

Non-isothermal kinetics: a different approach

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Abstract

The ability to produce computer generated DTG curves for first-, second- and third-order kinetic reaction equations of given peak heights and peak temperatures has simplified the comparison between experimental and computer generated DTG curves. This has been made possible by using mathematical equations, originally developed some years ago which have been suitably modified by more recent work. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

There are problems when using either isothermal or non-isothermal experimental methods to determine the reaction mechanism and the kinetic parameters of first-, second- and third-order solid state reactions. When using isothermal techniques, the method given by Sharp et al. [1] is often used to identify the reaction mechanism by comparison of the reduced time plot gained from experimental DTG data with the reduced time plot derived from the reaction equation. Many experimental reduced time plots do not fit any of the reduced time plots given in that paper. It is sometimes claimed that this could be due to the fact that the experimental data fits an unknown reaction equation, for which the reduced time plot has not yet been developed.

There are, however, other reasons which can cause the mismatch.

1. The data can be affected by the thermal lags in the system, for in many instances, mass loss

commences before the sample has reached the isothermal temperature. A recent paper has reported the effects of such thermal lags on reduced time plots for many of the known solid state reaction equations [2].

2. Sometimes multiple reactions occur simultaneously.

These multiple reactions will cause distortion of the reduced time plot, again making it difficult to identify the correct reaction mechanism.

The non-isothermal method is more frequently used, as it provides a quicker method by which the kinetic parameters: A , the pre-exponential factor and E , the activation energy, may be determined from the experimental data. However, when using this method, it is difficult to determine the 'correct' kinetic reaction equation to be applied to the collected data.

The general equation for the determination of the constants E and A has the form:

$$\ln \left[\left(\frac{d\alpha}{dt} \right) (\text{function of } \alpha) \right] = \ln A - \frac{E}{RT} \quad (1)$$

where $d\alpha/dt$ is the fractional rate of reaction at time t ; A , the pre-exponential factor (s^{-1}); E , the activation energy ($J \text{ mol}^{-1}$); T , the absolute temperature (K) and

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(function of α), the first differential function of the equation in α which describes the reaction process.

If the correct reaction equation has been selected, then a plot of Eq. (1) will be a straight line of slope $-E/R$ and intercept $\ln A$. However, this is rarely the case, for the plotted line is usually far from linear. In such a situation, the usual practice is to apply the experimental data to Eq. (1), using all the different functions of α in Eq. (1) to find which function produces the statistically best straight line. The values of E and A are then determined from the slope ($=E/R$) and intercept ($=\ln A$) of this best straight line. The reaction mechanism is assumed to be that which is described by the equation used to give the best straight line. This technique is not to be recommended as the curvature of a plot of Eq. (1) for any reaction mechanism can, in fact, be due to other causes, such as variation of E and to a lesser extent A , with reaction and/or temperature. Such variation will be considered in a paper to be published [3].

Much of the comment mentioned above concerning the choice of the correct equation applies to other equations which have been used to determine the parameters of the reaction [4–6].

In an attempt to find alternative methods by which to determine the reaction equation, together with A and E , computer generated DTG curves have been produced for all the known reaction mechanism equations with the idea of comparing such computer generated DTG curves with experimental DTG curves. To this end, factors such as half widths and other characteristics of experimental curves were compared with similar factors for computer generated curves [7–9]. This technique has been only partially successful for it is extremely difficult to match computer generated and experimental DTG curves, if the peak heights and peak temperatures do not coincide. In order to make comparison easier, it would be better if the computer generated DTG peak had the same peak height $(d\alpha/dt)_{\max}^1$ and peak temperature (T_{\max}) as the experimental curve. The difficulty of achieving this arises because the equation constants E and A are linked with $(d\alpha/dt)$ and (T_{\max}) in a complex manner, making it very difficult to produce a computer generated curve of the same peak height and peak temperature as that of an experimental DTG curve.

¹ Value of the peak of the DTG curve.

The mathematics of first-order reaction equations were investigated many years ago by Murray and White [10] who developed mathematical relations between the maximum rate of reaction $(d\alpha/dt)_{\max}$, the temperature at this maximum rate (T_{\max}), the heating rate β and the activation energy E . This equation is:

$$\left(\frac{d\alpha}{dt}\right)_{\max} = \frac{\beta E(1 - \alpha_{\max})}{RT_{\max}^2} \quad (2)$$

where α_{\max} : fraction reacted at the maximum rate; β : heating rate (degrees s^{-1}); R : gas constant (8.3145 J mol⁻¹ T⁻¹); T_{\max} : temperature of the maximum of the DTG curve.

Murray and White also developed mathematical expressions for α_{\max} and T_{\max} but more recent studies have shown that α_{\max} is sensibly constant at a value of 0.6 for first-order solid state reactions. Thus Eq. (2) can be written

$$\left(\frac{d\alpha}{dt}\right)_{\max} = \frac{0.4\beta E}{RT_{\max}^2} \quad (3)$$

Transposing,

$$E = \frac{2.5(d\alpha/dt)_{\max} RT_{\max}^2}{\beta} \quad (4)$$

Note that Eq. (4) does not contain A , the pre-exponential factor.

Hence substitution of the values for $(d\alpha/dt)_{\max}$ and T_{\max} from an experimentally produced DTG curve will give a value for E for the process, should the reaction be known to be a first-order reaction. In order, however, to draw the complete computer-generated curve it is necessary to find the value of A , the pre-exponential factor.

Referring again to [10] the authors also give a relationship between the factor A and other factors as given below

$$\ln A = \ln \beta + \ln E - \ln R - 2 \ln T_{\max} + \frac{E}{RT_{\max}} \quad (5)$$

(\ln : natural logarithm of the function).

Hence if the value of E found from Eq. (4) is substituted in Eq. (5), then A can be determined. These two values can then be used in the program given in [7] to produce a computer generated DTG curve.

Now that the computer generated and experimental DTG curves have the same peak temperature and peak

General Spreadsheet for 1st, 2nd and 3rd Order Reaction Equations
 All settings in marked boxes can be altered

Settings	Gas Const 8.3116	Heat Rare		10			
	Rate Max 0.002	1st temp		50			
	T step 5						

	Peak Temp	50	55	60	65	70	75	80
	Abs Temp	323	328	333	338	343	348	353
	(temp)^2	104329	107584	110889	114244	117649	121104	124609
1st Order	E	26014.23	26825.86	27649.95	28486.51	29335.54	30197.04	31071
	Ln A	4.417	4.567	4.717	4.867	5.017	5.167	5.317
	A	82.84741	96.25495	111.8323	129.9306	150.9578	175.388	203.7717
2nd Order	E	39266.76	40491.86	41735.77	42998.51	44280.06	45580.44	46899.63
	Ln A	9.681564	9.907979	10.13439	10.36081	10.58722	10.81364	10.58722
	A	16019.52	20090.02	25194.82	31596.73	39625.33	49693.98	62321.02
3rd Order	E	51091.77	52685.8	54304.32	55947.32	57614.81	59306.79	61023.25
	Ln A	14.72112	15.01572	15.31032	15.60492	15.89952	16.19412	16.48872
	A	2473447	3320820	4458493	5985918	8036622	10789870	14486350

Fig. 1. Part of spreadsheet for the calculation of *A* and *E* for given values of peak temperature and peak height for first-, second- and third-order reactions.

height, it is much simpler to make comparisons between the two curves. If the two curves match perfectly, then the experimental DTG reaction is indeed a first-order reaction with the same values of *E* and *A* which were used to generate the computer generated DTG curve.

Similar equations apply to second- and third-order reaction mechanisms and are as follows:

For a second-order reaction:

$$E = \frac{3.85(d\alpha/dt)_{\max} RT_{\max}^2}{\beta} \tag{6}$$

and

$$\ln A = \ln \beta + \ln E - \ln 2 - \ln R - 2T_{\max} + \frac{E}{RT_{\max}} \tag{7}$$

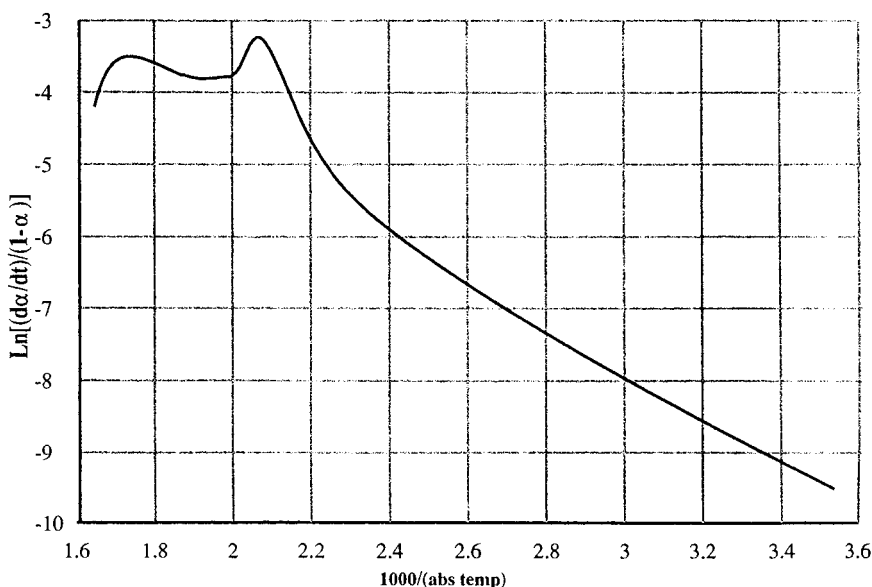


Fig. 2. In plot of the combination of two first-order reactions.

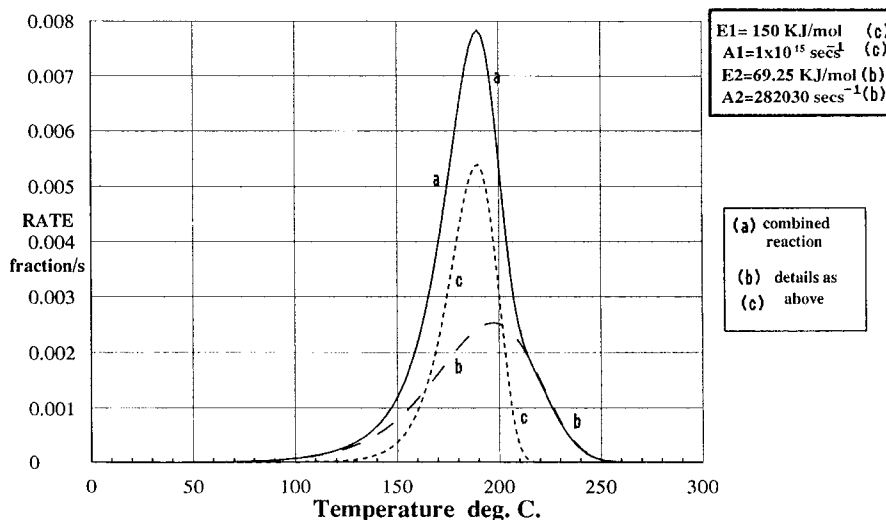


Fig. 3. DTG curves of two simultaneous reactions.

For a third-order reaction:

$$E = \frac{5(d\alpha/dt)_{\max} RT_{\max}^2}{\beta} \quad (6)$$

and

$$\ln A = \ln \beta + \ln E - \ln 3 - \ln R - 2T_{\max} + \frac{E}{RT_{\max}} \quad (7)$$

Using Eqs. (2)–(7), a universal spreadsheet (Fig. 1) has been devised, enabling the E and A values to be read off the chart for values of β , $d\alpha/dt$ and T_{\max} (the values given are only illustrative and do not represent real values).

Despite the improved ability to make comparisons between experimental and computer generated curves, they often still do not match for many reasons. If this is the case, it is often possible to gain further information from the experimental data when using Eq. (1). As stated above, if the correct reaction equation has been used and A and E are constant over the whole reaction, then the plot is a straight line. However, this curve can exhibit a 'hump' as shown in Fig. 2, whatever reaction equation is used and this can be indicative of more than one reaction mechanism occurring simultaneously. This is illustrated in Fig. 3 and is dealt with more fully in a paper to be published [3].

There are other reasons why experimental DTG curves do not conform to a specific reaction equation.

As well as the illustration given above, the DTG curve can be distorted due to a variation in A and E with both temperature and reaction. This situation is considered in the paper [3] mentioned above.

It is intended to produce similar equations to those for first-, second- and third-order reactions (Eqs. (2)–(7)) for other types of reaction mechanism.

2. Conclusions

The ability to produce a computer generated DTG curve of known maximum rate ($d\alpha/dt_{\max}$) and peak temperature (T_{\max}) makes it considerably easier to compare such curves with experimental DTG curves, rather than using factors, such as half widths, etc., as used in an earlier paper [7]. Accordingly, easier decisions can be made concerning the nature of the reaction involved, as to whether the correct reaction equation has been chosen or whether the reaction is of a more complex nature and requires further investigation.

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