

NUMERICAL SOLUTION OF NONISOTHERMAL RATE EQUATIONS AND ANALYSIS OF SOLUTIONS BY THE REICH-STIVALA METHOD

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(Received 30 November 1981)

ABSTRACT

Values of α have been obtained from the rate equation

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

by solving it numerically using a fourth order Runge-Kutta method for several values of n in the range 0-2. In each case, the solutions have been analyzed by the iterative method of Reich and Stivala. Calculated values of n and E were found to be virtually identical to those used in the differential equation.

INTRODUCTION

A great deal of attention has been focussed on the evaluation and approximation of the temperature integral

$$I = \int_0^T e^{-E/RT} dT \quad (1)$$

where E is the activation energy, T is the temperature (K) and R is the molar gas constant [1-8]. This attention arises from the fact that the usual nonisothermal rate equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta} (1-\alpha)^n e^{-E/RT} \quad (2)$$

where α is the fraction reacted, n is the reaction order, and β is the heating rate, cannot be solved exactly. Thus, the usual procedure is to represent the temperature integral as a truncated series [1,2,6]. Reich and Stivala obtained the equation

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

as a two point form of such an approximate equation [1,9]. Representing the left-hand side as $f(\alpha, T, n)$ and the right-hand side as $f(1/T)$, a linear relationship having an intercept of zero exists when the correct value of n is used. An iterative procedure was devised to determine the value of n giving the intercept closest to zero [10]. The slope of the line (E/R) is used to calculate E . One problem of using calculated test data is that the values of α are calculated using the approximate equation from which eqn. (3) is derived [10]. Two alternatives exist here. First, approximation of the temperature integral can be made to any desired accuracy [6,8] and test data can be generated to see if the series approximations of the temperature integral affect the outcome of the Reich–Stivala method. Second, the differential rate equation [eqn. (2)] can be solved by numerical methods and the results analyzed by the Reich–Stivala method. In either case, a valid test of the Reich–Stivala method can be made using data that are not obtained by means of the same equation which is used to derive the iterated function. This paper describes the numerical solution of eqn. (2) and the analysis of the (α, T) data by the Reich–Stivala method.

METHODS

Computational procedures

The rate equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta} (1 - \alpha)^n e^{-E/RT} \quad (2)$$

was solved numerically for various values of T using the previously selected values for E , A/β , and n . The numerical solution was carried out using a fourth order Runge–Kutta method. A comparison of the results obtained by this method with those obtained by several other methods has been made [11]. In general, the fourth order Runge–Kutta method is equal or superior to other methods in general use, especially when a large number of iterations per integration step are used. The computations were programmed for analysis using a Texas Instruments TI-59 programmable calculator. Two fourth order programs were used. The first involved a program adapted from that given by Meck [12] while the second made use of the Runge–Kutta program in the PROM Math/Utilities library module as a subroutine [13].

Validation of the procedures

Since eqn. (2) cannot be solved exactly, it is not possible to compare the results of a numerical solution with those obtained by analytical methods. Therefore, the computational techniques were tested by comparing such

results for an equation that can be solved analytically. The equation chosen was

$$\frac{dy}{dx} = x - y + 1 \quad (4)$$

which has been used to compare various numerical techniques [11], and it was solved subject to $y = 1$ at $x = 0$. The exact solution is

$$y = e^{-x} + x \quad (5)$$

Table 1 presents values of the exact solutions $y_n(x_n)$, the approximate solutions as determined by a computer solution [11], and the solutions calculated in this work. The procedure used 10 iterations in each $x_n - x_{n-1}$ interval. The data shown in Table 1 indicate that the fourth order Runge-Kutta method used in this work reproduced the exact solutions to nine decimal places when the TI-59 is used. This represents greater accuracy than the usual computer method [11] because the TI-59 computes with 13 digits internally.

Other equations have been used with similar results. Clearly, the accuracy of the computations is adequately established. This is necessary in order to attribute any inconsistencies in the computed results to their proper source. We have also found that certain types of computations that involve small differences in iterated parameters can be carried out more effectively with the TI-59 calculator than with small computers [14]. In cases such as the present one, it is frequently necessary to use a double precision routine with the computer to produce the same result as is obtained with the TI-59 calculator.

TABLE 1

Exact solutions of eqn. (4) and those obtained by Runge-Kutta methods ^a

x_n	Exact	Computer R-K of order four ^b	TI-59 R-K of order four
0.1	1.0048374180	1.0048375000	1.004837418
0.2	1.0187307531	1.0187309014	1.018730753
0.3	1.0408182207	1.0408184220	1.040818221
0.4	1.0703200460	1.0703202889	1.070320046
0.5	1.1065306597	1.1065309334	1.106530660
0.6	1.1488116360	1.1488119344	1.148811636
0.7	1.1965853038	1.1965856187	1.196585304
0.8	1.2493289641	1.2493292897	1.249328964
0.9	1.3065696597	1.3065699912	1.306569661
1.0	1.3678794412	1.3678797744	1.367879441

^a In each case the integration step size is 0.1 with 10 iterations per step.

^b Ref. 11, p. 206.

TABLE 2

Values of α computed^a with $E = 100 \text{ kJ mole}^{-1}$, $A/\beta = 3 \times 10^{10} \text{ min}^{-1}$ and $R = 8.3143 \text{ J mole}^{-1} \text{ deg}^{-1}$

T(K)	α							
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$	$n = 4/3$	$n = 5/3$	$n = 2$
380	0.00597	0.00597	0.00596	0.00596	0.00595	0.00595	0.00594	0.00594
390	0.01430	0.01427	0.01425	0.01424	0.01420	0.01417	0.01414	0.01410
400	0.03263	0.03246	0.03237	0.03228	0.03211	0.03194	0.03177	0.03160
410	0.07142	0.07056	0.07015	0.06974	0.06893	0.06815	0.06740	0.06666
420	0.15060	0.14676	0.14493	0.14317	0.13981	0.13666	0.13369	0.13089
430	0.30693	0.29065	0.28338	0.27660	0.26430	0.25140	0.24365	0.23485
440	0.60670	0.53996	0.51426	0.49189	0.45453	0.42423	0.39894	0.37737
450		0.89313	0.82452	0.77010	0.68720	0.62555	0.57706	0.53751
460				0.97868	0.88562	0.80441	0.73851	0.68436
470					0.98060	0.91931	0.85531	0.79767
480					0.99909	0.97298	0.92584	0.87497
490						0.99223	0.96354	0.92392
500							0.98235	0.95376

^a Shown to five decimal places. The values to nine decimal places were used in the Reich-Stivala analysis.

Reich–Stivala analysis

Implementation of the Reich–Stivala analysis of the computed (α , T) data was carried out using the algorithm developed for use with the TI-59 programmable calculator [15].

RESULTS AND DISCUSSION

The values chosen for the kinetic parameters used in the numerical solution of eqn. (2) were: $E = 100 \text{ kJ mole}^{-1}$, $A/\beta = 3 \times 10^{10} \text{ min}^{-1}$, $R = 8.3143 \text{ J mole}^{-1} \text{ deg}^{-1}$, and $n = 0, 1/3, 1/2, 2/3, 1, 4/3, 5/3$, and 2. The initial boundary conditions chosen were that $\alpha = 0$ at 340 K. Changing that condition to $\alpha = 0$ at 300 K did not materially change the computed α values or the results produced by Reich–Stivala analysis of them. The results of the Runge–Kutta method are shown in Table 2. Each of these sets of (α , T) data was then subjected to the Reich–Stivala analysis. As an example, Table 3

TABLE 3

Results of the Reich–Stivala analysis of the numerical solutions of the rate equation for $n = 1$, $E = 100 \text{ kJ mole}^{-1}$, and $A/\beta = 3 \times 10^{10} \text{ min}^{-1}$

Trial n	Intercept	–Slope	–Corr. coeff.
0.1	1.81366	42696	0.96803
0.2	1.69407	40719	0.96604
0.3	1.55815	38458	0.96445
0.4	1.40411	35881	0.96353
0.5	1.23014	32956	0.96365
0.6	1.03450	29652	0.96537
0.7	0.81560	25941	0.96947
0.8	0.57206	21799	0.97710
0.9	0.30285	17208	0.98920
1.0	0.00729	12156 ^a	0.99999
1.1	–0.31482	6638	0.90810
1.01	–0.02372	11625	0.99958
1.02	–0.05500	11089	0.99843
1.03	–0.08655	10549	0.99628
1.04	–0.11837	10004	0.99281
1.05	–0.15045	9455	0.98756
1.06	–0.18279	8901	0.97998
1.07	–0.21540	8342	0.96932
1.08	–0.24828	7779	0.95464
1.09	–0.28142	7210	0.93472

^a Calculated E is 101.06 kJ mole^{–1}.

TABLE 4

A summary of results computed by the Reich–Stivala analysis of numerical solutions

n		Intercept	–Slope	–Corr. coeff.	Calculated ^c $E(\text{kJ mole}^{-1})$
Actual ^a	Calcd. ^b				
0	0.02	–0.00007	12055.3	0.99964	100.231
1/3 ^d	0.34	0.00498	12129.4	0.99976	100.848
1/2	0.50	0.01046	12211.1	0.99998	101.526
2/3 ^d	0.67	0.00568	12137.1	0.99982	100.912
1	1.00	0.00729	12155.5	0.99999	101.065
4/3 ^d	1.34	–0.00348	11981.9	0.99983	99.621
5/3 ^d	1.67	–0.00374	11946.1	0.99999	99.323
2	2.00	0.00539	12112.4	0.99999	100.707

^a The value used in the numerical solution of eqn. (2).^b Value giving the intercept closest to zero in the Reich–Stivala analysis.^c Actual E used in eqn. (2) is 100 kJ mole^{–1}.^d Noninteger orders were input as $1 \div 3 = 0.333\dots$, etc.

shows the results as output of the Reich–Stivala analysis applied to the computed solutions for $n = 1$.

The results shown in Table 3 indicate quite clearly that the Reich–Stivala method identifies the correct order for this $n = 1$ case and that the resulting activation energy (101.06 kJ mole^{–1}) gives excellent agreement with the value of 100 kJ mole^{–1} used in the equation solved numerically. Table 4 provides a summary of the results obtained from the Reich–Stivala analysis for all the values of n used. These results clearly show that the Reich–Stivala method determines the order to within a maximum error of 0.02 and E to a maximum error of about 1.5 kJ mole^{–1} (1.5%) when n varies from 0 to 2. Although they are not presented here, other cases having other values of E and A/β were used with similar accuracy in the results.

The approximate integrated rate equation used by Reich and Stivala to obtain their function for iteration was based on the rate law shown in eqn. (2). While this method may not give the correct order if a rate law of a different form is followed [16], it is easily apparent that this method gives excellent results when the reaction does follow a rate law in the form of eqn. (2). In fact, in view of the uncertainties arising from sample-to-sample variations [17], it is safe to conclude that the Reich–Stivala method will accomplish all that the experimental data will allow if eqn. (2) represents the form of the rate law.

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