NUMERICAL SOLUTIONS AND AN ITERATIVE METHOD FOR A RATE LAW INVOLVING $(1 - \alpha)$ AND $[- \ln(1 - \alpha)]^n$

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ABSTRACT

Values of α at various temperatures have been obtained by numerical solution of the rate equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta}(1 - \alpha)[- \ln(1 - \alpha)]^n e^{-E/RT}$$

using a fourth-order Runge–Kutta method for cases where $n = 1/3$, $1/2$, and $2/3$. An iterative method has been derived using this equation as the rate law. In each case, the solutions have been analyzed by the iterative method. Calculated values of n and E were found to be virtually identical to those used in the solution of the differential equation for $n \geqslant 1/2$. Other iterative methods not based on this rate law do not give correct values for n and E. Specific errors have been determined in this work.

INTRODUCTION

A great deal of attention has been focused on the interpretation and use of the usual nonisothermal rate equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta}(1 - \alpha)^n e^{-E/RT} \tag{1}$$

where α is the fraction reacted, T is the temperature (K), E is the activation energy, n is the reaction order, A is the Arrhenius pre-exponential factor, and β is the heating rate [1]. Equation (1) is the basis of the Coats and Redfern and other methods for calculating n and E from (α, T) data [2]. These workers use a truncated series approximation of the temperature integral

$$I = \int_0^T e^{-E/RT} dT \tag{2}$$

Starting with the integrated form of eqn. (1), Reich and Stivala using a

truncated series for I derived the equation [3]

$$\ln\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right] = \frac{E}{R}\left(\frac{1}{T_{i+1}} - \frac{1}{T_i}\right) \tag{3}$$

Representing the left-hand side as $f(\alpha, T, n)$ and the right-hand side as $f(1/T)$, a linear relationship with an intercept of zero can be found when n has the correct value [4]. Therefore, linear regression is performed while iterating on n until the value of n giving the intercept nearest zero is found. This method proved to be accurate in calculating n and E for accurately derived (α, T) data based on eqn. (1) [5].

Recently, Criado and Ortega discussed the fact that kinetic data for reactions following a mechanism represented by a rate law different from eqn. (1) would be erroneously interpreted by the Reich and Stivala method [6]. It has been proposed that a rate equation such as

$$\frac{d\alpha}{dT} = \frac{A}{\beta}(1-\alpha)[-\ln(1-\alpha)]^n e^{-E/RT} \tag{4}$$

might be applicable in certain cases. In fact eqn. (4) represents a special case of the more general rate law

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\alpha^a(1-\alpha)^b[-\ln(1-\alpha)]^n e^{-E/RT} \tag{5}$$

where a, b, and n are constants [7]. Therefore, the present work was undertaken to provide numerical solutions to eqn. (4) and to provide an iterative method for analyzing them.

METHODS

The two-point form

In developing an iterative method for a particular rate law, it is necessary to derive a form in which the (α_i, T_i) data can be used. This form is most conveniently a two-point form so that some function $f(\alpha, T)$ can be computed for successive data points [4]. Starting with eqn. (4), rearrangement and integration using the Coats and Redfern approximation of the temperature integral gives eqn. (6), which is analogous to the two-point form of Reich and Stivala [4].

$$\ln\left[\frac{1}{(1-n)[-\ln(1-\alpha_0)]^{n-1}T^2} - \frac{1}{(1-n)[-\ln(1-\alpha_i)]^{n-1}T^2}\right]$$
$$= \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{6}$$

In this case, α_0 is a small initial boundary value of α. From eqn. (6), considering two points leads to

$$\ln\left\{\frac{\left(K^{n-1}/[-\ln(1-\alpha_i)]^{n-1}\right)-1}{\left(K^{n-1}/[-\ln(1-\alpha_{i+1})]^{n-1}\right)-1}\left(\frac{T_{i+1}}{T_i}\right)^2\right\}=\frac{E}{R}\left(\frac{1}{T_{i+1}}-\frac{1}{T_i}\right) \tag{7}$$

where $K=-\ln(1-\alpha_0)$.

Numerical solution of the rate equation

Equation (4) was solved numerically for various values of T using selected values for E, A/β, and n. The numerical solution was carried out using a fourth-order Runge–Kutta method similar to that previously described [5]. In order to avoid difficulties arising from division by zero, the initial value of α must be non-zero. Therefore, solutions were obtained subject to the initial condition that $\alpha=0.00001$ at $T=350$ K.

In order to determine what results are obtained if a method based on an incorrect rate law is used, the derived data were analyzed using several methods. The first two of these were based on a presumed rate law in the form of eqn. (1). In the first, a three-point iterative method [8] was carried out using the (α,T) data. Second, the iterative method of Reich and Stivala was carried out on the data as previously described [4,9].

To analyze the data correctly, values of E/R were calculated using eqn. (6) for successive pairs of (α, T) values. This was done in order to ascertain that E/R is constant at the correct value of n [3], and to verify the correctness of eqn. (6). This provides the basis for the iterative method based on a rate law in the form of eqn. (4).

Iterative method

Both the iterative method of Reich and Stivala and that based on eqn. (7) were carried out using a computer and programs in FORTRAN. In the case of the iterative method based on eqn. (7), the intercept is negative for trial values of n smaller than the correct value. The computation begins with $n=0$ and performs linear regression of f(α, T, n) vs. f($1/T$) to determine if the intercept is negative. If it is, n is incremented by 0.100001 and processing continues until a positive intercept results. At that point, the value of n is reduced to its previous value and incrementing is by 0.01 until the intercept is again positive. The process is then repeated using iterations where n is increased by 0.001. The value of n giving the intercept closest to zero is taken as correct and the slope is $-E/R$.

RESULTS AND DISCUSSION

One objective of this work was to determine numerical solutions for eqn. (4) and to develop an iterative method based on that rate law. Another objective was to determine what errors in n and E result when an iterative method based on eqn. (1) is used with (α, T) data obtained from eqn. (4).

Results of iterative methods from an incorrect rate law

The values chosen for the kinetic parameters used in the numerical solution of eqn. (4) were $E = 100$ kJ mole^{-1} and $A/\beta = 3 \times 10^{10}$ min^{-1}. Solutions were obtained for $n = 1/3$, $1/2$, and $2/3$. The results of the Runge–Kutta method applied to eqn. (4) are shown in Table 1. Each of these sets of (α, T) data was then subjected to analysis by the method of Reich and Stivala, which is based on the rate law of eqn. (1). As an example, Table 2 shows the results of applying the method of Reich and Stivala to the computed (α, T) solutions for the $n = 1/2$ case.

The results shown in Table 2 indicate that the method of Reich and Stivala will iterate to find a value of n where the intercept is close to zero and the correlation coefficient is high. However, the slope is such that a value of

TABLE 1

Values of α computed from eqn. (4) using a fourth-order Runge–Kutta method [a]

T (K)	α		
	$n = 1/3$	$n = 1/2$	$n = 2/3$
410	0.01044		
415	0.01827		
420	0.03148		
425	0.05334	0.01225	
430	0.08865	0.02422	
435	0.14394	0.04708	
440	0.22686	0.08950	0.01111
445	0.34384	0.16479	0.02726
450	0.49480	0.28929	0.06614
455	0.66553	0.47245	0.15525
460	0.82437	0.69357	0.33808
465	0.93518	0.88477	0.61349
470	0.98593	0.97976	0.90791
475		0.99904	0.99634

[a] Computed using $E = 100$ kJ mole^{-1}, $R = 8.31441$ J mole^{-1}, and $A/\beta = 3 \times 10^{10}$ min^{-1}.

TABLE 2

Output for the analysis of (α, T) data for the $n = 1/2$ case by the iterative method of Reich and Stivala [a]

Trial n	Intercept	$-$ Slope	E (kJ mole^{-1})	$-$ Corr. coeff.
0.000	2.6243	123 398		0.9309
0.100	2.4652	117 463	976.63	0.9275
0.200	2.2871	110 800	921.24	0.9243
0.300	2.0875	103 317	859.02	0.9215
0.400	1.8644	94 937	789.34	0.9196
0.500	1.6156	85 572	711.48	0.9190
0.600	1.3388	75 135	624.70	0.9205
0.700	1.0322	63 558	528.45	0.9256
0.800	0.6939	50 768	422.10	0.9372
0.900	0.3226	36 713	305.25	0.9610
1.100	$-$ 0.5194	4806	39.96	0.4285
1.010	$-$ 0.1158	20 141	167.46	0.9997
1.001	$-$ 0.0680	22 010	183.00	0.9960

[a] Based on rate law eqn. (1). Spurious result obtained at $n = 1.000$.

$E = 183.00$ kJ mole^{-1} is indicated while the actual value should be 100 kJ mole^{-1}. It must be pointed out that the three-point iterative method [8] does no better. In fact, the (α, T) data shown in Table 1 for $n = 1/2$ gave an apparent n of 0.92 and $E = 201.4$ kJ mole^{-1} by the three-point method. These results show that an iterative method based on an incorrect rate law will meet the conditions of iteration, but the resulting n and E values will not be correct if the reaction obeys a rate law given by eqn. (4).

Results from the present method

Because it is necessary here to show that a constant slope $(-E/R)$ is obtained, the (α, T) data shown in Table 1 were used to calculate E/R values [3]. Table 3 shows the values of E/R for the data obtained for $n = 2/3$. The value of $n = 2/3$ gives nearly constant E/R values and an average E of 99.7 kJ mole^{-1} over a large range of α values. Similar results are obtained using the (α, T) data for $n = 1/3$ and $1/2$. Based on this constancy of E/R, the iterative method based on eqn. (7) was performed on the (α, T) data, and the results are shown in Table 4 for the case when $n = 2/3$. The results shown in Table 4 indicate clearly that the iterative method developed for the application of eqn. (7) identifies the correct order for this $n = 2/3$ case and that the resulting activation energy of 100.85 kJ mole^{-1} is in good agreement with the value of 100 kJ mole^{-1} used in the

TABLE 3

Values of E/R calculated from eqn. (7) using α values for $n = 2/3$

T_1 (K)	T_2 (K)	E/R				
		$n = 0.50$	$n = 0.60$	$n = 2/3$ [a]	$n = 0.75$	$n = 0.9$
440	450	17277.7	14052.2	12005.0	9602.3	5856.9
445	450	17543.2	14160.6	12002.7	9462.0	5509.9
450	455	17754.4	14249.2	12000.8	9343.1	5209.1
455	460	17920.1	14320.6	11999.3	9243.1	4948.7
460	465	18049.1	14377.6	11998.1	9159.3	4723.0
465	470	18148.3	14422.3	11996.6	9098.1	4526.7
470	475	18181.8	14422.3	11966.1	9008.0	4343.9

[a] Average E/R value $= 11995.5$ corresponding to $E = 99.7$ kJ mole^{-1}.

numerical solution of eqn. (4). However, even using the correct iterating function shown in eqn. (7) the results for the $n = 1/3$ case are not accurate ($n = 0.253$ and $E = 112.66$ kJ mole^{-1}). This results from the numerical nature of the equations at small values of n.

TABLE 4

Output for the analysis of (α, T) data for the $n = 2/3$ case by the present iterative method

Trial n	Intercept	$-$ Slope	E (kJ mole^{-1})	$-$ Corr. coeff.
0.000	-0.4852	15936	132.50	0.9421
0.100	-0.4324	14443	120.09	0.9452
0.200	-0.3767	13067	108.65	0.9494
0.300	-0.3161	11904	98.98	0.9588
0.400	-0.2478	11088	92.19	0.9716
0.500	-0.1673	10832	90.06	0.9871
0.600	-0.0698	11357	94.43	0.9973
0.700	0.0452	12768	106.16	0.9994
0.610	-0.0591	11462	95.30	0.9982
0.620	-0.0482	11570	96.20	0.9985
0.630	-0.0370	11692	97.21	0.9991
0.640	-0.0258	11817	98.25	0.9989
0.650	-0.0143	11961	99.45	0.9998
0.660	-0.0027	12104	100.64	0.9997
0.670	0.0091	12264	101.97	1.0002
0.661	-0.0015	12121	100.78	0.9998
0.662	-0.0005	12130	100.85	0.9996

TABLE 5

Results of the analysis of (α, T) data from eqn. (4) by iterative methods [a]

	$n = 1/3$		$n = 1/2$		$n = 2/3$	
	eqn. (3)	eqn. (7)	eqn. (3)	eqn. (7)	eqn. (3)	eqn. (7)
Intercept	−0.0002	0.0000	−0.0680	0.0000	−0.0011	−0.0005
Calculated n [b]	0.995	0.253	1.001	0.490	0.953	0.662
−Slope	18368	13550	22010	12252	35404	12130
Calculated E [c]	152.72	112.66	183.00	101.87	294.37	100.85
−Corr. Coeff.	0.9998	1.0000	0.9960	0.9999	0.8874	0.9996

[a] (α, T) data computed using $E = 100$ kJ mole^{-1} and $A/\beta = 3 \times 10^{10}$ min^{-1}. Iterative method based on eqn. (3) was that of Reich and Stivala [4].
[b] Based on the intercept nearest zero.
[c] In kJ mole^{-1}.

Comparison of results from the iterative methods

The results for the $n = 1/2$ case shown in Table 2 indicate that analysis of (α, T) data by iterative methods based on eqn. (1) do not yield correct kinetic parameters when the reaction follows eqn. (4). An appropriate iterative method based on eqn. (7) does, however, yield acceptable kinetic parameters, at least for values of $n \geqslant 1/2$.

Table 5 shows a summary of the output of the two iterative methods applied to (α, T) data for various values of n. It is obvious that, while a method based on an incorrect rate law can not be expected to give correct kinetic parameters [6], the present work gives the first numerical comparison of results. Furthermore, the results shown in Table 5 indicate that, for the two rate laws tested here, the agreement gets worse for larger values of n.

We are currently developing a series of iterative methods corresponding to the rate laws of the most common mechanisms. Using these methods, it will be possible to test (α, T) data assuming a variety of mechanisms. It must be pointed out, however, that, even though a particular combination of n and iterated function gives an intercept of zero with a high correlation coefficient, the mechanism is not confirmed. In fact, a different choice of n and iterated function may also give an intercept of zero with a high correlation coefficient.

The results obtained in this work confirm the caution made by Criado and Ortega regarding iterative methods developed from one rate law being applied to data for a reaction following a different rate law [6]. Certainly no claim was made that the iterative method of Reich and Stivala would identify correct n and E values for a reaction that follows a rate law different from the one on which their derivation is based [4]. In fact, it now appears that the most definitive answer that can be given by the iterative analysis of (α, T) data is that, if one rate law applies, the kinetic parameters are n and E. If another rate law applies, the values may be greatly different (say n' and E'). Based on the iterative method used to analyze the data, nothing about the mechanism is ascertained and to identify n and E correctly requires that the actual rate law be known.

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