Thermochimica Acta, 231 (1994) 177–184
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01362-7

Use of databases in the kinetic analysis of two parallel first-order reactions

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(Received 31 March 1993; accepted 14 May 1993)

Abstract

In a previous publication by the author, a kinetic analysis of two consecutive irreversible first-order reactions was carried out in order to estimate values of the two rate constants k_1 and k_2. The procedure employed involved the use of the database PARADOX 3 which contained a powerful script language called PAL. A computer run was performed utilizing an algorithm based on a derived expression, and which involved an iteration method. The k values obtained were in satisfactory agreement with both theoretical and experimental values.

The aim of this paper is now to extend the preceding to a kinetic analysis of two parallel irreversible first-order reactions, each yielding a common product. Again, a PAL script was employed along with a somewhat modified algorithm. The k values are in satisfactory agreement with theoretical and with experimental data, where available.

INTRODUCTION

In previous publications [1, 2] a kinetic analysis of two consecutive irreversible first-order reactions (2CIFOR) was carried out using a database (PARADOX 3). Based on a derived expression values of two rate constants, k_1 and k_2, were estimated. These values were in satisfactory agreement with both theoretical and experimental corresponding values. In the previous article [1] it was noted that the aforementioned derived expression could also be applied to the case of two irreversible parallel first-order reactions, each yielding a common product (2IPFOR). It may also be mentioned that there were two typographical errors in ref. 1, i.e., [A] in the expression for F should be replaced with [B], and the same applies to the extent of reaction expression. These errors will not affect the final expressions nor the calculated values obtained for k_1 and k_2.

The aim of this paper is to expand the treatment of the kinetic analysis of 2CIFOR to 2IPFOR using the PAL language in PARADOX 3. Calculated values of k_1 and k_2 will be compared with corresponding theoretical and experimental values where available.

THEORETICAL ASPECTS

The 2IPFOR may be represented as in the following

$$A \xrightarrow{k_1} C + \ldots \tag{1a}$$

$$B \xrightarrow{k_2} C + \ldots \tag{1b}$$

In eqns. (1a) and (1b), C denotes a common product (CP). This CP may, for example, actually consist of two structural isomers which possess identical functional groups or where similar structures each yield the same gas (C), e.g. ammonia. Thus, concentrations of C could be estimated by means of a quantitative analysis of such functional groups, or in the latter case of the common gaseous product. Based on such values of C, various expressions can be derived as in the following. It can be shown that

$$[C] = [C_\infty] - [A_0]e^{-k_1t} - [B_0]e^{-k_2t} \tag{2}$$

where $[C_\infty] = [A_0] + [B_0]$ and $[C]/[C_\infty]$ is the degree of conversion, α. From eqn. (2), there follows

$$[C_\infty]\rho = k_1[A_0]e^{-k_1t} + k_2[B_0]e^{-k_2t} \tag{3}$$

where t denotes time and $\rho = d\alpha/dt$. Upon combining eqns. (2) and (3)

$$[C_\infty]\rho = k_1[A_0]e^{-k_1t} + k_2([C_\infty] - [C]) - k_2[A_0]e^{-k_1t} \tag{4}$$

From eqn. (4)

$$\rho - k_2(1 - \alpha) = (k_1 - k_2)([A_0]/[A_0] + [B_0])e^{-k_1t} \tag{5a}$$

It can be similarly shown that

$$\rho - k_1(1 - \alpha) = (k_2 - k_1)([B_0]/[A_0] + [B_0])e^{-k_2t} \tag{5b}$$

Upon taking natural logarithms of both sides of eqn. (5a) and subtacting the resultant expression from a similar expression consisting of different given values of α, ρ and t, there is finally obtained

$$\ln\{[\rho - k_2(1 - \alpha)]_0/[\rho - k_2(1 - \alpha)]\} = k_1(t - t_0) \tag{6}$$

In a similar manner, from eqn. (5b) it can also be shown that

$$\ln\{[\rho - k_1(1 - \alpha)]_0/[\rho - k_1(1 - \alpha)]\} = k_2(t - t_0) \tag{7}$$

From eqn. (6), if the left hand side is set equal to Y, then

$$Y = A_2X + A_1 \tag{8a}$$

where $A_2 = k_1$, $X = t - t_0$ and $A_1 = 0$. From eqn. (7), an equation similar to eqn. (8a) results

$$Y' - A_2'X + A_1 \tag{8b}$$

where Y' = left hand side of eqn. (7) and $A_2' = k_2$.

Using eqn. (8a), we can now employ the concepts of a computer algorithm previously devised and reported [3, 4] along with a PARADOX 3 based script (see the Appendix). However, this algorithm will be modified and values of k_1 and k_2 will again be determined via an iteration procedure wherein a minimum value of A_1 will be attained for the conditions employed.

APPLICATIONS OF THE METHOD

The procedure was tested using several sets of theoretical data. Thus, letting $k_1 = 0.0030$ (arbitrary units), $k_2 = 0.0020$ (arbitrary units) and $[A_0]/[B_0] = 0.5$, various values of α and ρ could be determined for various values of t (arbitrary units) by means of eqns. (2) and (3). These values are listed in Table 1 (Y2KS) along with derived values obtained from an iteration procedure (see the Y2KS script in the Appendix). The initial values used for t_0, α_0 and ρ_0 were calculated to be, respectively: 100, 0.2072 and 1.8325E-03 (see lines 18–20 of the script). The final values of k_2, which is equal to k_{2b} (see lines 60–62, 67 of the script), and not the value shown in Table 1, and k_1 were, respectively, 0.0020 and 0.0030, as anticipated (the k_1 value equals k_{1b} which is given in Table 1).

In using experimental data, it is expected that α and t will be given. Values of ρ can be obtained by the use of slopes from a plot of α versus t. However, such values may not possess a high enough accuracy as required. A preferred method would be to correlate the $\alpha - t$ data in terms of a fifth order polynomial. This was accomplished for the Y2KS table. The correlation coefficient was very high, $0.(9)_x$, where $x = 8$, and the following expression was obtained:

$$\alpha = -1.75\text{E-}04 + 2.33427\text{E-}03t - 2.8205\text{E-}06t^2 + 2.2698\text{E-}09t^3 - 1.198572\text{E-}12t^4 + 3.108974\text{E-}16t^5 \quad (9)$$

From eqn. (9), values of ρ could be readily estimated. Upon employing

TABLE 1

Theoretical data for k_1 and k_2 (Y2KS)

α	Rate $\times 10^3$	Time	X	k_2	Rate − $k_2(1-\alpha)$ $\times 10^5$	Y	tmp $\times 10^{10}$	k_{1b}	Intcpt$_1$
0.3702	1.4425	200	100	0.00218325	6.7488	0.4093	1.000	0.00300	−0.000066
0.4986	1.1383	300	200		4.3617	0.8458			
0.6000	0.9004	400	300		2.7099	1.3217			
0.6804	0.7136	500	400		1.5833	1.8591			
0.7441	0.5669	600	500		0.82058	2.5164			
0.7948	0.4512	700	600		0.31967	3.4591			
0.8352	0.3598	800	700		−0.000009	14.1825			

TABLE 2

Theoretical data for k_1 and k_2 (Y2KS2)

α	Rate $\times 10^3$	Time	X	k_2	Rate − $k_2(1-\alpha)$ $\times 10^4$	Y	tmp $\times 10^{10}$	k_{1b}	Intcpt$_1$
0.4506	1.60580	200	100	0.00264945	1.50214	0.5251	1.000	0.00450	−0.000051
0.5885	1.17680	300	200		0.86641	1.0754			
0.6900	0.86945	400	300		0.48121	1.6635			
0.7652	0.64713	500	400		0.25143	2.3126			
0.8214	0.48485	600	500		0.11715	3.0763			
0.8636	0.36541	700	600		0.041072	4.1244			
0.8955	0.27680	800	700		−0.0000008	16.1469			

these values of α and ρ for various values of t, the values of k_2 and k_1 obtained were, respectively, 0.0020 and 0.0030, as anticipated.

When $k_1 = 0.0045$, $k_2 = 0.0025$, $[A_0]/[B_0] = 0.4$ were assumed, values were obtained for α and ρ, as listed in Table 2 (Y2KS2). The initial values for t_0, α_0 and ρ_0 were, respectively, 100, 0.26153 and 2.21054E-03 (see lines 21–23 of the script). A computer run afforded the following values of k_2 and k_1, respectively: 0.0025 and 0.0045, as expected.

In order to ascertain that the ratio, $[A_0]/[B_0]$, had no effect on the outcome of the final results for the k values, run Y2KS2 was repeated using a new ratio of $[A_0]/[B_0] = 0.2$. Values of t, α and ρ are depicted in Table 3 (Y2KS3) along with other derived values. A computer run again afforded values of $k_2 = 0.0025$ and $k_1 = 0.0045$, as expected. Further, a 5th order polynomial was again utilized to correlate values of α and t. From the resulting expression, ρ could be obtained for the various values of t, and a computer run yielded $k_2 = 0.00251$ and $k_1 = 0.0045$. Thus runs Y2KS2 and Y2KS3 afforded k values which indicated that the effect of the ratio $[A_0]/[B_0]$ on the results for the k values was neglibile, as anticipated. It may be noted here that values of Y in both of the runs Y2KS2 and Y2KS3 were almost identical, as would be expected, and initial values of t_0, α_0 and ρ_0 were, respectively, 100, 0.2447 and 2.1007E-03 (see lines 24–26 of the script).

TABLE 3

Theoretical data for k_1 and k_2 (Y2KS3)

α	Rate $\times 10^3$	Time	X	k_2	Rate − $k_2(1-\alpha)$ $\times 10^5$	Y	tmp $\times 10^{10}$	k_{1b}	Intcpt$_1$
0.4268	1.56850	200	100	0.0025776	9.10191	0.5248	1.000	0.00450	−0.000053
0.5632	1.17850	300	200		5.24750	1.0756			
0.6659	0.89040	400	300		2.91720	1.6627			
0.7437	0.67593	500	400		1.52393	2.3120			
0.8029	0.51525	600	500		0.710714	3.0756			
0.8481	0.39416	700	600		0.249353	4.1222			
0.8827	0.30243	800	700		−0.000004	14.5383			

TABLE 4

Theoretical data for k_1 and k_2 (Y2KS4)

α	Rate $\times 10^3$	Time	X	k_2	Rate $- k_2(1-\alpha) \times 10^4$	Y	tmp $\times 10^{10}$	k_{1b}	Intcpt$_1$
0.4402	1.56900	200	100	0.0023956	2.27909	0.5004	1.000	0.00400	−0.00014
0.5750	1.15120	300	200		1.33081	1.0384			
0.6744	0.85312	400	300		0.731208	1.6372			
0.7484	0.63856	500	400		0.358333	2.3504			
0.8040	0.48264	600	500		0.131073	3.3561			
0.8463	0.36820	700	600		−0.0000003	14.9367			

In all the previous runs, the value of k_1 used was greater than the corresponding value of k_2. In Table 4 (Y2KS4), the value of k_2 used was now greater than that of k_1. Thus, $k_1 = 0.0020$ and $k_2 = 0.0040$, and $[A_0]/[B_0] = 1$. Initial values of t_0, α_0 and ρ_0 were, respectively, 100, 0.2555 and 2.1594E-03 (cf. lines 27–29 of the script). Unexpected results for k_1 and k_2 were obtained, which will be explained subsequently. Thus, from Table 4, the value of $k_{1b}(= k_1)$ was equal to 0.0040 and that of $k_{2b}(= k_2)$ was equal to 0.0020. From the preceding, there was a reversal of the k values. In order to ascertain the veracity of these results, three additional runs were carried out. In one of these runs, $k_1 = 0.0020$, $k_2 = 0.0025$ and $[A_0]/[B_0] = 0.5$; in another run, $k_1 = 0.0020$, $k_2 = 0.0025$ and $[A_0]/[B_0] = 1$; in the third additional run, $k_1 = 0.0020$, $k_2 = 0.0025$ and $[A_0]/[B_0] = 2$. In all these three runs, there was again a reversal of k values. Thus, in each of the three computer runs, $k_1 = 0.0025$ and $k_2 = 0.0020$.

The reversal of k values may be explained as follows. From eqn. (5a), it can be seen that in order for $\rho - k_2(1-\alpha)$ to possess a positive value, k_1 must be greater than k_2. Similarly, in order for $\rho - k_1(1-\alpha)$ to possess a positive value, k_2 must be larger than k_1. In the script, one of the limitations of the algorithm is that z_1 must not be negative in order that there not be a term consisting of the logarithm of a negative value (the algorithm also does not allow $z$diff to possess negative values by means of an automatic adjustment of k values; see lines 44 and 45). Based on the preceding, eqn. (5b) will predominate when k_2 is greater than k_1. In such a case, k_2 will assume the values of k_1 and vice versa, thereby leading to a reversal of values. The preceding now poses the problem of deciding whether or not a reversal of k values has occurred when these values have not been determined and are not known *a priori*. If the value of the ratio $[A_0]/[B_0]$ is known, then a possible solution is to employ the resulting computer k values and their corresponding reversed values in eqn. (2). After calculating several of α at various corresponding times, it will become apparent which k values provide the best agreement between calculated and actual α values. The pair of k values which afford the better agreement should be considered to be the preferred values. This method will not succeed when $[A_0] = [B_0]$. It may also be noted here that eqn. (2) was utilized to estimate the value of k_1 in the analysis of experimental data which will be described shortly.

In all of the results obtained for k_1 and k_2 listed in Tables 1–4, values of α and ρ were accurate to four or more significant figures. The k values may vary greatly when less accurate values are employed. With this in mind, we will now consider the utilization of experimental values.

Brown and Fletcher [5] studied the hydrolysis of diethyl-*t*-butylcarbinyl chloride (DBC). Ordinarily, a plot of the logarithm of the concentration of unhydrolyzed alkyl chloride versus time should afford a linear relationship from the slope of which the rate constant could be estimated. However, in the case of DBC no such relationship was observed. Instead, a first-order constant was found to vary from 0.739 at 0.50 h to 0.576 at 2.00 h to 0.470 at 5.00 h. However, after about 2.5 h, a linear relationship was obtained. This suggested that the unexpected behavior was the result of two simultaneous first-order reactions due to the presence of a mixture of two alkyl chlorides. One of these chlorides apparently hydrolyzed relatively rapidly and was essentially completely hydrolyzed at the end of a 2.5 h period, whereas the other hydrolyzed at a much slower rate. From the slope of the linear portion of the curve, a value of $0.38\ \mathrm{h}^{-1}$ was calculated (the B component). By correcting the experimental results for the hydrochloric acid contributed by the B component, a new set of rate data could be obtained from which the rate constant of the more reactive halide (the A component) could be determined and which was found to be equal to $k_1 = 1.58\ \mathrm{h}^{-1}$. The data also indicated that the more reactive halide was present to the extent of 35% and the less reactive halide to 65%.

The results obtained by Brown and Fletcher [5] for the k values of DBC involved a titration procedure. The resulting volumes were employed directly in the kinetic analysis used. Such volumes are at best only accurate to three significant figures. Thus, only the linear portion of the curve was utilized in the present paper for a computer run. From Fig. 4 of ref. 5, the following expression was developed between a time interval of 2.5–6 h.

$$\alpha = 1 - (0.1402)10^{-0.1733t+0.693} \tag{10}$$

Equation (10) allowed additional and consistent values of α to be obtained (with four significant figures) along with the corresponding times. Values reported by Brown and Fletcher [5] deviated only by about 0.2% from values estimated by eqn. (10). In the following, values of α (from eqn. (10)), α (from Brown and Fletcher [5]) and time (h) are listed in order: 0.7450, 0.744, 2.50; 0.7934, —, 3.03; 0.8289, 0.830, 3.50; 0.8599, 0.858, 4.00; 0.8838, —, 4.47; 0.9060, 0.905, 5.00; 0.9230, —, 5.50; 0.9369, 0.935, 6.00. The values of α and t were then correlated via a fifth-order polynomial. In this manner, values of ρ could be estimated at various values of α and its corresponding time. Then, by utilizing the script in the Appendix, the following results were obtained: $k_1 = 0.386\,\mathrm{h}^{-1}$ and $k_2 = 0.396\,\mathrm{h}^{-1}$ (average $= 0.391\,\mathrm{h}^{-1}$) with a low intercept value of 0.00012. Because these k values were approximately equal, there appears to be only one reactant (B) during the time interval employed. This is in agreement with statements made by Brown and Fletcher [5].

Although the results obtained by Brown and Fletcher [5], in the time interval of less than 2.5 h, are not considered to be sufficiently accurate to be utilized in the computer procedure used in this paper, another procedure can be employed to estimate k_1 by means of eqn. (2). In this procedure, a value of $k_2 = 0.39\,\mathrm{h}^{-1}$ was used along with initial compositions of A (C_A) and B (C_B) (from ref. 5) and values of α at times of 0.5, 1, 1.5 and 2.0 h (from ref. 5). Thus, four expressions resulted of the form

$$-k_1 t = \ln\{[(1-\alpha) - C_B e^{-k_2 t}]/C_A\} \tag{11}$$

From eqn. (11), four values of k_1 (h^{-1}) were calculated: 1.61, 1.58, 1.54 and 1.49 (with an average value of 1.56 ± 0.04).

ACKNOWLEDGMENT

I express my gratitude to Dr S.H. Patel for assistance in the preparation of the manuscript.

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APPENDIX: THE PARADOX 3 SCRIPT (Y2) FOR THE DATABASE ANALYSIS OF TWO IRREVERSIBLE PARALLEL FIRST-ORDER REACTIONS WITH A COMMON PRODUCT

```
                                          Script: D:\pdox35\sample\y2ks

; This database (Paradox 3) program allows the estimation of 2 rate
; constants (k1, k2) in parallel 1st-order irreversible reactions,
; cf. TA, 124 (1988) 139 and TA, 173 (1990) 253.

Clear  @5,5 ?? "Enter table to be analyzed (y2ks/y2ks2/y2ks3 or y2ks4): "
Accept "A8" Required To tbl  ; a non-blank value is required

Edit tbl
Echo Normal ; see changes in derived values on workspace during analysis

Intcpt1=100  [Intcpt1]=Intcpt1
sx=0 sy=0 sxx=0 sxy=0      ; initialize least squares params.
z=0 ztmp= 1E-01 [Tmp]=ztmp ; initialize value of z(K2) and its increment(ztmp)
ztmp2=1E-09 ;delimiting value of the increment

;-------------------select 1 of 4 tables to be analyzed---------------
;-------------------and provide initial values------------------------
```

```
If tbl="y2ks" Then
zalpha=.2072  zrate=1.8325E-03  ztime=100
Endif
If tbl="y2ks2" Then
zalpha=.26153 zrate=2.2105E-03 ztime=100
Endif
If tbl="y2ks3" Then
zalpha=.2447 zrate=2.1007E-03 ztime=100
Endif
If tbl="y2ks4" Then
zalpha=.256 zrate=2.1594E-03 ztime=100
Endif
NR=Nrecords(tbl)

While True
[K2]=z

For n From 1 To NR
zdiff=zrate-z*(1-zalpha)
Moveto [X]
Right Right
[]=[Rate]-z*(1-[Alpha])
z1=[]

;--------adjustment for possible negative log values---------

If (zdiff < 0) OR (zdiff/z1 < 0) Then Moveto [K2] Home z=z-ztmp
[K2]=z sx=0 sy=0 sxx=0 sxy=0 n=1 ztmp=ztmp/10 [Tmp]=ztmp Loop
Endif

Right [Y]=Ln(zdiff/z1)      ; LHS of eqn.
sx=sx+[X] sy=sy+[Y] sxy=sxy+[X]*[Y] sxx=sxx+[X]*[X]
Moveto [X]
Down
If Isblank([]) Then Del
Endif
Endfor

;----------calc least squares values of slope and intercept-----------


K1=(NR*sxy-sx*sy)/(NR*sxx-sx*sx)
Intcpt=(sy/NR)-K1*(sx/NR)

;-----------save values with the smallest intercept------------
If (Abs(Intcpt) < Abs(Intcpt1)) Then Intcpt1=Intcpt
k1b=k1  k2b=z  sx=0  sy=0  sxx=0  sxy=0
Endif
Moveto [K1b] Home [K1b]=k1b Right [Intcpt1]=Intcpt1

If ztmp < ztmp2 Then Do_It! Clear Clearall
@10,5  ?? "k2= "+strval(k2b)+",  "+"k1= "+strval(k1b)
@12,5  ?? "intercept= "+ strval(Intcpt1)
@14,5  ?? "Press a key to clear screen."
n=getchar() quitloop
Endif

z=z+ztmp   ; increment z(K2) values
Endwhile
```