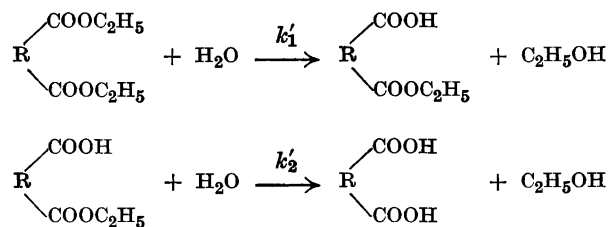# The Calculation of Velocity Constants for First- and Second-order Two-stage Reactions

SIGVARD WIDEQVIST

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

Several authors have been occupied with the problem of calculating the velocity constants for stage reactions. Among these authors should be mentioned Knoblauch[1], Meyer[2,3], Wegscheider[4], Skrabal[5], Ingold[6], Ritchie[7], and Homan[8].

As an example for a first-order two-stage reaction we may regard the catalytic hydrolysis by hydrochloric acid of symmetrical dialkyl esters. The dialkyl ester is first hydrolyzed to a monoalkyl ester, and the monoester is then hydrolyzed to a dicarboxylic acid:

$$R\begin{array}{l} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{array} + H_2O \xrightarrow{k_1'} R\begin{array}{l} \diagup COOH \\ \diagdown COOC_2H_5 \end{array} + C_2H_5OH$$

$$R\begin{array}{l} \diagup COOH \\ \diagdown COOC_2H_5 \end{array} + H_2O \xrightarrow{k_2'} R\begin{array}{l} \diagup COOH \\ \diagdown COOH \end{array} + C_2H_5OH$$
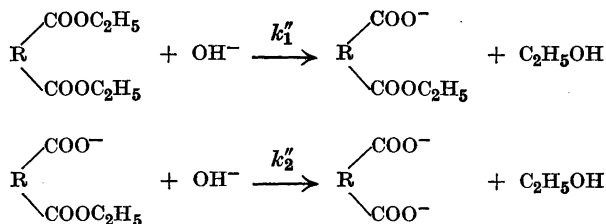
Let a be the initial concentration of the dicarboxylic ester, and let x be the fall in concentration of the same ester and y the rise in concentration of the dicarboxylic acid. Thus the concentration of the intermediate monoalkyl ester is $(x—y)$. When the first-stage reaction velocity constant is k_1' and k_2' that of the second-stage reaction, and ϑ is the time, we get the following differential equations:

$$dx/d\vartheta = k_1' \ (a—x) \tag{1}$$

$$dy/d\vartheta = k_2' \ (x—y) \tag{2}$$

A second-order two-stage reaction may be examplified by the saponification by alkali of symmetrical dicarboxylic esters:

$$R \diagdown \begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix} + OH^- \xrightarrow{k_1''} R \diagdown \begin{matrix} COO^- \\ COOC_2H_5 \end{matrix} + C_2H_5OH$$

$$R \diagdown \begin{matrix} COO^- \\ COOC_2H_5 \end{matrix} + OH^- \xrightarrow{k_2''} R \diagdown \begin{matrix} COO^- \\ COO^- \end{matrix} + C_2H_5OH$$

With the same assumptions as above and if b is the initial concentration of alkali and t is the time and $z = (x + y)$, we get the following differential equations:

$$dx/dt = k_1'' \ (a—x) \ (b—z) \tag{3}$$

$$dy/dt = k_2'' \ (x—y) \ (b—z) \tag{4}$$

The second-stage velocity constant (k_2' resp. k_2'') is easily determined by the use of monoalkyl ester, when a simple single-stage reaction is obtained. The determination of the first-stage constant (k_1' resp. k_1'') has been performed in several ways by use of approximative methods, but none of the investigators who have studied the reactions above have been able to obtain an exact, explicit mathematical expression for k_1. This problem is, however, to be solved in a simple way by the following method.

The two equation systems (1,2) and (3,4) may be treated in the same manner. For that reason we shall give both systems the same mathematical form. That is possible by a formal reduction of the reaction order for the second-order reaction. To do that we put

$$(b—z) \ dt = d\vartheta \tag{5}$$

On introduction of this expression into equ. (3) and (4) we obtain

$$dx/d\vartheta = k_1'' \ (a—x) \tag{3a}$$

$$dy/d\vartheta = k_2'' \ (x—y) \tag{4a}$$

These equations are from the mathematical point of view identical with equ. (1) and (2) for the first-order reaction.

When equ. (5) is integrated, we obtain

$$\vartheta = \int_0^t (b-z)\ \mathrm{d}t \tag{5a}$$

The quantity ϑ is the area between the curve $(b-z) = f\ (t)$ and the t-axis. As seen from that the *area* ϑ in the second-order reaction plays the same rôle as the *time* ϑ in the first-order reaction. Thus the substitution $(b-z)\ \mathrm{d}t = \mathrm{d}\vartheta$ involves a formal reduction of the reaction order.

The equation system (3, 4) has never been integrated, but approximative solutions may be obtained.

The equation system (1, 2) resp. (3a, 4a) is easily integrated. When the indices ' and " are discarded, we get from equ. (1)

$$k_1\vartheta = \ln\ a/(a-x) \tag{6}$$

or

$$x = a\ (1-e^{-k_1\vartheta}) \tag{7}$$

Putting this value of x into equ. (2) we get

$$\mathrm{d}y/\mathrm{d}\vartheta = k_2\ [a\ (1-e^{-k_1\vartheta})-y]$$

and

$$\mathrm{d}y/\mathrm{d}\vartheta + k_2y = k_2a\ (1-e^{-k_1\vartheta}) \tag{8}$$

On integration, we obtain

$$y = a\left[1 + \frac{k_2}{k_1-k_2}\ e^{-k_1\vartheta} - \frac{k_1}{k_1-k_2}\ e^{-k_2\vartheta}\right] \tag{9}$$

or

$$y = a\left[\frac{k_1}{k_1-k_2}\ (1-e^{-k_2\vartheta}) - \frac{k_2}{k_1-k_2}\ (1-e^{-k_1\vartheta})\right] \tag{9a}$$

During the reaction the quantity $(b-z)$ or z is measured. By addition of the equ. (7) and (9) we obtain

$$z = a\left[2 - \frac{k_1}{k_1-k_2}\ e^{-k_1\vartheta} - \frac{k_1-2k_2}{k_1-k_2}\ e^{-k_2\vartheta}\right] \tag{10}$$

As the velocity constant k_2 may be determined by a separate experiment, the equ. (10) contains only one unknown quantity, namely k_1. In spite of that, k_1 cannot be explicitly expressed because of the transcendent part $e^{-k_1\vartheta}$. We

shall therefore eliminate $e^{-k_1\vartheta}$ which is easily done in the following manner. Regard the function

$$z = f(\vartheta)$$

The area between the curve and the ϑ-axis is

$$A = \int_0^\vartheta f(\vartheta) \, d\vartheta = \int_0^\vartheta z \, d\vartheta \qquad (11)$$

Combining equ. (10) and (11) we get

$$A = a \int_0^\vartheta \left[2 - \frac{k_1}{k_1 - k_2} e^{-k_2\vartheta} - \frac{k_1 - 2k_2}{k_1 - k_2} e^{-k_1\vartheta} \right] d\vartheta \qquad (12)$$

On integration, we obtain

$$A = a \left[2\,t + \frac{k_1}{k_2\,(k_1 - k_2)} e^{-k_2\vartheta} + \frac{k_1 - 2k_2}{k_1\,(k_1 - k_2)} e^{-k_1\vartheta} - \frac{2k_2 + k_1}{k_1 k_2} \right] \qquad (13)$$

On elimination of $e^{-k_1\vartheta}$ between equ. (12) and (13) we get after simplification

$$k_1 \left[2k_2 a\vartheta - k_2 A - a\,(1 - e^{-k_2\vartheta}) \right] = k_2 z$$

or

$$k_1 = \frac{z}{2\,a\vartheta - \int_0^\vartheta z\,d\vartheta - \frac{a}{k_2}\,(1 - e^{-k_2\vartheta})} \qquad (14)$$

Equ. (14) is an exact, explicit expression for the velocity constant k_1. This expression is valid for both first- and second-order two-stage reactions. In a first-order reaction ϑ is identical with the time; in a second-order reaction ϑ is the area between the curve $(b - z) = f(t)$ and the t-axis, when t is the time. A and ϑ may be evaluated by means of graphical integration.

Example

The data of Ingold [6] for the saponification of dimethyl glutarate by sodium hydroxide at 20.30° have been treated by the method above. The initial concentrations for both dimethyl glutarate (a) and sodium hydroxide (b) are 0.001999 mole/l, and the second-stage velocity constant $k_2 = 1.12$. The results are reported in Table I, where $t =$ time in minutes, $A = \int_0^\vartheta z\,d\vartheta$ and $B = \frac{a}{k_2}\,(1 - e^{-k_2\vartheta})$.

5

Table 1. The saponification of dimethyl glutarate by sodium hydroxide according to Ingold [6].

t	$(b-z) \cdot 10^3$	$z \cdot 10^3$	$\vartheta \cdot 10^3$	$A \cdot 10^6$	$2 a \vartheta \cdot 10^6$	$B \cdot 10^6$	k_1
2.5	1.929	0.070	4.91	0.17	19.63	9.82	7.26
4.2	1.883	.116	8.15	0.48	32.58	16.08	7.24
6.0	1.839	.160	11.50	0.95	45.98	23.22	7.33
10.0	1.743	.256	18.66	2.45	74.59	36.61	7.21
12.0	1.699	.300	22.10	3.40	88.35	43.75	7.28
14.1	1.655	.344	25.62	4.54	102.43	50.90	7.32
16.0	1.619	.380	28.73	5.66	114.86	56.25	7.18
18.0	1.577	.422	31.93	6.94	127.64	62.50	7.25
20.0	1.539	.460	35.04	8.32	140.10	68.75	7.30
23.0	1.487	.512	39.58	10.52	158.24	77.68	7.31
26.0	1.435	.564	43.96	12.88	175.77	85.71	7.31
29.0	1.387	.612	48.20	15.37	192.69	93.76	7.32
32.0	1.345	.654	52.30	17.97	209.08	101.8	7.32
35.0	1.307	.692	56.27	20.64	224.90	109.0	7.25

Mean value　　7.277

For the first-stage reaction velocity constant Ingold reported the value $k_1 = 7.24$.

SUMMARY

A formula for the calculating of the first-stage velocity constant for a two-stage first- or second-order reaction has been deduced. The formula which makes use of graphical integration has been tested against the data of Ingold [6] for the saponification by alkali of dimethyl glutarate at 20.30°, whereby the value $k_1 = 7.277$ was obtained which is in good agreement with that of Ingold who reported $k_1 = 7.24$.

REFERENCES

1. Knoblauch, O. *Z. physik. Chem.* **26** (1898) 96.
2. Meyer, J. *Z. physik. Chem.* **66** (1909) 81.
3. Meyer, J. *Z. physik. Chem.* **67** (1909) 257.
4. Wegscheider, R. *Monatsh.* **36** (1915) 471.
5. Skrabal, A. *Monatsh.* **37** (1916) 137.
6. Ingold, Ch. K. *J. Chem. Soc.* (1931) 2170.
7. Ritchie, M. *J. Chem. Soc.* (1931) 3112.
8. Homan, J. D. H. *Rec. trav. chim.* **63** (1944) 189.