A CRITERION FOR DETERMINING THE MECHANISM OF SOLID STATE REACTIONS FROM TG DATA–CONSTANCY OF THE PRE-EXPONENTIAL FACTOR

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For incorrect mechanisms, the computed values of A vary as a function of the heating rate; the correct mechanism, however, yields a constant A.

Symbols

α	the fraction decomposed
A	pre-exponential factor
E^*	energy of activation
k	$= A \exp(-E^*/RT)$
q	the linear heating rate, dT/dt
R	gas constant
T	temperature, absolute
t	time
x	$= E^*/RT$
$f(\alpha)$	a function describing the dependence of $d\alpha/dt$ on α
$g(\alpha)$	the integral of $1/f(\alpha)$
$p^*(x)$	see Appendix for definition

The determination of the mechanisms of solid state reactions from thermogravimetric data is a subject of considerable interest. Many ingenious methods have been proposed by which the kinetic function, $f(\alpha)$, as well as the kinetic parameters may be derived from TG data. These methods are based on either the differential equation or its integral form.

Debate has also raged in the literature in regard to whether TG data can be analyzed to identify unambiguously the explicit form of the kinetic function. It has been suggested that the effect of $f(\alpha)$ on the dynamic curve is inherently masked by that of T being a linear function of t [1]. Actual experience of data analysis has also revealed that it is impossible to ascertain the right reaction mechanism from TG data [2–6]. Hence it is reiterated that the kinetic function should only be determined from isothermal data [1–2, 6–7].

We have now observed that, by the analysis of sets of TG data collected at various rates of heating, it is possible to distinguish among the kinetic functions.

Results

The mathematical model most frequently used for the kinetic description of thermogravimetric data is

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

It readily follows [8] that

$$g(\alpha) = \frac{A}{q} \int_0^T \exp\left(-E^*/RT\right) dT \tag{2}$$

Theoretical data are first generated using this Eq. (2), where the temperature integral is evaluated by numerical means; 700 weighted increments are used in each numerical integration. Typical data are presented in Table 1.

Table 1 Theoretical data—with $E^* = 20$ kcal mol^{-1}; $A = 1 \times 10^{12}$ min^{-1}; $g(\alpha) = -\ln(1-\alpha)$

α	T, K						
	at q = 1	2	5	10	20	50	100 deg min^{-1}
0.1000	313.549	320.062	329.085	336.245	343.715	354.097	362.363
0.2000	320.612	327.415	336.851	344.346	352.173	363.063	371.744
0.3000	325.185	332.180	341.888	349.604	357.666	368.893	377.849
0.4000	328.774	335.921	345.845	353.738	361.988	373.482	382.657
0.5000	331.884	339.165	349.278	357.325	365.740	377.469	386.837
0.6000	334.779	342.184	352.476	360.668	369.237	381.188	390.737
0.7000	337.659	345.190	355.659	363.997	372.722	384.895	394.627
0.8000	340.773	348.441	359.105	367.602	376.497	388.913	398.844
0.9000	344.694	352.535	363.447	372.146	381.257	393.984	404.170

Due to the fact that the temperature integral has no analytical closed form, approximations abound in the literature. The most accurate solution of Eq. (2) may be given [9] in the form

$$\frac{g(\alpha)q}{T^2 p^*(x)} = \frac{AR}{E^*} \exp\left(-E^*/RT\right) \tag{3}$$

where $p^*(x)$ may be evaluated from the van Tets or Schlömilch series or by numerical means [9].

The kinetic parameters are derived [9] from the theoretical data by linearizing

$$\ln \frac{g(\alpha)q}{T^2 p^*(x)} \quad vs. \quad 1/T$$

Typical results are given in Tables 2 and 3.

Table 2 Activation-energy values computed from the theoretical data in Table 1, using various mechanistic equations

Mechanism[+]	E^*, kcal mol^{-1}			R_{xy}
	at $q = 1$	10	100 deg min^{-1}	
D_1	29.46	29.49	29.54	-0.9884
D_2	32.68	32.74	32.80	-0.9942
$D_3 J$	36.80	36.87	36.95	-0.9987
$D_3 GB$	34.03	34.09	34.16	-0.9961
A_1	20.00	20.00	20.00	-1.0000
A_2	9.400	9.359	9.313	-1.0000
A_3	5.932	5.943	6.066	-1.0000
R_2	16.77	16.75	16.74	-0.9967
R_3	17.78	17.77	17.76	-0.9986

[+] See Table 4 for explanations.

Discussion

It can be readily seen that our method of data treatment [9] yields accurate kinetic parameters (both E^* and A) for the correct mechanism. However, the mechanism cannot be ascertained using R_{xy} as the criterion (see Table 2), even in the case of no-scatter theoretical data; this is in accord with the observations made by previous workers [1–7].

Table 3 Values of pre-exponential factor computed from the theoretical data in Table 1, using various mechanistic equations

Mechanism[+]	A, sec^{-1}				
	at $q=1$	5	10	50	100 deg min^{-1}
D_1	1.191×10^{16}	6.082×10^{15}	4.551×10^{15}	2.333×10^{15}	1.745×10^{15}
D_2	1.134×10^{18}	4.605×10^{17}	3.121×10^{17}	1.272×10^{17}	8.619×10^{16}
D_3J	1.950×10^{20}	5.900×10^{19}	3.524×10^{19}	1.072×10^{19}	6.407×10^{18}
D_3GB	2.247×10^{18}	8.282×10^{17}	5.386×10^{17}	1.994×10^{17}	1.296×10^{17}
A_1	1.665×10^{10}	1.667×10^{10}	1.666×10^{10}	1.667×10^{10}	1.666×10^{10}
A_2	1.047×10^{3}	2.241×10^{3}	3.106×10^{3}	6.630×10^{3}	9.181×10^{3}
A_3	3.926×10^{0}	1.153×10^{1}	1.861×10^{1}	6.034×10^{1}	1.047×10^{2}
R_2	4.175×10^{7}	5.269×10^{7}	5.815×10^{7}	7.332×10^{7}	8.086×10^{7}
R_3	1.464×10^{8}	1.718×10^{8}	1.839×10^{8}	2.157×10^{8}	2.307×10^{8}

[+] See Table 4 for explanations.

Table 4 Integral forms of the mechanistic functions

$g(\alpha)$	Rate-controlling factor	Symbol
1 α^2	1-Dimensional diffusion	D_1
2 $(1-\alpha)\ln(1-\alpha)+\alpha$	2-Dimensional diffusion	D_2
3 $[1-(1-\alpha)^{1/3}]^2$	3-Dimensional diffusion, Jander equation	D_3J
4 $\left(1-\dfrac{2}{3}\alpha\right)-(1-\alpha)^{2/3}$	3-Dimensional diffusion, Ginstling–Brounshtein equation	D_3GB
5 $-\ln(1-\alpha)$	Random nucleation/First order reaction	A_1/F_1
6 $[-\ln(1-\alpha)]^{1/2}$	Random nucleation, Avrami–Erofeev	A_2
7 $[-\ln(1-\alpha)]^{1/3}$	Random nucleation, Avrami–Erofeev	A_3
8 $1-(1-\alpha)^{1/2}$	Contracting area	R_2
9 $1-(1-\alpha)^{1/3}$	Contracting volume	R_3

Table 3 reveals that the computed values of the pre-exponential factor remain constant only for the correct kinetic function. For all incorrect kinetic functions tested, the calculated values of A show a drift with change in heating rate.

The criterion is a general one; it is found to hold good for all other mechanisms tested and at all ranges of E^*/RT.

Conclusion

The criterion of constancy of the computed A could prove an insensitive one for experimental data. However, this is to be contrasted with the use of R_{xy}, which is no criterion even for the no-scatter theoretical data.

Appendix

The solution to Eq. (2) is

$$g(\alpha) = \frac{AE^*}{qR} p(x) \tag{4}$$

where

$$p(x) = \int_x^\infty \frac{e^{-u}}{u^2} du \tag{4a}$$

$$= \frac{e^{-x}}{x^2} p^*(x) \tag{4b}$$

The function $p^*(x)$ may be evaluated from the van Tets or Schlömilch series or by numerical means [9].

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Zusammenfassung — Für unrichtige Mechanismen stellen die errechneten Werte für A eine Funktion der Aufheizgeschwindigkeit dar. Im Falle eines korrekt festgestellten Mechanismus erhält man A als Konstante.

Резюме — В случае неправильно установленных механизмов реакций вычисленные значения A изменяются в зависимости от скорости нагрева, тогда как корректный механизм реакции приводит к постоянству A.