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Problems
Задачи

SIMPLE TECHNIQUE FOR DETERMINING THE FORWARD RATE CONSTANT OF REVERSIBLE REACTION

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Abstract. The forward rate constant of reversible reactions can be used to estimate the concentration of the reactants at a given time (and then the products by using stoichiometric coefficients), to control the quality of the products, to calculate the backward rate constant (by using equilibrium constant), to determine the activation energy, and to predict the reaction mechanisms. Most commonly, the determination of a forward rate constant is done by using the equilibrium concentrations. However, this approach is inefficient since to a certain extent a lot of reactions takes a long time to reach an equilibrium state. The method without using equilibrium concentration is also introduced. Nevertheless, it cannot be used to determine the backward rate constant. This study presents a simple and appropriate technique, using irreversible approach on three data at the early stages of a reversible reaction. The data for first order for both directions and first order for forward and second order for back reaction were obtained from literatures. The results were then compared with that obtained from conventional technique. The results show that, with error percentage less than 5%, the new technique is valid and reliable.

Keywords: forward rate constant; reversible reaction; irreversible approach; equilibrium concentrations; simple technique

If the activities are taken as the concentrations, for a homogeneous system at equilibrium:

$$aA(g) \underset{k_b}{\overset{k_f}{\longleftrightarrow}} pP(g) + qQ(g) \tag{1}$$

by the equilibrium law, the value of K_c is:

$$K_c = \frac{[P]_{eq}^{p}[Q]_{eq}^{q}}{[A]_{eq}^{a}} \tag{2}$$

In this expression, [A], [P], and [Q] are the molar concentrations of the respective components at equilibrium. Each concentration term is raised to a power given by its stoichiometric coefficient.

The equilibrium constant (K_c) is only a function of temperature. It should be constant if the temperature does not change. Theoretically, at a constant temperature, the value for *Kc* should be the same for each regardless of the initial conditions and technique of determination. In most text-books, the value of *Kc* is determined with thermodynamic approach. Unfortunately, in many reactions, this will be a tedious job because it requires a relatively long time of experiments (and thus require greater production costs) to reach an equilibrium state. The equilibrium constant can be also calculated with kinetic approach. For some reasons, this approach is even more favourable than the thermodynamic approach. Although the formation reaction of an industrial product is an exothermic reaction, because of kinetics consideration, the process is still being done at high temperatures. The products will be less, but the time required much shorter. A catalyst does not change the equilibrium position but speed up reaction to reach the equilibrium state. The concept of thermodynamics just states that if the concentration of one reactant is made in excess then the equilibrium will shift toward products. However, the concept of kinetics states which reagent that should be made in excess. Save for economic consideration, it is the reactant with highest order that should be made in excess.

The equilibrium constant obtained by kinetics approach is denoted as $K_{kin.}$ This constant is calculated from the equation:

$$K_{kin} = k_f / k_b \tag{3}$$

where *kf* and *kb* are the forward and backward rate constant, respectively. Of the two, the forward rate constant k_f has more important role in studying an equilibrium system. The forward rate constant can be used to determine the concentration of the reactants at any given time (which is then used to determine the products) and to control the quality of the products, i.e. when a reaction should be stopped (because the target has been achieved and prolonging the reaction is ineffective). In addition, it can be employed to calculate the backward rate constant, to estimate the activation energy, and to predict the reaction mechanisms (Patiha & Firdaus, 2016).

The integral method is most widely used for the determination of k_f value. For first order reaction, the integral equation is

$$\ln[A] = \ln[A_o] - k_f t \tag{4}$$

or

$$\ln\frac{[A]}{[A_o]} = k_f t \tag{5}$$

The value of k_f is obtained from the slope of the linear curve of ln[A] vs t of Eq. (4) or ln([A]/[A_o] vs t of Eq. (5).

For second order reaction, the integral equation is:

$$\frac{1}{[A]} = \frac{1}{[A_o]} + k_f t \tag{6}$$

The value of k_f is obtained from the slope of the linear curve of 1/[A] vs t.

The value of k_f can be calculated without using equilibrium concentration. In this case, the influence of back reaction on the reaction rate is not taken into account. Nevertheless, most commonly the equilibrium concentration is included in the calculation (Schafer et al., 2010; Alberty, 1987a).

The better equation for studying reversible reaction which is first order for both directions is:

$$\frac{x_e}{[A_o]} \ln\left[\frac{x_e}{(x_e - x)}\right] = k_f t \tag{7}$$

and for first order for forward and second order for back reaction is

$$\frac{x_e}{2[A_o] - x_e} \ln\left[\frac{[A_o]x_e + x([A_o] - x_e)}{[A_o](x_e - x)}\right] = k_f t \tag{8}$$

where [A_o], x, x_e, k_f, and t are the initial concentration, amount reacted, amount reacted at equilibrium, the forward rate constant, and the time, respectively.

A practical technique for the determination of k_f by differential method with the initial rate has been discussed (Levine, 2009). However, save for zero-order reaction, the value of a rate constant, k, obtained by the differential method will not be the same with the integral method. Thus, only in the zero-order reaction, the rate is independent of reactants concentration. The initial rate method only gives best result if the fraction reacted less than 5% (Casado et al., 1986). Moreover, the value obtained by differential method should be checked with integral method (Laidler, 1987).

Nevertheless, the initial rate approach for the determination of k_f is still interesting. The forward rate law of a reversible reaction has a linear form (not fractal). At the early stages of a reaction, the inter-influences between the reactant and product are relatively small. The reaction rates vary linearly with time. It is nearly like in the irreversible reactions. Therefore, the determination of the rate constant can be done using the calculated rate from the data at the early stages of the reaction and being treated like irreversible reaction. Thus, indeed, the determination should by integral method.

A unified integral equation for easier determination of the order of a reaction has also been introduced (Patiha, 2011):

$$t_i = (\beta)^{(i-1)(1-n)} t_\beta \tag{9}$$

or in a logaritmic form

$$\log t_i = (1-n)\log\beta(i-1) + \log t_\beta \tag{10}$$

where β is the unreacted fraction of the reactant, t_β is the (first) time needed for the reactant to react until left β fraction, and t_i is next observation time if β are always made constant.

The order of a reaction, can be predicted from Eq. (9). For example, the t_i for a first order reaction is independent of β and the half-live for a second order reaction is 2 β. But, the better is obtained from the slope of the curve of log t_i vs (i-1) of Eq. (10). Then, the value of k_f can be calculated from the equation of

$$k_f = -\ln(\beta)/t_\beta \ for \quad n = 1 \tag{11}$$

or

$$k_f = \frac{\beta^{(1-n)} - 1}{\left[(n-1)[A_o]^{(n-1)}\right]} \frac{1}{t_\beta} \qquad \text{for } n \neq 1 \tag{12}$$

Based on above discussion, there are three goals of this study, i.e. first, to compare the validity of the two methods, that with and without using the equilibrium concentrations data, in the determination of k_f; second, to present a new technique for the determination of k_f, using irreversible approach on the 3 data at the very beginning of a reaction; and third, the main goal, to prove the validity and reliability of both conventional and the new methods by comparing the k_f values obtained with that from standard.

Methodology

The framework to solve the three goals listed are as follows. First, the observed physical properties of reactant(s) and product(s) in any reversible reactions are influenced by the previous and the next observations. The reverse reaction will shift the equilibrium position. The influences depend on the type of the reversible reactions. Normally, for a reaction with the same first order for both directions, the concentration of the product should be higher than when the reaction is irreversible. This is because, the addition of reactant concentration (by reverse reaction) will shift the equilibrium position toward product. However, if the reverse reaction is of the second order, the amount of product will be nearly the same. This is because the reverse reaction last faster. Second, the forward rate law (and as well the backward) of a reversible reaction has a linear form (not fractal). Therefore, the rate constants can be determined from the rate counted from observational data at the very beginning of a reaction until near equilibrium state. However, the rate at the beginning of a reaction is the most appropriate because the rate at this condition is more linear with concentration. Applying the effect of back reaction will give the more exact concentrations. But, the effect can be measured sufficiently from two sequential observations at the early stages of the reaction. There is no need to use equilibrium concentrations in the calculation.

The conclusions will be taken with the following way. A method is claimed valid if the method is applicable for all cases. It is claimed reliable if the difference of percentage error of the values of k_f obtained from the method with that obtained from standard is less than 5%. The standard for first order for both directions is Eq. (7) and for first order for forward and second order for back reaction is Eq. (8).

The data used for studying are taken from literatures i.e. two for first order ↔ first order (Wright, 2004; Wilkinson, 1980) and three for first order ↔ second order types (Persada, 2012; Alberty, 1987b).

Table 1. Data and calculations for determining rate constant for the isomerization of *cis*-1-ethyl-2- methylcyclopropane (Wright, 2004)

Time (s)	*[Cis] (M)*	*A*	*B*	*C*
0	0.01679			
400	0.01406	-0.24958	-0.17745	0.18373
1000	0.01102	-0.62891	-0.42107	0.46297
1600	0.00892	-1.01261	-0.63249	0.74544
2100	0.00775	-1.31450	-0.77309	0.96767
∞	0.00443			
k_f		$6.28 \times 10^{-4}\ s^{-1}$	$3.52 \times 10^{-4} s^{-1}$	$4.62 \times 10^{-4} s^{-1}$

$A = = \ln \{([Cis] - \infty) / ([Cis_o] - \infty)\}$; $B = \ln ([Cis]/[Cis_o])$; $C = \frac{x_e}{Cis_o} \ln \frac{x_e}{(x_e - x)}$

Table 2. Data and calculations for determining rate constant for an isomerization reaction (Wilkinson, 1980)

Time (h)	*Reaction (%)*	*A*	*B*	*C*
0	100			
1	72.5	-0.49899	-0.32158	0.34929
2	56.8	-0.96009	-0.56563	0.67207
3	45.6	-1.50122	-0.78526	1.05086
4	39.5	-1.99720	-0.92887	1.39804
∞	30.0			
k_f		13.99 x 10^{-5} s^{-1}	5.67 x 10^{-5} s^{-1}	9.79 x 10^{-5} s^{-1}

$A = = \ln \{([Cis] - \infty) / ([Cis_o] - \infty)\}$; $B = \ln([Cis]/[Cis_o])$; $C = \dfrac{x_e}{Cis_o} \ln \dfrac{x_e}{(x_e - x)}$

Table 3. Data and calculations for determining first order rate constant for the hydrolysis of methyl acetate (Persada, 2012)

Time	*[HAc.] (M)*	*[MAc.] [M]*	*A*	*B*	*C*
0		0.57064	0		
10 min.	0.00358	0.56706	-0.00767	-0.00629	0.00630
20 min.	0.00766	0.56298	-0.01648	-0.01351	0.01352
30 min.	0.01124	0.55940	-0.02427	-0.01986	0.01991
40 min.	0.01495	0.55569	-0.03241	-0.02655	0.02657
50 min.	0.01890	0.55174	-0.04115	-0.03368	0.03371
4 days 0.46880		0.10184	1.02895	1.00907	1.04951
k_f			8.29x10^{-4} min.$^{-1}$	6.78x10^{-4} min.$^{-1}$	6.79x10^{-4} min.$^{-1}$

$A = \ln([MAc.] - \infty) / ([MAc.]_o - \infty)$; $B = \ln[MAc.]/[MAc.]_o$; $C = \dfrac{x_e}{2[A_o] - x_e} \ln\left[\dfrac{[A_o]x_e + x([A_o] - x_e)}{[A_o](x_e - x)}\right]$

Table 4. Data and calculations for determining first order rate constant for the hydrolysis of methyl acetate

Time (min.)	[*HAc.*] (M)	[*MAc.*] [M]	ln [*MAc.*]	ln ([*MAc.*]/ ln [*MAc.*]o)	Literature
0		0.1000			
1.25	0.0045	0.0955	-2.3486	-0.0460	
10.20	0.0298	0.0702	-2.6564	-0.3538	
19.55	0.0494	0.0506	-2.9838	-0.6812	
31.20	0.0667	0.0333	-3.4022	-1.0996	
40.75	0.0757	0.0243	-3.7173	-1.4147	
50.50	0.0830	0.0170	-4.0745	-1.7720	
k_f			3.50x10^{-2}	3.50x10^{-2}	3.50x10^{-2}min-1

Table 5. Data of the NaOH volume used in the titration of the aliquots of equal volume of the solution at different time and calculations for determining constants for hydrolysis of methyl acetate at 25 ^{o}C (Alberty, 1987a)

Time (s)	v (cm3)	(39.81-v) (cm3)	ln (39.81-v)	(39.81-v) (cm3)	ln [(39.81-v)-∞]	Literature
0				14.05		
339	26.34	13.47	2.6005	13.47	2.4097	
1242	27.80	12.01	2.4857	12.01	2.2690	
2745	29.70	10.11	2.3135	10.11	2.0503	
4546	31.81	8.00	2.0794	8.00	1.7334	
∞	39.81			2.34		
k_f		-	1.23 x 10^{-4}s^{-1}		1.60 x 10^{-4}s^{-1}	1.22 x 10^{-4}s^{-1}

Table 6. Data and calculations for determining first order rate constant using the new technique

Source	***Time***	***Rev. con.***	***A2 irrev.***	***A1 Correction Factor***	***Irrev.***	***kf***	***Error %***
Table 1	0	0.01679			0.01679		
	400 s	0.01406		-9.84x10-5	0.01396		
	1000 s	0.01102	0.010774 < A2				
						4.61x10^{-4}s^{-1}	0.22

Table 2	0	100			100		
	1 hour	72.5		-2.11875	70.38		
2 hour		56.8	52.5625 < A2				
						$9.76x10^{-5}s^{-1}$	0.31
Table 3	0	0.57064					
	10 min.	0.56706		-2.6x10-4	0.566799		
	20 min.	0.56298	0.56350 > A2				
						$6.75x10^{-4}min^{-1}$	0.59
Table 4	0	0.1000					
	1.25 s	0.0955		+1.863x10-4	0.09569		
	10.20 s	0.0702	0.06868 < A2				
						$3.53x10^{-2}min^{-1}$	0.86
Table 5	0	13.47					
	903 s	12.01		+0.07	12.08		
	2406 s	10.11	9.923 < A2				
						$1.21x10^{-4}\ s^{-1}$	0.82
	0	14.05					
	339 s	13.47		-8.188x10-3			
	1242 s	12.01	12.04 > A2				
						kf# $1.26x10^{-4}\ s^{-1}$	3.28

Results

In accordance with previous statements on the influence of the concentration of product(s), some empirical equations are introduced.

To make easier, for reversible reaction which is first order for forward reaction, Eq. (5) is modified into:

$$k_{f^*} = -\left(\ln {}^{[A_1]}\!/_{[A_o]}\right)/t_1 \tag{13}$$

$$[A_2]_{irr.} = \left[anti\ln(-k_{f^*}t_2\right][A_o] \tag{14}$$

$$[A_1]_{irr} = [A_1] - C \text{ first order of back reaction;} \tag{15}$$

$$[A_1]_{irr.} = [A_1] + C \text{ second order of back reaction; } [A_2]_{irr.} < [A_2] \tag{16}$$

$$[A_1]_{irr.} = [A_1] + C \text{ second order of back reaction; } [A_2]_{irr.} < [A_2] \tag{17}$$

where the correction factor is

$$C = \pm({}^{t_1}\!/_{t_2})([A_2] - [A_2]_{irr.}) \tag{18}$$

and

$$k_f = -\left(\ln {}^{[A_1]_{irr.}}\!/_{[A_o]}\right)/t_1 \tag{19}$$

where k_f^*, k_f, $A_2]_{irr.}$, $[A_2]$, $[A_o]$, t_1, t_2, $[A_1]_{irr.}$, $[A_1]$, and C, are the forward rate constant for the first observation, the forward rate constant for the reaction, the second theoretical irreversible concentration, the second observation, the initial concentration, the time for the first observation, the time for the second observation, the first theoretical irreversible concentration, the first observation, and the correction factor respectively.

Three examples of calculations are as follows:

(1) Applying Eq. (13), onto the first observation (t = 400) in Table 1: $k_{f^*} = -\left(\ln({}^{0.01406}\!/_{0.01679})\right)/400s = 4.436x10^{-4}s^{-1}$; By Eq. (14): $[A_2]_{irr.}$ = [anti ln (-4.436x10^{-4}x1000)]0.01679 = 0.01078 M; By Eq. (18), the correction factor C =± (400/1000)x(0.01102 – 0.01078) = ± 9.6 x 10^{-5} M. Because the reverse reaction first order, C = - 9.6 x 10^{-5} M. Then by Eq. (15): $[A_1]_{irr.}$ = (0.01406 - 9.6 x 10^{-5}) = 0.013964 M. And last, by Eq. (19), $k_f = -\left(\ln({}^{0.013964}\!/_{0.01679})\right)/400s = 4.61x10^{-4}s^{-1}$.

(2) Applying Eq. (13), onto the first observation (t = 903) in Table 6: $k_{f^*} = -\left(\ln({}^{12.01}\!/_{13.47})\right)/903s = 1.27x10^{-4}s^{-1}$; By Eq. (13) $[A_2]_{irr.}$ = [anti ln (-1.27x10^{-4}x2406)]x13.47 = 9.923 cm^3; By Eq. (17), the correction factor C =± (903/2406)x(10.11 – 9.923 cm^3) = ± 0.07 cm^3. Because the reverse reaction is second order and $[A_2]_{irr.}$ (=9.923 cm^3) < A_1 (= 10.11cm^3) then C = 0.07 cm^3. Then by Eq. (16): $[A_1]_{irr.}$ = (12.01 + 0.07) cm^3= 11.94 cm^3. And last, by Eq. (19), $k_f = -\left(\ln({}^{11.94}\!/_{0.01679})\right)/903s = 1.21x10^{-4}s^{-1}$.

(3) Applying Eq. (13), onto the first observation (t = 339) in Table 5: $k_{f^*} = -\left(\ln({}^{13.47}\!/_{14.05})\right)/339s = 1.244x10^{-4}s^{-1}$; By Eq. (15) $[A_2]_{irr.}$ = [anti ln (-1.244x10^{-4}x1242)]x14.05 = 12.04 cm^3; By Eq. (18), the correction factor C =± (339/1242)x(12.01 – 12.04 cm^3) = ± 8.188 x 10^{-3} cm^3. Because the reverse reaction is second order and $[A_2]_{irr.}$ (= 12.04) cm^3 > A_1 (= 12.01 cm^3) then C = - 8.188 x 10^{-3} cm^3. Then by Eq. (17): $[A_1]_{irr.}$ = (13.47 - 8.188 x 10^{-3})

cm^3= 13.462 cm^3. And last, by Eq. (19), $k_f = -\left(\ln\left(13.462/14.05\right)\right)/339s = 1.26x10^{-4}s^{-1}$. The recapitulation of the calculation is presented in Table 7.

Discussion

Before entering further discussion, it is important to give some explanations on the hydrolysis of methyl-ethanoate data used in this study. As seen in Table 7, the reaction has three different values of k_f. This is because the data obtained from experiment with different temperature.

The data in Table 4 is not accompanied with equilibrium concentration data. Thus, it is not used as consideration concerning the use of equilibrium concentration in the determination of k_f. The standard use for the error percentage is from the source. The data in Table 5 is without initial concentration. There are 2 ways used for the determination of k_f using the new technique. First by assuming that $[A_o]$ is the data observed at 339 second. Second, $[A_o]$ is taken from the abscissa of linear curve of ln (39.81-*v*) *vs t* (Table 5 column 4). The standard use for the error percentage is from the source of the data.

Table 7. Recapitulation of the calculations of k_f values

Values	**Method***				**Literature**
	1	**2**	**3**	**4**	
kf	$5.74 \text{ x } 10^{-4} \text{ s}^{-1}$	$3.52 \text{ x } 10^{-4} \text{ s}^{-1}$	$4.61 \text{ x } 10^{-4} \text{ s}^{-1}$	$4.62 \text{ x } 10^{-4} \text{ s}^{-1}$	
Error (%)	**35.93**	**23.81**	**0.22**		
kf	$13.99 \text{ x } 10^{-5} \text{ s}^{-1}$	$5.67 \text{ x } 10^{-5}\text{s}^{-1}$	$9.76 \text{ x } 10^{-5}\text{s}^{-1}$	$9.79 \text{ x } 10^{-5}\text{s}^{-1}$	
Error (%)	**42.90**	**42.08**	**0.31**		
kf	$8.29 \text{ x } 10^{-4} \text{ s}^{-1}$	$6.78 \text{ x } 10^{-4} \text{ s}^{-1}$	$6.75 \text{ x } 10^{-4} \text{ s}^{-1}$	$6.79 \text{ x } 10^{-4} \text{ s}^{-1}$	
Error (%)	**22.09**	**0.15**	**0.59**		
kf	-	$3.50 \text{ x } 10^{-5} \text{ s}^{-1}$	$3.53 \text{ x } 10^{-5} \text{ s}^{-1}$		$3.50 \text{ x } 10^{-5} \text{ s}^{-1}$
Error (%)		**0**	**0.86**		
kf	$1.60 \text{ x } 10^{-4} \text{ s}^{-1}$	$1.23 \text{ x } 10^{-4} \text{ s}^{-1}$	$1.21 \text{ x } 10^{-4} \text{ s}^{-1}$		$1.22 \text{ x } 10^{-4} \text{ s}^{-1}$
Error (%)	**31.15**	**0.82**	**0.82**		
kf#	$1.60 \text{ x } 10^{-4} \text{ s}^{-1}$	$1.23 \text{ x } 10^{-4} \text{ s}^{-1}$	$1.26 \text{ x } 10^{-4} \text{ s}^{-1}$		$1.22 \text{ x } 10^{-4} \text{ s}^{-1}$
Error (%)	**31.15**	**0.82**	**3.28**		

* **1.** Calculation with equilibrium concentration
2. Calculation without equilibrium concentration
3. Calculation using New Technique
4. Calculation using integral equation for reversible reaction (standard)

There are some facts from Table 7 that should be pointed out here to be discussed. First, the use of equilibrium concentrations in the determination of k_f values for first ↔ first and first ↔ second order of reversible reactions always gives percentage error much higher than 5%. Second, the determination of k_f without using equilibrium concentrations only gives percentage error lower than 5% in the first ↔ second order of reversible reactions. Third, the new technique always gives k_f values with percentage error lower than 5% either in the first ↔ first or first ↔ second order of reversible reactions.

The explanations are as follows. It has been pointed out that, implicitly, the observed concentration of the reactant left in reversible reactions should be lower in the first ↔ first and nearly the same in the first ↔ second order with that from irreversible reactions. That is to say, it is reasonable enough to assume that both values are the same.

By Eq. (9), for first order reaction, t_i are independent of the unreacted fraction, β, and valid for forward and backward reactions. However, the rate becomes slower for forward and faster for back reaction. So, the influences of back reaction on the rate of the forward reaction will not constant. The $[A_1]$ are dominantly influences by $[A_o]$ and $[A_2]$ but $[A_2]$ by $[A_o]$, $[A_1]$, and $[A_3]$. Thus, the value of β will not be the same, espesially for first ↔ first order reaction type. This facts are confirmed by the different values of k_f^* for $[A_1]$ with $[A_2]$. For that reason, a correction factor is needed. Using the suitable correction factor on the observation data will make it valid for both, first ↔ first and first ↔ second order reaction.

However, the back reaction in the first ↔ second order reaction, will accelerate the forward reaction. The effects can make the values of β constant or be made constant by the using of the suitable correction factor.

The correction of the observed data with equilibrium concentration will not give the same β. Eq. (5) is a fractal, a division will give different results, especially if the equilibrium concentration is high. As seen in all of the examples of calculation given, the calculated value of k_f are always differ either in first ↔ first order or first ↔ second reactions. This statement is confirmed in Table 7.

Implementation

It is expected the same results for the reactions with the same order for the forward and reverse reactions. It has also been stated that, the observed concentration of the product for first ↔ second reversible reaction will be the same when the reaction is irreversible. But if the difference of the order of both directions are higher, the theoretical concentrations of reaction components will be different Then, some new empiric equations are needed.

Second, the concentration of the reactant at a given time, can be calculated using the value of k_f. These values can be used to determine concentration of product(s) using the stoichiometric coefficient. Thus, it is possible to find a new technique to determine k_b, using the first 3 data at the outset of the reaction and to determine K_{kin} by Eq. (3),

Conclusion

The irreversible approach on the first three data at the outset of the reversible reactions is suitable for the determination of k_f. The new technique is valid and reliable.

Recommendation

It is recommended to use the an irreversible approach on the first three data at the outset of the reaction for determination of k_f for reversible reactions with higher difference orders of forward with backward reactions.

REFERENCES

Alberty, R.A. (1987a). *Solution manual to accompany physical chemistry*. New York: John Wiley & Sons.

Alberty, R.A. (1987b). *Physical chemistry*, New York: John Wiley & Sons..

Casado, J., Lopez-Quintela, M.A. & Lorenzo-Barral, F.M. (1986). The initial rate method in chemical kinetics: evaluation and experimental illustration. *J. Chem. Educ., 63*, 450 – 452.

Laidler, K.J. (1987). *Chemical kinetics*. New York: Harper Collins Publisher.

Levine, I.N. (2009*). Physical chemistry*. New York: McGraw-Hill.

Patiha (2011). *Kajian Krirtis terhadap Persamaan-persamaan dan Teknik untuk Penentuan Tetapan Michaelis-Menten*. Surakarta: FMIPA UNS.

Patiha & Firdaus, M. (2016). Determination of the rate and the equilibrium constant with kinetics approach. *Chemistry, 25*, 686 – 694.

Persada, W.R. (2012). *Pendekatan Kinetika terhadap Reaksi Kesetimbangan; Studi Kasus pada Data Pustaka dan Reaksi Hidrolisis Metil Asetat.* Surakarta: FMIPA UNS..

Schafer, W., Klunker, J., Schelenz, T., Meier, T. & Symonds, A. (2010). *Laboratory experiments chemistry.* Gottingen: Phywe Systeme GmbH.

Wilkinson, F. (1980). *Chemical kinetics and reaction mechanisms.* New York: Van Nostrand Reinhold Company.

Wright, M.R. (2004). *An introduction of chemical kinetics*. West Sussex: John Wiley & Sons.

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