

UNIT 5

ORDER OF REACTION

Dr. Shashi Kiran Misra
School Of Pharmaceutical Pharmacy

Determination of order of reaction

- 1. SUBSTITUTION METHOD**
- 2. INITIAL RATE METHOD**
- 3. DATA PLOTTING METHOD**
- 4. HALF-LIFE DETERMINATION METHOD**

SUBSTITUTION METHOD

The data accumulated in a kinetic study may be substituted in the integrated form of the equations which describes the various orders. When the equation is found in which the calculated **k** values remain constant the reaction is considered to be of that order.

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad (\text{For first order reactions})$$

$$k = \frac{1}{t} \left[\frac{1}{a} - \frac{1}{a-x} \right] \quad (\text{For second order reactions})$$

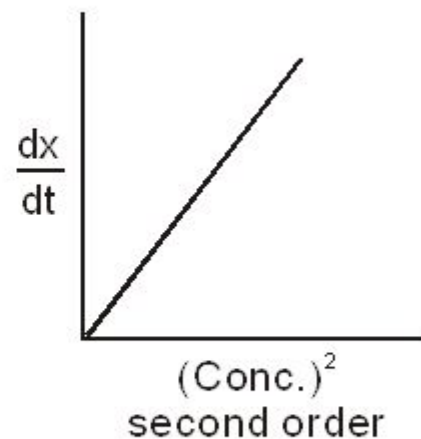
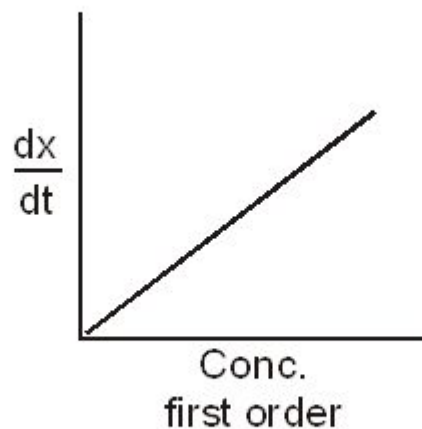
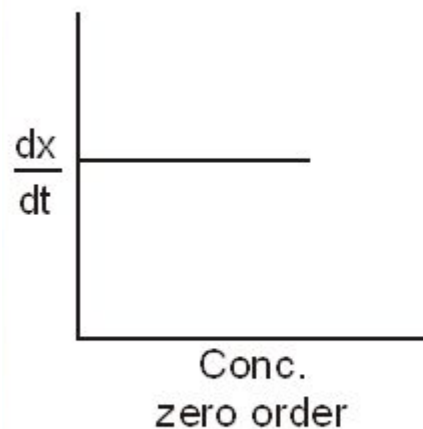
$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] \quad (\text{For third order reactions})$$

GRAPHICAL (DATA PLOTTING) METHOD

If a straight line results when concentration is plotted against time the reaction is zero order.

If plot of $1/c$ against time is linear then it is second order.

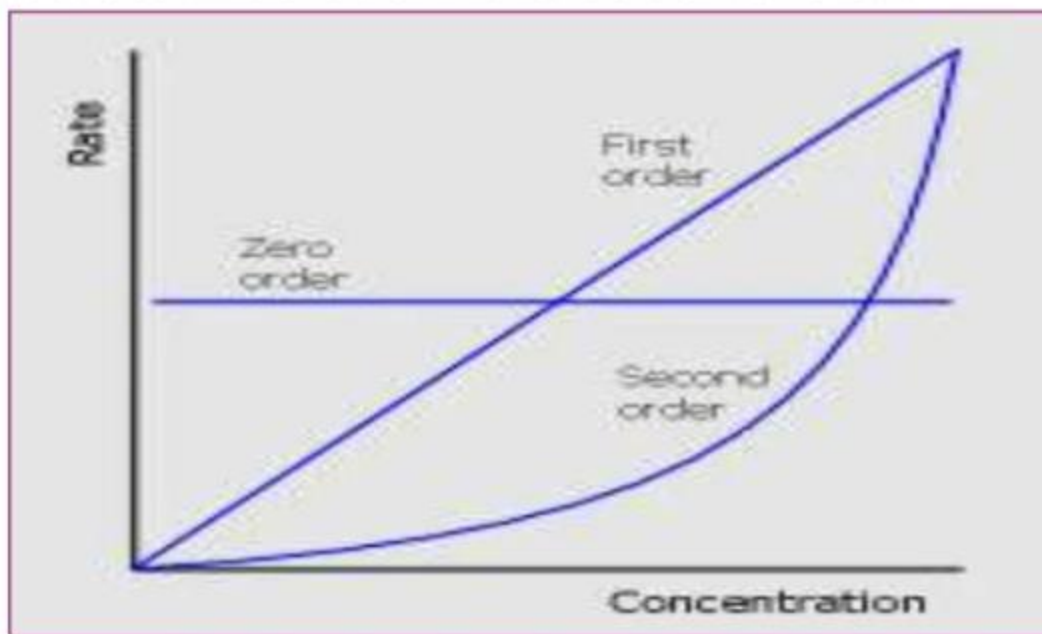
If plot of $\log c$ against time is linear then it is first order reaction.



Graphical representation of rate versus concentrations

INITIAL RATE METHOD

- Graphs are plotted of rate of reaction against concentration and the initial rate determined from the gradient at time = 0.
- If it is a straight line the reaction is first order.
- A line which is independent of concentration is zero order.
- If a curve is obtained then it is second order.



Half- life method

| Order | Rate Law | Concentration-Time Equation | Half-Life |
|-------|------------------|--|------------------------------|
| 0 | rate = k | $[A] = [A]_0 - kt$ | $t_{1/2} = \frac{[A]_0}{2k}$ |
| 1 | rate = $k [A]$ | $\ln[A] = \ln[A]_0 - kt$ | $t_{1/2} = \frac{\ln 2}{k}$ |
| 2 | rate = $k [A]^2$ | $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$ | $t_{1/2} = \frac{1}{k[A]_0}$ |

Determination of $t_{10\%}$ by Arrhenius equation

- Temperature influences rate and order of reaction. So shelf life of product can be obtained under exaggerated condition.
- It is said that for every 10°C rise, rate of reaction increases by 2-3 times.
- For this **Arrhenius equation** is used

$$K = Ae^{-E_a/RT}$$

where ; A= frequency factor,
R= gas constant,
K = rate constant,
E_a = energy of activation

- Therefore, $\text{Log } K = \log A - \frac{E_a}{2.303RT}$
- Graph of **log K** vs **1/T** gives **straight line** with slope $\frac{E_a}{2.303R}$
& intercept at **t=0**

Shelf-life

- Shelf-life is the time period during which a drug product is expected to remain within the approved specification for use, provided that it is stored under the conditions defined on the container label

$$t_{0.9} = 0.1 \frac{[D]_0}{k_0} \quad (\text{zero order})$$

$$t_{0.9} = \frac{0.105}{k_1} \quad (\text{first order})$$

DIFFERENCE BETWEEN HALF LIFE AND SHELF LIFE

■ Half-life ($t_{1/2}$ or $t_{0.5}$) and Shelf-life($t_{0.9}$)

- The *Half-life* is the time taken for half of the reactant to decompose
- The *shelf-life* is the time required for 10% of the material to disappear (which is the time require for remaining material is 90%)
- For example, in *zero-order reaction*, the half-life and shelf life can be derived

$$0.5 A_0 = A_0 - kt_{0.5}$$

$$t_{0.5} = \frac{0.5 A_0}{k}$$

$$0.9 A_0 = A_0 - kt_{0.9}$$

$$t_{0.9} = \frac{0.1 A_0}{k}$$

Reference

- Physical; pharmacy by Alfred martin, second edition , **355-377**.
- The theory and practice of industrial pharmacy by Lachman, **760**.
- Pharmaceutics the science of dosage form design by AULTON, **119-128**