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On-line method for isothermal kinetic analysis

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Abstract

The kinetic analysis of any isothermal process is based on compliance with the equational form $g(\alpha) = kt$, which requires an a priori knowledge of the final property change Δp_∞. It is therefore imperative that this equation is not applied to incomplete reactions. A new on-line method has therefore been developed here which gives analytical solutions to well known mechanisms of reaction without recourse to Δp_∞. In some cases, where $\Delta p_\infty k$ appears as a product or exponential terms are to be found, computer based numerical methods have been adopted to solve the equations. The deciphering of the mechanism and the evaluation of k without waiting for the completion of a TG run has been demonstrated with a hypothetical TG curve.

Keywords: Accelerating rate equation; Decelerating rate equation; Kinetic analysis; On-line method; Sigmoid rate equation

1. Introduction

After reviewing current methods of evaluating the rate constant k and pointing out some of the inherent weaknesses of the non-isothermal method [1], a technique is outlined for the determination of k during the course of an actual isothermal experiment. In isothermal kinetic studies involving at least one solid phase, the rate constant is usually represented by an equational form

$$g(\alpha) = kt \tag{1}$$

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Table 1
Commonly used solid-state reaction mechanisms

Rate mechanisms		$g(\alpha) = f(kt)$ functional form	$\alpha = f(kt)$ functional form
1. Accelerating rate equations			
Power law	E1	$\alpha^{1/n} = kt$	$\alpha = (kt)^n$
Exponential law	P1	$\ln \alpha = kt$	$\alpha = \exp(kt)$
2. Sigmoid rate equations (nucleation and growth control)			
Avrami–Erofeev	A2	$[-\ln(1-\alpha)]^{-1/2} = kt$	$\alpha = 1 - 2\exp(-kt)$
Avrami–Erofeev	A3	$[-\ln(1-\alpha)]^{-1/3} = kt$	$\alpha = 1 - 3\exp(-kt)$
Avrami–Erofeev	A4	$[-\ln(1-\alpha)]^{-1/4} = kt$	$\alpha = 1 - 4\exp(-kt)$
Prout–Tompkins	B1	$\ln \frac{\alpha}{1-\alpha} = kt$	$\alpha = \frac{\exp(kt)}{1+\exp(kt)}$
3. Deceleratory rate equations			
3.1. Based on diffusion mechanism			
One-dimensional diffusion	D1	$\alpha^2 = kt$	$\alpha = \sqrt{kt}$
Two-dimensional diffusion	D2	$(1-\alpha)\ln(1-\alpha) = kt$	–
Three-dimensional diffusion	D3	$[1-(1-\alpha)^{1/3}]^2 = kt$	$\alpha = 1-(1-\sqrt{kt})^3$
Ginstling–Brounshtein	D4	$[1-(2\alpha/3)]-(1-\alpha)^{2/3} = kt$	–
Anti-Jander (counter diffusion)		$[(1+\alpha)^{1/3}-1]^2 = kt$	$\alpha = (1+\sqrt{kt})^3 - 1$
3.2. Based on geometric models			
Contracting area	R2	$[1-(1-\alpha)^{1/2}] = kt$	$\alpha = 1-(1-kt)^2$
Contracting volume	R3	$[1-(1-\alpha)^{1/3}] = kt$	$\alpha = 1-(1-kt)^3$
3.3. Based on order of reaction			
First order	F1	$-\ln(1-\alpha) = kt$	$\alpha = 1-\exp(-kt)$
Second order	F2	$1/[1-\alpha] = kt$	$\alpha = 1 - 1/(kt)$
Third order	F3	$1/[1-\alpha]^2 = kt$	$\alpha = 1 - 1/\sqrt{kt}$

where $g(\alpha)$ is a function of the fraction reacted at time t at an arbitrary constant temperature.

The function $g(\alpha)$ can take different forms depending on the type of reaction that occurs, and such forms have been reviewed by Brown and co-workers [2,3]. A summary of these functional forms is given in Table 1. One way of obtaining k is to calculate all the available functions of $g(\alpha)$ and to find the one which gives the best linear compliance with Eq. (1). Most of the methods so far reported in the literature make use of α, which is the fraction converted and is measured by means of any property p that changes linearly and continuously with the reaction during the course of an isothermal experiment as a function of time. The property chosen must be sufficiently sensitive to represent the change of the state and must be linearly proportional to the number of reactant or product molecules. In thermal analysis, such a property which is monitored as a function of time can be any one of the following, viz.: the instantaneous weight during thermogravimetry, the intensity of a characteristic line in high temperature X-ray diffractometry, the enthalpy in dynamic calorimetry, the volume in thermomechanical measurement, or the physical dimension in dilatometry. The term α is generally defined by

$$\alpha = \frac{|(p_t - p_0)|}{|(p_\infty - p_0)|} = \frac{\Delta p_t}{\Delta p_\infty} \tag{2}$$

where p_t is the value of the property at any instant of time, p_0 is the value of the property at the initial time, and p_∞ is the value of the property after infinite time (symbolizing completion of the reaction).

In general, the methods of kinetic analysis are based on the very definition of α. That is, one can compute the fraction converted only with the knowledge of p_∞ after completion of the reaction. Quite often one comes across situations where reactions in a solid medium seldom proceed to completion for a variety of reasons, such as low temperature and limitations in the solid-state transport processes. Such reactions designated as incomplete reactions are therefore unsuitable for the determination of kinetic constants because of their dependence on the numerical value of p_∞. However, the present trend of computer based automation-cum-data processing could facilitate the determination of kinetic constants, even without recourse to the value of p_∞, if the mathematical solutions could be suitably reformulated. The steps involved in such an approach are described in this work, along with its application to a numerically simulated TG curve for the purpose of illustration.

2. Mathematical formulation

Eq. (1) above can be rewritten as

$$\alpha = f(k,t) \tag{3}$$

and various $g(\alpha)$ equational forms listed in Table 1 correspond to different mechanisms. For two distinct instants of time t_1 and t_2, Eqs. (2) and (3) yield

$$\alpha_{t1} = \Delta p_{t1}/\Delta p_\infty = f(k,t_1) \tag{4}$$

$$\alpha_{t2} = \Delta p_{t2}/\Delta p_\infty = f(k,t_2) \tag{5}$$

The ratio of the weight changes R is obviously given by the ratio of α_{t1} and α_{t2}

$$R = \Delta p_1/\Delta p_2 = f(k,t_1)/f(k,t_2) \tag{6}$$

Eq. (6) can be solved algebraically for k for the different mathematical forms of $g(\alpha)$ in Table 1, and such solutions are summarized in Table 2. It should be noted at this juncture that, for all except a few of the mechanisms, the algebraic solutions could be found in the present study.

The exceptional cases are mainly those mechanisms based on nucleation and growth, such as Avrami–Erofeev equations, which have exponential terms rendering algebraic solutions difficult, if not impossible. However, the numerical solution, viz., the Newton–Raphson approach, can be employed for elucidating the roots of Eq. (6) when an analytical route is not feasible. A brief description of this iteration method, along with initial guessed values, are given in the Appendix. In addition, the rate equations based on a power law, such as $\alpha^{1/n} = kt$, cannot be solved for an exclusive k. Instead, the algebraic roots lead to n, the power law exponent, and k^n

Table 2
Analytical solutions for k with weight ratio R

Rate mechanisms		Solution for rate constant k	Remarks
1. Accelerating rate equations			
Power law	P1	$n = \ln(R)/\ln(t_1/t_2) \quad k\Delta w_\infty^{1/n} = \frac{\Delta w_t^{1/n}}{t_i}$	$k\Delta w_\infty^{1/n}$ could not be separated
Exponential law	E1	$k = \frac{\ln(R)}{(t_1 - t_2)}$	
2. Sigmoid rate equations			
Avrami–Erofeev	A2	$(R-1) + 2\exp(-kt_1) - 2\exp(-kt_2) = 0$	Solution can be obtained by Newton–Raphson method. Refer to appendix for the method
Avrami–Erofeev	A3	$(R-1) + 3\exp(-kt_1) - 3\exp(-kt_2) = 0$	
Avrami–Erofeev	A4	$(R-1) + 4\exp(-kt_1) - 4\exp(-kt_2) = 0$	
Prout–Tompkins	B1	$0 = \frac{\exp[k(t_1 - t_2)][1 + \exp(kt_2)]}{[1 + \exp(kt_1)]} - R$	
3. Deceleratory rate equations			
3.1. Based on diffusion mechanism			
One-dimensional diffusion	D1	Solution is similar to power law with $n = 0.5$	
Three-dimensional diffusion	D3	$(Rt_2^{3/2} - t_1^{3/2})k - (Rt_2 - t_1)\sqrt{k} \cdot 3 + 3(Rt_2^{0.5} - t_1^{0.5}) = 0$	
Anti Jander (counter diffusion)		$(Rt_2^{3/2} - t_2^{3/2})k + (Rt_2 - t_1)\sqrt{k} \cdot 3 + 3(Rt_2^{0.5} - t_1^{0.5}) = 0$	
3.2. Based on geometric models			
Contracting area	R2	$k = \frac{2t_1 - 2Rt_2}{t_1^2 - t_2^2 R}$	
Contracting volume	R3	$(Rt_2^3 - t_1^3)k^2 - (Rt_2^2 - t_1^2) \cdot 3k + 3(Rt_2 - t_1) = 0$	
3.3. Based on reaction order			
First order	F1	$R[1 - \exp(-kt_2)] - [1 - \exp(-kt_1)] = 0$	Newton–Raphson method can be used to obtain rate constant
Second order	F2	$k = \frac{(Q-1)}{(Qt_2 - t_1)}$	
Third order	F3	$k = \frac{(Q^{\#} - 1)^2}{[(Q^{\#})\sqrt{t_1} - \sqrt{t_2}]^2}$	

Note: $R = \Delta w_1/\Delta w_2$; $Q = Rt_1/t_2$; $Q^{\#} = R\sqrt{t_1/t_2}$.

Table 3
Numerical values of hypothetical TG curves chosen for Figs. 1 and 2

Time/s	Delta W (ΔW) values for	
	Fig. 2	Fig. 1
10	1.3216	0.2151
70	3.2341	1.4117
130	4.2075	2.4619
190	4.9025	3.3838
250	5.4482	4.1929
310	5.8977	4.9030
370	6.2789	5.5263
430	6.6086	6.0734
490	6.8980	6.5536
550	7.1546	6.9751
610	7.3942	7.3450

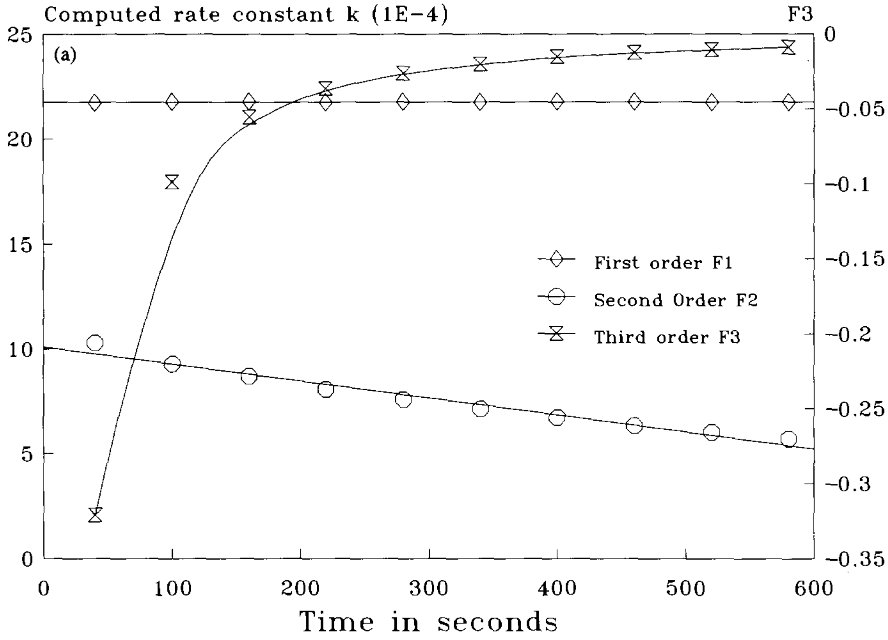
Note: $\Delta W_{\infty} = 10.0000$.

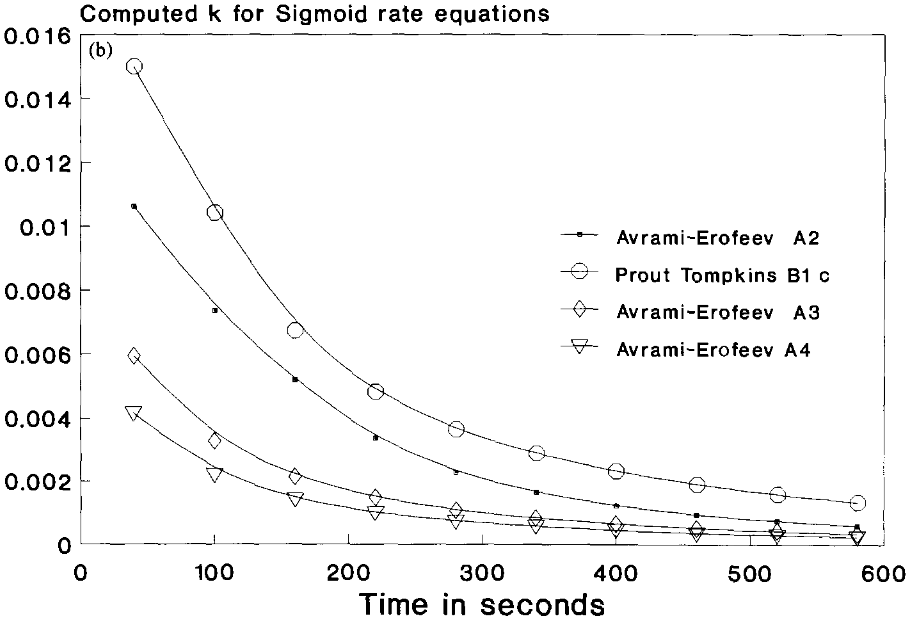
multiplied by Δp_{∞}, as is pointed out in Table 2. Further, some of the equations which are based on diffusion controlled mechanism (viz., the Ginstling–Brounshtein equation D4 and two-dimensional diffusion D2, have defied all our attempts at solution for their roots. Perhaps the following polynomial approximation suggested by Bar-Gadda [4] may lead to solutions of the D4 and D2 equations.

2.1. Evaluation of k with numerical simulation

Two hypothetical TG curves as given in Table 3 are taken for testing the analytical solutions listed in Table 2. Both the approaches developed in the earlier section, viz., those of analytical solutions and numerical methods, have been applied to the different models and the values of k have been computed as a function of time. Typical results of such computations are presented in Fig. 1(a)–(d). In the case of the mechanism that is operative for the reaction under investigation, k has to be independent of time. If k does not have a constant value, this indicates that the mechanism under consideration is not operative. In addition to these two distinct categories, possibilities exists for marginal variation of k with time, which makes it difficult to select between the two options (see Fig. 2(a)–(d)). Under these circumstances, one resorts to the computation of α and Δp_{∞} using the derived values of k. A cursory look at the values of α and Δp calculated thus will usually reveal the acceptability or otherwise of the mechanism being considered. This point is illustrated with the help of Table 4. It is obvious that values of α that are either greater than unity or negative and those values of Δp_{∞} noncomparable in magnitude to the values of Δp_0 or nonconstancy of Δp_{∞} are untenable. It is thus easy to reject the mechanisms that have given rise to such k values.

In this manner, numerical simulation has been carried out on all fourteen mechanisms, and it is found that the present on-line method can be readily adopted





c The computed k for Prout-Tompkins mechanism is only approximate value.

Fig. 1. (a), (b).

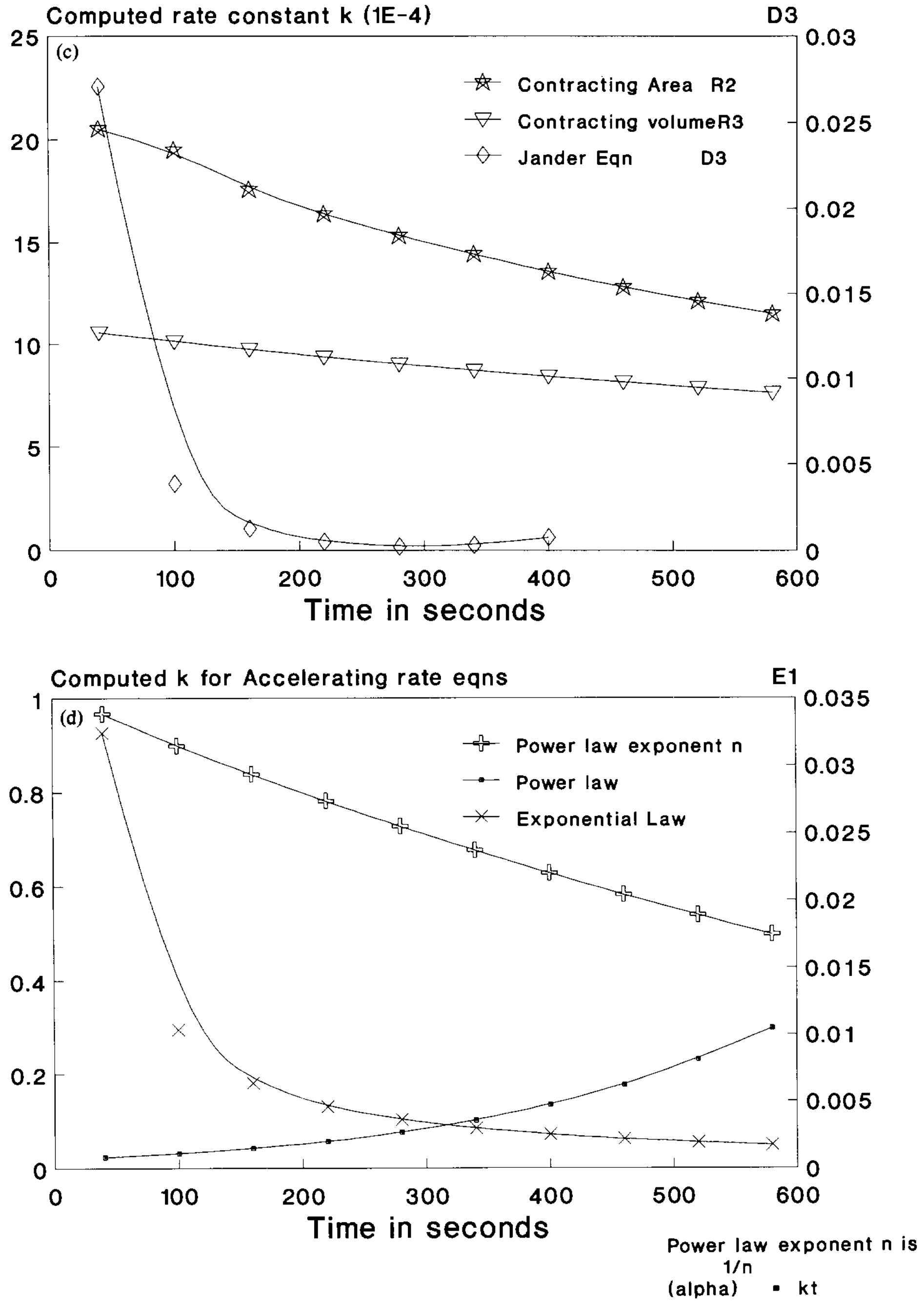
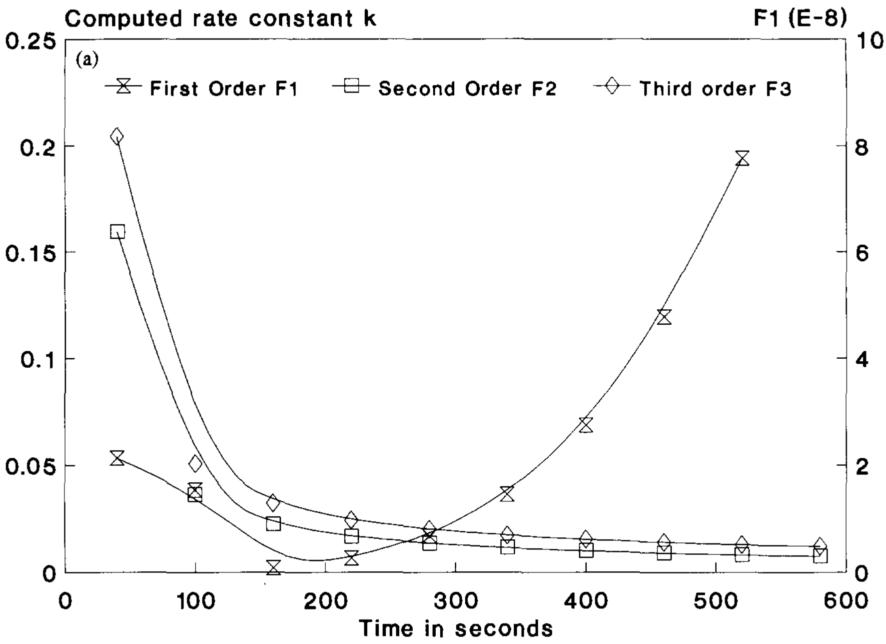
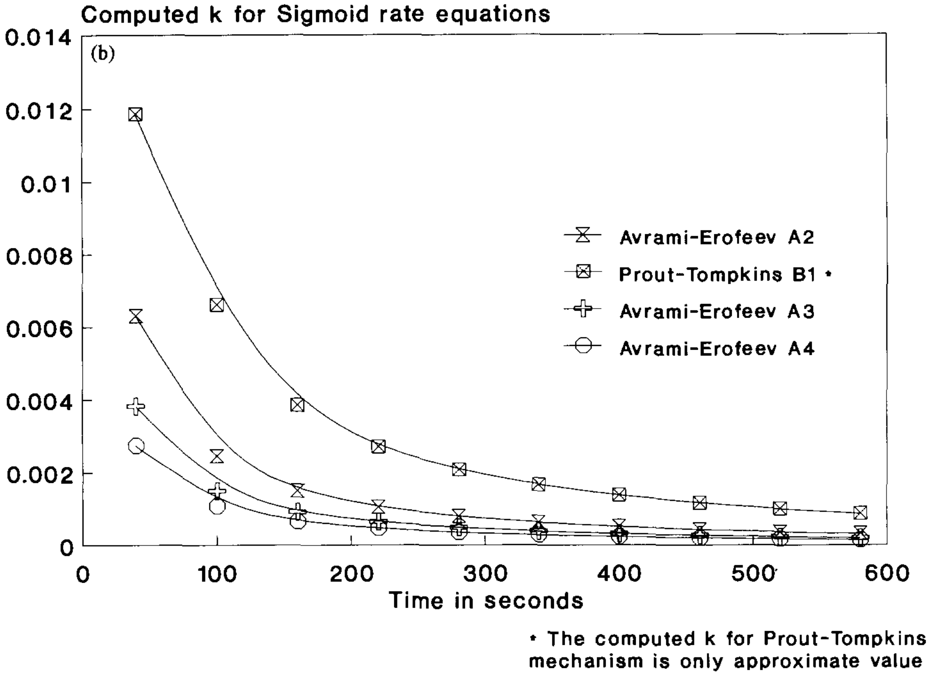


Fig. 1. Illustration of the method for generation of the rate constant *k* vs. time *t* using the data of the hypothetical TG curve (Table 3), which is following the F1 reaction mechanism for various reaction mechanisms: (a), based on reaction order; (b), based on nucleation and growth; (c), based on diffusion and geometric models; (d), based on accelerating rate expressions.





* The computed k for Prout-Tompkins mechanism is only approximate value

Fig. 2. (a), (b).

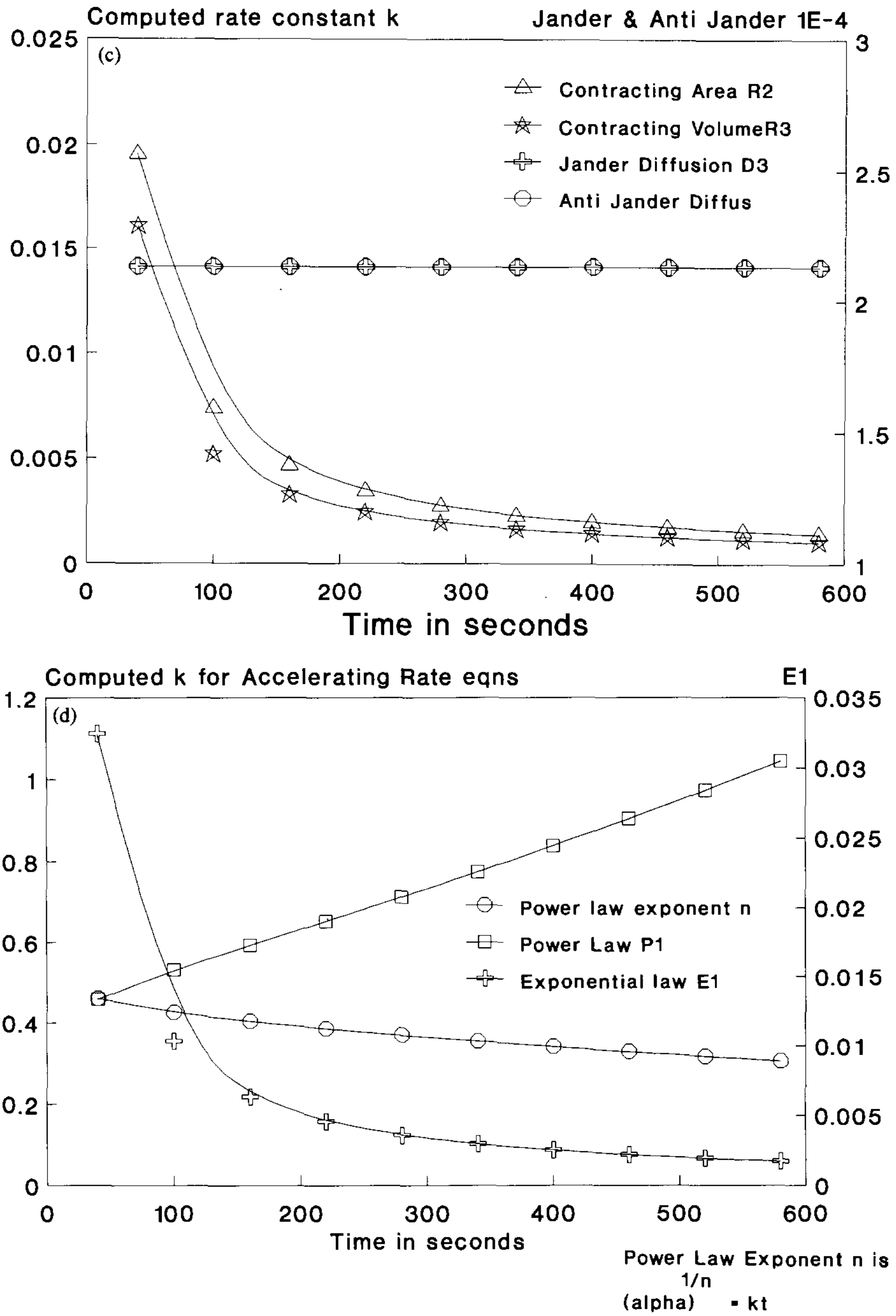


Fig. 2. Plot of computed rate constant k as a function of reaction time t for the hypothetical TG curve which is following the D3 reaction mechanism, which exhibits marginal variation of k with time for certain reaction mechanisms among various reaction mechanisms: (a), based on reaction order; (b), based on nucleation and growth; (c), based on diffusion and geometric models; (d) based on accelerating rate expressions.

Table 4
Computed α values and final weight loss ΔW for D3, F3, R3, A4 and anti-Jander mechanisms (which exhibited marginal variation in k vs. t plots; Fig. 2) using this computed k for the respective mechanism by this on-line method from the hypothetical TG curve, which follows the D3 mechanism

3-D diffusion mechanism D3		Third order reaction mechanism F3		Contracting volume mechanism R3		Avrami–Erofeev mechanism A4		Anti-Jander 3-dimensional counter diffusion mechanism	
α	ΔW_α	α	ΔW_α	α	ΔW_α	α	ΔW_α	α	ΔW_α
0.3234	10.0001	0.7357	4.3962	1.0021	3.2274	−2.3003	−1.4060	−0.3234	−10.001
0.4207	10.0000	0.6106	6.8906	0.9658	4.3564	−2.4792	−1.6971	−0.4207	−10.000
0.4902	10.0000	0.5958	8.2287	0.9479	5.1718	−2.5313	−1.9368	−0.4902	−10.000
0.5448	10.0000	0.5949	9.1585	0.9421	5.7827	−2.5637	−2.1251	−0.5448	−10.000
0.5898	10.0000	0.5984	9.8561	0.9410	6.2676	−2.5884	−2.2785	−0.5898	−10.000
0.6279	10.0000	0.6037	10.4003	0.9418	6.6666	−2.6089	−2.4067	−0.6279	−10.000
0.6609	10.0000	0.6100	10.8343	0.9437	7.0032	−2.6269	−2.5158	−0.6609	−10.000
0.6898	10.0000	0.6167	11.1852	0.9459	7.2922	−2.6430	−2.6099	−0.6898	−10.000
0.7155	10.0000	0.6237	11.4710	0.9484	7.5436	−2.6577	−2.6920	−0.7155	−10.000
0.7384	10.0000	0.6309	11.7046	0.9510	7.7646	−2.6714	−2.7642	−0.7384	−10.000

to clarify the mechanism that is operative in the condensed phase reaction without waiting for the completion of the reaction.

3. Application of on-line method to real TG curves

The foregoing discussion on numerical simulation has been restricted to a hypothetical TG curve instead of a real one. Nevertheless, the on-line method can be readily adapted to real experimental TG curves if the following precautions are taken.

(a) The weight record should be devoid of apparent weight changes, as achieved by suitable incorporation of blank corrections during the TG run itself, in order to derive the full benefit of the on-line method. It must be mentioned that the zero-time corrections should be also carried out a priori so that the initial weight change Δp_0 is free from error. A mathematical method for correcting zero-time errors during the course of the isothermal experiment itself is under development [5].

(b) The weight record should be a sufficiently smooth one, free from fluctuations, as could be attained by incorporation of computer programs based on Fourier analysis; otherwise, erratic values of k might be obtained.

Even though the above method is applicable for any isothermal experiment, in general thermogravimetry constitutes a major field of activity for high temperature solid-state kinetic studies, which in turn encompass many high temperature factors (e.g., compatibility, decomposition, corrosion, preparation, degradation etc.). Application of the above method to experimental techniques other than thermogravimetry should be possible provided that the change in the relevant property is smooth and devoid of "apparent" changes, and also free from zero-time errors or with the possibility of in situ correction of such errors.

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Appendix: Newton–Raphson method of finding the root

Consider $x = x_1$ as a known rough approximation to a root of $f(x) = 0$. Suppose that the exact root is at $x = x_1 + h$, so that $f(x_1 + h) = 0$. As h is a small value compared with x, by Taylor's expansion

$$f(x_1 + h) = 0 = f(x_1) + hf'(x_1) + h^2/2!f''(x_1) + \ \ldots$$

Neglecting terms in h^2 and other higher order terms results in

$$h \approx -f(x_1)/f'(x_1)$$

Table A1
Initial approximate roots for various mechanisms which depend on the Newton–Raphson method for the solution of the rate constant k

Mechanism	Initial root k for iteration purpose
A2	$k=\frac{(1-R)}{2(t_1-Rt_2)}$
A3	$k=\frac{(1-R)2}{3(t_1-Rt_2)}$
A4	$k=\frac{(1-R)3}{4(t_1-Rt_2)}$
R3	$k=\frac{(Rt_2-t_1)}{(Rt_2^2-t_1^2)}$
B1	$t_2(t_1-t_2)k^2+(2t_1-Rt_1-t_2)k+2(1-R)=0$

Note: the above equations are not analytical solutions for the rate-constant, since they are obtained by ignoring some terms (higher order terms in expansion).

where $f'(x_1)$ is the value of the differential coefficient of $f(x)$ at $x=x_1$. Consequently, a second approximation to the root is

$$x_2=x_1+h=x_1-\frac{f(x)}{f'(x_1)}$$

This approach may be used iteratively for improving the approximate root to the desired degree of accuracy. The initial approximate roots for iteration purpose for the rate mechanisms that are controlled by nucleation and growth are given in Table A1.

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