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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA
XXXI. Derivation of a non-linear kinetic compensation law

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Abstract

The kinetic compensation effect observed in heterogeneous non-isothermal kinetics is only an apparent effect. In general, the correlation derived between the kinetic parameters E and log A from TG curves can be described by means of a non-linear compensation law, expressed by Eq. (14). This equation may become approximately linear in certain particular cases, i.e. it may change into an isokinetic relation. The validity of the non-linear compensation law has been tested by using over 1000 sets of kinetic parameters reported earlier.

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

Introduction

It has been observed that the kinetic compensation effect (CE) apparently also operates in thermal decomposition reactions [1, 2]. In general, the CE obeys the following linear compensation law (CL):

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

A is the pre-exponential factor in the Arrhenius equation and E is the activation energy. The logarithmic form of the Arrhenius equation yields for the temperature T_i the expression

$$\log A = (RT_i \ln 10)^{-1}E + \log k_i \tag{2}$$

Obviously, if a CE operates in a set of processes, this implies the existence of an isokinetic temperature T_i at which the rate constants of all processes have the same value k_i. Accordingly, the compensation parameters a and b in Eq. (1) merely have the meanings

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$$a = (RT_i \ln 10)^{-1} \quad \text{and} \quad b = \log k_i \tag{3}$$

In studies of the thermal decompositions of solids, thermogravimetric (TG) investigations are frequently performed under dynamic temperature conditions, mainly by using constant heating rates q. A considerable number of calculation techniques have been developed to derive kinetic parameters from TG curves.

The basic relation utilized in a major proportion of calculation techniques is

$$\frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \frac{A}{q}\exp\{-E/RT\}\mathrm{d}T \tag{4}$$

where α is the transformation degree and n is the apparent reaction order. Its integrated form [3]

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

where

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

is the equation of a TG curve. In fact, Eq. (5) represents a family of functions depending on three parameters, n, E and A. Thus, calculation techniques aiming at deriving kinetic parameters are in fact variational methods, allowing us to obtain the parameter values n, E and A that ensure the best fit of Eq. (5) to the experimental TG curve, i.e. these parameters are simply mathematical, variational parameters, without any clear physical meaning. They are not real kinetic parameters and they have nothing to do with the reaction order, activation energy or activation entropy of any process that actually occurs in the system. They are the kinetic parameters of a hypothetical n-th-order homogeneous reaction, the conversion of which simulates the expeirmentally found TG curve.

Compensation effect in TG kinetics

The rate constant of the hypothetical homogeneous reaction simulating the TG curve vanishes at low temperatures. It increases with increasing T, and it must attain a finite value at the temperature of decomposition of the solid. Thus, if a certain number of substances have approximately the same decomposition temperature, there will be a relatively narrow temperature interval in which the rate constants of the thermal decompositions of all these substances will have almost the same value. Consequently, a linear CL of type (1) will operate, and, in expression (3) for the slope a of the straight line $\log A$ *vs.* E, T_i will represent simply the decomposition temperature [4].

As shown earlier [5], a linear relation of type (1) may be valid for a set of TG curves situated in the same temperature interval, but it may also be consistent with TG curves corresponding to very different decomposition temperatures. In the latter case, with increasing E the TG curves will be shifted towards higher temperatures if k_i has relatively large values, but towards lower ones if k_i has low values.

In our earlier papers, the thermal decompositions of a considerable number of substances were studied under dynamic temperature conditions and almost 1200 sets of kinetic parameters n, E and $\log A$ have been reported. For substances with related structures, or for a given compound studied under different working conditions, the kinetic parameters derived frequently obeyed the kinetic CL (1). We tested the hypothesis that in expression (3) for the parameter a, T_i means a certain decomposition temperature. Since the definition and the experimental determination of the decomposition temperature are very difficult, we suggested to take in relation (3) the mean value of $T_{0.1}$ (i.e. the temperature at which the conversion attains a degree of 0.1) for T_i [6]. The calculated

$$a' = (R\overline{T_{0.1}}\ln 10)^{-1} \tag{6}$$

was observed to be very close to the slope a of the straight line (1).

In a previous paper [7], all the experimental data published earlier were processed by dividing them into smaller sets on the basis of the $T_{0.1}$ values, irrespective of the nature of the chemical process. For each set, the parameters a and b were derived by performing a linear regression analysis. In all $T_{0.1}$ intervals, the linearity of the $\log A$ *vs.* E plots was observed to be very good, the correlation coefficient values always being higher than 0.99. The isokinetic temperature corresponding to the parameter a obtained did not differ very much from $T_{0.1}$. As concerns the parameter $b=\log k_{0.1}$, its values were situated between –2.3 and –4 and were generally close to –3. This result allowed us to define a 'theoretical' pre-exponential factor [8] by means of the relation

$$\log A' = (RT_{0.1}\ln 10)^{-1}E - 3 \tag{7}$$

i.e. by taking $T_i = T_{0.1}$ and $\log k_i = -3$ in Eqs (3).

In the present paper, we set out to test approximation (7) for the kinetic parameters reported earlier. For this purpose, 1152 pairs of $T_{0.1}$ and E values were used to calculate $\log A'$ values and the latter were compared with $\log A$ values derived directly from the TG curves. The results are presented in Table 1. In this Table, the number N of $\log A'$ values satisfying the condition

$$|\log A' - \log A| \leq \Delta \tag{8}$$

is given for different Δ values. u and v are the parameters of the equation

$$\log A = u\log A' + v \tag{9}$$

These parameters were established by means of linear regression; r is the correlation coefficient. Obviously, if Eq. (7) gave the exact values of $\log A$, one would have $u=r=1$ and $v=0$. It is clear from Table 1 that Eq. (7) may be considered to be a quite good approach. Nevertheless, in the plot $\log A$ *vs.* $\log A'$ the points are rather scattered, since only about 20% of them satisfy condition (8) for $\Delta=0.1$.

Table 1 Testing of Eq. (7)

Δ	*N*	*u*	*v*	*r*
0.1	252	0.999	0.008	0.9999
0.2	468	0.997	0.022	0.9999
0.3	687	0.994	0.043	0.9999
0.4	846	0.992	0.066	0.9998
0.5	960	0.990	0.078	0.9998
0.6	1044	0.988	0.107	0.9998
2.0	1152	0.987	0.117	0.9996

Derivation of a non-linear compensation law

In order to obtain a better approach, the correlation between T_i, $T_{0.1}$ and k_i was studied. Let us consider the equation of the TG curve, i.e. Eq. (5). The exponential integral $p(x)$ may be approximated [9, 10] as

$$p(x) \approx e^{-x}\frac{x-2}{x^3} \tag{10}$$

which leads to the expression

$$\frac{E}{R}p(x) = \left(1 - \frac{2RT}{E}\right)\frac{RT^2}{E}\exp\{-E/RT\} \tag{11}$$

On the other hand, if a CE operates, A will obey Eq. (2). Thus, for $\alpha=0.1$, by combining Eqs (2), (5) and (11), we obtain

$$\log\left(1 - \frac{2R}{E}T_{0.1}\right)T_{0.1}^2 - (RT_{0.1}\ln 10)^{-1}E = \log\left[g(0.1)\frac{qE}{Rk_i}\right] - (RT_i\ln 10)^{-1}E \tag{12}$$

Equation (12) allows us to calculate $T_{0.1}$ as a function of T_i, k_i, E, n and q. As an example, apparently first-order reactions were considered for $q=10$ K min^{-1}=

Table 2 $T_{0.1}$ values calculated by means of Eq.(12). n=1, q=1/6 K s^{-1}, T_i=400 K

E/ kJ mol^{-1}	logk_i				
	–5	–4	–3	–2	–1
50	535	454	394	347	309
100	473	436	404	377	353
200	440	422	407	392	378
400	422	413	406	398	391
800	412	408	404	400	396

1/6 K s^{-1}. Some illustrative results are presented in Table 2. Inspection of this Table shows that with increasing E the $T_{0.1}$ value may decrease (logk_i=–4 or –5), but it may also increase (logk_i=–2 or –1). The interval $\Delta T_{0.1}$ in which $T_{0.1}$ varies as a function of E also depends upon k_i and it has a minimum value $\Delta_m T_{0.1}$ at a certain k_i. The log k_i values corresponding to $\Delta_m T_{0.1}$, as well as those for which $T_{0.1}$=T_i, are given in Table 3. It may be seen that, with decreasing E, the log k_i value corresponding to $T_{0.1}$=T_i approaches the value at which $T_{0.1}$ becomes practically independent of E and this value is not very far from –3. Consequently, the approximations T_i=$T_{0.1}$ and log k_i=–3 are justified to some extent, but these are very rough approximations. At any rate, an apparent CE may be expected if the thermal decomposition occurs in approximately the same temperature interval, but the exact relation between A and E is more complicated than the simple linearity expressed by Eq. (2).

Table 3 logk_i values corresponding to $\Delta_m T_{0.1}$ and to $T_{0.1}$=T_i

T_i/ K	$\Delta_m T_{0.1}$	E/kJ mol^{-1}				
		50	100	200	400	800
400	–3.2	–3.1	–2.8	–2.6	–2.3	–2.0
800	–3.7	–3.6	–3.4	–3.1	–2.9	–2.6
1200	–4.0	–3.9	–3.7	–3.5	–3.2	–2.9

A better approximation may be obtained by combining Eqs (5) and (11), which leads for α=0.1 to the expression

$$\log A = (RT_{0.1}\ln 10)^{-1}E + \log[g(0.1)qE] - \log\left[RT_{0.1}^{2}\left(1-\frac{2RT_{0.1}}{E}\right)\right] \qquad (13)$$

In general, $2RT_{0.1}/E<0.2$. Among the 1152 cases considered in the present paper, there are only 13 exceptions and even in these cases $2RT_{0.1}/E$ does not exceed 0.25. On the other hand, in all cases $-1<n<4$ and consequently $-1.02<\log g(0.1)<-0.91$. Since log$R$=0.92, we always have

$$-1.94 < \left[\log g(0.1) - \log R\left(1 - \frac{2RT_{0.1}}{E}\right)\right] < -1.73$$

Therefore, by taking −1.85 for the expression in square brackets, the approximation seems to be quite realistic and instead of Eq. (7) we obtain

$$\log A' = (RT_{0.1}\ln 10)^{-1}E + \log(qE/T_{0.1}^{2}) - 1.85 \qquad (14)$$

Equation (14) allows us to derive better approximations of the pre-exponential factor. Equation (14) was tested as for Eq. (7) and the results are presented in Table 4. Obviously, Eq. (14) is a much better approximation than Eq. (7): the slope of the straight line log*A* *vs.* log*A'* is nearer to 1, the ordinate intercept is nearer to 0 and the correlation coefficient is higher for Eq. (14) than for Eq. (7). The values are much less scattered and over 80% of the log*A* – log*A'* pairs satisfy condition (8) for Δ=0.1.

Table 4 Testing of Eq. (14)

	N	*u*	*v*	*r*
0.1	956	0.999	0.002	0.99999
0.2	1020	0.998	0.036	0.99999
0.3	1067	0.998	0.034	0.99999
0.4	1104	0.998	0.042	0.99998
0.5	1119	0.998	0.042	0.99997
0.6	1125	0.998	0.042	0.99996
2.0	1152	0.997	0.063	0.99989

We can conclude that Eq. (14) describes the correlation between log*A* and *E* very well, i.e. for the kinetic parameters derived from TG curves it is a much better CL than Eq. (1). Obviously, it is not a linear CL and therefore it is not an isokinetic relation.

Some particular cases of a linear CL

Equation (14) may become an isokinetic relation if $\log(qET_{0.1}^{-2})$ ≈const.. This happens, for example, when kinetic parameters are derived from a single TG curve by means of different calculation techniques. In this case, the q and $T_{0.1}$ values are identical and E varies in a relatively narrow interval. Thus, it is not surprising that, in a kinetic analysis of the TG curves of some lanthanide complexes, with the use of 19 different conversion functions $g(\alpha)$, the kinetic parameters obeyed a linear CL with correlation coefficients higher than 0.999 [11] and T_i corresponding to the slope of the straight line was found to be close to $T_{0.1}$ [7].

Table 5 Kinetic parameters obeying a linear compensation law

Compound	q/ K min^{-1}	$T_{0.1}$/ K	E/ kJ mol^{-1}	log$A$	logA'	Ref.
[Co(NCO)$_2$py$_4$]	5	323	45.6	4.0	4.08	20
[Co(NCS)$_2$(*o*-tol)$_2$]	2	355	59.7	5.1	5.12	21
[Co(NCS)$_2$(*o*-tol)$_2$]	5	364	55.2	4.6	4.61	21
[Co(NCS)$_2$(*p*-anis)$_2$]	5	385	62.7	5.2	5.20	21
[Co(DH)$_2$(*p*-Br-an)$_2$]NCS	15	408	61.0	4.9	4.91	13
[Co(DH)$_2$(*p*-phenet)$_2$]NCS	10	417	66.9	5.5	5.52	13
CaC$_2$O$_4$·H$_2$O	10	423	63.0	5.0	4.70	19
[CoCl$_2$(*m*-tol)$_2$]	5	425	76.5	6.1	6.10	16
CaC$_2$O$_4$·H$_2$O	7.5	431	74.0	5.7	5.81	19
[Co(NioxH)$_2$py$_2$]NCS·1.5H$_2$O	10	436	78.0	6.3	6.33	18
[CoCl$_2$(*m*-tol)$_2$]	5	441	81.1	6.3	6.30	16
[CoCl$_2$(*m*-tol)$_2$]	15	443	73.2	6.0	6.00	16
[Co(DiphH)$_2$(*o*-et-an)$_2$]Br	10	444	74.4	5.7	5.70	12
[CoCl$_2$(*m*-tol)$_2$]	10	447	79.8	6.3	6.30	16
[Co(NCS)$_2$(*m*-xyl)$_2$]	1	447	81.1	6.2	6.23	21
[Co(DiphH)$_2$(an)$_2$]Cl	10	448	77.7	6.0	6.02	12
[Co(NCS)$_2$(*p*-tol)$_2$]	10	453	81.1	6.2	6.32	17
[CoCl$_2$(*m*-tol)$_2$]	15	454	74.8	5.7	5.71	16
[CoBr$_2$(*m*-tol)$_2$]	15	455	79.4	6.2	6.24	15
[CoBr$_2$(*m*-tol)$_2$]	10	456	81.5	6.3	6.30	15
[Co(NCS)$_2$(py)$_4$]	5	456	87.1	6.7	6.68	20
[CoBr$_2$(*m*-tol)$_2$]	15	457	76.1	5.8	5.80	15
[CoBr$_2$(*m*-tol)$_2$]	10	458	83.6	6.5	6.50	15
[Co(NCS)$_2$(*p*-tol)$_2$]	15	458	77.8	6.0	5.99	17
[Co(DiphH)$_2$(*m*-tol)$_2$]Cl	10	461	86.1	6.7	6.73	12
[Co(NCS)$_2$(py)$_4$]	10	467	86.1	6.7	6.59	20
[Co(NCO)$_2$(py)$_4$]	10	473	93.8	7.3	7.35	20
[Co(NCO)$_2$(py)$_4$]	15	476	85.3	6.5	6.49	20
[Co(NioxH)$_2$(*o*-phenet)$_2$]Br	10	481	96.1	7.4	7.41	14
[Co(DiphH)$_2$(*m*-am-phen)$_2$]NCS	10	494	99.5	7.5	7.51	23
[Co(NioxH)$_2$(an)$_2$]Br	10	495	97.4	7.2	7.24	14
(benzimidH)$_2$[PtCl$_6$]	10	605	183.9	12.9	12.96	22

Symbols: DH$_2$=dimethylglyoxime; NioxH$_2$=cyclohexanedione-dioxime; DiphH$_2$=diphenylglyoxime; an=aniline; tol=toluidine; et-an=ethylaniline; am-phen=aminophenol; anis=anisidine; phenet=phenetidine; xyl=xylidine; py=pyridine; benzimid=benzimidazole

Obviously, in this case the CE is a mere mathematical effect with no physical meaning.

According to Eq. (14), a nearly linear CL may be expected if approximately the same heating rate is used and the $T_{0.1}$ values of the processes involved are close to each other. In this case, the isokinetic temperature which may be derived by means of linear regression does indeed indicate a certain decomposition temperature [7], as presumed by Garn [4].

However, these are not the only possibilities, since $\log(qET_{0.1}^{-2})$ may be almost constant even if $T_{0.1}$ varies in a relatively large interval. In order to illustrate this possibility, some selected experimental data are presented in Table 5 in the sequence of increasing $T_{0.1}$. It may be seen that both E and $\log A$ display a clearly increasing tendency in the same sequence. The 32 sets of kinetic parameters presented obey a linear kinetic CL (1) and, by means of linear regression, the following compensation parameters can be derived:

$$a=0.0646 \text{ and } b=1.057$$

the correlation coefficient being $r=0.997$. The isokinetic temperature calculated from a is $T_i=809.4$ K, i.e. a value several hunderds of degrees higher than the decomposition temperature.

In general, in homogeneous kinetics the validity of a linear CL is believed to indicate an analogous reaction mechanism. In TG kinetics, a similar conclusion may not be drawn. Inspection of Table 5 shows that the processes involved are very different; moreover, the papers cited in this Table include numerous kinetic parameters characterizing TG curves of the same substances recorded under not very different working conditions, which do not obey the above CL at all. The validity of the CL for the kinetic parameters presented in Table 5 is a simple coincidence. It merely happens that the product $qET_{0.1}^{-2}$ has almost the same value.

A more correct description of the correlation between E and $\log A$ is given by Eq. (13), for which Eq. (14) is a very good approximation. As seen from Table 5, for $\log A'$ values calculated by means of Eq. (14), the agreement with the $\log A$ values derived directly from the TG curves is excellent.

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