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New Approaches
Нови подходи

DETERMINATION OF THE RATE AND THE EQUILIBRIUM CONSTANT WITH KINETIC APPROACH

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Abstract. So far, the kinetic approach for determination of the rate constants of reversible reaction is still using the equilibrium concentration. Basically, this is thermodynamic concept. This technique is not only needs a long time for the experiments but also gives only the exact value of the forward rate constant. The exact value of backward rate constant must be determined based on the postulated reaction mechanism. This study presents a simple technique on the determination of the exact value of both forward and backward rate constants using irreversible approach on three data at the early stages of a reaction and then used for the determination of equilibrium constant. This theoretical study is supported with statistical analysis on the experimental data adapted from the literatures. The results showed that the technique is valid and reliable.

Keywords: forward rate constant, backward rate constant, equilibrium constant, irreversible approach, chemical kinetics

Introduction

For most homogeneous reversible reactions, the value of K in the reaction:

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

is given by the equation:

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

By Eq. (2), all of the reaction components must be in the equilibrium condition. In most textbooks, the value of K 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 consequently will require greater production costs) to reach the equilibrium state.

The equilibrium constant can also be determined with kinetic approach. The obtained equilibrium constant is denoted as K_{kin}. This constant is calculated from the equation:

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

where k_f and k_b are the forward and backward rate constant, respectively.

For some reasons, this approach is even more favorable 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 are less, but the required time is shorter. The concept of thermodynamics just states that if the concentration of one reactant is prepared in excess then the equilibrium will shift toward products but the concept of kinetics states which reagent that should be made in excess in order to yield more product. It is the reactant with the highest order that should be made in excess. The rate constant tells us when the reaction must be stopped in order to save the production costs.

The determination of K_{kin} can be done either by differential and/or integral method; the later is more widely used. But there are at least 3 problems that could interfere. First, there are a number of integral equations which are complicated and vary depending on the order of the reaction in both directions. Data should be tested onto all of these equations to obtain the best one by linearity test. Second, it is only the forward rate constant k_f that can be obtained. The value of the backward reaction rate constant k_b, can only be determined by the postulated of the most possible mechanism that can take place (Wilkinson, 1980). This is contrary to the kinetics concept i.e. the reaction mechanism is deduced based on the rate law and not vice versa (Espenson, 1995; Levine, 2009). Third, the integral equations are still using the equilibrium concentration. It is not only impractical but also impressed using thermodynamics for kinetics learning.

A practical technique based on differential method for the determination of k_f with the initial rate method has been introduced (Horiuti & Nakamura, 1967). However, for the integral method, the value of k_b should be determined based on estimation of reaction mechanisms that may occur. It also stated that the value kinetic equilibrium constant K_{kin} is not always the same with thermodynamic equilibrium constant K. Both constants are related with equation:

$$K = K_{kin}^{\ s} \tag{4}$$

where s is the stoichiometric number. This concept applies mostly to the reaction that takes place in multiple steps.

The value of s can be vary, depend on the postulated mechanism. For example, the reaction of iron (II) with mercury (II):

$$2Fe^{2+}(aq) + 2Hg^{2+}(aq) \underset{k_b}{\overset{k_f}{\Leftrightarrow}} 2Fe^{3+}(eq) + Hg_2^{2+}(aq) \tag{5}$$

is found to have the initial rate of

$$v_f = k_f[Fe^{2+}]_{eq}[Hg^{2+}]_{eq} \tag{6}$$

By a postulated mechanism (Levine, 2009), it gives

$$K = \frac{[Fe^{3+}]^2[Hg_2^{2+}]}{[Fe^{2+}]^2[Hg^{2+}]^2} \tag{7}$$

Here the value of $s = 1$.

With different postulated mechanism (Adamson, 1986), it provides

$$K = \frac{[Fe^{3+}][Hg_2^{2+}]^{1/2}}{[Fe^{2+}]Hg^{2+}]} \tag{8}$$

here $s = 2$.

This is not the whole problems. First, the initial rate method only gives best result if the fraction reacted less than 5% (Casado et al., 1986). Second, for zero-order reaction, the value of the rate constant, k, obtained by the differential method will not be the same as those obtained with the integral method. This is because, only in the zero-order reaction that the rate is independent of reactants concentration. In differential method, the value of the rate constant of a zero-order reaction is calculated using equation:

$$-(\Delta A/\Delta t) = k \tag{9}$$

and in integral method by basically the same equation:

$$-d[A] = kdt \tag{10}$$

For first-order reaction, differential method using equation:

$$-(\Delta A/\Delta t) = k[A] \tag{11}$$

and integral method using different formula:

$$\ln\frac{[A]}{[A_o]} = -k_A t \tag{12}$$

As for the initial rate method, the determination of k_f will use the modification of Eq. (11), i.e.:

$$-(\Delta A/\Delta t) = k[A_o] \tag{13}$$

The differential method is easier but the integral method gives the more exact value of a rate constant (Laidler, 1987). The weakness of the integral method is that one should test a number of equations on a data in order to obtain the most appropriate equation. However this can be avoided with the use of the unified integral equation (Patiha, 2013):

$$t_\beta = \{F(\beta)/k_A\}[A_o]^{(1-n)} \tag{14}$$

where

$$F(\beta) = -\ln\beta \quad \text{for} \quad \text{n} = 1 \tag{15}$$

$$F(\beta) = \frac{1}{(n-1)}\left[\frac{1}{\beta^{(n-1)}} - 1\right] \quad \text{for} \quad \text{n} \neq 1 \tag{16}$$

Here, β, t_β, $F(\beta)$, k_A, n are the fraction of A unreacted, the time –interval, the integrated form of the rate law, the rate constant, and the order of the reaction respectively.

As a fraction, β eliminates the solvent effects (on the observation of the physical properties of the reaction components) in the calculation process. If β is constant then $F(\beta)$ will also has a constant value. Thus, the calculated value of t_β with Eq. (14), will be unique for different values of n. As an example, for $n = 1$, the value of t_β is independent of initial concentration $[A_o]$. Each observation will have the same value of t_β. If, for example the half-live of a reaction = t_β, all the next half-life will be have the same value = t_β. For $n = 0$, the half-live is directly proportional to $[A_o]$. If the first half-live of a reaction = t_β then the second half-life will be 0.5 t_β. Or conversely, experiment with observation on constant t_β (this easier to be performed) will give the same β for $n = 1$ and 2β for $n = 0$. Then, the value of k_A is calculated using Eq. (15) for $n = 1$ or Eq. (16) for $n \neq 1$.

The next problem is to find the technique of obtaining the value of k_b without the necessity of postulating the possible reaction mechanism and using only three data at the early stages of the reaction.

The forward and backward rate law of reversible reactions has a linear form (not fractal). Therefore, the determination of the rate constants can be done using the calculated rate from the observational data at the beginning of the experiment until the reaction approaching the equilibrium. However, the value of the rate at the beginning of the reaction is the most appropriate because the rate at this condition is linear with concentration. For this reason, in this study, both k_f and k_b value will be determined using three data at the outset of experiment.

Based on the previously discussion, the main purposes of this study are: to obtain a new technique for the determination of the forward rate constant, backward rate constant, and equilibrium constant of reversible reactions without using the equilibrium concentrations, to prove the validity and reliability of the technique, and to prove the failure of the initial rate method for determination of forward rate constant.

Methodology

This research is a literature study. The first goal is approached with the assumption that the reactions are irreversible for both directions. Because both sample reactions are the first order for both directions, Eq.(12) will be used for the determination the value of both k_f and k_b. As for the initial rate method, Eq. (13) will be used for the determination of k_f. Eq. (3) is then employed for the determination of K_{kin}.

The second goal is accomplished by comparing the values of the constants (k_f, k_b, and K_{kin}) obtained using the new technique by thermodynamic approach. The technique is claimed valid if the difference of the values is less than 5%.

The third goal is achieved by comparing the values of k_f obtained by initial rate method with that obtained by the integral method and the new technique. The initial rate method is claimed fail if the difference of k_f values obtained from initial rate method and integral method are more than 5%.

This study uses two data, i.e., from a problem of an opposing unimolecular isomerization reaction (Wilkinson, 1980) which is presented in Table 1 and the data of *cis-trans* isomerization of: 1-ethyl-2-methyl cyclo-propane at 425,6 °C (Wright, 2004) which can be seen in Table 2.

Table 1. The variation percentage of *R* with time in the opposing unimolecular reaction $R \underset{k_b}{\overset{k_f}{\Longleftrightarrow}} P$ (Wilkinson, 1980)

t / hour	0	1,0	2,0	3,0	∞
% R	100	72,5	56,8	45,6	30

The calculated values of k_f, k_b, and K of this reaction are $9.72\text{x}10^{-5}$ s^{-1}, $4.17\ \text{x}10^{-5}$ s^{-1}, and 2.33, respectively.

Table 2. The Variation of concentration with time in the isomerization of *cis*-1-ethyl-2- methylcyclopropane (Wright, 2004)

t / s	0	400	1000	1600	∞
[cis] / mol dm-3	0,01679	0,01406	0,01102	0,00892	0.00443

The calculated values of k_f, k_b, and K of this reaction are $4{,}60\text{x}10^{-4}$ s^{-1}, $1{,}65\text{x}10^{-4}$ s^{-1}, and 2.79, respectively.

Discussion and implementation

Discussion

The observed concentrations of the reactants at certain time of reversible reactions are always higher than irreversible reactions (Table 3). This is because, in reversible reactions, the addition of a reactant (by back reaction) will shift the equilibrium position towards products. The difference between the two values indicates the product addition by reversible reaction.

Applying Eq. (12) onto the second observation in Table 1 gives the value of $k_f = 8.93\text{x}10^{-5}$ s^{-1}. Using this value for calculating the theoretical value of the third observation gives 52.6%. The difference is (56.8 – 52.6)% = 4.2%. For the second observation, this caused by backward reaction to initial concentration and forward reaction to the third. Thus, the addition of product caused by reversible reaction (the correction factor) is (4.2/2) % = 2.1 %. Therefore, the second observation should be (72.5 – 2.1)% = 70.4%. This is in accordance with Eq. (14). For first order reaction, the same t_β will give the same β. Thus, if the forward reaction is irreversible, the value of k_f is $9.75\text{x}10^{-5}$ s^{-1}.

From Table 1, the concentration of the product P at the second observation is (100 – 72.5)% = 27.5 %. The backward reaction, reduces P concentration into (27.5 – 2.1) = 25.4 % and forward reaction increase P concentration into (27.5 + 2.1) % = 29.6 %. By applying Eq. (11), $\ln(25{,}4 / 29.6) = - k_b \text{ x } 60 \text{ x } 60$, and $k_b = 4.25\text{x}10^{-5}$ s^{-1}. Employing Eq. (3), the value of K_{kin} can be calculated = ($9.75\text{x}10^{-5}$ s^{-1} /$4.25\text{x}10^{-5}$ s^{-1}) = 2.29. The percentage error of k_f, k_b, and K_{kin} can be calculated as follows:

$k_f = [\,(9.75 \text{ x } 10^{-5} - 9.72 \text{ x}10^{-5}\,)/\, 9.72 \text{ x}10^{-5}\,] \text{ x } 100\ \% = 0.31\%$;
$k_b = [\,(4.25 \text{ x } 10^{-5} - 4.17 \text{ x } 10^{-5}\,)/\, 4.17 \text{ x}10^{-5}\,] \text{ x } 100\ \% = 1.92\%$;
$K_{kin} = [(2.33 - 2.29) / 2.33] \text{ x } 100\ \% = 1.72\%$.

The resume of the calculations is presented in Table 3.

Applying Eq. (12) onto the second observation in Table 2 gives the value of $k_f = 4.43 \text{ x } 10^{-4}$ s^{-1}. Using this value for calculating the theoretical value of the third observation gives 0.01078. The difference is (0.01102 – 0.01078) = 0.00024. For the second observation, this caused by backward reaction to initial concentration and forward reaction to the third. However, as seen in Table 2, the observation was not taken at the same time-interval so the data is analyzed as follows. Because the second observation was done at 400 s and the third at 1000 s then the correction factor is (0.00024 /2.5) = 0,00009, and the second observation should be (0.01406 – 0.00009) = 0.01397. Thus, if the forward reaction is irreversible, the value of $k_f = 4.60 \times 10^{-4}\ s^{-1}$.

From Table 2, the concentration of the product (the trans) at the second observation is (0,01679 - 0,01406) = 0,00273. The backward reaction, reduces produk concentration into (0,00273 - 0.00009) = 0.00264 and forward reaction increase product concentration into (0,00273 +0.00009) = 0.00282. Then, by Eq. (11), ln (= 0.00264 / 0.00282) = - k_b x 60 x 60, and $k_b = 1.65 \times 10^{-4}$ s. And by Eq. (3) the value $K_{kin} = (4.60 \times 10^{-4}\ s / 1.65 \times 10^{-4}\ s) = 2.79$. The error percentage of k_f = [(4.60 x 10^{-4} - 4.60 x 10^{-4})/ 4.60 x 10^{-4}] x 100 % = 0 %; of k_b = [(1.65 x 10^{-4} – 1.65 x 10^{-4})/ 1.65 x 10^{-4}] x 100 % = 0 % ; and of K_{kin} = [(2.79 – 2.79) / 2.79] x 100 % = 0 %. The resume of the calculations is presented in Table 3.

Table 3. Results of data Analysis of Table 1 and Table 2

	Table 1			Table 2		
	105 kf	105kb	Kkin	104kf	104kb	Kkin
Literatur	9.72	4.17	2.33	4.60	1.65	2.79
New method	9.75	4.25	2.29	4.60	1.65	2.79
% error	0.31	1.92	1.72	0	0	0

As seen in Table 3, the percentage errors of k_f, k_b, and K_{kin} for both reactions are always less than 5 %. It can be concluded that the new method is easier and valid - easier because uses only three observations and valid because percentage difference are smaller than the higher allowed of errors in using physical properties for observation.

Quite interesting to discuss the fact that the percentage differences error for Table 1 are higher than for Table 2. One of the possible reasons is caused by the difference of β values.

If only the second observation in Table 1 is 56.8%, then applying Eq. (12) onto the "second" observation gives the value of $k_f^* = 7.86 \times 10^{-5}$ s. Using this value for calculating the theoretical value of the "third" observation gives 42.8%. The difference is (45.6 – 42.8)% = 2.8%. For the "second" observation, this caused by backward reaction to initial concentration and forward reaction to the "third". The addition of product caused by reversible reaction (the correction factor) is (2.8/2)% = 1.4%. So, the "second" observation should be (56.8 – 1.4) % = 55.4 %. If the forward reaction is irreversible, the value of k_f is 8.20 x 10^{-5} s^{-1}. The error percentage = [(9.72 x 10^{-5} - 8.20 x 10^{-5})/ 9.72 x 10^{-5}] x 100 % = 15.61 %. It is larger.

By similar way, if only the second observation in Table 2 is 0.00892, then Applying Eq. (12) onto the "second" observation gives the value of $k_f^* = 6.32 \times 10^{-4}\ s^{-1}$.

Using this value for calculating the theoretical value of the "third" observation gives 0.00610. The difference is (0.00892– 0.00610) = 0.00282. For the "second" observation, this caused by backward reaction to initial concentration and forward reaction to the "third". As seen in Table 2, the observation was not taken at the same time-interval so the data is analyzed as follows. Because the "second" observation was done at 1000 s and the "third" at 1600 s then the correction factor is (0.00282 / 4) = 0,00071, and the "second" observation should be (0.00892 – 0.00071) = 0.00821. Then, if the forward reaction is irreversible, the value of k_f = 7.15 x 10^{-4} s. The error percentage = [(7.15 x 10^{-4} - 4.60 x 10^{-4})/ 4.60 x 10^{-4}] x100 % = 55.43 %; it is also larger. Then, smaller β will give larger error percentage.

Table 4. The difference of calculated value of k_f by differential and integral method

	Table 1				Table 2			
	Diff.	New meth.	Diff.	New meth.	Diff.	New meth.	Diff.	New meth.
105 kf-diff.	7.64	8.93	7.64	8.93	4.07	4.44	4.07	4. 44
105 kf-int. rev	9.72				4.60			
105 kf-int. irrev			9.75				4.60	
% error	21.40	8.13	21.64	8.41	11.52	3.48	11.52	3.48

diff = differential; int. = integral; meth. = method

The last fact to be discussed is about the possible failure of initial rate method to determine the correct value of k_f. It has been stated earlier, that for $n \neq 0$, the value of the rate constant, k, obtained by the differential method will not be the same as those obtained with the integral method. Eq. (11) is used for differential method (as initial rate) and Eq. (12) for integral method and using the first and the second data in both Table 1 and Table 2. As seen in Table 4, the errors percentage obtained from initial rate method are higher than allowed. These facts can be caused by the high percentage of reaction reacted (more than 5 %). But, the most possible is from the form the difference of the equations used in each method.

Implementation

The data used for this study are first-order in both directions reactions. The results may be valid for all reversible reactions with the same order for forward and backward reaction. However it must not be the same for reversible reactions with different order.

The products at the near end of a reaction are less than at the outset. The amount of product can be predicted from the forward rate constant. Thus, waiting until equilibrium condition will be time-wasting and cost-consuming. A special attention should be paid for the higher value of β. As has been discussed, the smaller value of β tend to cause larger percentage error.

Conclusion

A simple technique for the determination of the forward rate constant, backward rate constant, and equilibrium constant of reversible reactions without using the equilibrium concentrations was presented. The results showed that this technique is valid and reliable. The initial rate method is not suited for determination of forward rate constant for first order of reversible reaction.

REFERENCES

Adamson, A.W. (1986). *A textbook of physical chemistry.* New York: Academic Press.

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.

Espenson, J.H. (1995). *Chemical kinetics and reaction mechanisms,* New York: McGraw-Hill.

Horiuti, J. & Nakamura, T. (1967). Theory of heterogeneous catalysism (pp. 1 – 74). In: Eley, D.D. (Ed.). *Advances in catalysis.* New York: Academic Press.

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

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

Patiha (2013). Penentuan Tetapan Laju Reaksi Balik dan Tetapan Kesetimbangan dengan Pendekatan Reaksi Searah dan Hukum Laju Reaksi Maju. *Alchemy*, *9*, 145 – 155.

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

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

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