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Use of spreadsheets in the kinetic analysis of two consecutive first-order reactions

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Abstract

The present author developed an expression in a previous report that could be applied to the determination of the two rate constants, k_1 and k_2, for two consecutive irreversible first-order reactions (2CIFR). This expression was solved utilizing various computer methods and rate data (which could be obtained from conversion (α) versus time (t) curves). Thus, BASICA (IBM), Lotus spreadsheets, and the Paradox data base were employed.

The usual expressions developed for 2CIFR can be converted into dimensionless parameters and variables (DPV). One investigator (to be mentioned subsequently) developed a procedure whereby these DPV could be used to solve for k_1 and k_2 in 2CIFR. His method was rather tedious in that it involved plotting, superposing, and displacement measurements.

In the present paper, a Lotus spreadsheet will be utilized to analyze 2CIFR for k-values. By means of this analysis, which utilizes dimensionless variables, these k-values will be obtainable in a matter of seconds once the experimental data is provided.

Keywords: Consecutive irreversible first-order reactions; Rate constant; Spreadsheet

1. Introduction

A mathematical expression was recently devised by the author for the concurrent evaluation of two rate constants, k_1 and k_2, for two consecutive irreversible first-order reactions (2CIFR) [1]. This expression was solved by the use of various computer procedures and rate data (which can be obtained from α–t curves). Thus, BASICA (IBM) was employed [1] as well as the spreadsheet, Lotus 1-2-3, release 2.2 [2], and the data base Paradox, versions 3 and 3.5 [3,4].

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The usual expressions developed for 2CIFR can be converted into dimensionless parameters and variables (DPV) [5]. Swain [6] devised a procedure whereby these DPV could be utilized to solve for k_1 and k_2 in 2CIFR. His rather tedious method involved the use of graphs, superposition, and the subsequent measurements of displacements.

In the present paper, a spreadsheet, Lotus 1-2-3, release 2.2 (DOS) and 4 (Windows) will be employed to analyze 2CIFR for values of k_1 and k_2. By means of this analysis, the k-values will be obtainable in a matter of seconds once the experimental data is provided.

2. Theoretical aspects

The 2CIFR may be represented as in the following

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} + \mathrm{gas} \tag{1A}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C} + ..\mathrm{gas}. \tag{1B}$$

In Eqs. (1A) and (1B), A, B, and C denote the starting material, the intermediate product, and the final product, respectively. The use of isothermal TG should enable the estimation of the extent of the reaction depicted in Eqs. (1) on the basis of the amount of gas liberated.

In order to calculate k_1 and k_2 in 2CIFR, reaction times were utilized at three conversions, i.e., 15, 35, and 70% (denoted as t_{15}, t_{35}, and t_{70}, respectively). In this

Table 1
Theoretical vs. calculated k-values at various kappa values using one time ratio (cf. Table 3)

Kappa	Theoretical k-values and corresponding t-values				Calculated k-values	
	k_1	k_2	t_{15}	t_{70}	k_1	k_2
0.100	0.0150	0.0015	23.270	413.000	0.0150	0.0015
0.333	0.0360	0.0120	9.280	80.300	0.0360	0.0118
0.400	0.1000	0.0400	3.300	26.500	0.1000	0.0380
0.500	0.0120	0.0060	27.100	200.700	0.0120	0.0056
0.600	0.2500	0.1500	1.280	8.948	0.2530	0.1380
0.700	0.0028	0.0020	112.700	753.000	0.0028	0.0019
0.800	0.0500	0.0400	6.232	40.060	0.0510	0.0390
0.900	0.0450	0.0405	6.840	42.860	0.0451	0.0404
0.999	0.0500	0.0499	6.081	37.240	0.0499	0.0508
2.000	0.1500	0.3000	1.844	10.230	0.1490	0.3077
3.000	0.2500	0.7500	1.036	5.650	0.2590	0.6210
4.000	0.0750	0.3000	3.280	18.080	0.0831	0.1813

respect, the following expression [1] was used for various fixed values of k_1 and k_2.

$$2(1-\alpha) = K_1 \exp(-k_1 t) + K_2 \exp(-k_2 t) \tag{2}$$

where $K_1 = (k_1 - 2k_2)/(k_1 - k_2)$ and $K_2 = k_1/(k_1 - k_2)$. In Tables 1 and 2, various theoretical values of t_{15}, t_{35}, and t_{70} are given for various k_1 and k_2 values (kappa $(\kappa) = k_2/k_1$).

A dimensionless expression was also used, i.e.,

$$\delta = 2 - [(1-2\kappa)/(1-\kappa)]\exp(-\tau) - [1/(1-\kappa)]\exp(-\tau\kappa) \tag{3}$$

where the κ represents kappa, $\tau = k_1 t$, and $50\delta = P\%$ reaction (thus for $P = 50$, $\delta = 1$; for $P = 100$, $\delta = 2$, etc.). From Eq. (3), various values of τ could be ascertained for κ at P-values of 15, 35, and 70%. Thus, for example, at $P = 70$, τ-values (τ_{70}) could be calculated for various values of κ at $P = 70$. Then κ can be obtained as a function of $\tau_{70}/\tau_{15} (= t_{70}/t_{15})$. A plot of $\log(\kappa)$ versus $\log(t_{70}/t_{15})$ is depicted in Fig. 1. A quartic polynomial was derived correlating $\log(\kappa)$ and $\log(t_{70}/t_{15})$ (cf. line B9 of Table 3). In this table, T7015T denotes t_{70}/t_{15} and K7015K in line B10 of Table 3 now denotes κ for the ratio t_{70}/t_{15}. Lastly, from the preceding, τ_{15} could be correlated with K7015K by means of a polynomial of the 6th degree (cf. line B11 of Table 3). Also, from the preceding, $k_1 = \tau_{15}/t_{15}$ and $k_2 = k_1 \times$ K7015K. Thus, in Table 3, $k_1 = 0.3427/0.367 = 0.934$ and $k_2 = k_1 \times 0.1921 = 0.1794$, as indicated on line A27 of Table 3. In these calculations, values in cells B5, C5, A36, and B36 of Table 3 were utilized. Besides using two reaction times and one ratio (t_{70}/t_{15}) to estimate values of k_1 and k_2, three reaction times and three time ratios were also employed, i.e., t_{70}/t_{15}, t_{70}/t_{35}, and t_{35}/t_{15} (cf. Tables 2 and 4). Similar k-value calculations, as noted in the preceding, were also carried out in Table 4.

Table 2
Theoretical vs. calculated k-values at various kappa values using three time ratio (cf. Table 4)

Kappa	Theoretical k-values and corresponding t-values					Average calculated k-values	
	k_1	k_2	t_{15}	t_{35}	t_{70}	k_1	k_2
0.100	0.0150	0.0015	23.270	71.870	413.000	0.0150	0.0015
0.333	0.0360	0.0120	9.280	25.710	80.300	0.0360	0.0120
0.400	0.1000	0.0400	3.300	8.970	26.500	0.1010	0.0397
0.500	0.0120	0.0060	27.100	71.800	200.700	0.0120	0.0059
0.600	0.2500	0.1500	1.280	3.300	8.948	0.2520	0.1478
0.700	0.0028	0.0020	112.700	287.000	753.000	0.0028	0.0019
0.800	0.0500	0.0400	6.232	15.700	40.060	0.0500	0.0402
0.900	0.0450	0.0405	6.840	17.020	42.860	0.0451	0.0408
0.999	0.0500	0.0499	6.081	15.000	37.240	0.0500	0.0512
2.000	0.1500	0.3000	1.844	4.292	10.230	0.1480	0.3007
3.000	0.2500	0.7500	1.036	2.362	5.650	0.2560	0.6196
4.000	0.0750	0.3000	3.280	7.438	18.080	0.0814	0.1884

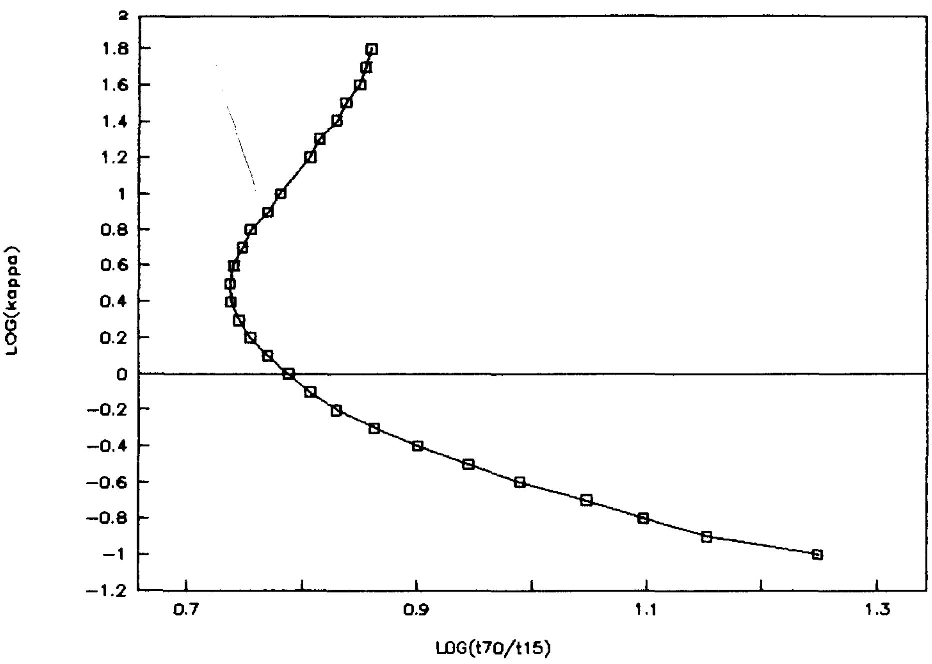
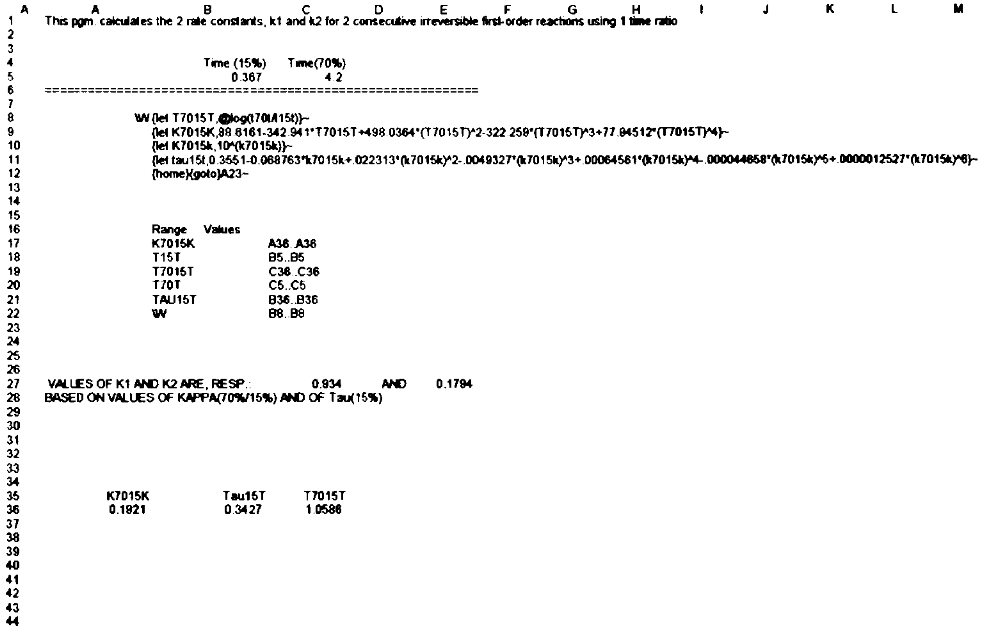


Fig. 1

3. Results and discussion

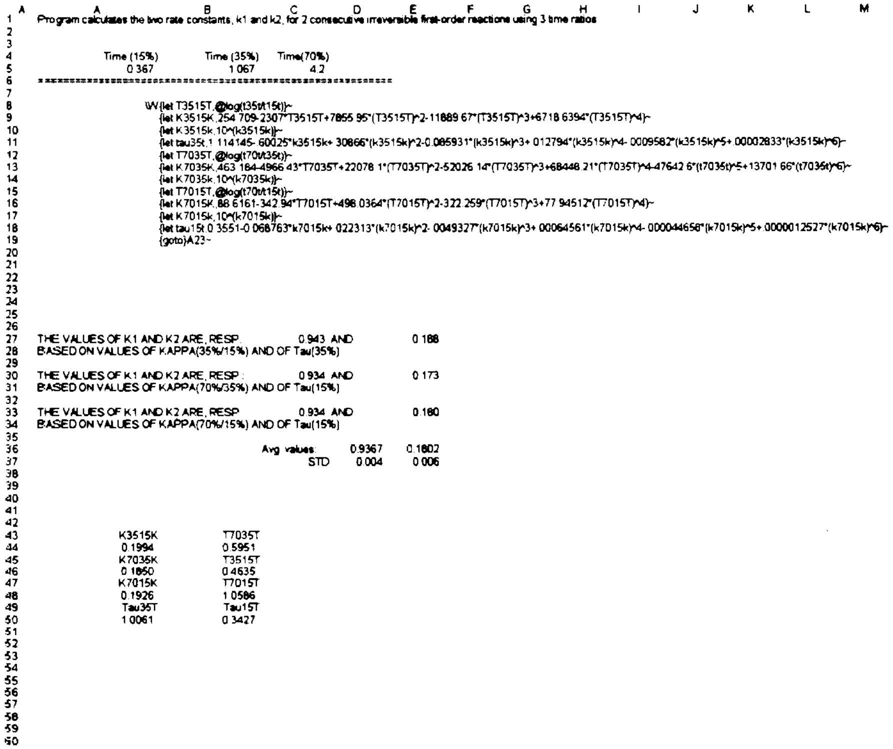
The Lotus worksheet in Table 3 was employed to obtain the calculated values of k_1 and k_2 in Table 1. Similarly, the worksheet in Table 4 was used to obtain the calculated k-values in Table 2. As an illustration, experimental data [6] for t_{15} and t_{70} were entered into cells B5 and C5, respectively (cf. Table 3). Then the run command was given for the macro, lines A8–A12 (alt-W for DOS and ctrl-W for Windows). Within a few seconds, the results for k_1 and k_2 appeared in cells C27 and E27, respectively, i.e., 0.934 and 0.1794 h^{-1} (the reaction times were in hours. The average reported results [6] were $k_1 = 0.937$ h^{-1} and $k_2 = 0.180 h^{-1}$, in excellent agreement with the spreadsheet results. Similar average k-values were obtained in Table 4 using three time ratios. In obtaining his results, Swain also utilized three time ratios, i.e., t_{70}/t_{35}, t_{70}/t_{15} and t_{35}/t_{15}, and reported the average of his results. In Table 3, only one ratio, i.e., t_{70}/t_{15}, was used since it was observed that this time ratio alone could afford calculated k-values which were in excellent agreement with corresponding theoretical values. However, this good agreement (cf. Table 1) only held up to a κ-value of 2.0, after which it became increasingly poor as κ was increased to a value of four. This could be accounted for as follows. From Fig. 1, it can be observed that in the plot of $\log(\kappa)$ versus $\log(t_{70}/t_{15})$, at a value of $\log(\kappa)$ of ca. 0.4 ($\kappa = 2.5$), the curve starts to turn back toward the previous portion of the curve causing double values of $\log(\kappa)$ for corresponding singular

Table 3



```
A       A                     B                C           D          E          F         G          H         I         J         K         L         M
1    This pgm. calculates the 2 rate constants, k1 and k2 for 2 consecutive irreversible first-order reactions using 1 time ratio
2
3
4                          Time (15%)    Time(70%)
5                              0.367           4.2
6    ==========================================================
7
8                  W{let T7015T,@log(t70t/t15t)}~
9                    {let K7015K,88.6161-342.941*T7015T+498.0364*(T7015T)^2-322.259*(T7015T)^3+77.94512*(T7015T)^4}~
10                   {let K7015k,10^(k7015k)}~
11                   {let tau15t,0.3551-0.068763*k7015k+.022313*(k7015k)^2-.0049327*(k7015k)^3+.00064561*(k7015k)^4-.000044658*(k7015k)^5+.0000012527*(k7015k)^6}~
12                   {home}{goto}A23~
13
14
15
16                   Range    Values
17                   K7015K              A36..A36
18                   T15T                B5..B5
19                   T7015T              C36..C36
20                   T70T                C5..C5
21                   TAU15T              B36..B36
22                   W                   B8..B8
23
24
25
26
27    VALUES OF K1 AND K2 ARE, RESP.:              0.934         AND        0.1794
28   BASED ON VALUES OF KAPPA(70%/15%) AND OF Tau(15%)
29
30
31
32
33
34
35             K7015K                Tau15T          T7015T
36             0.1921                0.3427          1.0586
37
38
39
40
41
42
43
44
```

Table 4



```
A       A                     B                C           D          E          F         G          H         I         J         K         L         M
1    Program calculates the two rate constants, k1 and k2, for 2 consecutive irreversible first-order reactions using 3 time ratios
2
3
4               Time (15%)          Time (35%)    Time(70%)
5                   0.367               1.067          4.2
6    ===========================================================
7
8                          W{let T3515T,@log(t35t/t15t)}~
9                            {let K3515K,254.709-2307*T3515T+7855.95*(T3515T)^2-11889.67*(T3515T)^3+6718.6394*(T3515T)^4}~
10                           {let K3515k,10^(k3515k)}~
11                           {let tau35t,1.114145-.60025*k3515k+.30866*(k3515k)^2-0.085931*(k3515k)^3+.012794*(k3515k)^4-.0009582*(k3515k)^5+.00002833*(k3515k)^6}~
12                           {let T7035T,@log(t70t/t35t)}~
13                           {let K7035K,463.184-4966.43*T7035T+22078.1*(T7035T)^2-52026.14*(T7035T)^3+68448.21*(T7035T)^4-47642.6*(t7035t)^5+13701.66*(t7035t)^6}~
14                           {let K7035k,10^(k7035k)}~
15                           {let T7015T,@log(t70t/t15t)}~
16                           {let K7015K,88.6161-342.94*T7015T+498.0364*(T7015T)^2-322.259*(T7015T)^3+77.94512*(T7015T)^4}~
17                           {let K7015k,10^(k7015k)}~
18                           {let tau15t,0.3551-0.068763*k7015k+.022313*(k7015k)^2-.0049327*(k7015k)^3+.00064561*(k7015k)^4-.000044658*(k7015k)^5+.0000012527*(k7015k)^6}~
19                           {goto}A23~
20
21
22
23
24
25
26
27   THE VALUES OF K1 AND K2 ARE, RESP.                 0.943  AND              0.188
28   BASED ON VALUES OF KAPPA(35%/15%) AND OF Tau(35%)
29
30   THE VALUES OF K1 AND K2 ARE, RESP.:                0.934  AND              0.173
31   BASED ON VALUES OF KAPPA(70%/35%) AND OF Tau(15%)
32
33   THE VALUES OF K1 AND K2 ARE, RESP.                 0.934  AND              0.180
34   BASED ON VALUES OF KAPPA(70%/15%) AND OF Tau(15%)
35
36                                          Avg. values:      0.9367      0.1802
37                                                  STD       0.004       0.006
38
39
40
41
42
43                 K3515K              T7035T
44                  0.1994             0.5951
45                 K7035K              T3515T
46                  0.1850             0.4635
47                 K7015K              T7015T
48                  0.1926             1.0586
49                  Tau35T              Tau15T
50                  1.0061             0.3427
51
52
53
54
55
56
57
58
59
60
```

values of $\log(t_{70}/t_{15})$. Thus, a polynomial correlation would not be expected to afford calculated k-values in good agreement with theoretical k-values when κ exceeded a value of two, as indicated in Table 1. In order to present a more complete picture, average k-value results are also presented in Table 2 using the three ratios t_{70}/t_{35}, t_{35}/t_{15}, and t_{70}/t_{15} and expressions given in Table 4. These average k-value results, also agreed well with the theoretical, and similar limitations apply as previously indicated for the t_{70}/t_{15} ratio. Finally, it should be mentioned that the ultimate validity of the calculated k-values should be established by comparing conversion values (experimental or theoretical) with corresponding conversion values calculated by using these k-values in Eq. (2).

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