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KINETIC COMPENSATION DUE TO PSEUDO REACTION MECHANISMS

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Abstract

Two kinds of compensation mechanism are suggested: a genuine one due to thermodynamic factors and a pseudo one arising from experimental or data-processing artifacts. It is computationally demonstrated that the choice of reaction mechanism strongly influences the kinetic parameters determined in thermal analytical studies. It is further shown that the kinetic parameters determined at different heating rates by using a pseudo reaction mechanism exhibit kinetic compensation that gives the temperature of the experiment as the so-called isokinetic temperature. A rule of thumb relating to the magnitude of the isokinetic temperature is suggested to differentiate genuine compensation from pseudo compensation.

Keywords: compensation mechanism, isokinetic temperature, kinetic parameters, pseudo reaction mechanisms, thermodynamic factors

Introduction

The widely varying kinetic parameters reported for the decompositions of solids following the use of thermal analysis have been a topic of several experiments and discussions [1–7], some controversies [8, 9] and even an outright protest [10]. Though these parameters sometimes span a wide spectrum of values, they are connected by a relationship that has come to be known as kinetic compensation [1], of the form

$$\ln A = a + bE \tag{1}$$

where E is the activation energy and A is the frequency factor. Considerable disagreement exists as to the factors that give rise to the compensation effect.

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While some authors indicate the Arrhenius equation as responsible for the observed compensation [6, 11], others attribute compensation to artifacts produced by experimental conditions and the inadequate processing of experimental data [12, 13]. An attempt has also been made to probe the physicochemical factors behind the compensation phenomenon [14].

Theory and simulation

The rate equation

$$\mathrm{d}x/\mathrm{d}t = f(x)K(T) \tag{2}$$

where x is the fraction reacted and $f(x)$ is the function describing the reaction mechanism, is the starting point for any kinetic study. The rate constant $K(T)$ is generally taken to follow the Arrhenius form

$$K(T) = A\exp(-E/RT) \tag{3}$$

where A is the pre-exponential factor and E is the activation energy. In instances where the reaction rate is known to depend on other parameters such as pressure P, $f(x)$ will be modified $f(x,P)$. The integral form of Eq. (2) is given by

$$\int_0^x \mathrm{d}x/f(x) = A\int_0^t \exp(-E/RT)\mathrm{d}t \tag{4}$$

For experiments at a fixed heating rate, β, the above integral can be expressed after suitable manipulation as

$$\int_0^x \mathrm{d}x/f(x) = AE/\beta R\int_0^\infty \exp(-y)/y^2\mathrm{d}y \tag{5}$$

where $y = E/RT$. The integral on the RHS is not an exact one and suitable approximations are used in kinetic studies. A numerical integration performed by this author confirmed that the approximation used by Ozawa [15] gives sufficiently accurate results. With this approximation, Eq. (5) becomes

$$g(x) = \log\int_0^x \mathrm{d}x/f(x) = \log A + \log(E/\beta R) - 2.315 - 0.4567E/RT \tag{6}$$

In thermogravimetric studies, the experimental variable is the weight change, which is proportional to the fraction transformed, x, and the kinetic parameters A and E are generally determined by using Eq. (6) or other similar relationships. The experimental variables in Eq. (6) are the fraction x and the temperature T. It has been shown that the temperature lag in anisothermal experiments can considerably alter both the kinetic plot and the kinetic parameters [16]. If some pseudo reaction mechanism $f'(x)$ is used instead of the actual one $f(x)$, the error due to such a pseudo reaction mechanism and the uncertainty in the fraction transformed will result in an error in the value of $g(x)$. This uncertainty, and also that due to an incorrectly measured temperature, will follow the relationship obtained from Eq. (6).

$$\delta g(x) = \log A - \log A_{\varphi} + (\log E - \log E_0) \qquad (7)$$

$$- 0.4567/RT(E - E_0) - 0.4567(E/R)(1/T - 1/T_0)$$

where $\delta g(x)$ is $g(x) - \int_0^{x+\delta x} f'(x)\mathrm{d}x$, $f'(x)$ being the pseudo reaction mechanism, δx is the uncertainty in determination of x, T_0 is the correct temperature and A_0 and E_0 are the actual kinetic parameters. If $T = T_0 = T_E$, the experimental temperature, then Eq. (7) becomes (after neglecting smaller terms)

$$\delta g(x) = \log A - 0.4567E/RT_E - \log A_0 - 0.4567E_0/RT_E \qquad (8)$$

Equation (8) is similar to the kinetic compensation equation with

$$b = 0.4567/RT_E \qquad (9)$$

and

$$a = \delta g(x) + \ln A_0 - 0.4567E_0/RT_E \qquad (10)$$

when the kinetic parameters are determined at a fixed value of x, 'a' will be a constant and Eq. (8) is equivalent to Eq. (1). When $\delta g(x)$ is zero, A and E will coincide with A_0 and E_0 in the absence of genuine compensation. If genuine compensation exists, Eq. (7) will still hold good with $\delta g(x) = 0$, and again Eq. (8) becomes analogous to Eq. (1). The genuine compensation equation can also be obtained by a different method by assuming an isokinetic temperature [17]. Differentiation of the logarithm of Eq. (3) gives

$$\mathrm{d}K(T)/K = \mathrm{d}\ln A - \mathrm{d}E/RT \tag{11}$$

At the isokinetic temperature, T_i, $\mathrm{d}K = 0$ for all pairs of A and E values, and Eq. (11) becomes

$$\mathrm{d}\ln A = \mathrm{d}E/RT_i \tag{12}$$

Integration of Eq. (12) with the limits of the isokinetic temperature and any other temperature gives

$$\ln A - \ln A_0 = E/RT_i - E_0/RT_i \tag{13}$$

which is the equation for genuine compensation.

In the present simulation study, the validity of Eqs (8), (9) and (10) is demonstrated. For the simulation, the values of the different parameters used are $A = 3\times10^8 \cdot \mathrm{sec}^{-1}$, $E = 30$ kcal/mole, $f(x) = (1 - x)^2$ and $f'(x) = (1 - x)^4$. The local activation energy is determined at each temperature by numerically evaluating the gradient, $R(-\mathrm{d}g(x)/\mathrm{d}(1/T)$.

Results and discussion

Table 1 gives a sample of different kinetic parameters obtained at different heating rates and temperatures. The widely varying kinetic parameters obtained in the simulation study of the reaction kinetics clearly show the importance of choosing the correct reaction mechanism. The kinetic parameters in Table 1 satisfy the kinetic compensation relationship of Eq. (1). At a fixed temperature, T_E, a plot of ln A *vs.* E gave a straight line with gradient b given by Eq. (9). This shows that a false reaction mechanism gives rise to pseudo kinetic compensation as an artifact. It should also be mentioned here that the assumption of an incorrect pressure dependence of the reaction will yield similar compensation, and the above analysis applies equally well with $g(x,p)$ replacing $g(x)$. The plot of ln $K(T)$ *vs* $1/T$ in Fig. 1 for four sets of E and ln$A$ values shows a sharp point of concurrence. It is appropriate at this point to dwell upon the controversy regarding such a concurrence [8, 9]. The sharp point of concurrence in Fig. 1 is due to the fact that the kinetic parameters are derived precisely, using numerical methods, in contrast with the experimental determination. It has been shown by Zsakó and Somasekharan [9] that uncertainties in the kinetic parameters convert the point of concurrence into an intersecting domain, sometimes stretching far and wide. Under these circumstances, it appears that a criterion based on a point of concurrence to decide the nature of the observed compensation cannot be a successful one. A better criterion the decide whether the observed compen-

Table 1

Heating rate/ $\text{deg}\cdot\text{min}^{-1}$	Temperature/ K	E/ $\text{kcal}\cdot\text{mole}^{-1}$	ln$A$
0.10	555.1	80.5	72.2
0.10	539.2	71.3	63.2
0.10	529.8	65.7	57.6
0.10	520.6	57.3	49.2
0.25	555.1	72.2	62.8
0.25	539.2	59.5	50.5
0.25	529.8	51.3	42.4
0.25	520.6	44.4	35.4
0.50	555.1	61.8	52.0
0.50	539.2	48.9	39.5
0.50	529.8	42.6	33.2
0.50	520.6	37.9	28.6
1.00	555.1	51.0	41.1
1.00	539.2	40.9	31.3
1.00	529.8	36.8	27.3
1.00	520.6	34.2	24.6
2.00	555.1	42.3	32.4
2.00	539.2	35.8	26.2
2.00	529.8	33.6	23.9
2.00	520.6	32.1	22.4

sation is genuine or an artifice is the value of the isokinetic temperature, T_i. For pseudo compensation, T_i will be in the experimental temperature range as given by Eq. (9), whereas this may not generally hold for genuine compensation. The kinetic compensation observed in the thermal dissociation of solids reported in the literature generally has values of isokinetic temperature that lie in the experimental temperature range [1, 18]. It is surprising that the domain of intersection in the log $K(T)$ *vs* $1/T$ plot is confined to the domain of experimental temperatures [19], in contrast with what is feared in light of the fact shown by Zsakó and Somasekharan [9] that small uncertainties in kinetic parameters tend to spread the domain of intersection to a large extent. In this context, it is worth

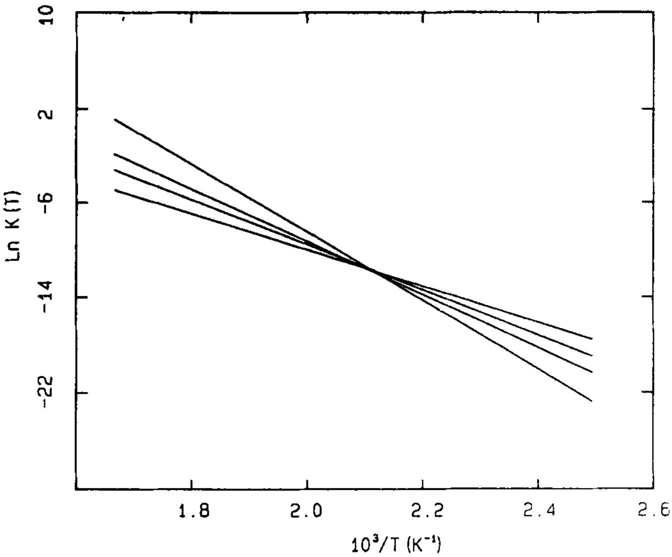

Fig. 1 Plot of ln *K*(*T*) *vs* 1/*T* for four sets of kinetic parameters obtained by simulation

mentioning the mechanism of compensation observed in an altogether different field, structural relaxation in metallic glasses [20]. The value of *b* reported for the glass $Fe_{40}Ni_{40}B_{20}$ in Ref. [20] gives an isokinetic temperature of about 1030 K, well above the experimental temperature range; and this may perhaps provide an excellent example of genuine compensation. The author has shown that the phenomenon of compensation extends to the kinetics of crystallization too for the glass $Fe_{40}Ni_{40}B_{20}$ [17].

References

1 J. Zsakó and H. E. Arz, J. Thermal Anal., 6 (1974) 651.
2 P. D. Garn, Thermochim. Acta, 135 (1988) 71.
3 N. Koga and H. Tanaka, Thermochim. Acta, 135 (1988) 79.
4 R. K. Agrawal, J. Thermal Analysis, 35 (1989) 909.
5 J. H. Flynn, J. Thermal Anal., 36 (1990) 1579.
6 N. Koga and J. Sesták, Thermochim. Acta, 182 (1991) 201.
7 P. Budrugeac and E. Segal, Thermochim. Acta, 184 (1991) 25.
8 R. K. Agrawal, J. Thermal Anal., 31 (1986) 73.
9 J. Zsakó and K. N. Somasekharan, J. Thermal Anal., 32 (1987) 1277.
10 R. F. Shlensky, J. Thermal Anal., 20 (1981) 519.
11 P. D. Garn, J. Thermal Anal., 13 (1978) 581.
12 M. Arnold, G. Veress, J. Paulik and F. Paulik, J. Thermal Anal., 17 (1979) 507.
13 R. R. Krug, W. G. Hunter and R. A. Grieger, J. Phys. Chem, 90 (1976) 2335.

14 A. Lesnikovich and S. V. Levchik, J. Thermal Anal., 30 (1985) 237.
15 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
16 R. V. Muraleedharan, Thermochim, Acta, 179 (1991) 341.
17 R. V. Muraleedharan, Phys. Stat. Solidi (a), 125 (1991) K83.
18 B. Pacewska and J. Physiak, Thermochim. Acta, 167 (1990) 145.
19 R. K. Agrawal, J. Thermal Anal., 31 (1986) 73.
20 Structural relaxation in Amorphous $Fe_{40}Ni_{40}B_{20}$, A. Van den Beukel in Rapidly Solidified Materials, Proc. of an Int. Conf., San Diego, California 1986, (Eds. P. W. Lee and R. S. Carbonara) p.193.

Zusammenfassung — Es werden zwei Arten von Kompensationsmechanismen vorgeschlagen: einen echten im Zusammenhang mit thermodynamischen Faktoren und einen Pseudo-Kompensationsmechanismus, der sich aus experimentellen oder Datenverarbeitungsfehlern ergibt. Es wird rechnerisch gezeigt, daß die Wahl des Reaktionsmechanismus die in thermischen Untersuchungen bestimmten kinetischen Parameter stark beeinflußt. Weiterhin wird gezeigt, daß die unter Anwendung eines Pseudoreaktionsmechanismus bei verschiedenen Aufheizgeschwindigkeiten ermittelten kinetischen Parameter eine kinetische Kompensation aufweisen, aus welchem sich die Temperatur des Experimentes als sogenannte isokinetische Temperatur ergibt. Es wird eine ungefähre Berechnung bezüglich der Größe der isokinetischen Temperatur vorgeschlagen, um tatsächliche von Pseudokompensation zu unterscheiden.