Notes on Espenson Method for Determining Catalyzed Reaction Fitting-Constants

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Abstract. Espenson states that many catalyzed reactions can be represented in a unified equation. Based on the basic assumption that the catalyzed reaction occurs in 2 reaction mechanisms (zeroth-order and first-order), he also introduced a time-lag-based equation for determining the fitting-constants, q and κ, using a combination of outset and near-end data. A new method, compiled based on the outset and near-end data separately, has been introduced. This study aims to demonstrate the inaccuracy of Espenson Method. The study was carried out theoretically, and the inaccuracies were tested by applying both methods to the literature data. Assessment is based on the \(k_{obs}\) and \(\kappa\) values. The results showed that Espenson Method does not always use basic assumptions. The average percentage difference in the mean value of \(k_{obs}\), relative to the new method was 14.24% and for \(\kappa\) was 52.23%. The \(q\) value is not constant; \(q\) is not the maximum velocity. Doubling [Cat.] will double \(q\), but \(k_{obs}\) and \(\kappa\) are the same. Therefore, \(q\) is simply a maximum relative velocity. The real constant is \(k_{obs}\) as the observed catalyst constant.

1. Introduction

The overall rate of homogeneously catalyzed reaction is strictly the sum of the rate of catalyzed and non-catalyzed processes. However, since the non-catalyzed reaction is usually very much slower than the catalyzed process, the rate expression is simply denoted as the rate of catalyzed reaction as expressed in Eq. (1).

\[
v = k_c[Cat.][A]
\]  

(1) 

Where \(v\), \(k_c\), and [Cat.] are the rate, catalytic constant, and catalyst concentration, respectively. Espenson states that many catalyzed reactions can also be represented in a unified Eq. (2).

\[
v = \frac{q[A]}{\kappa+[A]}
\]  

(2) 

Where \(v\), \(q\) and \(\kappa\), and \([A]\), are rate, fitting-constants, and concentration of the solution, respectively [1]. The fitting-constants \(q\) and \(\kappa\) represent the role of catalyst in a reaction. When Eq. (1) is compared to Eq. (2), \(q\) can be related to \(k_c[Cat.]\), and it is assumed to be Eq. (3).

\[
q = k_c[Cat.]
\]  

(3) 

Inserting (3) into (2) gives the result of Eq. (4).
It is difficult to calculate the correct value of \( q \) and \( \kappa \) in Eq. (2). This is because the plot of \( v \) against \([A]\) is hyperbolic. However, if \([A]\) \( \gg \) \( \kappa \), Eq. (2) becomes equal to \( q \) as written in Eq. (5), in which the reaction follows zeroth-order to \([A]\).

\[
v = q \tag{5}
\]

Using the integral method (IM), the constant \( q = - \) slope of the linear plot of \([A]\) against \( t \). Next, if \([A]\) \( \ll \) \( \kappa \), Eq. (2) becomes equal to Eq. (6).

\[
v = \frac{q[A]}{\kappa} \tag{6}
\]

As written in Eq. (6), the reaction is first-order to \([A]\). The constant \((q/\kappa) = \) slope of the linear plot of \( v \) against \([A]\); thus, \( \kappa \) can be determined using the values of \((q/\kappa)\) and \( q \).

Espenson introduced an equation to calculate the correct value of \( q \) and \( \kappa \). This equation is based on the basic assumptions that catalyzed reactions occur in two different mechanisms, zeroth-order and first-order following Eq. (7).

\[
k \ln[A]_t + [A]_t = -\kappa \ln[A]_0 + [A]_0 - kt \tag{7}
\]

The fitting-constants \( q \) and \( \kappa \) are then determined by the Time-lag (T-l) method using Eq. (8).

\[
[A]_t - [A]_{t+\Delta} = -\kappa(\ln[A]_t/[A]_{t+\Delta}) + k\Delta \tag{8}
\]

Where \( \Delta \) is the time-lag; the larger \( \Delta \), the better. The constant \( \kappa = - \) slope and \( q = (\) intercept \( /\Delta) \) of the linear plot of the incremental concentrations differences of \(([A]_t - [A]_{t+\Delta}) \) against the logarithm of their ratios \((\ln [A]_t/[A]_{t+\Delta})\).

Three problems arise. First, there is a need for a new method that obeys the basic assumptions of catalyzed reaction (Eq. (5) and Eq. (6)). Second, during the reaction process, enzyme concentration will be constant, but the substrate decreases. Then, as long as the catalyzed reaction is followed until near-end, depending on the initial catalyst and substrate concentration, the reaction can occur as zeroth-order at the outset and first-order at near-end or always as the first-order reaction. In all of the present equations for fitting-constants determination, there is no check for the real rate law. This can cause problems. For example, if the former occurs, it will be in accordance with the basic assumptions of Espenson Method, however, contrary to the time-lag method principle.

Accordingly, the time-lag method is meant to obtain the fixed value of the rate constant of a single reaction order reaction. It is used when the final reading of solution physical properties of a reaction can not or difficult to obtained [2, 3]. The well-known is of Guggenheim [4], Swinbourne [5], Kezdy, Jaz, and Bruylants [6] for first-order reaction and Tobey [7] and Espenson [8] for the second-order reaction. If the latter happens, it will be in accordance with the time-lag method principle; however, it is contrary to the Espenson Method’s basic assumptions. Second, the logical consequences of Eq. (5), Eq. (7), and Eq. (8); \( q \) should be determined under the condition of \([A]\) \( \gg \) \( \kappa \). In Espenson method, the fitting-constants are determined using the combination of the outset and near-end data. Third, because the catalyzed reaction is first-order to \([Cat.]\) then, the value of \( q \) is not constant. A new notion is needed.

Therefore, the present study aims to introduce a new method based on Eq. (5) and Eq. (6), to prove that Espenson method can not be directly used for fitting-constants determination and to introduce a better notion for \( q \) and the real constant in catalyzed reaction.
2. Method

2.1. Reaction model

This study theoretically used two models. The first is the autocatalysis oxidation of Ta6Br122+ by VO2+[9]. The second model is the reaction of acetone with bromine, catalyzed by \( H^+ \) (from ionization of \( HCl \))[10]:

\[
H^+ + CH_3C(O)CH_3 + Br_2 \rightarrow CH_3C(O)CH_2Br + Br^- + H^+ \tag{9}
\]

In this reaction, \( H^+ \) is also produced, then \( H^+ \) is an autocatalyst. It is believed that, at room temperature, this reaction takes place by the following mechanism:

\[
K_1 \equiv \frac{k_1}{k_{-1}} \text{ fast & equilibrium (10a)}
\]

\[
[CH_3C(OH)CH_3]^+ \leftarrow [CH_3C(OH) = CH_2] + H^+ \text{ fast & equilibrium (10b)}
\]

\[
[CH_3C(OH) = CH_2] + Br_2 \rightarrow [CH_3C(OH)CH_2Br] + Br^- \text{ slow (10c)}
\]

\[
[CH_3C(OH)CH_2Br] \leftarrow [CH_3C(O)CH_2Br] + H^+ \text{ fast & equilibrium (10d)}
\]

According to Eq. (10c), the rate law is

\[
-d[Br_2]/dt = k_3[CH_3C(OH) = CH_2][Br_2] \tag{11}
\]

Based on Eq. (11), by the Steady State Approximation, after some steps, the rate law is

\[
-d[Br_2]/dt = \frac{k_3k_2[CH_3C(OH)CH_3]^+[Br_2]}{k_{-2}[H^+] + k_3[Br_2]} \tag{12}
\]

Intermediate \( [CH_3C(OH)CH_3]^+ \) are product in Eq. (10a) and reactant in Eq. (10b). Because Eq. (10a) is an acid-base reaction, then, it can be assumed that mostly, \( [CH_3C(OH)CH_3]^+ \) are from Eq.(10a), or

\[
[CH_3C(OH)CH_3]^+ = K_4[CH_3C(O)CH_3][H^+] \tag{13}
\]

Inserting Eq. (13) into Eq. (12) gives

\[
-d[Br_2]/dt = \frac{k_3k_2K_3[CH_3C(O)CH_3][H^+][Br_2]}{k_{-2}[H^+] + k_3[Br_2]} \tag{14}
\]

Or

\[
-d[Br_2]/dt = \frac{k_3k_2K_3[CH_3C(O)CH_3][H^+][Br_2]}{[k_{-2}/k_3][H^+] + [Br_2]} \tag{15}
\]

Because \( k_2 \) and \( k_3 \) have the same unit (= \( M^{-1} \cdot t^{-1} \)), the denominator unit is \( M \).

At first sight, Eq. (15) is not yet similar to Eq. (4) because, in this model, there are three reactants, \( CH_3C(O)CH_3, Br_2 \), and the catalyst \( H^+ \) (from \( HCl \)). However, if \( [CH_3C(O)CH_3] \) is made in excess, the rate will depend only on \( [Br_2] \) and \( [H^+] \) or
\[-d[Br_2]/dt = \frac{k_{obs}[H^+][Br_2]}{(k_{-2}/k_3)[H^+]+[Br_2]}\] (16)

where

\[k_{obs} = k_2 K_1 CH_2 C(O)CH_3\] (17)

Further, if

\[(k_{-2}/k_3)[H^+] = \kappa\] (18)

Eq. (18) becomes

\[-d[Br_2]/dt = \frac{k_{obs}[H^+][Br_2]}{\kappa+[Br_2]}\] (19)

If \([Br_2] >> \kappa\), Eq. (19) becomes

\[-d[Br_2]/dt = k_{obs}[H^+]\] (20)

the reaction is first-order to \([H^+]\) and zeroth-order to \([Br_2]\). Or, based on Eq. (3), Eq. (20) becomes

\[-d[Br_2]/dt = k_{obs}[H^+] = q\] (21)

If \([Br_2] << \kappa\), Eq. (19) becomes

\[-d[Br_2]/dt = \frac{k_{obs}[H^+][Br_2]}{\kappa}\] (22)

The reaction is first-order to \([H^+]\) and to \([Br_2]\). Inserting Eq. (21) into Eq. (22) gives

\[-d[Br_2]/dt = \frac{q[Br_2]}{\kappa}\] (23)

And inserting Eq. (21) into Eq. (19) gives

\[-d[Br_2]/dt = \frac{q[Br_2]}{\kappa+[Br_2]}\] (24)

The fitting-constants of the reaction can be determined using Eq. (21) and Eq. (23) by following the changes of \([Br_2]\) concentration spectrophotometrically at 400 nm.

2.2. Framework and Execution Technique.

2.2.1. Integral-based Modified Method

Eq. (8) of Espenson method is an integral equation. Thus, the new method should be based on the integral equation. Eq. (21) is based on Eq. (3) and Eq. (5). Therefore, the integral form of Eq. (21) is

\[\frac{k_{obs}[H^+][Br_2]}{\kappa+[Br_2]}\] (25)

The value of \((k_{obs}[H^+]) = q = -\) slope of the linear plot of \([Br_2]\) against \(t\). Eq. (23) is based on Eq. (6). Therefore, the integral form of Eq. (23) is expressed in Eq. (26)
The value of \((q/\kappa)\) is the negative slope of the linear plot of \(\ln [Br_2]\) against \(t\).

2.2.2. Required Data

As discussed, the catalyzed reaction can be zeroth-order at the outset and first-order at near-end or always first-order. This needs two data. By using Eq. (3), or more specifically by using Eq. (21), \(q\) is first-order to \([H^+]\). This also needs two data. However, by changing \([H^+]\) in the condition of the same \(Br_2\) concentration, three experimental data will suffice.

Concentration data of the autocatalysis for fitting-constants determination of autocatalysis oxidation of \(Ta_6Br_{12}^{2+}\) by \(VO_2^+\) is presented in Table 1. However, this cannot meet the purposes of this study. The effect of catalysis concentration changes cannot be obtained yet. To cope with, the reaction of Acetone with Bromine autocatalyzed by \(H^+\) (\(HCl\)) is also used. The absorption data in the absorbance unit (measure at 400 nm) is presented in Table 2. Later, as needed, it will be changed into molar concentration using an absorbance index of 160 \(M^{-1} cm^{-1}\).

| Time (s\(^{-1}\)) | \(t\) | \(t + \Delta\) | \(t - (t + \Delta)\) | \(\ln \{t / (t + \Delta)\}\) |
|-------------------|-------|----------------|-----------------|-------------------|
| 5                 | 0.908 | 0.338         | 0.570           | 0.988             |
| 10                | 0.748 | 0.274         | 0.474           | 1.004             |
| 15                | 0.616 | 0.221         | 0.395           | 1.025             |
| 20                | 0.505 | 0.177         | 0.328           | 1.048             |
| 25                | 0.414 | 0.140         | 0.274           | 1.084             |

2.2.3. Data analysis

Data analysis for data in Table 1 and Table 2 will be analyzed using Espenson Method and New Method. Because the new method is based on the basic assumptions and with the integral method, this method is used as the standard. The results of the analysis are presented in Table 3 and Table 4. The reaction is first-order at the outset as well as at near-end; for New Method, there are no \(q\) and \(\kappa\) values.

2.2.4. Execution

Based on the objectives of this study, a method will be claimed to be applicable if, first, it meets all the requirements for fitting-constant determination; and second, if \(q\) value is not constant, the value changes with the change of \([H^+]\).

3. Results and Discussion

3.1. First case

The new method is based on the basic assumption of catalyzed reactions and uses the integral method for data analysis. The integral method provides a relatively accurate rate constant value; then, it will be used as a standard.

3.2. Second case

The validity of Espenson method for determining the fitting-constants catalyzed reaction is relative to the new method.
Table 2. Absorbance data for fitting-constants determination in the reaction of acetone 0.8 M with bromine 0.01 catalyzed by $H^+$ (0.050, 0.100, and 0.200) $M \text{HCl}$; $\Delta_1 = 1260 \text{ s}$, $\Delta_2 = 570 \text{ s}$, and $\Delta_3 = 210 \text{ s}$ [10]

| t/s | t   | $t_{\Delta 1}$ | $t-t_{\Delta 1}$ | ln($t : t_{\Delta 1}$) |
|-----|-----|----------------|------------------|----------------------|
| 10  | 0.468 | 0.059 | 0.409 | 2.071 |
| 20  | 0.463 | 0.055 | 0.408 | 2.130 |
| 30  | 0.458 | 0.052 | 0.406 | 2.176 |
| 40  | 0.454 | 0.050 | 0.404 | 2.206 |
| 50  | 0.449 | 0.047 | 0.402 | 2.257 |
| 60  | 0.444 | 0.044 | 0.400 | 2.312 |

As shown in Table 3, the autocatalysis oxidation of Ta$_6$Br$_{12}^{2+}$ by VO$_2^+$, yields the values of $q$ (= 1.40x10$^{-6}$) and $\kappa$ (= 3.00x10$^{-5}$). However, these values are questionable. For the same data, the new method finds that the reaction is first-order either at the outset or near-end of the reaction. So as, in the reaction of Acetone with Bromine, autocatalysis by $H^+$.

Table 3. Results of data analysis of autocatalysis oxidation of Ta$_6$Br$_{12}^{2+}$ by VO$_2^+$ for the new method and Espenson method

| n trial | A       | B       | r       | Order | $(q / \kappa)$ s | $q \cdot M^1$ s | $\kappa \cdot M^1$ |
|---------|---------|---------|---------|-------|-----------------|-----------------|-------------------|
| Outset  | $1.01 \times 10^{-5}$ | $-2.46 \times 10^{-7}$ | -0.9941 | - | - | - | - |
| $l$     | -11.411 | -3.93x10$^{-2}$ | -1.000 | $l$ | 3.93x10$^{-2}$ | - | - |
| $0$     | 3.78x10$^{-6}$ | -9.86x10$^{-8}$ | -0.9942 | - | - | - | - |
| Near-end| $l$     | -12.370 | -4.40x10$^{-2}$ | -0.9998 | $l$ | 4.40x10$^{-2}$ | - | - |

As shown in Table 4, there are 3 possible values for $q$ and $\kappa$. At $[H^+]$ of 0.200 $M$, Espenson Method gives the values of $q$ (= 1.33x10$^{-5}$) and $\kappa$ (= 4.38x10$^{-4}$). The new method finds that in this condition, the reaction is also first-order both at the outset and near-end of the reaction. Based on its basic assumptions, Espenson Method is invalid under these conditions. To be used, the reaction must be of zeroth-order.
As shown in Table 6, the true value of $q$ and $\kappa$ are obtained from the concentration of $[H^+] 0.050 \text{ M}$ or $0.100 \text{ M}$. In these conditions, at the outset, the zeroth and near-end reactions are first-order to $[B_r_2]$.

This is the weakness of Espenson Method. There is no prior cheque to the real reaction order of reaction at the outset and at the near-end. However, this is precisely the essence of the New Method. The $q$ value is determined when the reaction is zeroth-order (at the outset) and is then used to determine $\kappa$ from the value of $q/\kappa$ obtained when the reaction is first-order (at near-end). So, there is no need for additional equations or techniques.

However, actually, the main weakness of Espenson method is in relation to the unified equation of Eq. (2). Based on Eq. (8), the value of $q = \text{intercept} / \Delta$. Mathematically, $(A_t - A_{t+\Delta}) / \Delta \approx v$. Thus, if $v = q$ then,

$$\kappa = 0$$

Eq. (27) at the same time states that $q$ and $\kappa$ in Eq. (2) cannot be determined using a combination of outset and near-end data.

3.3. Third case: The better notion for $q$ and the real constant.

By using Eq. (3), the $q$ value depends on the catalyst concentration; and by using Eq. (21), $q$ is first-order to $[H^+]$. That is, doubling the catalyst concentration will double the rate. Using Table 6. data, for the new method: $(6.09 \times 10^{-6} / 2.96 \times 10^{-6}) = 2.06$ and for Espenson Method $(5.42 \times 10^{-6} / 2.44 \times 10^{-6}) = 2.22$. Since the reaction order is an integer or half-integer, the value must be 2; thus, the reaction is still first-order to $[H^+]$. The new method gives closer value and so better.

As also shown in Table 6, $q$ values are not constant by either the new method or Espenson Method. However, dividing the $q$ value by the catalyst concentration yields a constant $k_{obs}$ value. After division, at $[H^+]$ of 0.050 M and 0.100 M, the new method gave almost the same values for $k_{obs}$ (mean 6.005x10^{-5}), and Espenson Method also gave nearly the same values for $k_{obs}$ (mean 5.15 x 10^{-5}). This means that the constant is $k_{obs}$. The notion that $q$ is a constant or as maximum velocity is biased. The better notion for $q$ is the maximum relative velocity. The value obtained by the new method is higher than that of Espenson Method. The percentage difference of $k_{obs}$ values in both methods, relative to the new method is 14.24 %. That is pretty high. In analytical chemistry, as a rule, the maximum allowable percentage difference is up to 7%.

It is quite interesting to discuss the fact that $\kappa$ values of the new method are also higher than Espenson Method. The percentage difference is 52.23 %, which is very high because the $\kappa$ value depends on $q$. In the new method is $q$ is the “maximum” velocity. Therefore, its value (with the New Method) is higher (compared to Espenson Method), which makes the $\kappa$ value higher. Espenson Method combined the outset and near-end data. However, a pancake made from 1 kg of wheat and 0.5 of eggs does not taste the same as 0.5 kg of wheat and 1 kg of eggs, or the same weight of wheat and eggs.
### Table 4. Results of data analysis of the reaction of acetone with bromine catalyzed by HCl using Espenson method

| $H^+ M$ | A    | B          | r     | $q M^{-1}s$ | $k_{obs} s$ | $\kappa M^{-1}s$ | $\chi^2$ |
|---------|------|------------|-------|-------------|-------------|------------------|-----------|
| 0.050   | 0.4921 | -3.98x10^{-2} | -0.9660 | 0.4921 : (1260x160) = 2.44x10^{-6} | 4.88x10^{-5} | 3.98x10^{-2} : 160 = 2.49x10^{-4} |          |
| 0.100   | 0.4941 | -4.41x10^{-2} | -0.9897 | 0.4941 : (570x160) = 5.42x10^{-6} | 5.42x10^{-5} | 4.41x10^{-2} : 160 = 2.76x10^{-4} |          |
| 0.200   | 0.4472 | -7.01x10^{-2} | -0.9897 | 0.4472 : (210x160) = 1.33x10^{-5} | 2.13x10^{-3} | 7.01x10^{-2} : 160 = 4.38x10^{-4} |          |

### Table 5. Effect of catalyst concentration $[H^+]$ changes on the reaction order, $n$, and fitting-constant, $q$, and ($q/\kappa$), in the reaction of acetone with bromine; $\Delta_1 = 1260$ s, $\Delta_2 = 570$ s, and $\Delta_3 = 210$ s by the New Method

| $[H^+]$ (M) | $n_{trial}$ | A    | B          | r     | $q$ | Abs | $t$ | $n_{trial}$ | A    | B          | r     | $q$ | Abs | $t$ | $n$ | ($q/\kappa$) s |
|-------------|-------------|------|------------|-------|-----|-----|-----|-------------|------|------------|-------|-----|-----|-----|-----|----------------|
| 0.050       | 0           | 0.473 | -4.47x10^{-4} | -0.9996 | 0   | 4.74x10^{-4} | 0   | 0.061       | -2.89x10^{-4} | -0.9962 | -    | 0.050 | 0           | 0.473 | -4.47x10^{-4} | -0.9996 | 0   | 4.74x10^{-4} | 0   | 0.061       | -2.89x10^{-4} | -0.9962 | -    |
| 0.100       | 0           | 0.493 | -9.74x10^{-4} | -0.9999 | 0   | 9.74x10^{-4} | 0   | 0.078       | -6.00x10^{-4} | -0.9968 | -    | 0.100 | 0           | 0.493 | -9.74x10^{-4} | -0.9999 | 0   | 9.74x10^{-4} | 0   | 0.078       | -6.00x10^{-4} | -0.9968 | -    |
| 0.200       | 0           | 0.471 | -1.66x10^{-3} | -0.9995 | ?   | -    | 0   | 0.117       | -1.04x10^{-3} | -0.9957 | -    | 0.200 | 0           | 0.471 | -1.66x10^{-3} | -0.9995 | ?   | -    | 0   | 0.117       | -1.04x10^{-3} | -0.9957 | -    |

### Table 6. Comparison of the values of $q$ (in $M s^{-1}$ unit) and $\kappa$ (in $s^{-1}$ unit) and Percentage difference (P-D) in %) in the reaction of acetone with bromine catalyzed by HCl.

| $[H^+] M^{-1}$ | $q M^{-1}s$ | $k_{obs} 10^5s$ | $\bar{x} 10^6s$ | $P-D$ % | $\sigma x$ | $\kappa 10^4M^{-1}$ | $\bar{x} 10^4M^{-1}$ | $P-D$ % | $\sigma x$ |
|----------------|-------------|----------------|-----------------|---------|-----------|-------------------|-------------------|---------|-----------|
| 0.050          | 2.96x10^{-6} | 5.92          | 6.005           | 1       | 8.50x10^{-7} | 5.24               | 5.495             | 1       | 2.55x10^{-5} |
| 0.100          | 6.09x10^{-6} | 6.09          | 6.333           | 1       | 5.68x10^{-7} | 5.75               | 5.333             | 3.48x10^{-5} |
| 0.200          | -            | -             | -               | -       | -          | -                 | -                | -       | -          |
| 0.050          | 2.44x10^{-6} | 4.88          | 5.150           | 14.24   | 2.70x10^{-6} | 2.49               | 2.625             | 52.23   | 1.35x10^{-5} |
| 0.100          | 5.42x10^{-6} | 5.42          | 5.42            | 14.24   | 2.70x10^{-6} | 2.76               | 6.125             | 52.23   | 1.35x10^{-5} |
| 0.200          | 1.33x10^{-5} | 6.65          | 6.65            | 14.24   | 2.70x10^{-6} | 4.38               | 4.38              | 52.23   | 1.35x10^{-5} |
Last but not least, it is interesting to talk about the impracticality of the integral method. As seen in Table 3. and Table 4., two equations must be used to determine the real reaction order at the outset and near-end. Literally, such treatment can be avoided by using the single integral based equation of

\[ t_i = \beta^{(i-1)(1-n)} t_\beta \]  

(28)

Where \( \beta, t_\beta, t_i, i, \) and \( n \) are the remaining reactant fraction, first time observation, following observations, observation, and reaction order, respectively [10, 11, 12]. However, to be used, measurements must be at the same \( \beta \).

Eq. (28) can be used to guess the order of a reaction from the given data. If \( \beta \) is made the same as \( \beta \) in \( t_\beta \), then for first-order reaction \( t_i \) will always the same with \( t_\beta \) and for zeroth-order reaction, \( t_2 = \beta x t_\beta \). For example, as shown in the data, the first, the second, and the \( i^{th} \) half-life of a reaction are always 20 seconds, then the reaction must be first-order. However, if the reactions occurred under the same condition, and the half-life time is 20, 10, 5, …. seconds, then the reaction must be a zeroth-order reaction. The data in Table 1 were measured at certain time, following the theory of the latter. This treatment also resulted in the difference in the \( \kappa \) values obtained.

4. Conclusions
Espenson method is not recommended for determining the fitting-constants based on the unified equation for the catalyzed reaction. A new method for determining the fitting-constant of the catalyzed reaction (in the unified equation) has been introduced using the integral-based modified method, which is more reliable. A better notion of the concept of \( q \) is the maximum relative velocity, not the maximum velocity. The real constant is \( k_{obs} \) (or \( k_c \) if there is only one substrate).

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