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REVIEW AND IMPROVED TECHNIQUE OF THE INITIAL RATE METHOD

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Abstract. It is claimed that, in certain circumstances, initial-rate method (*IRM*) has advantages over the integral method (*IM*). But, the *IRM* will only be effective if the concentration change is less than 5 % and the rate constant (*k*) obtained should be checked with *IM*. There are two main purposes of this research. First, to prove that the claim is invalid and the *IRM* can be used on broader concentration changes. In addition, the rate law model used in the claimed is invalid for reaction that takes place in two mechanisms. Second, to find a new form of *IRM* equation, which does not require *IM* checks. This study used the oxidation of formic acid with bromine as a reaction model. The values of *n* and *k* of this reaction at two mechanisms were determined by the *IM*, and then by the conventional *IRM*, the method used in the claim, and by the new *IRM* generated by this study. All of *k* values are compared by using *IM* as the standard. The proposed method is claimed valid if the error percentage of *k* is less than 5 %. Despite the shortcomings, the results show that the new *IRM* is valid and more reliable.

Keywords: initial rate method; integral method; rate constant; reaction order

Introduction

The differential method (*DM*) is believed to be the most reliable one for determining the rate law of a reaction (Laidler, 1987). By this method, the order, *n*, with respect to a particular reactant can be directly determined; not by *trial and error* (as in the integral method, *IM*). However, the rate, *v*, is not always proportional to every concentration. The initial rate of a reaction is defined as the rate of the reaction at the instant in which the reactants are first mixed. The rate at the beginning of a reaction is the most appropriate because at this condition, the rate is more linear with concentration. However, the exact initial rate v_o, is not easily determined. A statistical method has been introduced. As long as the percent error of the reaction followed less than 5%, the setting up solution can be considered valid. It has been proved that under this condition, in certain circumstances, the initial rate method (*IRM*), has advantages over *IM*. For example, the *IRM* can be used to simultaneously determine k_1 and k_2 in a reaction of the type

$$v_o = k_1[C_o] + k_2[C_o]^2 \tag{1}$$

whereas only k_2 by *IM*. The value of k_1 is determined from the intercept and k_2 from the slope of the linear graph of

$$v_o /[C_o] = k_1 + k_2[C_o] \qquad (2)$$

By Eq. (2) and using the diazotization of *p*-anisidine (initial concentration 3 x 10^{-4} *M*) in aqueous perchloric acid (initial concentration 0.1 *M*) as the study object, the rate equation is

$$v_o = k_1[nitrite]_0 + k_2[nitrite]_0^2 \qquad (3)$$

and $k_1 = 2.60 \text{ X } 10^{-5}$ s^{-1} and $k_2 = 5.40 \text{ X } 10^{-3}$ M^{-1} s^{-1}. (Casado et al., 1986).

There are two problems that arise related to the above statement. First, the recommendation to restrict the percentage of reaction should be followed by a maximum of 5%. It is expected that such limitation is caused by the use of graphical method for determination. However, graphical method is not recommended for determining the order, *n*, and the rate constant, *k*, of a reaction (Levine, 2003). The shelf life of a pharmaceutical product is $t_{0.1.}$ (Tan et al., 1994). It is not enough reason that the shelf life of a pharmaceutical product cannot be determined by *IRM.* A reaction which has the rate law such as in Eq. (1) will always take place in two different reaction mechanisms. The two mechanisms could take place simultaneously (competing) or in two successive steps (consecutive). Thus, the value of the two constants cannot be determined easily.

It is reported that the plot of $v_o /[C]_o$ versus $[C]_o$ gives both of k_1 and k_2 values simultaneously. The plot of $[C]^{-1}$ against *t* would overlook $k_1[C]$. This is for sure not an overlooking. In *IM*, the plot of $[C]^{-1}$ against *t* will never give the constants for *first*- or *other*-order of a reaction. Any [*C*] that appropriate for *first*-order is not suitable for *other*-orders. By concept, a *first*-order reaction means, doubling [*C*] will make a reaction last 2^1 or 2 times faster and second-order reaction means, doubling [*C*] will make a reaction last 2^2 or 4 times faster. Thus, it is unlikely that v_o for *first*-order is used for *second*-order reaction (and conversely). In thermodynamic, to determine the absolute entropy of a liquid near the absolute temperature 0°*K*, the curve of Cp/T versus T, only use data in the solid phase (Rastogi & Misra, 1980). It is more appropriate to use a model of integral equation that can give the two constant values simultaneously (Espenson, 1995; Brynildson et al., 1987). However, it is also possible that one found that for eq. (1), there is only one order, a non-integer, between *1* and *2*, say *1.38.* Though*,* the order is usually integers or half-integers (Levine, 2003).

Besides, the term of $v_o /[C]_o$ in Eq. (1) is basically give the accurate value of *k* for *first*-order reaction (k_1). This is because the accurate value of $v_o/[C]_o$ is obtained if $[C]_o \rightarrow 0$. This case is similar with the method for the determination molecular weight of gases by limiting density (or Regnault) method (Crockford & Nowell, 1975). The consequences, the term of $k_2 [C]_o$ is ambiguous. It is correct mathematically but meaningless from chemical point of view. It is $v_o/[C]_o^2$ that gives the accurate value k_2, that is if $[C]_o \rightarrow 0$. It stands to reason; the $[C]_o$ data used must be from the condition of *second*-order reaction.

Second, the *IRM* is believed to give the exact *n* value, but it is uncertain *k* value. The *k* value obtained must be checked with the exact value obtained from *IM* (Laidler, 1987). In fact, save for *zeroth*-order reaction, the calculated value of the apparent *k* obtained by the *IRM* method are always differ with that from *IM*. There is a missing link here. Both *IM* and *IRM* are derived from the same rate expression. Therefore, it is unlikely that a *k* value obtained from *IRM* (and then given the notation k_{IRM}) at a certain condition, is uncertain. It is expected just caused by experimental technique and/or mathematical reasoning. However, *IM* itself is impractical in some aspects. The true *n* can only be determined by trial and error, using some integral equations to find the best fit equation.

In continuation of our previous reports in the field of chemical kinetics (Patiha & Firdaus, 2016; Firdaus & Patiha, 2017), we discuss here an improved technique for the initial rate method. Based on the above statement, there are two goals of this research. The first goal is to prove that, there is no need in initial rate method to restrict the percentage of reactions followed to a maximum of 5%. Also, to provide evidence that the *CM* (Casado Method), the method used as reported by Casado et al. (1986), cannot be used to simultaneously determine the two constants of the reaction that takes place in two mechanisms. The second is to introduce an alternative *IRM* model, a valid and reliable method to determine the correct order and the accurate value of *k* and no need for *IM* checks.

Methodology

The two goals will be confirmed by using the oxidation of formic acid by bromine as the model.

$$HCOOH + Br_2 \rightarrow CO_2 + 2Br + 2H^+ \tag{4}$$

At room temperature, this reaction is believed to take place by the following reaction mechanism {Hodgson et al., 1998):

$$\begin{gathered} HCOOH \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} HCOO^- + H^+ \\ HCOO^- + Br_2 \xrightarrow{k_2} CO_2 + H^+ + 2Br^- \end{gathered} \tag{5}$$

At first sight, the reaction is of the second order. But in highly acidic media, such as in the presence of $HClO_4$, the reaction is found to be of the *first*-order with respect to $[Br_2]$:

$$-d[HCOOH]/dt = \frac{k[HCOOH][Br_2]}{[H^+]} \tag{6}$$

Actually, by the steady-states approximation, its rate law is

$$-d[HCOOH]/dt = \frac{k_1[HCOOH][Br_2]}{(k_{-1}/k_2)[H^+]+[Br_2]} \tag{7}$$

In an excessive of [*HCOOH*], the rate law of the reaction is

$$-d[HCOOH]/dt = k'[HCOOH]^{0.5}[Br_2] \tag{8}$$

The reaction is *halved*-order relating to [*HCOOH*] and *first*-order with regard to [Br_2] (Patiha & Firdaus, 2016).

Theoretically, when the initial $[Br_2]_\text{o}$ is slightly greater than $(k_{-1}/k_2)[H^+]$, at the beginning starting point, the reaction is *zeroth*-order relating to [Br_2] and, end before the final stage, becomes *first*-order. The first step of Eq. (5) takes place very fast and thus therefore $(k_{-1}/k_2)[H^+] >> [Br_2]$, and the reaction is *first*-order relating to [Br_2]. Because this step is reversible, then after a while, [Br_2] will be higher than $(k_{-1}/k_2)[H^+]$, and the reaction becomes *zeroth*-order. However, it is also possible that at equilibrium, $[HCOOH]_\text{eq} = [Br_2]_\text{eq}$ and the reaction becomes *one* and *halved*-order; Eq. (8). However, the reaction is always *first*-order, whenever at the early stage, $[Br_2]_\text{o}$ is lower than $(k_{-1}/k_2)[H^+]$. Thus, the reaction will take place in two different mechanisms. For a rate law with a summation, there are two possible reaction types; competing or consecutive. Since this reaction is consecutive, the initial rate law of the reaction is

$$v_o = k_1[A_\text{o}] + k_2 \tag{9}$$

The k_1 value can be calculated from the slope and k_2 from the intercept of the linear plot of v_o versus $[A_\text{o}]$. The kinetics of the reaction is followed by monitoring the decrease of [Br_2] at 400 (ε = 160 M^{-1} cm^{-1}) nm and room temperature. The required time each Br_2 reacts by 10% (or constant of fraction-left = β = 90%) are then recorded.

The data were obtained from a single run for each experiment which was taken at the same β, and the observed value at the end of one period is regarded as the initial value for a new interval. The difference between each pair was divided with the time difference, and denote as v_o. The data (from the two conditions) and their setting are depicted in Tables 1 and 2.

The data in Tables 1 and 2. will be analyzed using the integral equation of:

$$[A]-[A_o] = k_A t \text{ for n=0} \tag{10}$$

$$[A]^{0.5} = [A_o]^{0.5} - 0.5k_A t \text{ for n=0,5} \tag{11}$$

$$\ln \frac{[A]}{[A_o]} = -k_A t \quad \text{for n=1} \tag{12}$$

$$[A]^{-0.5} = [A_o]^{-0.5} + 0.5k_A t \quad \text{for n=1,5} \tag{13}$$

$$[A]^{-1} = [A_o]^{-1} + k_A t \quad \text{for n=2} \tag{14}$$

Table 1. The data and setting of Br_2 absorbance, *A*, in oxidation of formic acid by bromine at early-stage

No.	Data		Δt/s	Data Setting		
	t/s	*A*		A_o	*A*	$(A_o\text{-}A)/\Delta t = v_o$
0.	0	0.267	15	0.267	0.240	$1.80\text{x}10^{-3}$
1.	15	0.240	15	0.240	0.216	$1.60\text{x}10^{-3}$
2.	30	0.216	14	0.216	0.194	$1.57\text{x}10^{-3}$
3.	44	0.194	15	0.194	0.175	$1.27\text{x}10^{-3}$
4.	59	0.175	16	0.175	0.157	$1.13\text{x}10^{-3}$
5.	75	0.157	15	0.157	0.141	$1.07\text{x}10^{-3}$
6.	90	0.141		0.141		

Table 2. The data and setting of Br_2 absorbance, *A*, in oxidation of formic acid by bromine at near-end

No.	Data		Δt/s	Data Setting		
	t/s	*A*		A_o	*A*	$(A_o\text{-}A)/\Delta t = v_o$
0.	308	0.050	50	0.050	0.045	$1.00\text{x}10^{-4}$
1.	358	0.045	40	0.045	0.041	$1.00\text{x}10^{-4}$
2.	398	0.041	41	0.041	0.037	$0.98\text{x}10^{-4}$
3.	439	0.037	39	0.037	0.033	$1.03\text{x}10^{-4}$
4.	478	0.033	30	0.033	0.030	$1.00\text{x}10^{-4}$
5.	508	0.030	30	0.030	0.027	$1.00\text{x}10^{-4}$
6.	538	0.027		0.027		

The true order *n* and the accurate value of k_A is that from the equation with regression coefficient closer to ± 1.0000. The values obtained are used as the standard.

The data is then analyzed with conventional *IRM* equation:

$$v_o = k_{IRM}[A_o]^n \tag{15}$$

where v_o, k_{IRM}, and *n* are the initial rate, the rate constant (for *IRM*), and the reaction order respectively. From the slope, the reaction order, *n,* can be determined and the rate constant *k* can be obtained from the intercept of a straight line of double-logarithmic plot of log v_o versus log $[A_o]$.

$$\log v_o = \log k_{IRM} + n \log[A_o]$$

The data is also analyzed by Eq. (9) and the equation that will be introduced. A method is claimed valid if, relative to the standard (*IM*), its error percentage (*EP*) of k_A is less than 5%.

The first goal

If an experiment is done in a single run and each observation is taken at constant fraction-left:

$$\beta = [A]/[A_o] \tag{17}$$

the time, $t_{i,}$ needed in each observation is:

$$t_{\beta-i} = (\beta)^{(i-1)(1-n)} t_\beta \tag{18}$$

where $t_{\beta-i}$, β, and t_β are the interval-time, fraction-left, and the first interval-time, respectively (Patiha, 2011). If the initial observation is $[A_o]$ then $[A_1] = \beta[A_o]$, $[A_2] = \beta^2[A_o]$, or $[A_{i\,=}\ \beta^i[A_o]$.

$$v_{o-i} = ([A_o]-[A_i])/t_i = k_{A-i}[A_o]^n$$

$$v_{o-i} = (1-\beta^i)[A_o]/t_i = k_{A-1}[A_o]^n \tag{19}$$

$$(1-\beta^i)[A_o]^{(1-n)}/t_i = k_{A-1} \tag{20}$$

Based on the basic of initial rate concept (the rate of the very beginning of a reaction), the example of the effect of changing the fraction reacted on the value of k_A will be given from the initial rate of $([A_o] - [A_1])$ and $([A_o] - [A_2])$.

From Eq. (18): $t_{\beta\text{-}1} = t_\beta = t_1$ and $t_{\beta\text{-}2\,=}\beta^{(1-n)}t_\beta$; then by Eq. (20), for $([A_o] - [A_1])$:

$$(1-\beta)[A_o]^{(1-n)}/t_\beta = k_{A-1} \tag{21}$$

and for $([A_o] - [A_2])$

$$(1-\beta^2)[A_o]^{(1-n)}/t_2 = k_{A-2}$$

Because $t_2 = t_{\beta\text{-}1} + t_{\beta\text{-}2} = t_\beta + t_{\beta\text{-}2}$, then

$$(1-\beta^2)[A_o]^{(1-n)}/(t_\beta + t_{\beta-2}) = k_{A-2} \tag{22}$$

But by Eq. (18), $t_{\beta\text{-}2\,=}\beta^{(1-n)}t_{\beta\,,}$ then

$$t_{\beta\text{-}2} = t_{\beta}(1 + \beta^{(1\text{-}n)}) \tag{23}$$

Inserting Eq. (23) into Eq. (22), after some steps gives

$$\{(1+\beta)(1-\beta)[A_o]^{(1-n)}\}/t_{\beta}\{1+(\beta)^{(1-n)}\} = k_{A-2} \tag{24}$$

As an example, for *zeroth*-order reaction: Eq. (24) becomes

$$\begin{gathered}(1+\beta)(1-\beta)[A_o]/t_{\beta}(1+\beta) = k_{A-2} \\ (1-\beta)[A_o]/t_{\beta} = k_{A-2}\end{gathered} \tag{25}$$

and Eq. (21) becomes

$$(1-\beta)[A_o]/t_{\beta} = k_{A-1} \tag{26}$$

Comparing Eq. (25) with Eq. (26) gives $k_{A-2} = k_{A-1}$. For *zeroth*-order reaction, there is no influence in the changing of the amount fraction reacted. That is not so for *first*-order reaction. But, both values are comparable and by Eq. (18), directly proportional to the fraction-reacted (= 1- β) and inversely to the time. This fact is then used to formulate a new model of *IRM* which is need no *IM* checks.

The validity of Eq. (9) will also be tested using the combined data of *first*- and *zeroth*-order (Tables 1 and 2). The equation is invalid if the *EP* of k_1 and k_2 values with that obtained from *IM* is higher than 5%.

The second goal: *the new method* (*NM*)

Based on the previous discussion, there are three factors that affect the value of *k* and cause it different from *IM*: the fraction-reacted (= 1- β) the time, and the general form of *IM*. Because the time variable is already included in v_o, the time factor is excluded. So, if the apparent rate constant for initial rate is given the symbol of k_{IRM} , to get the real value of k_A, k_{IRM} must be divided by (1-β) and crossed with general form of *IM*, *F(β)*. This is given in the following equation:

$$k_A = \left({}^{F(\beta)}\!/_{(1-\beta)}\right)k_{IRM} \tag{27}$$

or

$$k_{IRM} = \left({}^{(1-\beta)}\!/_{F(\beta)}\right)k_A \tag{28}$$

The first expression on the right side of Eq. (27) is the correction factor (*CF*) to obtain k_A from k_{IRM}. Conversely, the first expression on the right side of eq. (28) is the *CF* to obtain k_{IRM} from k_A.

The integrated form of *F*(*β*) is obtained the following way. Generally, if, in a homogeneous reaction,

$$\mathrm{a}A + \ldots.. \rightarrow \mathrm{p}S + \ldots.. \tag{29}$$

the concentration of reactant *A* is made much less than the concentration of other species, the rate *v* at time *t* is experimentally found to be

$$v = - 1/a\ d[A]/dt = k\ [A]^n \tag{30}$$

$$v_A =- d[A]/dt = k_A\ [A]^n \tag{31}$$

Dividing Eq. (31) with $[A_o]$ gives

$$-\frac{d\big[[A]/[A]_o\big]}{dt} = k_A[A]_o^{(n-1)}\big[[A]/[A]_o\big]^n \tag{32}$$

Introducing Eq. (17) to Eq. (32) offers

$$-d\beta / dt = k_A[A_o]^{(n-1)}\beta^n \tag{33}$$

$$-d\left(\frac{\beta}{\beta^n}\right) = k_A[A_o]^{(n-1)}dt$$

$$-\int d\left(\frac{\beta}{\beta^n}\right) = k_A[A_o]^{(n-1)}\int dt \tag{34}$$

The general integral of the term in the left side of Eq. (34) is introduced as *F* (*β*) or

$$F(\beta) = k_A[A_o]^{(n-1)}t_\beta \tag{35}$$

There are two solutions for *F* (*β*):

$$F(\beta) = -\ln\ \beta \text{ for n = 1} \tag{36}$$

and

$$F(\beta) = \frac{[A_o]^{(1-n)}}{(n-1)}\left[\beta^{(1-n)} - 1\right] \text{ for n} \neq 1 \tag{37}$$

The difference between the *IRM* method and *NM* is in the determination of the rate constant. The constant for *NM* is determined by variance analysis. The value obtained is then multiplied with their corresponding *CF* (Eq. (36) or Eq. (37)):

$$k_A = k_{NM} \text{ for n = 0} \tag{38}$$

or,

$$k_A = k_{NM}\left[\frac{-\ln\beta}{(1-\beta)}\right] \qquad \text{for n = 1} \tag{39}$$

In this study (β) = 0.9. Because the unit in both Table 1 and Table 2 is in absorbance then, in the unit of *M* (molarity), Eq. (38) becomes

$$k_A = k_{NM}/160 = k_{NM}\ 6.25\text{x}10^{-3}\ M\,s^{-1} \quad \text{for n = 0} \tag{40}$$

and Eq. (39) becomes

$$k_A = k_{NM}\left[\frac{-\ln 0.9}{(0.1)}\right]s^{-1} = k_{NM}\ \text{x}\ 1.0536\ s^{-1} \qquad \text{for n = 1} \tag{41}$$

The *NM* is claimed valid if the *EP* of k_A values is lower than 5% and reliable if its *EP* is lower than other methods.

Description

Before entering the discussion, the following definitions are required. The initial rate method is the rate that depends on the initial concentration of the reagent. The conventional initial rate method (*IRM*) is the method that using the plot of log initial rate versus initial concentration for the determination of *n* and *k* or by using Eq. (16). The *CM* is the method used in the main reference. The new method (*NM*) is the method that using correction factor, Eq. (38) or Eq. (39) in the calculation. This method uses variance analysis for the determination of *n* and *k.* The true order is that with lower deviation standard.

The results of all calculations are presented in Tables 3 and 4. In all tables, the notation *r* is the regression coefficient and $\chi^{\sigma n}$ is the deviation standard for variance analysis which is introduced as *NM*.

Table 3. The results of data analysis of Table 1

	A	*B*	*r*	*n*	*CF/* s^{-1}	k_1 / s^{-1}	*E P / %*	k_2 / Ms^{-1}	*E P / %*
IM	0.01127	1.31x10^{-3}	0.99606	0					
	0.51184	-1.57x10^{-3}	-0.99931	0.5					
	-2.17x10^{-3}	**-7.08x10^{-3}**	**-0.99986**	**1**		**7.08x10^{-3}**			
	1.90817	8.28x10^{-3}	0.99950	1.5					
	3.49182	3.89x10^{-2}	0.99763	2				-	
IRM	**-2.14404**	**1.03923**	**0.98096**	**≈1**	1.0536	7.56x10^{-3}	**6.78**		
CM	**-4.38x10^{-3}**	**6.97x10^{-3}**	0.98012		1.0536	7.34x10^{-3}	**3.67**		
NM		$\ddot{x}$	$\chi^{\sigma n}$						
		1.41x10^{-3}	2.67x10^{-4}	0					
		6.75x10^{-3}	**2.61x10^{-4}**	**1**	1.0536	**7.11x10^{-3}**	**0.42**		

There are two interesting points in Table 3. First, *IM, IRM*, and *NM*, show that, when the initial $[Br_2]_o$ is greater than $(k_{-1}/k_2)[H^+]$, the reaction is of the *first*-order with respect to Br_2. By *IM*, the reaction is *first*-order (its regression coefficient is higher than *other*-order) with k_1 = 7.08x$10^{-3}M\,s^{-1}$. By *IRM*, the order is 1.03923 ≈ *1* = *first*-order. By *NM,* it is also *first*-order (lower deviation standard) with k_1 = 7.11x$10^{-3}M\,s^{-1}$.

Second, by *IRM*, it is just assumed as *first*-order. This is because nearer to *1.00* with k_1 = 7.56x$10^{-3}M\,s^{-1}$. By *CM*, there are two possible values of *k,* but the first is meaningless because *k* must have positive value. Then, by Eq. (9), the reaction is of the *first*-order with respect to Br_2 with k_1 = 7.34x$10^{-3}M\,s^{-1}$.

Table 4. The results of data analysis of Table 2.

	A	*B*	*r*	*n*	*CF*	*k_1/ s^{-1}*	*E P / %*	*k_2 / Ms^{-1}*	*E P / %*
IM	$-2.56\text{x}10^{-5}$	$1.00\text{x}10^{-4}$	0.99998	*0*	$6.25\text{x}10^{-3}$			**$6.25\text{x}10^{-7}$**	
	0.23788	$-2.78\text{x}10^{-4}$	-0.99843	*0.5*					
	0.22621	$-2.65\text{x}10^{-4}$	-0.99922	*1*				-	
	4.27148	$7.56\text{x}10^{-3}$	0.99370	*1.5*					
	17.25431	$8.13\text{x}10^{-2}$	0.98898						
IRM	**-4.01854**	**-0.01361**	**-0.16395**	*≈0*	$6.25\text{x}10^{-3}$			**$5.99\text{x}10^{-7}$**	**4.16**
CM	**$1.02\text{x}10^{-4}$**	**$-3.68\text{x}10^{-5}$**	-0.17197		$6.25\text{x}10^{-3}$	**$6.38\text{x}10^{-7}$**		**$6.38\text{x}10^{-7}$**	**2.08**
NM		$\ddot{x}$	$\chi^{\sigma n}$						
		$1.00\text{x}10^{-4}$	**$1.46\text{x}10^{-6}$**	*0*	$6.25\text{x}10^{-3}$			**$6.25\text{x}10^{-7}$**	**0**
		$2.63\text{x}10^{-3}$	$4.65\text{x}10^{-4}$	*1*					

There are also two interesting points in Table 4. First, *IM, IRM*, and *NM*, show that, when the initial $[Br_2]_o$ is lower than $(k_{-1}/k_2)[H^+]$, the reaction is of the *zeroth*-order with respect to Br_2. By *IM*, the reaction is *zeroth*-order (its regression coefficient is higher than *other*-order) with k_2 = 6.25x10^{-7} $M\ s^{-1}$. By *IRM*, the order is -0.01361 ≈ *0* = *zeroth*-order with k_2 = 5.99x10^{-7}$M\ s^{-1}$. By *NM,* it is also *zeroth*-order (lower deviation standard) k_1 = 6.38x10^{-7} $M\ s^{-1}$.

Second, by *IRM*, it is also just assumed as *zeroth*-order. This is because nearer to *0.00.* By *CM*, there are also two possible values of *k,* but the second is meaningless because *k* must have positive value. Then by Eq. (7), k_2 = 6.38x10^{-7}$M\ s^{-1}$.

Table 5. The results of data analysis of the combination of data from Table 1 and Table 2

	A	*B*	*r*	*n*	*CF*	*k_1/ s^{-1}*	*E P / %*	*k_2 / Ms-1*	*E P / %*
A	$-2.50\text{x}10^{-4}$	$7.88\text{x}10^{-3}$	0.99712	1	1.0536	$8.30\text{x}10^{-3}$	17.23		
B	$-1.40\text{x}10^{-4}$	$7.43\text{x}10^{-3}$	-0.99779	1	1.0536	$7.83\text{x}10^{-3}$	10.59		
C	-2.60x10-^{4}	$8.05\text{x}10^{-3}$	0.99755	1	1.0536	$8.48\text{x}10^{-3}$	19.77		
D	$-1.42\text{x}10^{-4}$	$7.38\text{x}10^{-3}$	0.99857	1	1.0536	$7.78\text{x}10^{-3}$	9.89		

Note: *A* is the combination of the first 3 data of Table 1 and the first 3 data of Table 2.
B is the combination of the first 3 data of Table 1 and the last 3 data of Table 2.
C is the combination of the last 3 data of Table 1 and the first 3 data of Table 2.
A is the combination of the last 3 data of Table 1 and the last 3 data of Table 2.
All combinations give two possible values of *k* but one of them are meaningless.

Discussion

The first goal

By Eq. (21), for ($[A_o]$ - $[A_1]$) in Table 2 (for *zeroth*-order) gives $k_{A\text{-}1\,=}$ {(1 - 0.9) x 0.050}/50= 1.00x10^{-4}$A\ s^{-1}$/ 160 = 6.25x10^{-7} $M\ s^{-1}$. By Eq. (20), for ($[A_o]$ - $[A_2]$) gives $k_{A\text{-}2\,=}$ (1-0.9^2) x 0.050/90=1.06x10^{-4}$A\ s^{-1}$/ 160 = 6.60x10^{-7} $M\ s^{-1}$. Their error percentage = [(6.60x10^{-7} - 6.25x10^{-7}): 6.25x10^{-7} x100 %]= 5.6%. The error percentage is large. But this is not because the theory is wrong. This is an experimental error. By Eq. (18) $t_{\beta-2}$ should be 45, then t_{β}= 50 + 45 = 95 *s* and k_{A-2} = (1-0.9^{2}) x 0.050/95=1.00x10^{-4}*A s*$^{-1}$/ 160 = 6.25x10^{-7} *M s*$^{-1}$. The error percentage is 0.00 %. Different fraction gives the same rate constant.

By Eq. (18), $t_{\beta-1}$ = $t_{\beta-2}$ and in Table 1 = 15 *s*. By Eq. (21), for *first*-order = ([A_o] - [A_1]) in Table 2 gives k_{A-1} = {(1 - 0.9)}/15 = 6.67x10^{-3}*s*$^{-1}$. For ([A_o] - [A_2]) gives k_{A-2} = {(1-0.9^{2})} /30 = 6.33x10^{-3} *s*$^{-1}$. Their error percentage=[(6.66x10^{-3}-6.33x10^{-3}): 6.66x10^{-3} x 100%] = 4.95%. It is also large. But by Eq. (40), k_{A-1} = 6.66x10^{-3} x (-ln 0.9 / 0.1) = 7.02x10^{-3} and k_{A-2}= 6.33x10^{-3}*s*$^{-1}$x (-ln 0.81 / 0.19) = 7.02x10^{-3}. The *EP* is 0.00 %. The same rate constant can be obtained at different fractions.

Due to the correction factor, by *NM* the value of error percentage are the same, including for *first*-order reaction. Thus, it is not a necessity to restrict the percentage of reaction followed to maximum 5%.

The model used in this study is slightly different from that of the main reference. However, by the same principle, both discuss the reaction that takes place in two different reaction mechanisms. Based on Table 3 and Table 4 the *CM* always gives twovalues of *k* but one of them is always negative.

In Table 3, the slope is positive which means the reaction is of the *first*-order. By Eq. (9), this value is from k_1. The intercept is negative which thus the k_2 value cannot be obtained; a constant must have positive value.

In Table 4 the intercept is positive which means the reaction is of the *zeroth*-order. By Eq. (9), this value is the value of k_2. This is in accordance with the theory: if [*C*] → 0, plotting the intercept of v_o versus [*C*] gives the value of *k* of *zeroth*-order reaction and so must be positive then $v_o = k_2$.

To be valid, *CM* should be able to give simultaneous value of k_1 and k_2 for every combination. In Table 5, there are two values, but once again, only one in each of them are positive; that is the slope. By Eq. (9) and in our model, this gives the value of k_1. And, differ with that in Table 3. and Table 4 all with large *EP.* One of the possible reason is that the data are not at the same level of concentration. But, whatsoever, the *CM* is not always suitable for data analysis of reaction with 2 successive mechanisms.

The second goal

There is a fundamental premise difference in the determination of a rate law by *IM* and by conventional *IRM*. By *IM*, the premise is that, for an experimental data, there must be a most probably fixed rate law. In contrast, in conventional *IRM*, the results of data analysis using Eq. (9) will give a certain order and its rate constant value. If the experiment is done correctly then the results of both methods (k_A and k_{IRM}) will be attributable. For example, if from the calculation by Eq. (9), the order obtained, let say, 0.875, then it will be assumed to be *first*-order. This is because the order reaction usually integer or half-integer and 0.875 is nearer *1* than *0.5.* The value of the calculated rate constant is the value for the *0.875th*-order and not for *first*-order (as in *IM*).

The greater the order difference (with that from *IM*) the greater the difference. Thus, for this reason, most chemists recommend the need to check the *IRM* value.

There is an alternative way of determining the order. That is by variance analysis; and introduced as the new method: the *NM*. The spirit is resembled with *IM*. Both give the most possible rate law.

It is interesting to compare the values obtained by *IRM*, *CM*, and *NM*. In Table 3, the *IRM* gives *EP* = 6.78 %, *CM* gives *EP* = 3.67 %, and *NM* = 0.42 % for k_1. In Table 4, the *IRM* gives *EP* = 4.16 %, *CM* gives *EP* = 2.08 %, and *NM* = 0.00 % for k_2. The *EP* for *NM* are always lower than 5%. Then, it can be concluded that of the 3 models, the *NM* is the best. These values are obtained after using their correspondence correction factor; However, by Eq. (38) or Eq. (39), the value k_{IRM} can be determined if k_A is known. That is to say, that any k_{IRM} value is fixed. There is no need of *IM* checks for *k*.

However, all of the above conclusions apply only to certain conditions; at the out-set or at the nearly-end of the reaction. Thus, for the reaction which takes place in two reaction mechanisms the *IRM*, *CM*, or *CN* cannot be used, in one step, to determine the rate constant. The initial rate method cannot be used to determine both constants simultaneously. Compared with *IM*, this method is also impractical because rate is the difference of to concentrations. But, by *IRM*, a rate law can be determined directly from the change of product concentration.

Implementation

There are two cases that can be discussed further as the possible implication of this research.

First case

It is about enzymatic reaction which has the rate law:

$$v = \frac{v_{\max}[S]}{K_M + [S]} \tag{42}$$

where v, v_{max}, $[S]$, and K_M are the rate, the maximum rate, the substrate concentration, and the Michaelis-Menten constant, respectively (Michaelis & Menten, 1913). Mostly, K_M is determined by *IRM* (Briggs & Haldane, 1925).

Theoretically, enzymatic reaction takes place in 2 successive reaction mechanisms. If the substrate concentration, $[S] >> K_M$, the reaction is *zeroth*-order relating to [S]. However, as the reaction proceed, $[S]$ will decrease and because K_M constant then, $[S] << K_M$, and the reaction becomes *first*-order with respect to [S]. That is to say, the reaction takes place in 2 successive mechanisms.

There are two equations that most commonly used in the determination of K_M : the Lineweaver-Burk equation and the Eadie–Hofstee equation (Lineweaver & Burk, 1934; Eadie, 1942; Hofstee, 1959). Both equations derived from eq. (42) and use *IRM* for K_M determination but, mostly give different values. Some even claimed that the second is better and superior than the first (Dowd & Riggs, 1965).

The first problem: there is no explanation of the source of the data used for the calculation, from the condition when the reaction is *zeroth*-order, *first*-order or mix. It is stand to reason that using data from one condition will not represent the reaction as whole. The second is that eq. (42) is resemble with Langmuir isotherm and the Lineweaver-Burk equation is very much resembled with Langmuir equation: which is unreliable for K_d determination (Patiha et al., 2016).

Second case

As with *IM*, the introduced method is impractical. Unified integral equations have been introduced (Tan et al., 1994). An improvement was also given (Patiha, 1998). Because, by the *NM* is the value of *k* is determined by variance analysis then it is impractical. Unified *NM* is open to be invented. It is possible to invent a new *IRM* modification formula for *DM*, with which, the true order and the accurate value of apparent rate constant obtained will always be the same with that from integral method.

Conclusions

The *IRM* is not suitable for simultaneous determination of constants of reaction which take places in 2 mechanisms. There is no necessary to restrict the percentage of reaction followed to a maximum of 5%. The *CM* cannot be (always) used to simultaneously determine the two constants of the reaction that takes place in two mechanisms. The *NM* is valid and more reliable and there is no need of *IM* checks for *k*.

Recommendations

It is recommended to invent a new, valid, and reliable method for determining K_M of Michaelis-Menten equation and to derive a unified form of *DM* equation, which does not require *IM* checks.

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