

CHEMICAL KINETICS

Dr. Jagot

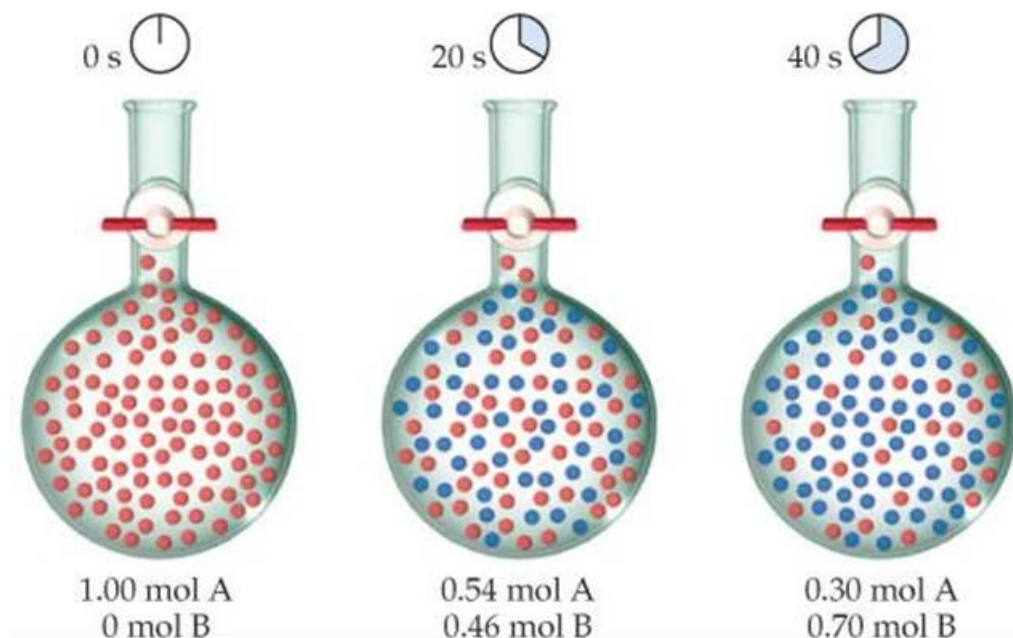
Factors That Affect Reaction Rates

- The speed at which a chemical reaction occurs is called the ***reaction rate***.
- The portion of chemistry that deals with the study of reaction rates is known as ***chemical kinetics***.
- Four factors that affect the rate of a reaction:
 - 1. *Physical state of the reactants***: the more readily reactant molecules collide with each other, the more rapidly they react. With heterogeneous reactions, the reaction is limited by the area of contact of the reactants. Thus, heterogeneous reactions involving solid reactants are faster when the surface area of solid is increased.

2. ***Reactant concentrations***: The rate of most reactions increases as the concentration of one or more of the reactants increases. This is due to the increased frequency of collisions between reactant molecules.
3. ***Reaction temperature***: Reaction rates generally increase as temperature is increased. This is due to increased kinetic energy of the molecules, which results in more frequent collisions between reactants, and collisions with more energy.
4. ***The presence of a catalyst***: Catalysts are agents that speed up the rates of reactions without themselves being used up. They affect the kinds of collisions (and therefore alter the mechanism) that lead to reaction.

Reaction Rates

- Reaction rate is measured in terms of changes in concentration of reactants or products per unit of time.
- The units are usually molarity per second (M/s).



Progress of a
hypothetical
reaction $A \longrightarrow B$

- The rate of this reaction can be expressed either as the rate of disappearance of reactant A or the rate of appearance of product B.

$$\begin{aligned}\text{Average rate of appearance of B} &= \frac{\text{change in concentration of B}}{\text{change in time}} \\ &= \frac{[B] \text{ at } t_2 - [B] \text{ at } t_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}\end{aligned}$$

$$\begin{aligned}\text{Average rate of disappearance of A} &= - \frac{\text{change in concentration of A}}{\text{change in time}} \\ &= - \frac{[A] \text{ at } t_2 - [A] \text{ at } t_1}{t_2 - t_1} = - \frac{\Delta[A]}{\Delta t}\end{aligned}$$

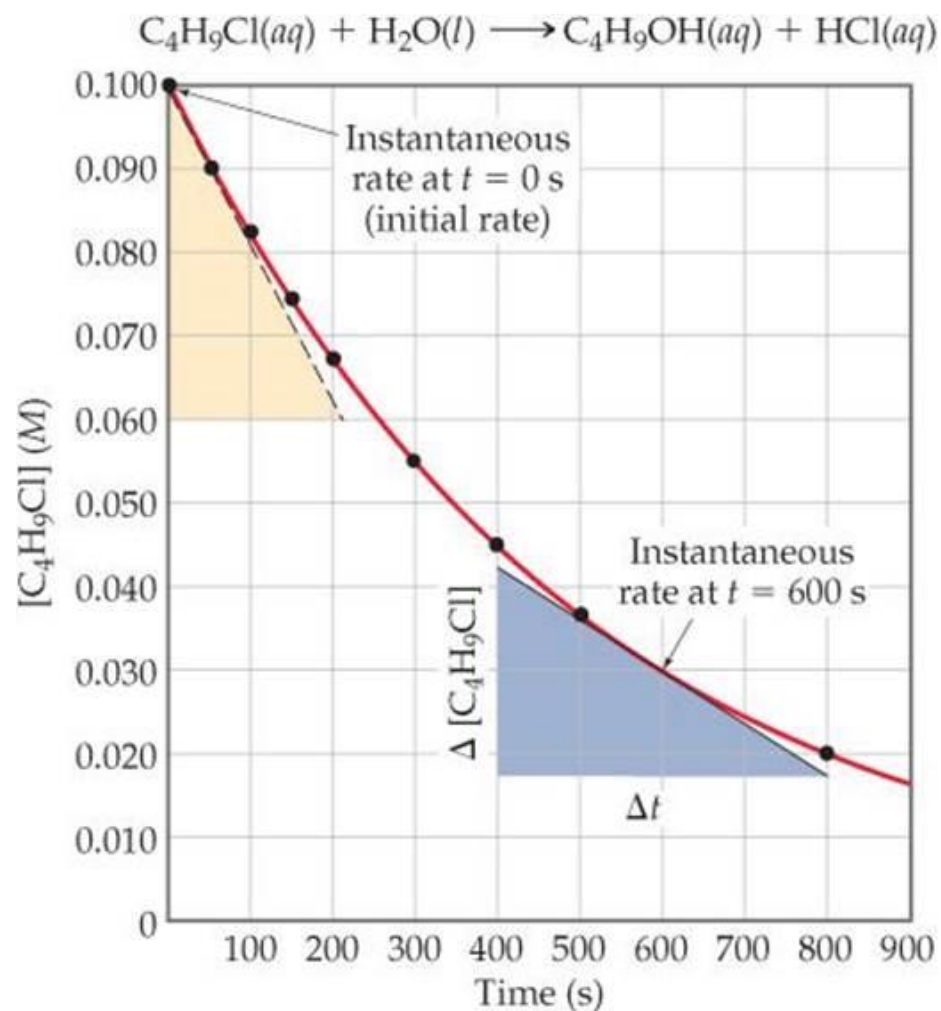
Note the minus sign in this equation – used to indicate that concentration decreases. Rates always expressed as positive quantities.

NB! Brackets are used to indicate molarity

- Sample exercise:
 - a) From the data given in the figure provided, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.
 - b) Calculate the average rate of appearance of B over the time interval from 0 s to 40 s.

Ans: a) $1.2 \times 10^{-2} \text{ M/s}$, b) $1.8 \times 10^{-2} \text{ M/s}$

Instantaneous Rate



It is typical for rates to decrease as a reaction proceeds because the concentration of reactants decreases over time.

- Graphs showing how the concentration of a reactant or product changes with time allow us to evaluate the ***instantaneous rate*** of a reaction, *which is the rate at a particular instant during the reaction.*
- Determined from the slope of the curve at a particular point in time.
- For example, to determine the instantaneous rate at 600 s, we construct horizontal and vertical lines to form the blue right triangle in the graph.
- The slope of the tangent line is the ratio of the height of the vertical side to the length of the horizontal side:
- Instantaneous rate =
$$-\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.017 - 0.042) M}{(800 - 400) s} = 6.3 \times 10^{-5} M/s$$

- Sample exercise:

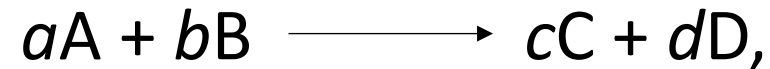
Using the graph in the previous slide,

- a) calculate the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 0$ s (the initial rate).
- b) Determine the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 300$ s.

Ans: a) $1.9 \times 10^{-4} \text{ M/s}$, b) $1.1 \times 10^{-4} \text{ M/s}$

Reaction Rates and Stoichiometry

- The rate of appearance of product = the rate of disappearance of reactant.
- In general, for the reaction;



Where a , b , c , and d are the coefficients of the balanced equation, the rate is given by:

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

- Sample exercise:

- a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2\text{O}_3(\text{g}) \longrightarrow 3\text{O}_2(\text{g})$?
- b) If the rate at which O_2 appears, $\Delta[\text{O}_2]/\Delta t$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[\text{O}_3]/\Delta t$?

a)
$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

- b) Solving for the rate at which O_3 disappears:

$$-\frac{\Delta[\text{O}_3]}{\Delta t} = \frac{2}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{2}{3} (6.0 \times 10^{-5} \text{ M/s}) = 4.0 \times 10^{-5} \text{ M/s}$$

- Practice exercise:

If the rate of decomposition of N_2O_5 in the reaction

$2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ at a particular instant is $4.2 \times 10^{-7} \text{ M/s}$, what is the rate of appearance of (a) NO_2 and (b) O_2 at that instant?

Ans: a) $8.4 \times 10^{-7} \text{ M/s}$, b) $2.1 \times 10^{-7} \text{ M/s}$

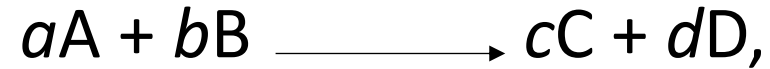
Concentration and Rate Laws

- For the reaction $\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$, the table below shows that changing the concentration of either reactant changes the initial reaction rate.

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

- When the $[\text{NH}_4^+]$ is doubled, while keeping the $[\text{NO}_2^-]$ constant, the rate doubles.
- Likewise, when the $[\text{NO}_2^-]$ is doubled, while keeping the $[\text{NH}_4^+]$ constant, the rate doubles.
- Thus the rate is directly proportional to the $[\text{NO}_2^-]$ and $[\text{NH}_4^+]$.
- This is expressed as: $\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$.
- This equation is known as a **rate law**.
- The constant k is called the **rate constant**. The magnitude of k changes with temperature.

- For the general reaction;



the rate law generally has the form:

$$\text{Rate} = k[A]^m[B]^n$$

Once we have both the rate law and the k value for a reaction, we can calculate the reaction rate for any set of concentrations.

The exponents m and n are generally small whole numbers.

These exponents are called ***reaction orders***.

Reaction Orders: The Exponents in the Rate Law

- Consider again the reaction between ammonium ions and nitrite ions:

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

Because the exponent of $[\text{NH}_4^+]$ is 1, the rate is first order in NH_4^+ .

The rate is also first order in NO_2^-

The ***overall reaction order*** is the sum of the orders with respect to each reactant represented in the rate law.

Thus in the above reaction, the overall reaction order is $1 + 1 = 2$.

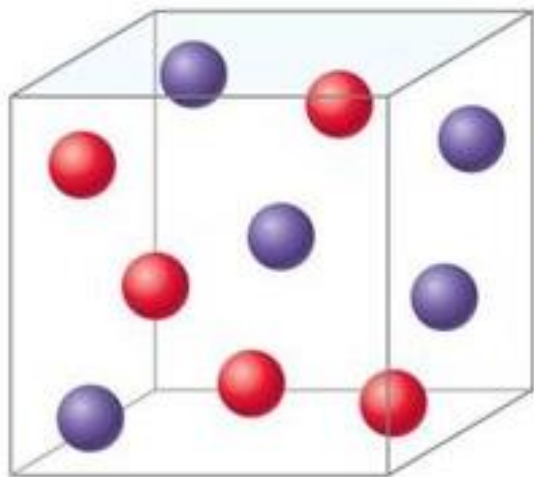
The reaction is *second order overall*.

- The exponents in a rate law indicate how the rate of reaction is affected by each reactant concentration.
- Thus the rate doubles when the $[\text{NH}_4^+]$ doubles, and triples when the $[\text{NH}_4^+]$ triples.
- Likewise for $[\text{NO}_2^-]$.
- If a rate law is second order with respect to a reactant, $[\text{A}]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple because $[2]^2 = 4$.
- Tripling the concentration causes the rate to increase ninefold: $[3]^2 = 9$.
- If the rate law is zero order with respect to a reactant, changing the concentration of that reactant has no effect on the rate of reaction.

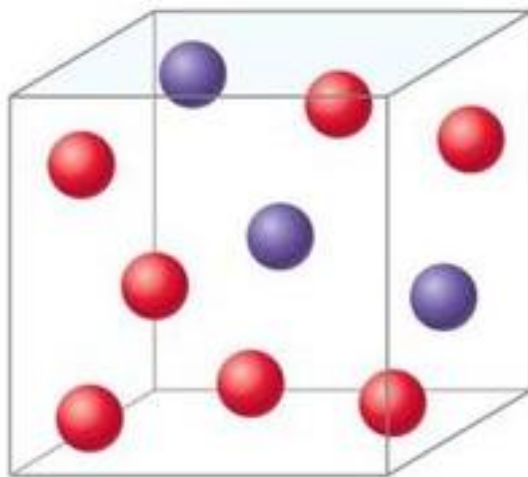
- The exponents in a rate law are not necessarily the same as the coefficients in a balanced equation.
- *For any reaction, the rate law must be determined experimentally.*
- In most rate laws, reaction orders are 0, 1, or 2. However, reaction orders can also be fractional, or even negative.

- Sample exercise:

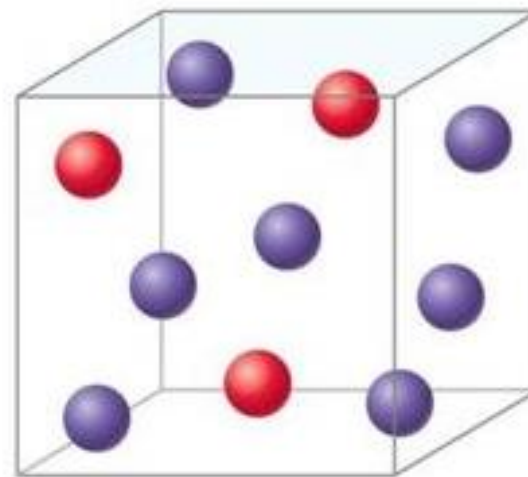
Consider a reaction $A + B \longrightarrow C$ for which the rate $= k[A][B]^2$. Each of the following boxes represents a reaction mixture in which **A** is shown as red spheres and **B** as purple ones. Rank these mixtures in order of increasing rate of reaction.



(1)



(2)



(3)

Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate: Box 1: Rate = $k(5)(5)^2 = 125k$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (box 2), and the highest is $147k$ (box 3). Thus, the rates vary in the order $2 < 1 < 3$.

- Practice exercise:

Assuming that $\text{rate} = k[A][B]$, rank the mixtures represented in the Sample Exercise in order of increasing rate.

Ans: $2 = 3 < 1$

Magnitudes and Units of Rate Constants

- In general, a large value of k (10^9 or higher) means a fast reaction, and a small value of k (10 or lower) means a slow reaction.
- The units of the rate constant depend on the overall reaction order of the rate law.
- In a reaction that is second order overall, for example, the units of rate constant must satisfy the equation:

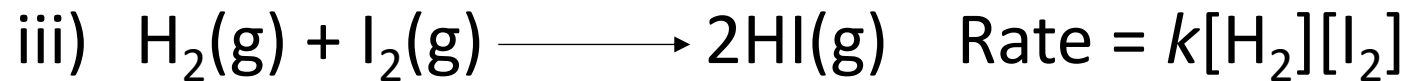
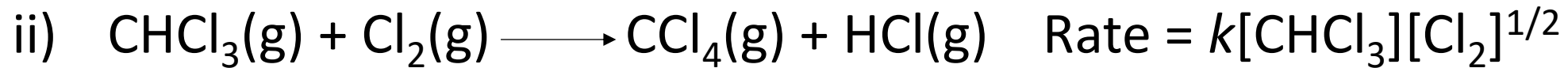
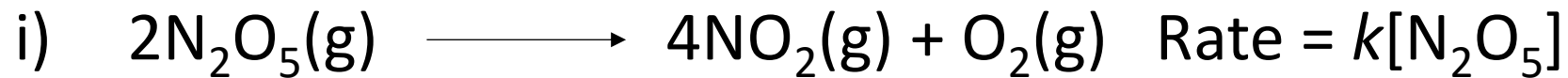
$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^2$$

Hence, we have:

$$\text{Units of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/s}{M^2} = M^{-1}s^{-1}$$

- Sample exercise:

- a) What are the overall reaction orders for the reactions described below.
- b) What are the units of the rate constant for the rate law in equations (i), (ii) and (iii).



- a) i. first order overall
ii. 1 and a half order overall
iii. Second order overall

b) i. Units of rate constant = $\frac{\text{units of rate}}{(\text{units of concentration})} = \frac{M/s}{M} = s^{-1}$

ii. Units of rate constant = $\frac{\text{units of rate}}{(\text{units of concentration})^{3/2}} = \frac{M/s}{M^{3/2}} = M^{-1/2}s^{-1}$

iii. Units of rate constant = $\frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/s}{M^2} = M^{-1}s^{-1}$

Using Initial Rates to Determine Rate Laws

Sample exercise:

The initial rate of a reaction $A + B \longrightarrow C$ was measured for several different starting concentrations of A and B, and the results are as follows:

Experiment number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine (a) the rate law for reaction, (b) the rate constant, (c) the rate of the reaction when $[A] = 0.050\text{ M}$ and $[B] = 0.100\text{ M}$.

Solve: a) comparing experiments 1 and 2, we see that when the [B] is doubled while holding [A] constant, the rate stays the same. Thus reaction is zero order with respect to B. Comparing experiments 1 and 3, the rate increases fourfold when the [A] is doubled while holding [B] constant. Thus reaction is second order in A.

$$\text{Hence, rate law} = k[A]^2[B]^0 = k[A]^2$$

b) Using rate law and data from experiment 1, we have;

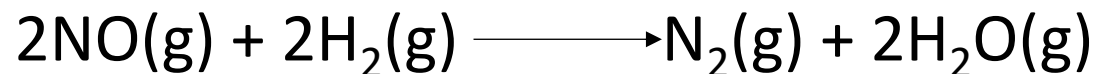
$$k = \frac{\text{rate}}{[A]^2} = \frac{4.0 \times 10^{-5} \text{ M/s}}{(0.100 \text{ M})^2} = 4.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$$

c) Using the rate law and the rate constant, we have:

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1})(0.050 \text{ M})^2 = 1.0 \times 10^{-5} \text{ M/s}$$

- Practice exercise:

The following data were measured for the reaction of nitric oxide with hydrogen:



Experiment number	[NO] (M)	[H ₂] (M)	Initial Rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

- Determine the rate law for this reaction.
- Calculate the rate constant.
- Calculate the rate when [NO] = 0.050 M, and [H₂] = 0.150 M.

Ans: (a) rate = $k[\text{NO}]^2[\text{H}_2]$; b) $k = 1.2 \text{ M}^{-2}\text{s}^{-1}$, c) rate = $4.5 \times 10^{-4} \text{ M/s}$

The Change of Concentration With Time

- **First-Order Reactions**

- A first-order reaction is one whose rate depends on the concentration of a single reactant raised to the first power, i.e;

$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]$$

- Using an operation called integration, this relationship can be transformed into an equation that relates the initial concentration of A, $[A]_0$, to its concentration at any other time t , $[A]_t$:

$$\ln[A]_t - \ln[A]_0 = -kt \quad \text{or} \quad \ln \frac{[A]_t}{[A]_0} = -kt$$

- The function 'ln' is the natural logarithm.

- The equation can also be rearranged to:

$$\ln[A]_t = -kt + \ln[A]_0$$

- Given any three of the following quantities, we can solve for the fourth: k , t , $[A]_0$, and $[A]_t$.

- Thus, you can use these equations to determine:

- 1) the concentration of a reactant remaining at any time after the reaction has started,
- 2) the time interval required for a given fraction of a sample to react, or
- 3) the time interval required for a reactant concentration to fall to a certain level.

- Sample exercise: Using the Integrated First-Order Rate Law

The decomposition of a certain insecticide in water at 12 °C follows first-order kinetics with a rate constant of 1.45 yr^{-1} . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$. Assume that the average temperature of the lake is 12 °C.

- a) What is the concentration of the insecticide on June 1 of the following year?
- b) How long will it take for the insecticide concentration to decrease to $3.0 \times 10^{-7} \text{ g/cm}^3$?

We have: $\ln[A]_t = -kt + \ln[A]_0$

Where $t = 1.00 \text{ yr}$, $k = 1.45 \text{ yr}^{-1}$, and $[A]_0 = 5.0 \times 10^{-7} \text{ g/cm}^3$

Substituting into the equation:

$$\begin{aligned}\ln[insecticide]_{t=1yr} &= -(1.45 \text{ yr}^{-1})(1.00 \text{ yr}) + \ln(5.0 \times 10^{-7}) \\ \ln[insecticide]_{t=1yr} &= -1.45 + (-14.51) = -15.96 \\ [insecticide]_{t=1yr} &= e^{-15.96} = 1.2 \times 10^{-7} \text{ g/cm}^3.\end{aligned}$$

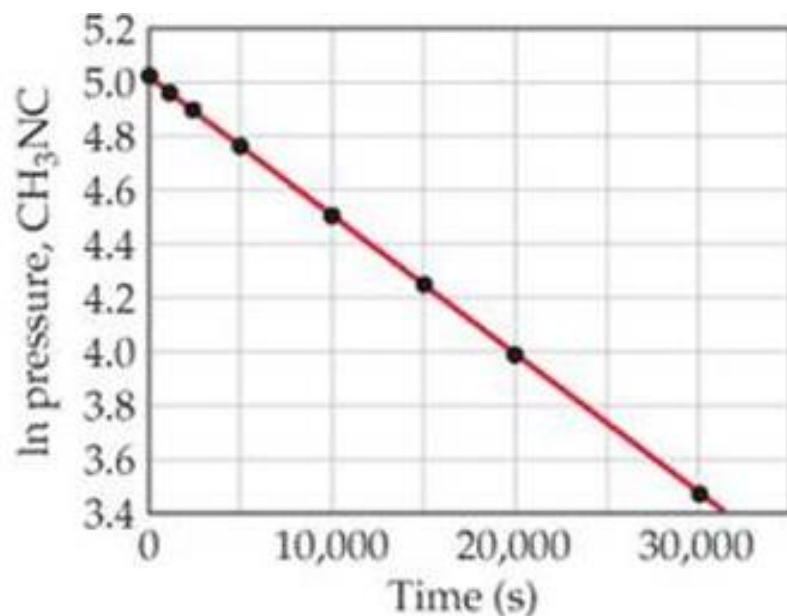
$$\begin{aligned}\text{b) } \ln(3.0 \times 10^{-7}) &= -(1.45 \text{ yr}^{-1})(t) + \ln(5.0 \times 10^{-7}) \\ t &= - [\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})] / 1.45 \text{ yr}^{-1} \\ &= - (-15.02 + 14.51) / 1.45 \text{ yr}^{-1} = 0.35 \text{ yr}\end{aligned}$$

- For a first-order reaction, a graph of $\ln[A]_t$ versus time gives a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$.

$$\ln[A]_t = -kt + \ln[A]_0$$

$$y = mx + c$$

- A reaction that is not first-order will not yield a straight line.



For example, for the conversion of methyl isonitrile (CH_3NC) to its isomer acetonitrile (CH_3CN), a plot of **ln pressure of CH_3NC over time** yields a straight line, indicating that the reaction is a first-order process.

- **Second-Order Reactions**

- A second-order reaction is one whose rate depends either on a reactant concentration raised to the second power, or on the concentrations of two reactants each raised to the first power.
- Let's assume that $\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]^2$
- The integrated rate law: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
- This equation also has the format for a straight line graph.
- If a reaction is second-order, a plot of $1/[A]_t$ versus t yields a straight line with a slope k and y-intercept $1/[A]_0$.
- Half life of a second-order reaction: $t_{1/2} = \frac{1}{k_r[A]_0}$

- **Zero-Order Reactions**

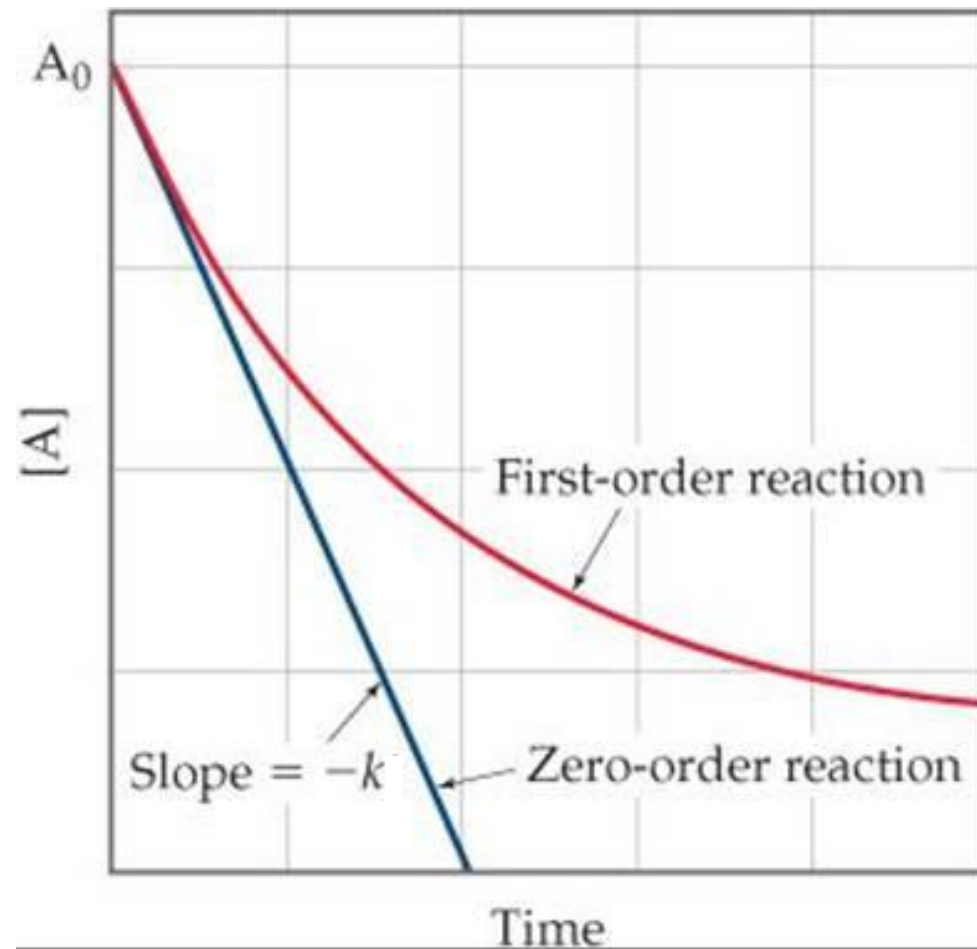
- A zero-order reaction is one in which the rate of disappearance of A is independent of [A].
- The rate law for a zero-order reaction is:

$$\text{rate} = - \frac{\Delta[A]}{\Delta t} = k$$

- The integrated rate law for a zero-order reaction is:

$$[A]_t = -kt + [A]_0$$

This is the equation for a straight line with vertical intercept $[A]_0$ and slope $-k$.



Comparison of first-order and zero-order reactions for the disappearance of reactant A with time.

- **Half-Life**

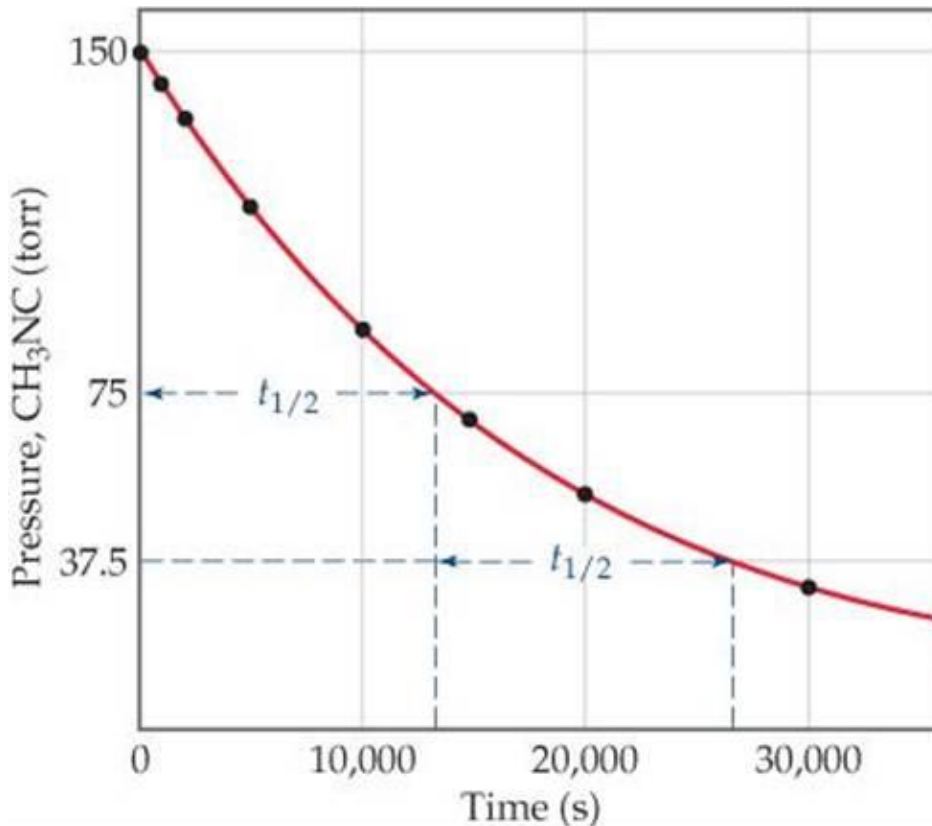
- The half-life of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to reach half of its initial value, $[A]_{t_{1/2}} = \frac{1}{2} [A]_0$

- A fast reaction has a short half-life.
- The half-life for a first-order reaction is calculated as:

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

- Thus, $t_{1/2}$ for a first-order reaction does not depend on the initial concentration of any reactant.

- If, for example, the concentration of a reactant is 0.120 M at some instant in the reaction, it will be $0.5(0.120\text{ M}) = 0.060\text{ M}$ after one half-life.
- After one more half-life passes, the concentration will drop to 0.030 M , and so on.



*In a first-order reaction, the concentration of the reactant decreases by **one-half** in each of a series of regularly spaced time-intervals, each interval equal to $t_{1/2}$.*

- The half-life of second-order reactions and other reactions depends on reactant concentrations, and therefore changes as the reaction progresses.

- Half-life for a second-order reaction is calculated as:

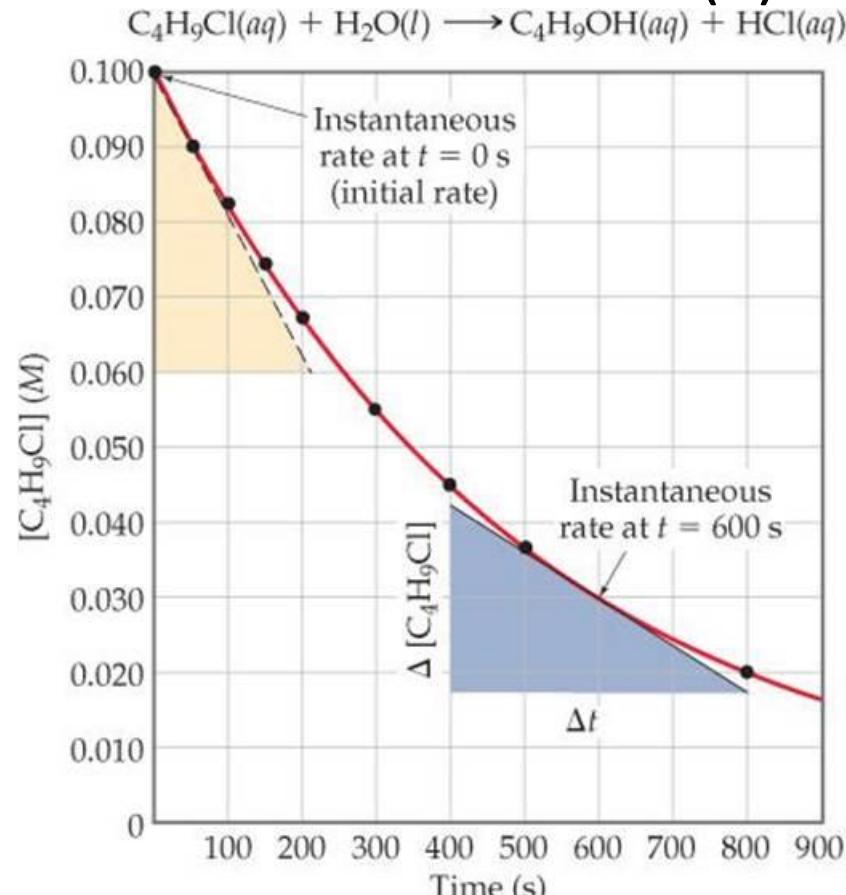
$$t_{1/2} = \frac{1}{k[A]_0}$$

- Thus, the lower the initial concentration of reactant, the longer the half-life.

- Sample exercise:

The reaction of $\text{C}_4\text{H}_9\text{Cl}$ with water is a first-order reaction.

- Use the graph below to estimate the half-life for this reaction.
- Use the half-life from (a) to calculate the rate constant.



- a) From the graph, we see that the initial value of $[\text{C}_4\text{H}_9\text{Cl}]$ is 0.100 M . The half-life is the time required for $[\text{C}_4\text{H}_9\text{Cl}]$ to decrease to 0.050 M , which we can read off the graph. This point occurs at approximately 340 s .
- b) Solving for k , we have:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340\text{ s}} = 2.0 \times 10^{-3}\text{ s}^{-1}$$

- Practice exercise:
 - a) Calculate $t_{1/2}$ for the decomposition of the insecticide described in the previous sample exercise.
 - b) How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Ans: a) 0.478 yr

b) it takes two half-lives, $2(0.478 \text{ yr}) = 0.956 \text{ yr}$