# A NOVEL METHOD FOR THE DETERMINATION OF ORDER OF A REACTION AND RATE CONSTANT

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## Abstract

*This study reports the derivation of a novel method for the determination of the order of a reaction and its rate constant, from experimental data. The derived expression is:*

$$w = \frac{\tau}{t_{1/2}} = \frac{(e^{n-1}-1)}{(2^{n-1}-1)}$$

*And*

$$k = \frac{C_o^{1-n}}{1-n}\sqrt{\frac{(1-2^{n-1})(1-e^{n-1})}{\tau \times t_{1/2}}}$$

*Where k is the rate constant at a suitable temperature*
*$\tau$ is the time constant*
*$t_{1/2}$ is the half-life*
*$C_0$ is a suitable concentration at which the half-life and time constant where recorded.*
*n is the order of the reaction.*

**Key Words**: kinetics, reaction order, rate constant, initial rate method, rate law, extent of conversion, temperature, pressure, reaction mechanism.

### 1.0 INTRODUCTION

Kinetics is concerned with the dynamics of chemical reactions such as the way by which reactions take place and the rate (speed) of the process. The keystone for a reaction mechanism is its rate law. It describes the relation between the velocity of a reaction and the concentration of chemical reactants (Perry, 2007). The initial rate method, *when it is applicable*, provides a clean, simple path to the rate law. The italicized qualifier is important. However, in practice, the method of initial rates is only rarely used for several reasons. The data obtained at the beginning of a reaction, where the rate is largest and the time interval is smallest, is usually less reliable than that obtained at later times, when the rate is less. It is undesirable to base an analysis on one's least reliable data. Second, and more important, the method of initial rates uses only a small fraction of the concentration time data; the rest is wasted. Third, to apply the initial rate method requires that full concentration-time profiles be collected for each run in order to extract the slope of the concentration-time plot at t=0. Collection of this much data requires a lot of experimental effort. Most of the resulting data is then ignored if the initial rate method is used. For these reasons and others, chemists have developed other methods for determining rate laws from data, which make use of all of the data collected (anonymous).

Determination of the value of the rate constant is of great importance, since it helps to determine the value of the rate of any reaction applying its rate equation.

In the industrial applications of kinetics, knowledge of chemical rate equation is essential in establishing the optimum conditions of pressure, temperature, feed composition, space velocity, extent of conversion and recycling (Smith, 1983). Experimental reaction data must be fitted into a useful reaction rate equation in order to be used in the simulation of reactor design and sizing (Jack et al).

For the Finite Difference Methods of Numerical Analysis technique to be successful, however, it is important that the time intervals over which average rates are calculated be short relative to the total reaction time.

## 1.1 DERIVATION OF EQUATIONS

Assume a reaction: $A \rightarrow P$

$$\left. \frac{-C_a^{1-n}}{1-n} \right|_{C_0}^{C_t} = kt \big|_0^t$$

$$-C_t^{1-n} + C_0^{1-n} = kt(1-n)$$

$$C_0^{1-n} - C_t^{1-n} = kt(1-n)\dots\dots\dots\dots(1)$$

$at\ t_{1/2}\ c_t = 0.5c_0$

substituting for $t_{1/2}$ in equation (1)

$$C_0^{1-n} - (C_0 \times 0.5)^{1-n} = kt_{1/2}(1-n)$$

$$C_0^{1-n}\left[1 - \left(\frac{1}{2}\right)^{1-n}\right] = kt_{1/2}(1-n)$$

$$t_{1/2} = \frac{C_0^{1-n}(1 - 2^{n-1})}{k(1-n)}\dots\dots\dots\dots(2)$$

$at$ tau, $\tau$=time constant, $C_t = \left(\frac{C_0}{e}\right)$

substituting for $\tau$ in equation (1)

$$C_0^{1-n} - C_t^{1-n} = kt(1-n)$$

$$C_0^{1-n} - (C_0 \times \left(\frac{1}{e}\right)^{1-n} = k\tau(1-n)$$

$$C_0^{1-n} - C_0^{1-n}\left(\frac{1}{e}\right)^{1-n} = k\tau(1-n)$$

$$C_0^{1-n}\left[1 - e^{n-1}\right] = k\tau(1\text{-}n)$$

$$\tau = \frac{C_0^{1-n}(1 - e^{n-1})}{k(1-n)}\dots\dots\dots\dots(3)$$

dividing equation (3) by equation (2)

$$\left(\frac{\tau}{t_{1/2}}\right) = \frac{C_0^{1-n}(1 - e^{n-1})}{k(1-n)} \div \frac{C_0^{1-n}(1 - 2^{n-1})}{k(1-n)}$$

$$\frac{\tau}{t_{1/2}} = \frac{1 - e^{n-1}}{1 - 2^{n-1}} = \left|\frac{1 - e^{n-1}}{1 - 2^{n-1}}\right| = w$$

let $w = \dfrac{\tau}{t_{1/2}}$

$therefore\ w = \dfrac{e^{n-1} - 1}{2^{n-1} - 1}\dots\dots\dots\dots(4)$

also multiply equation (3) by equation (2)

$$C_0^{1-n}(1 - 2^{n-1}) \times C_0^{1-n}(1 - e^{n-1}) = k\tau(1\text{-}n) \times kt_{1/2}(1-n)$$

$$C_0^{2(1-n)} \times (1 - 2^{n-1})(1 - e^{n-1}) = k^2 t_{1/2}\tau(1-n)^2$$

$$k^2 = \frac{C_0^{2(1-n)} \times (1 - 2^{n-1})(1 - e^{n-1})}{(1-n)^2 \times t_{1/2} \times \tau}$$

$$k = \sqrt{\frac{C_0^{2(1-n)} \times (1 - 2^{n-1})(1 - e^{n-1})}{(1-n)^2 \times t_{1/2} \times \tau}}$$

$$k = \frac{C_0^{1-n}}{1-n}\sqrt{\frac{(1 - 2^{n-1})(1 - e^{n-1})}{t_{1/2} \times \tau}}\dots\dots\dots\dots(5)$$

$$k^2 = \frac{C_0^{2(1-n)} \times (1-2^{n-1})(1-e^{n-1})}{(1-n)^2 \times t_{1/2} \times \tau}$$

$$k = \sqrt{\frac{C_0^{2(1-n)} \times (1-2^{n-1})(1-e^{n-1})}{(1-n)^2 \times t_{1/2} \times \tau}}$$

$$k = \frac{C_0^{1-n}}{1-n} \sqrt{\frac{(1-2^{n-1})(1-e^{n-1})}{t_{1/2} \times \tau}} \quad .........................(5)$$

Thus it is evident from equation (4), that there are only two variables, time constant and half-life. Therefore if various values of *n* are substituted into equation (4), we would eventually obtain a corresponding value of *w*. Hence a table is constructed below. This table could be used as a reference in the determination of the order of a reaction.

The table is:

| n(order of the reaction with respect to A ) | w(ratio of time constant to half-life) |
|---|---|
| 0.1 | 1.28 |
| 0.2 | 1.29 |
| 0.3 | 1.31 |
| 0.4 | 1.33 |
| 0.5 | 1.34 |
| 0.6 | 1.36 |
| 0.7 | 1.38 |
| 0.8 | 1.40 |
| 0.9 | 1.42 |
| 1.0 | 1.44 |
| 1.1 | 1.47 |
| 1.2 | 1.49 |
| 1.3 | 1.51 |
| 1.4 | 1.54 |
| 1.5 | 1.57 |
| 1.6 | 1.59 |
| 1.7 | 1.62 |
| 1.8 | 1.65 |
| 1.9 | 1.69 |
| 2.0 | 1.72 |
| 2.1 | 1.75 |
| 2.2 | 1.79 |
| 2.3 | 1.83 |
| 2.4 | 1.86 |
| 2.5 | 1.90 |
| 2.6 | 1.95 |
| 2.7 | 1.99 |
| 2.8 | 2.03 |
| 2.9 | 2.08 |
| 3.0 | 2.13 |

*Table of w and n*

The value of w for n=1, is not obtained from equation (4). Because it has been stated during integration that n cannot be 1. The value of w was obtained thus:
For first order:

$$t_{1/2} = \frac{0.693}{k}, \quad \tau = \frac{1}{k}$$

$$\frac{\tau}{t_{1/2}} = \left(\frac{1}{k}\right) \div \left(\frac{0.693}{k}\right)$$

$$w = \left(\frac{1}{k}\right) \times \left(\frac{k}{0.693}\right)$$

$$w = \left(\frac{1}{0.693}\right) = 1.44$$

## 1.2 THE METHOD FOR THE DETERMINATION OF THE ORDER

The method involves, finding a way of getting w from the experimental data. The **w** obtained is now checked up in the table for the corresponding value of **n**; thus its order is determined.

Let us assume that you were given the data on the rate of change of concentration with time.

| Concentration | $C_0$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
|---|---|---|---|---|---|
| TIME | $t_0$ | $t_1$ | $t_2$ | $t_3$ | $t_4$ |

**Step1**
Plot a graph of concentration (on the y-axis) against time (on the x-axis).
**Step2**
Choose or pick a reference concentration (within the boundary of the concentration given) or if the initial concentration is given, just adopt it.
**Step3**
If the reference concentration is $C_O$ find the
Value of $0.5C_O$ and $(1/e)C_O$
**STEP4**
Extrapolate the values $0.5C_O$ to the curve and $(1/e)C_O$ to the curve, the respective time values will be $t_{1/2}$ and respectively
**Step5**
From the values of half-life and time constant,
Calculate **w**,

The value obtained is now looked-up in the table and the corresponding n value is the order of the reaction with respect to A.

The graph of w against **n** is shown below
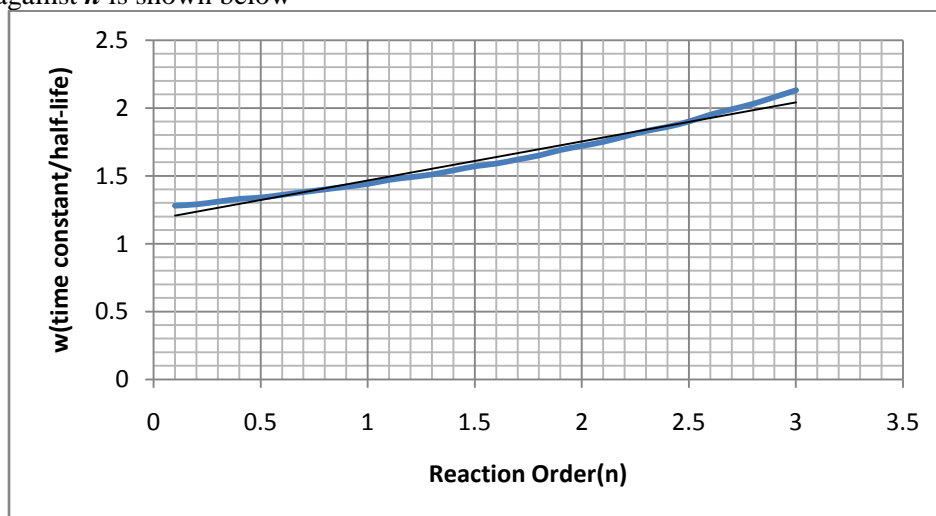
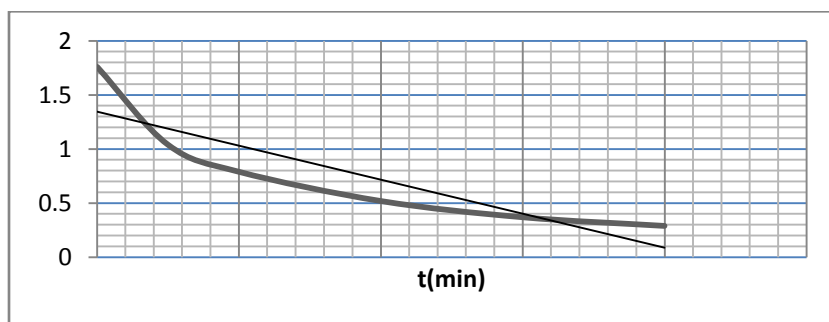## 1.3 APPLICATION OF THE PRESENT THEORY AND DISCUSSION

PROBLEM **1**

### Extracted from (Clyde R Metz, 1976)

The reaction between ozone and carbon disulphide was studied at 29.5$^{o}$C with excess $CS_2$ to find the order of the reaction with respect to ozone from the following data by Olszyna and Hieecklan, prove that the reaction is second order and determine the pseudo second order rate constant.

| t(min) | 0.0 | 0.5 | 1.0 | 2.0 | 3.0 | 4.0 |
|---|---|---|---|---|---|---|
| Pressure of ozone(torr) | 1.76 | 1.04 | 0.79 | 0.52 | 0.37 | 0.29 |

### Determination of order by proposed method

Using a computer software plot the graph (Microsoft excel)



Let the reference concentration be $C_O$=1.76

$0.5C_O = 0.5(1.76)=0.88$

$$\frac{1}{e}C_o = \frac{1}{e}\times 1.76 = 0.6475$$

$$at \ \frac{1}{2}C_o, \ t = t_{\frac{1}{2}}$$

$$at \ \frac{1}{e}C_o, \ t=\tau$$

from the graph $t_{\frac{1}{2}} = 0.7526$

$\tau = 1.311$

$$w = \frac{\tau}{t_{\frac{1}{2}}} = \frac{1.311}{0.7526}$$

$w = 1.742 \approx 1.74$

*from* the table the corresponding value of n is 2.1
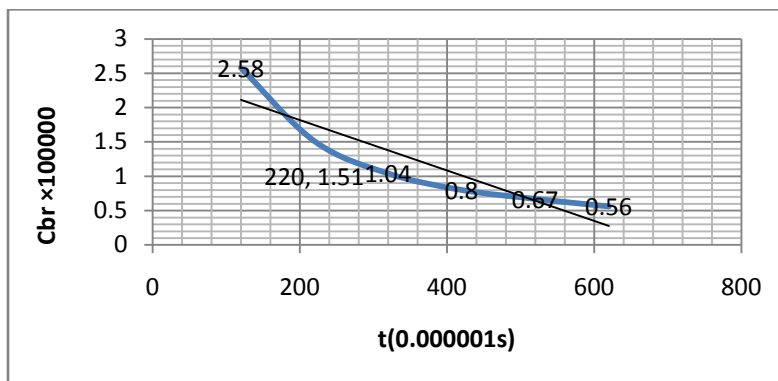
## PROBLEM 2

Extracted from (Clyde R. Metz, 1976)

The concentration of bromine at various times after flash photolysis of a bromine-$SF_6$ mixture with $C_{Br}/C_{SF6}=3.2(10^{-2})$ were reported by Degraft and Lang as

| $C_{Br}\times 10^5 M$ | 2.58 | 1.51 | 1.04 | 0.80 | 0.67 | 0.56 |
|---|---|---|---|---|---|---|
| $T(10^{-6}s)$ | 120 | 220 | 320 | 420 | 520 | 620 |

If these data were for the reaction $2Br \rightarrow Br_2$ show that the reaction is a pseudo-second order and calculate k.

## Determination of order by proposed method

Using a computer software plot the graph( Microsoft excel)



Let the reference concentration be $C_t = 2.58$ at $t=120$

$$\frac{1}{2}C_t = 0.5 \times 2.58 = 1.290$$

$$\frac{1}{e}C_t = \frac{1}{e} \times 2.58 = 0.949$$

$$at\ \frac{1}{2}C_t,\ t=t_{\frac{1}{2}}$$

$$at\ \frac{1}{e}C_t,\ t= \tau$$

from the graph $t_{\frac{1}{2}} = 134.8$

*from* the graph $\tau = 228.7$

$$w = \frac{\tau}{t_{\frac{1}{2}}} = 1.6965 \approx 1.70$$

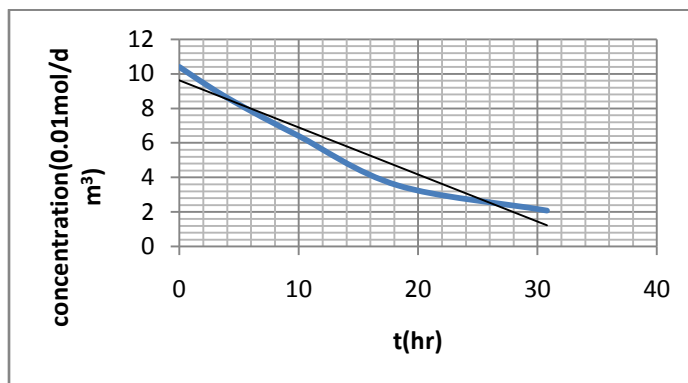from the table the corresponding value n is 1.9

### PROBLEM 3

Extracted from (Peter Atkins et al)

The data below apply to the reaction $(CH_3)_3CBr\ +\ H_2O \rightarrow (CH_3)_3COH\ +\ HBr$, determine the order of the reaction, the rate constant and molar concentration of 2-methyl-2-bromopropane after 43.8hr.

| t/hr | 0 | 3.15 | 6.2 | 10.00 | 18.30 | 30.8 |
|------|---|------|-----|-------|-------|------|
| $(CH_3)_3CBr$ $(0.01mol/dm^3)$ | 10.39 | 8.96 | 7.76 | 6.39 | 3.53 | 2.07 |

## DETERMINATION OF ORDER BY PROPOSED METHOD

Using a computer software plot the graph (Microsoft excel)



Let the reference concentration be $C_o = 10.39$ at t=0

$$\frac{1}{2}C_o = 0.5 \times 10.39 = 5.195$$

$$\frac{1}{e}C_o = \frac{1}{e} \times 10.39 = 3.822$$

$$at \ \frac{1}{2}C_o, \ t = t_{\frac{1}{2}}$$

$$at \ \frac{1}{e}C_o, \ t = \tau$$

from the graph $t_{\frac{1}{2}} = 12.96$

*from* the graph $\tau = 17.09$

$$w = \frac{\tau}{t_{\frac{1}{2}}} = 1.3186 \approx 1.32$$

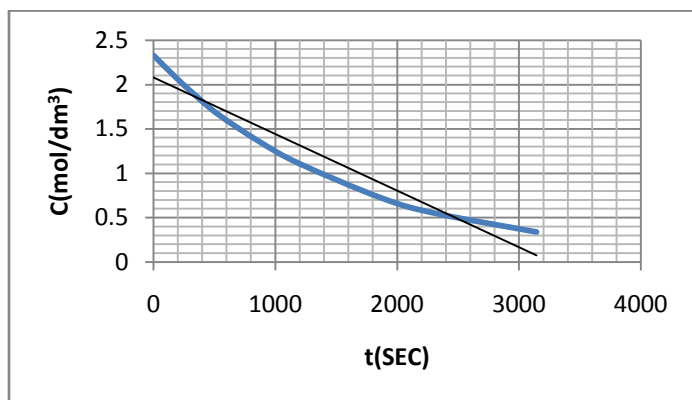from the table the corresponding value n is 0.4

## PROBLEM 4

Extracted from (Kween W.R. et al, 1982)

Dinitrogen pentoxide, $N_2O_5$ decomposes on standing to produce dinitrogentetraoxide, nitrogendioxide and oxygen. The decomposition is first order.

| t(sec) | 0 | 184 | 319 | 526 | 867 | 1198 | 1877 | 2315 | 3144 |
|---|---|---|---|---|---|---|---|---|---|
| C(molL$^{-1}$) | 2.33 | 2.08 | 1.91 | 1.67 | 1.36 | 1.11 | 0.72 | 0.55 | 0.34 |

## DETERMINATION OF ORDER BY PROPOSED METHOD

Using a computer software plot the graph (Microsoft excel)



Let the reference concentration be $C_o = 2.33$ at t=0

$$C_o = 0.5 \times 2.33 = 1.165$$

$$\frac{1}{e}C_o = \frac{1}{e} \times 2.33 = 0.857$$

$$at \ \frac{1}{2}C_o, \ t=t_{\frac{1}{2}}$$

$$at \ \frac{1}{e}C_o, \ t= \tau$$

from the graph $t_{\frac{1}{2}} = 1107.1$

*from* the graph $\tau = 1618.4$

$$w = \frac{\tau}{t_{\frac{1}{2}}} = 1.4618 \approx 1.46$$

from the table the corresponding value n is 1.1
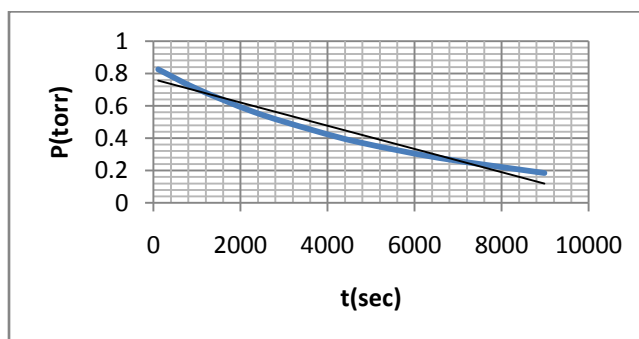
### PROBLEM 5

Extracted from (Clyde R. Dillard et al)

Determine the order of reaction and value of the specific rate constant for the decomposition of $N_2O_5$ from the following data

| t(sec) | 110 | 980 | 2310 | 3670 | 4770 | 6580 | 8988 |
|--------|-----|-----|------|------|------|------|------|
| P(torr) | 0.826 | 0.708 | 0.562 | 0.449 | 0.372 | 0.277 | 0.184 |

## DETERMINATION OF ORDER BY PROPOSED METHOD

Using a computer software plot the graph (Microsoft excel)

Let the reference concentration be $C_o = 0.826$ at $t=110$

$$\frac{1}{2}C_o = 0.5 \times 0.826 = 0.413$$

$$\frac{1}{e}C_o = \frac{1}{e} \times 0.826 = 0.304$$

$$at\ \frac{1}{2}C_o,\ t=t_{\frac{1}{2}}$$

$$at\ \frac{1}{e}C_o,\ t=\tau$$

from the graph $t_{\frac{1}{2}} = 5933.3$
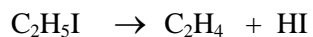
*from* the graph $\tau = 4013.1$

$$w = \frac{\tau}{t_{\frac{1}{2}}} = 1.479 \approx 1.48$$

from the table the corresponding value n is 1.1

**PROBLEM 6**

Extracted from (Raymond Chang, 2005)

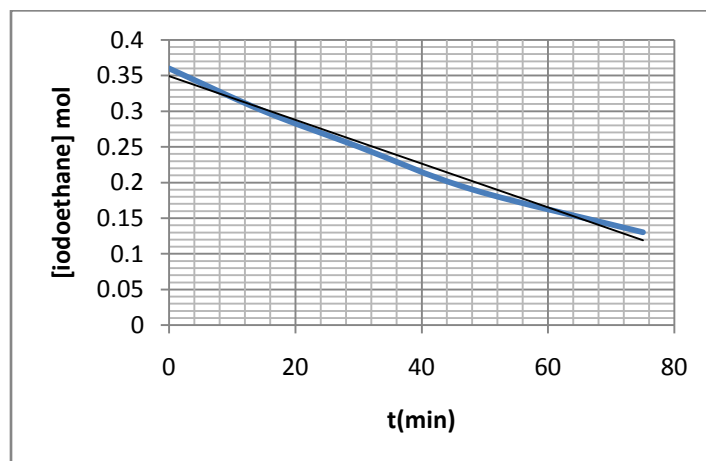Ethyl iodide decomposes at a certain temperature in the gas phase as follows:

$C_2H_5I \quad \rightarrow \quad C_2H_4 \ + \ HI$

From the following data determine the order of the reaction and rate constant

| Time(min) | 0 | 15 | 30 | 48 | 75 |
|---|---|---|---|---|---|
| [$C_2H_5I$] mol | 0.36 | 0.30 | 0.25 | 0.19 | 0.13 |

**DETERMINATION OF ORDER BY PROPOSED METHOD**

Using a computer software plot the graph (Microsoft excel)

Let the reference concentration be $C_o = 0.36$ at t=0

$$\frac{1}{2}C_o = 0.5 \times 0.36 = 0.18$$

$$\frac{1}{e}C_o = \frac{1}{e} \times 0.36 = 0.132$$

$$at \ \frac{1}{2}C_o, \ t=t_{\frac{1}{2}}$$

$$at \ \frac{1}{e}C_o, \ t= \tau$$

from the graph $t_{\frac{1}{2}} = 51.35$
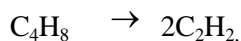
*from* the graph $\tau = 73.92$

$$w = \frac{\tau}{t_{\frac{1}{2}}} = 1.4395 \approx 1.44$$

from the table the corresponding value n is 1.0

**PROBLEM 7**
Extracted from (Raymond Chang, 2005)
Cyclobutane decomposes to ethylene according to the equation below:
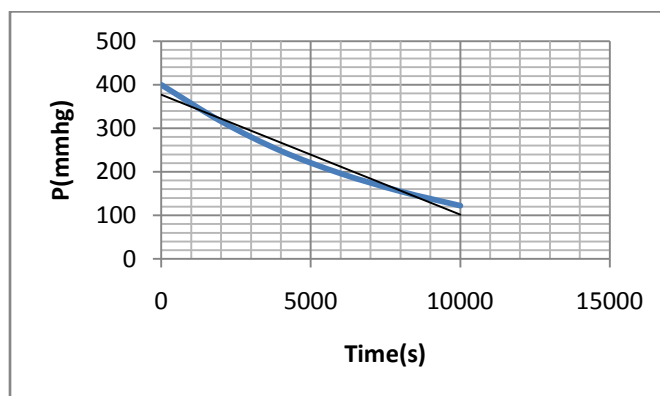
$C_4H_8 \quad \rightarrow \quad 2C_2H_{2,}$

Determine the order of the reaction and the rate constant based on the following pressures which were recorded when the reaction is carried out at $430^0C$ in a constant-volume vessel.

| Time(s)  | 0   | 2000 | 4000 | 6000 | 8000 | 10000 |
|----------|-----|------|------|------|------|-------|
| P(mmHg)  | 400 | 316  | 248  | 196  | 155  | 122   |

## DETERMINATION OF ORDER BY PROPOSED METHOD

Using a computer software plot the graph (Microsoft excel)

Let the reference concentration be $C_o$ =400 at t=0

$$\frac{1}{2}C_o = 0.5 \times 400 = 200$$

$$\frac{1}{e}C_o = \frac{1}{e} \times 400 = 147.15$$

$$at \ \frac{1}{2}C_o, \ t=t_{\frac{1}{2}}$$

$$at \ \frac{1}{e}C_o, \ t= \tau$$

from the graph $t_{\frac{1}{2}} = 5832.9$

*from* the graph $\tau = 8409.2$

$$w = \frac{\tau}{t_{\frac{1}{2}}} = 1.4416 \approx 1.44$$

from the table the corresponding value n is 1.0

## 1.4 CONCLUSION

This method and its accuracy will be limited by the source of the experimental data, experimental errors and whatever errors that exist in this theoretical reasoning and analysis. From the worked illustrations there still remains a margin of error, noticeably ±0.1 in the results of the order of the reaction. These errors hypothetically may be caused by the inherent errors in the experimental data and/or the errors in the computer plotting and extrapolation of the curve.

Recall the equation on which this method is based:

$$w = \frac{\tau}{t_{1/2}} = \frac{(e^{n-1} - 1)}{(2^{n-1} - 1)}$$

An experimental method that would determine both the time-constant and half-life accurately at a specified concentration ($C_0$) would also specify accurately the order of the reaction and indirectly the rate constant.

### 1.4.1 EXPERIMENTAL PROCEDURE

Assume a hypothetical reaction

A  +  B  →   P

Assume A is the reactant specie whose order we intend to determine

**Step1**

Measure the concentration of A before reaction=$C_o$

Measure accurately two equal volumes of A into two separate reaction vessels

**Step2**

Calculate $0.5C_O$ AND $(1/e) C_o$

**Step3**

To the first volume of A react with B and determine the time taken for the reaction of A to be $0.5C_O$, the time determined is the half-life.

**Step4**

To the first volume of A react with B and determine the time taken for the reaction of A to be $(1/e) C_0$, the time determined is the time constant.

**Note**

Step3 and step4 should be carried out using suitable instrumental analytical techniques

**Step5**

Calculate $\dfrac{\tau}{t_{\frac{1}{2}}}$

And check the value obtained with the corresponding value in the table. And calculate k.

The above experiment is yet to be demonstrated due to unavailability of suitable analytical equipment and reagents. We would appreciate help or suggestion to help us out.

Kindly note that the problems used for illustration in this paper are exactly as presented in the original texts.

*References*

Yang, K.H., & Hougen, O.A. (1950). Determination of Mechanism of Catalyzed Gaseous

Reactions. Chemical Engineering Progress, 46 (3), 146-157

Perry, R. H., 2007. Chemical engineers' handbook. 8th ed., McGraw-Hill Professional.

Smith, J. M., 1983. Chemical engineering kinetics. 3rd ed., McGraw-Hill, International Student edition

Clyde R. Metz: theory and problems of physical chemistry, schuam's outline series Mcgraw-Hill book company, 1976.

Peter Atkin's et al: physical chemistry Oxford university press, New York, eight edition.

Kween W.R. et al: chemistry; facts, patterns, and principles ELBS and Addison Wesley publishers, London, 1982 edition.

Clyde R. Dillard, David E. Goldberg: Chemistry reactions, structure and properties, new Macmillan company, New York.

Raymond Chang: chemistry(eight edition), Mcgraw-Hill higher education 2005.