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Numerical data for the evaluation of kinetic parameters of solid state decompositions by the non-isothermal method

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Abstract

Determination of the kinetic parameters of the thermal decomposition of solids usually requires a knowledge of the function $g(\alpha)$, describing the mechanism of decomposition. An effective and fast method is described for the determination of kinetic parameters from a single non-isothermal curve. Numerical data in the form of a ready reference table are given from which the kinetic parameters can be obtained once the correct form of $g(\alpha)$ has been established.

INTRODUCTION

The methods of determining the mechanism and kinetics of solid state decompositions of the type

$$a\mathrm{A(s)} \rightarrow b\mathrm{B(s)} + c\mathrm{C(g)} \tag{1}$$

from non-isothermal data are usually based on the equation

$$\ln g(\alpha) = \ln\left(\frac{ZE}{qR}\right) + \ln p(x) \tag{2}$$

where α is the fraction decomposed at temperature T, $g(\alpha)$ is a function of α which depends on the mechanism of decomposition, Z is the pre-exponential factor, E the activation energy of the reaction, q the rate of heating, R the gas constant and $p(x)$ an exponential integral given by

$$p(x) = \int_x^{\infty} (\mathrm{e}^{-x}/x^2)\,\mathrm{d}x \tag{3}$$

x being equal to E/RT [1–3].

It has been shown graphically that ln $p(x)$ is linearly related to $1/T$ and that the temperature range within which the linear relationship exists depends on the value of E [3]. It is thus evident from eqn. (2) that a plot of ln $g(\alpha)$ vs. $1/T$ should be a straight line for a function describing the correct mechanism of the reaction. It is also clear from eqn. (2) that the slope of the plot of ln $g(\alpha)$ vs. $1/T$ is equal to that of ln $p(x)$ vs. $1/T$,

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since $\ln(ZE/qR)$ is a constant. A series of $\ln p(x)$ vs. $1/T$ plots can be prepared, each corresponding to a particular value of E. By finding the $\ln p(x)$ vs. $1/T$ plot with the same slope as that of the experimental $\ln g(\alpha)$ vs. $1/T$ plot for the function describing the correct mechanism, the value of E for the reaction can be obtained.

To simplify the above procedure, we present here numerical data in the form of a ready reference table, for the easy determination of the values of E and Z from a knowledge of the experimental values of slope (S_{expt}) and intercept (I_{expt}) of $\ln g(\alpha)$ vs. $1/T$ plots.

COMPUTATION OF NUMERICAL DATA

The computation involves the determination of (i) the temperature range over which a plot of $\ln p(x)$ vs. $1/T$ gives a straight line for each selected value of E and (ii) the slope S and intercept I of this straight line. This requires the evaluation of the $p(x)$ function.

It is well known [4] that the $p(x)$ function cannot be expressed in a closed form, although several approximations exist [5–7]. Several authors [8,9] have compared the values of $p(x)$ obtained from these approximation methods with those obtained numerically by means of Simpson's procedure [10]. They found that the error involved in the $p(x)$ function calculated from the approximation methods is very large (of the order of several hundred per cent). We have calculated the values of $p(x)$ numerically by means of Simpson's procedure using an IBM computer (version DOS 4.00) for a given activation energy at several temperatures in the range 200–2000 K. The values of $\ln p(x)$ were then plotted vs. $1/T$ and the linear range was determined from the plot. Values of $\ln p(x)$ for some selected E values are given in Table 1 and some typical plots of $\ln p(x)$ vs. $1/T$ are shown in Fig. 1. Using this procedure we have determined the temperature range for each E value from 40 to 800 kJ mol^{-1} at intervals of 40 kJ mol^{-1}. The results are given in Table 2.

It can be seen that for $E = 40$ kJ mol^{-1}, the linear relationship is valid up to 600 K, whereas for $E = 321$–800 kJ mol^{-1}, it is valid up to 2000 K (Table 2). It is thus clear that all data points of $\ln p(x)$ vs. $1/T$ plots for $T \leqslant 600$ K will fall on a straight line for all values of E ranging from 40 to 800 kJ mol^{-1}. Therefore, the slope of the $\ln p(x)$ vs. $1/T$ plot for a given E value (in the above range) can be determined using the equation

$$\frac{\mathrm{d}\ln p(x)}{\mathrm{d}(1/T)} = \frac{\ln[p(x)]_2 - \ln[p(x)]_1}{(1/T_2) - (1/T_1)} \tag{4}$$

where T_1 and T_2 are any two temperatures below 600 K, such that $T_2 > T_1$ and $[p(x)]_1$ and $[p(x)]_2$ are the values of $p(x)$ at T_1 and T_2 respectively.

For accurate results, the least-squares method can be used for the evaluation of the slope and intercept, in which all values of $\ln p(x)$ corresponding

TABLE 1
Values of ln $p(x)$

T (K)	E (kJ mol^{-1})						
	40	100	200	300	400	600	800
200	−32.13	−70.04	−129.85	−190.80	−251.52	−372.60	−493.45
300	−23.31	−49.19	−88.95	−129.85	−170.52	−251.52	−332.27
400	−17.16	−38.59	−70.04	−99.21	−129.85	−190.80	−251.52
500	−14.33	−32.13	−57.57	−82.43	−105.35	−154.27	−202.96
600	−12.39	−27.76	−49.19	−70.04	−88.95	−129.85	−170.52
700	−10.96	−24.59	−43.15	−61.14	−78.90	−112.36	−147.30
800	−9.86	−20.97	−38.59	−54.43	−70.04	−99.21	−129.85
900	−8.98	−18.72	−35.01	−49.19	−63.12	−88.95	−116.26
1000	−8.26	−17.16	−32.13	−44.97	−57.57	−82.43	105.35
1100	−7.66	−15.88	−29.75	−41.50	−53.00	−75.68	−96.42
1200	−7.14	−14.80	−27.76	−38.59	−49.19	−70.04	−88.95
1300	−6.70	−13.88	−26.06	−36.12	−45.94	−65.26	−84.33
1400	−6.31	−13.09	−24.59	−33.99	−43.15	−61.14	−78.90
1500	−5.96	−12.39	−23.31	−32.13	−40.72	−57.57	−74.18
1600	−5.65	−11.77	−20.97	−30.50	−38.59	−54.43	−70.04
1700	−5.37	−11.22	−19.69	−29.05	−36.70	−51.66	−66.38
1800	−5.12	−10.72	−18.72	−27.76	−35.01	−49.19	−66.12
1900	−4.89	−10.27	−17.90	−26.60	−33.50	−46.97	−60.20
2000	−4.68	−9.86	−17.16	−25.55	−32.13	−44.97	−57.57

to different temperatures in the linear range are taken into account. The values of slope S and intercept I calculated by this method are given in Tables 3 and 4 respectively, for E values ranging from 40 to 800 kJ mol^{-1} at

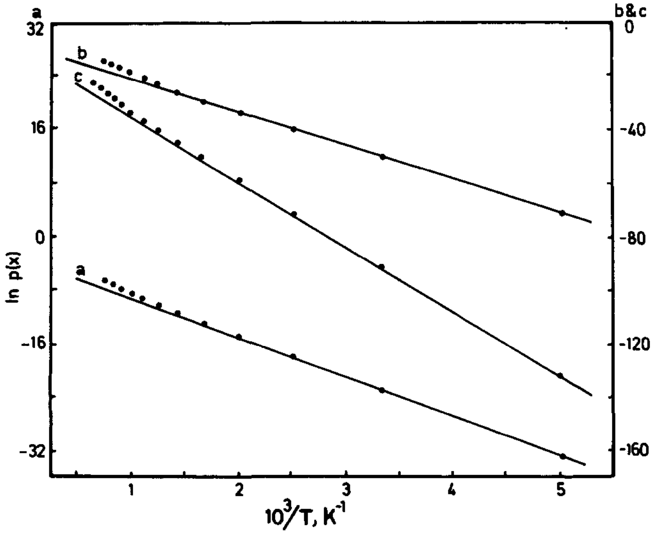

Fig. 1. Plot of ln $p(x)$ vs. $1/T$: a, $E = 40$ kJ mol^{-1}; b, $E = 100$ kJ mol^{-1}; c, $E = 200$ kJ mol^{-1}.

TABLE 2

Activation energy E and temperature range

E (kJ mol^{-1})	Temperature range (K)
40	$\leqslant 600$
80	$\leqslant 700$
120	$\leqslant 800$
160	$\leqslant 900$
200	$\leqslant 1000$
240	$\leqslant 1200$
280	$\leqslant 1500$
320	$\leqslant 1800$
321–800	$\leqslant 2000$

intervals of 4 kJ mol^{-1}. From a knowledge of S_{expt}, one can easily read out the values of the activation energy from this table by matching the slope values. Knowing E, Z can be calculated as follows. In the linear range, ln $p(x)$ can be written as

$$\ln p(x) = S(1/T) + I \tag{5}$$

Substituting eqn. (5) in eqn. (2), we obtain,

$$\ln g(\alpha) = \ln\left(\frac{ZE}{qR}\right) + S(1/T) + I \tag{6}$$

It is clear from eqn. (6) that

$$I_{\mathrm{expt}} = \ln\left(\frac{ZE}{qR}\right) + I \tag{7}$$

Z can now be calculated using eqn. (7). Knowing E and Z, the rate constant k of the reaction at a particular temperature can be obtained from the Arrhenius relation:

$$k = Z\,\mathrm{e}^{-E/RT} \tag{8}$$

A plot of E vs. S revealed an excellent linear relationship (correlation coefficient, $r = 0.99998$) between these two quantities (see Fig. 2). The equation of this straight line is found to be

$$E\ (\mathrm{kJ\ mol^{-1}}) = -8.3249(S/10^3) - 5.3699 \tag{9}$$

Either Table 3 or eqn. (9) can be used to estimate the value of E from the experimental slope of the ln $g(\alpha)$ vs. $1/T$ plot.

It must be pointed out that there are some difficulties in determining the correct kinetic function, $g(\alpha)$, from non-isothermal data. For instance, Criado and Morales [11] have shown that with non-isothermal data, it is impossible to distinguish between reactions described by a first-order kinetic

TABLE 3

Values of slopes ($S \times 10^{-3}$)

E (kJ mol^{-1})	0	4	8	12	16	20	24	28	32	36
40	−6.00	−6.49	−6.96	−7.40	−7.84	−8.31	−8.84	−9.25	−9.72	−10.16
80	−10.52	−11.14	−11.60	−11.96	−12.43	−12.89	−13.30	−13.71	−14.20	−14.68
120	−15.16	−15.68	−16.16	−16.26	−16.74	−17.22	−17.70	−18.18	−18.66	−19.14
160	−19.63	−20.16	−20.65	−21.13	−21.67	−22.09	−22.62	−23.10	−23.58	−23.92
200	−24.40	−24.97	−25.45	−25.93	−26.41	−26.89	−27.42	−27.90	−28.38	−28.86
240	−29.34	−29.86	−30.34	−30.82	−31.30	−31.71	−32.23	−32.71	−33.19	−33.67
280	−34.22	−34.70	−35.18	−35.66	−36.14	−36.62	−36.69	−37.17	−37.65	−38.61
320	−39.09	−39.57	−40.00	−40.49	−40.97	−41.45	−41.93	−42.41	−42.89	−43.37
360	−43.85	−44.33	−44.82	−45.30	−45.78	−46.26	−46.74	−47.22	−47.68	−48.16
400	−48.64	−49.12	−49.61	−50.09	−50.57	−51.05	−51.53	−52.01	−52.49	−52.97
440	−53.45	−53.94	−54.42	−54.90	−55.37	−55.86	−56.34	−56.82	−57.30	−57.78
480	−58.26	−58.74	−59.22	−59.70	−60.19	−60.67	−61.15	−61.63	−62.11	−62.59
520	−63.08	−63.56	−64.04	−64.52	−65.01	−65.49	−65.97	−66.45	−66.93	−67.41
560	−67.89	−68.37	−68.85	−69.34	−69.82	−70.30	−70.80	−71.28	−71.76	−72.24
600	−72.72	−73.20	−73.68	−74.16	−74.65	−75.13	−75.61	−76.09	−76.57	−77.05
640	−77.53	−78.01	−78.49	−79.00	−79.48	−79.96	−80.44	−80.93	−81.41	−81.89
680	−82.37	−82.85	−83.33	−83.81	−84.29	−84.77	−85.26	−85.74	−86.22	−86.73
720	−87.21	−87.69	−88.17	−88.66	−89.14	−89.62	−90.10	−90.58	−91.06	−91.54
760	−92.02	−92.50	−92.99	−93.47	−93.95	−94.47	−94.95	−95.43	−95.91	−96.39
800	−96.87									

TABLE 4

Values of intercepts (I)

E (kJ mol^{-1})	0	4	8	12	16	20	24	28	32	36
40	−2.46	−2.64	−2.85	−3.30	−3.67	−3.88	−3.87	−4.33	−4.49	−4.76
80	−5.38	−4.94	−5.12	−5.69	−5.81	−5.98	−6.32	−6.64	−6.71	−6.78
120	−6.85	−6.78	−6.84	−7.56	−7.62	−7.68	−7.74	−7.79	−7.85	−7.90
160	−7.95	−7.79	−7.84	−7.89	−7.93	−7.98	−7.85	−7.89	−7.93	−8.10
200	−8.15	−7.89	−7.93	−7.96	−8.00	−8.04	−7.94	−7.98	−8.01	−8.05
240	−8.08	−8.00	−8.03	−8.06	−8.09	−8.12	−8.05	−8.08	−8.11	−8.14
280	−7.98	−8.01	−8.03	−8.06	−8.09	−8.11	−9.48	−9.51	−9.53	−8.05
320	−8.07	−8.10	−8.09	−8.12	−8.14	−8.17	−8.19	−8.21	−8.24	−8.26
360	−8.28	−8.30	−8.32	−8.35	−8.37	−8.39	−8.41	−8.43	−8.39	−8.41
400	−8.43	−8.45	−8.47	−8.49	−8.51	−8.53	−8.55	−8.56	−8.58	−8.60
440	−8.62	−8.64	−8.65	−8.67	−8.61	−8.62	−8.64	−8.66	−8.67	−8.69
480	−8.71	−8.73	−8.74	−8.76	−8.77	−8.79	−8.81	−8.82	−8.84	−8.85
520	−8.77	−8.78	−8.80	−8.81	−8.83	−8.84	−8.86	−8.87	−8.89	−8.90
560	−8.91	−8.93	−8.94	−8.96	−8.97	−8.98	−8.88	−8.90	−8.91	−8.92
600	−8.94	−8.95	−8.96	−8.98	−8.99	−9.00	−9.02	−9.03	−9.04	−9.05
640	−9.07	−9.08	−9.09	−8.98	−8.99	−9.00	−9.01	−9.03	−9.04	−9.05
680	−9.06	−9.07	−9.09	−9.10	−9.11	−9.12	−9.13	−9.14	−9.15	−9.03
720	−9.04	−9.05	−9.06	−9.07	−9.09	−9.10	−9.11	−9.12	−9.13	−9.14
760	−9.15	−9.16	−9.17	−9.18	−9.19	−9.06	−9.07	−9.08	−9.09	−9.10
800	−9.11									

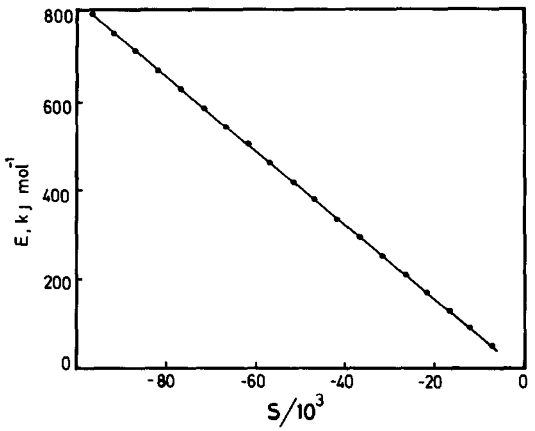

Fig. 2. Plot of activation energy E vs. slope S.

equation and those governed by the Prout–Tompkins or Avrami–Erofeev mechanisms. They have also pointed out the impossibility of identifying unambiguously between diffusion-controlled and phase-boundary-controlled reactions by non-isothermal methods [12]. Such difficulties do not arise when the isothermal method is followed. But this method of obtaining kinetic data involves a series of experiments at different temperatures which is laborious. The non-isothermal method, which enables a range of temperatures to be investigated relatively quickly is more convenient and Wendlandt [13] has pointed out several advantages of this method. It is suggested by many authors [14–17] that simultaneous kinetic analysis of one isothermal curve for the identification of the reaction mechanism, i.e. the correct $g(\alpha)$ and one non-isothermal curve for the determination of kinetic parameters, would constitute an effective and fast method. The numerical data as well as the straight-line equation proposed in this paper can be used very efficiently for obtaining kinetic parameters, once the correct form of $g(\alpha)$ has been established.

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