will be referred to as compensation parameters.

In some earlier papers we presumed the compensation parameter a to be determined by the bond strength of the leaving group [8, 11, 13, 17, 26, 28–30], or at least to be correlated with some characteristics of the decomposition reaction, irrespective of working conditions [41]. According to Garn [42, 43] the compensation effect (*CE*) is only an apparent one and it is due to the use of the Arrhenius equation in non-isothermal kinetics. The validity of the *CE* for a set of TG curves means that with all decomposition processes involved there is a temperature T_i at which the rate constant of all the processes has approximately the same value k_i. Obviously, logarithmation of the Arrhenius equation yields for this isokinetic temperature the following relation

$$\lg A = (RT_i \ln 10)^{-1} E + \lg k_i \tag{8}$$

i.e. the meaning of the compensation parameters is

$$a = (RT_i \ln 10)^{-1} \qquad \text{and} \qquad b = \lg k_i \tag{9}$$

Since under the dynamic temperature conditions of the TG analysis the rate constant increases in time beginning from a practically zero value at room temperature, it seems likely to presume that in the case of substances which begin to undergo a pyrolysis at about the same temperature, at the beginning of the thermal decomposition there will be a relatively narrow temperature interval in which rate constants attain the same value k_i. In order to verify this hypothesis, we proposed to take for T_i the mean value of the temperatures $T_{0.1}$ at which the conversion becomes equal to $\alpha=0.1$ [15]. As observed [15–19, 22, 24, 25, 31, 32] the calculated

$$a' = (R\overline{T_{0.1}} \ln 10)^{-1} \tag{10}$$

value is very close to the slope a of the straight line (8).

Since in general the stronger bonded the leaving group in the crystal lattice the higher the decomposition temperature, in some cases the contradiction between Garn's and our hypotheses is not very important.

According to Agrawal [44] the *CE* observed in TG kinetics [9, 45, 46] is not a true one. In his vue a *CE* is true if 1) by plotting ln$k$ *vs.* T^{-1} one obtains a single point of concurrence of the straight lines and 2) in the point of concurrence $\ln k_i \neq 0$.

In the study of the *CE* the Arrhenius plot ln$k$ *vs.* T^{-1} instead of a ln$A$ *vs.* E linear regression has been correctly advocated by many authors [47–51], but in TG kinetics no rate constants are directly measured, only lg$A$ and E values are derived. Since we have no basis to presume that these formal parameters do determine a real rate constant as claimed by Eq. (2) [52, 53], a plot of ln$k$ values derived from lg$A$ and E values cannot give more information than a lg$A$ *vs.* E linear regression [54]. The single point of concurrence advocated by Agrawal cannot be the criterion of the true or false character of *CE* since all data are affected by experimental errors and even in the case of the truest *CE* the ln$k$ *vs.* T^{-1} straight lines will intersect each other in a finite domain $\Delta \ln k$, ΔT^{-1} [55]. As shown, the dimensions of this domain are correlated to the correlation coefficient r of the linear regression lg$A$ *vs.* E [54]. Agrawal's second criterion $\ln k_i \neq 0$ is a non sense, since the $\ln k_i$ values depend on the units in which k_i is expressed. Therefore, by taking k_i for the unit of the rate constant, the 'truest' *CE* becomes 'false' [54]. Consequently, the true or false character of *CE* cannot be established on the basis of Agrawal's criteria.

Compensation effect and the equation of TG curves

According to our above presumption that the isokinetic temperature may be approximated as $T_i \approx T_{0.1}$, for this temperature the Eq. (5) of the TG curves becomes

$$g(0.1) = \frac{AE}{Rq}\,p(x_{0.1}) \qquad \text{with} \qquad x_{0.1} = E/RT_{0.1} \tag{11}$$

In the case of the exponential integral, as a first approach, the following series expansion may be used [37, 56]:

$$p(x) \approx \mathrm{e}^{-x}\,\frac{x-2}{x^3} \tag{12}$$

From Eqs (11) and (12) one obtains

$$\mathrm{lg}A = (RT_{0.1}\,\ln 10)^{-1}E + \mathrm{lg}[g(0.1)qI]$$

with (13)

$$I = \frac{E^2}{RT_{0.1}^2 E - 2RT_{0.1}}$$

By comparing Eq. (13) with Eq. (8) one observes that they have the same shape and the former describes a *CE* if the product $g(0.1)qI$, i.e. k_i in the latter, has approximately a constant value. In order to test the constancy of this product, we analyzed our experimental data, viz the heating rates used and the n, $T_{0.1}$ and E values derived. This analysis showed that in about 95% of the cases one had

$$-1 \le \mathrm{lg}g(0.1) \le -0.93$$

$$-1.08 \le \mathrm{lg}q \le -0.60$$

$$-1.60 < \mathrm{lg}I \le -0.60$$

$$-3.68 < \mathrm{lg}[g(0.1)qI] < -2.13$$

This means that a perfect linearity in a lg$A$ *vs.* E plot cannot be expected, but if a linearity is observed, for the ordinate intercept lgk_i a value of about −3 seems to be likely.

Compensation effect for narrow $T_{0.1}$ intervals

All our experimental data published earlier have been processed by dividing them in smaller sets on the basis of $T_{0.1}$ values. In order to derive the parameters a and b of Eq. (7), for each set a linear regression analysis has been performed. Results are presented in Table 2. In this table $(T_{0.1})$ indicates the temperature in-

Table 2 lg$A$ *vs.* E linearizations in narrow $T_{0.1}$ intervals

$(T_{0.1})$	$\overline{T_{0.1}}$	T_i	$\lg k_i$	r	n
312–323	317.5	317.4	–3.16	0.9981	29
323–333	327.9	318.5	–3.38	0.9988	47
333–345	339.0	338.3	–3.06	0.9996	14
345–357	350.9	353.9	–2.88	0.9996	15
357–370	363.6	360.2	–3.20	0.9955	41
370–385	377.4	371.2	–3.07	0.9994	47
385–392	388.3	384.3	–2.97	0.9998	53
392–400	396.0	390.6	–3.03	0.9998	55
400–408	404.0	403.6	–2.82	0.9996	80
408–417	412.4	408.7	–3.05	0.9991	88
417–425	421.1	421.1	–2.93	0.9996	89
425–435	430.1	433.1	–3.26	0.9995	105
435–444	439.6	431.2	–3.26	0.9997	93
444–454	449.4	434.0	–3.53	0.9997	54
454–465	459.8	464.9	–2.96	0.9998	55
465–476	470.6	467.3	–3.02	0.9996	43
476–488	481.9	483.3	–2.94	0.9999	22
488–500	493.8	489.2	–3.08	0.9998	70
500–513	506.3	500.5	–2.87	0.9998	30
513–556	533.3	523.6	–3.33	0.9989	21
556–625	588.2	609.4	–2.82	0.9951	10
625–667	645.2	645.6	–3.32	0.9945	9
667–714	689.7	684.5	–3.44	0.9992	14
714–769	740.7	737.5	–3.17	0.9933	14
769–909	833.3	856.9	–2.98	0.9970	8
909–100	952.4	948.8	–3.97	0.9934	5
1000–1350	1111.1	1115.7	–2.30	0.9984	14
				Total	1125

terval in which the experimental $T_{0.1}$ value is comprised, $\overline{T_{0.1}}$ stands for the arithmetical mean of the experimental $T_{0.1}$ data, T_i and $\lg k_i$ stand for the isokinetic parameters derived from the parameters of the straight line accordingly to Eq. (8), r stands for the correlation coefficient of the linear regression and n for the number of sets of kinetic parameters processed.

As seen from Table 2, the correlation coefficients indicate a very good, sometimes excellent linearity, the $\overline{T_{0.1}}$ and T_i values are very close to each other and in 21 cases (from the overall 27 ones) T_i is situated inside the $(T_{0.1})$ interval. By means of linear regression the following relation between T_i and $\overline{T_{0.1}}$ could be established

$$T_i = 1.015\,\overline{T_{0.1}} - 9.2$$

which is very near to the equality of these magnitudes.

Further, the $\lg k_i$ values obtained are all situated in the above given $\lg[g(0.1)qI]$ interval, i.e. in the theoretically expected $\lg k_i$ interval. The arithmetical mean of $\lg k_i$ values is about −3.1, i.e. it is very close to the middle of the expected $\lg[g(0.1)qI]$ interval, which is equal to −2.9.

Intersection of the lg*k* *vs.* T^{-1} straight lines

By taking the logarithm of Eq. (2), one obtains

$$\lg k = \lg A - E(RT\ln 10)^{-1} \tag{14}$$

It is obvious that in a $\lg k$ *vs.* T^{-1} plot, each $\lg A$ and E pair determines a straight line. The intersection of two such straight lines corresponds to an isokinetic point. If there are n straight lines, the number of intersections will be equal to $n(n-1)/2$. If in the case of these n pairs of kinetic parameters a kinetic *CE* operates, the major part of the intersections must be situated in a relatively narrow temperature interval. In order to investigate these intersections we have chosen the $T_{0.1}$ interval comprised between 425 and 435 K in which we have 105 pairs of $\lg A$ and E values derived from TG curves (Table 2). Consequently, the number of the possible intersections is equal to 5460. The number of real intersections is less, since there are TG curves from which identical kinetic parameters have been derived. Therefore, the straight lines corresponding to Eq. (14) are also identical and no intersection point can be given. The co-ordinates of the intersection points have been calculated for each pair of different straight lines. The distribution of the intersections along the $\tau = 10^3T^{-1}$ axis is visualized in Fig. 1. In this figure the number of intersections situated between $\tau - 0.05$ and $\tau + 0.05$, i.e. in a τ interval of $\Delta\tau = 0.1$, is plotted *vs.* τ. As seen, a very sharp maximum appears at $\tau = 2.35$. We mention that the $\overline{\tau_{0.1}} = 10^3\overline{T_{0.1}^{-1}}$ average value for the corresponding TG curves is equal to 2.325. This means that the major part of the intersections are situated near to $\overline{T_{0.1}}$.

Further, we took τ intervals of different widths around $\tau = 2.35$ and we determined the following magnitudes: the number of intersections inside the interval (n), the mean value of the τ parameters at the intersections $(\overline{\tau_i})$, standard deviation of these τ parameters from their arithmetical mean (σ_τ), mean value

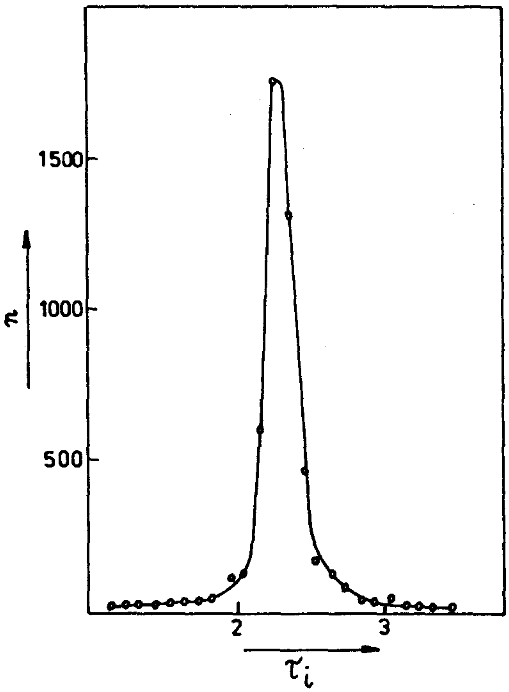

Fig. 1 Number of intersections of the lg$k$ *vs.* T^{-1} straight lines in different τ intervals of a width of 0.1 units

Table 3 Isokinetic characteristics for TG curves with $425 < T_{0.1} < 435$ K

$\Delta\tau_i$	n	$\overline{\tau_i}$	σ_τ	$\overline{\lg k_i}$	σ_k
0.1	1755	2.354	0.027	–3.16	0.31
0.3	3678	2.371	0.069	–3.23	0.58
0.5	4381	2.378	0.098	–3.28	0.79
0.7	4683	2.378	0.120	–3.28	0.96
0.9	4910	2.380	0.146	–3.29	1.13
1.1	5031	2.384	0.162	–3.32	1.24
1.3	5106	2.385	0.176	–3.33	1.34
1.5	5171	2.386	0.192	–3.34	1.43
1.7	5235	2.390	0.209	–3.36	1.54
1.9	5274	2.391	0.222	–3.36	1.63
2.1	5305	2.390	0.234	–3.36	1.70
2.3	5329	2.390	0.245	–3.36	1.76
2.5	5354	2.391	0.258	–3.36	1.86
2.7	5370	2.390	0.267	–3.36	1.91
2.9	5388	2.388	0.279	–3.34	1.98

of lg$k$ at the intersections ($\overline{\lg k_i}$) and standard deviation of the individual lg$k$ values from their arithmetical mean (σ_k). Results are presented in Table 3.

As seen from this table, by taking larger and larger intervals, having the same center $\tau=2.35$, neither $\overline{\tau}_i$ nor $\overline{\lg k_i}$ show any important modification, only the standard deviations σ_τ and σ_k increase monotonously. $\overline{\tau}_i$ remains all the time very near to the $\tau_i=2.369$ value corresponding to $T_i=422.1$ K given in Table 2 for this set of 105 TG curves. Similarly, the $\overline{\lg k_i}$ values do not differ essentially from the $\lg k_i=-3.26$ value obtained by means of linear regression (Table 2). All these results are consistent with the validity of Eq. (8) and the existence of an 'isokinetic' temperature. It is significant, that by using 90% of all theoretically possible intersections the standard deviation of the τ_i values is only 6%. By taking into account the very high value of the correlation coefficient, formally the existence of a kinetic *CE* cannot be denied.

Is in TG kinetics the CE 'true' or 'false'?

The excellent linearity of the lg$A$ *vs.* E plots and the existence of an isokinetic temperature suggests the idea that in TG kinetics a CE operates.

According to Eyring's absolute rate theory [57] in homogeneous kinetics the validity of a (7) type relation implies a linear relation between the activation enthalpy $\Delta H^{\neq}$ and the activation entropy $\Delta S^{\neq}$ of the reaction. The kinetic *CE* is thought to have the same meaning also in heterogeneous catalysis. A linear $\Delta S^{\neq}$ *vs.* $\Delta H^{\neq}$ dependence has been reported frequently, both for homogeneous reactions [58–61] and for heterogeneous catalysis [62–65].

In TG kinetics one has no basis to presume either the parameter lg$A$ to be correlated to the activation entropy of an actual process, or the parameter E to imply the activation enthalpy of some real process. These parameters are derived by means of a curve fitting method, by presuming *ab ovo* the validity of a (5) type relation. But this presumption is based upon at least 11 not justified hypotheses [53] and consequently, one can tell nothing concerning the physical meaning of the parameters E and A.

Even if we accept that

$$E=\Delta H^{\neq}+RT \qquad \text{and} \qquad A=kT/h\,\exp\{\Delta S^{\neq}/R\}$$

(k and h stand for Boltzmann's constant and Planck's constant, respectively), as claimed by the absolute rate theory [57], it is embarrassing that T_i is always situated in the incipient period of the thermal decomposition and lgk_i is always close to −3. With homogeneous reactions the picture is completely different. To illustrate the validity of this statement, we present in Table 4 T_i and lgk_i values for some reactions occurring in aqueous solutions of $[\mathrm{Co(en)_2AX}]^{2+}$ type complexes [66], where A stands for NH_3, aliphatic or aromatic amines, pyridine or pyridine derivatives and X stands for Cl or Br. The aquation reaction consists of

$$[\mathrm{Co(en)_2AX}]^{2+} + \mathrm{H_2O} = [\mathrm{Co(en)_2A(H_2O)}]^{3+} + \mathrm{X^-}$$

The assisted aquation is the same reaction in the presence of Hg^{2+} or Tl^{3+} ions and the olation reaction means

$$[\mathrm{Co(en)_2AX}]^{2+} + \mathrm{OH^-} = [\mathrm{Co(en)_2A(OH)}]^{2+} + \mathrm{X^-}$$

In Table 4 n stands for the number of $\Delta H^{\neq}$–$\Delta S^{\neq}$ pairs used for deriving the isokinetic parameters. As seen from this table, the isokinetic temperatures are not inside the temperature range in which rate constants can be experimentally determined, but they depass even the boiling point of aqueous solutions. Further, the isokinetic rate constants are not close to each other, they may differ even by 10 orders of magnitude. These differences are thought to indicate different reaction mechanisms.

Table 4 Isokinetic characteristics for some reactions of $[\mathrm{Co(en)_2AX}]^{2+}$ type complexes in aqueous solutions

Reaction	T_i	$\lg k_i$	n
Aquation	373.5	-2.68	110
Assisted aquation	486.6	3.23	31
Olation	488.9	8.28	25

By taking into account these different features of *CE* in homogeneous kinetics and TG kinetics, the latter one seems to be a false *CE*. Nevertheless, as working hypothesis, let us accept the idea that the special features of the *CE* in TG kinetics would be due to the similar mechanism of all thermal decompositions entailing gas evolution. Thus, by modifying the working conditions, or by substituting in a complex compound one ligand for another, the TG curve might undergo a modification in such a way that e.g. the increase in $\lg A$ value compensates for the increase in E. But what can be told in the following situation? By studying the pyrolysis of $M(NCS)_3 \cdot 3Ala$ type complexes, where M stands for La, Ce, Pr, Nd and Ala for *dl*–(α)–alanine, from a single TG curve kinetic parameters have been derived, by using Eq. (5) with 19 different conversion functions $g(\alpha)$. This graphical plot of $\ln A$ *vs.* E yielded excellent straight lines separately for each compound studied, i.e. a clear *CE* was observed [67].

It is worth mentioning that this *CE* presents exactly the same features as the above discussed ones. Thus, e.g. with $Pr(NCS)_3 \cdot 3Ala$ the isokinetic parameters derived from the 19 $\ln A$ –E pairs by means of linear regression are the following $T_i = 481$ K and $\lg k_i = -2.54$, the correlation coefficient being equal to $r = 0.9996$. Meanwhile, from TG data a $T_{0.1} = 467$ K value results. Obviously, in this case no real compensation effect may arise, since the kinetic parameters have been derived from the same TG curve. Nothing is modified, except the shape of a mathematical function in processing the same experimental data. Nevertheless, T_i and $T_{0.i}$ values are very close to each other, and lgk_i does not differ essentially from –3, exactly as with all other cases of *CE* observed in TG kinetics.

On the basis of the above discussions, the final conclusion may be only that the compensation effect observed in heterogeneous non isothermal kinetics (TG kinetics) cannot be a true kinetic compensation effect, it is rather a 'mathematical', apparent effect.

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