CHEMICAL KINETICS: ORDER, MOLECULARITY, RATE LAWS, AND REACTION MECHANISMS

1. CONCEPT OF ORDER AND MOLECULARITY

Molecularity: Refers to the number of reactant molecules involved in an **elementary step** of a reaction mechanism. It is a theoretical concept, determined by the reaction stoichiometry for that specific elementary step, and must be an integer (1, 2, or 3). For a single elementary step, like A + B -> Products, the molecularity is 2.

Order of Reaction: Is determined **experimentally** from the rate law. It describes how the rate of a reaction depends on the concentration of reactants. The order can be zero, fractional, or an integer.

Key Differences:

- Molecularity applies to elementary steps, while order applies to the overall reaction.
- Molecularity is theoretical and always an integer, while order is experimental and can be any real number.
- For a single-step (elementary) reaction, the order is equal to its molecularity. For multi-step reactions, the overall order is determined by the rate-determining step, and it may not match the molecularity of any single step.

2. RATE LAWS FOR ZERO, 1ST, 2ND, AND N-TH ORDER REACTIONS

For a general reaction: aA + bB -> Products

The experimentally determined rate law is typically of the form: **Rate = $k[A]^x[B]^y$**

Where:

- **k** is the rate constant.
- **x** and **y** are the partial orders with respect to reactants A and B, respectively.
- The **overall order** of the reaction is the sum of the partial orders ($n = x + y$).

Zero-Order Reaction (n=0)

- Rate Law: **Rate = k** (Rate is independent of reactant concentrations).
- Integrated Rate Law: $[A]_t = [A]_0 - kt$
- Half-life: $t_{1/2} = [A]_0 / (2k)$

First-Order Reaction (n=1)

- Rate Law: **Rate = k[A]**
- Integrated Rate Law: $\ln[A]_t = \ln[A]_0 - kt$ or $[A]_t = [A]_0 e^{-kt}$
- Half-life: $t_{1/2} = \ln(2) / k \approx 0.693 / k$ (Independent of initial concentration)

Second-Order Reaction (n=2)

- Rate Law: **Rate =** $k[A]^2$ (or Rate = k[A][B] if order with respect to A and B are both 1)
- Integrated Rate Law (for Rate = $k[A]^2$): $1/[A]_t = 1/[A]_0 + kt$
- Half-life (for Rate = $k[A]^2$): $t_{1/2} = 1 / (k[A]_0)$

n-th Order Reaction

- Rate Law: **Rate =** $k[A]^n$
- Integrated Rate Law (for $n \neq 1$): $1/[A]_t^{(n-1)} = 1/[A]_0^{(n-1)} + (n-1)kt$
- Half-life (for $n \neq 1$): $t_{1/2} = (2^{(n-1)} - 1) / ((n-1)k[A]_0^{(n-1)})$

Units of Rate Constant (k):

Order (n)	Units of k
0	$M\ s^{-1}$
1	s^{-1}
2	$M^{-1}\ s^{-1}$
n	$M^{(1-n)}\ s^{-1}$

3. DETERMINATION OF ORDER OF A REACTION

a) Differential Method

By varying the initial concentration of one reactant and measuring the initial rate, one can determine the order. For a reaction Rate = $k[A]^x$:

$\text{Rate}_1 = k[A]_1^x$

$\text{Rate}_2 = k[A]_2^x$

Taking the ratio: $\mathbf{Rate_2 / Rate_1 = ([A]_2 / [A]_1)^x}$. Solving for x, often using logarithms.

b) Half-life Method

This method uses the relationship between half-life ($t_{1/2}$) and initial concentration ($[A]_0$). From the half-life equations derived earlier:

$t_{1/2} \propto 1/[A]_0^{(n-1)}$

By comparing half-lives at different initial concentrations, the order 'n' can be determined.

4. RATE DETERMINING STEP (RDS) AND STEADY STATE APPROXIMATION (SSA)

Rate Determining Step (RDS): In a multi-step reaction mechanism, the overall rate of the reaction is limited by the slowest step, which is called the rate-determining step.

Steady State Approximation (SSA): For reactive intermediates (species formed and consumed during the reaction), we assume their concentration remains approximately constant (steady state) throughout most of the reaction. This means the rate of formation of the intermediate is equal to its rate of consumption. This approximation simplifies the derivation of rate laws for complex reactions.

5. OPPOSING, CONSECUTIVE, AND PARALLEL REACTIONS (FIRST ORDER STEPS ONLY)

a) Opposing Reactions

Consider A ↔ B. The net rate is the difference between the forward and reverse rates. If both are first order:

Rate = $k_f[A] - k_r[B]$

At equilibrium, Rate = 0, so $k_f[A]_{eq} = k_r[B]_{eq}$, leading to the equilibrium constant $K_{eq} = k_f/k_r$.

b) Consecutive Reactions

A → B → C. Both steps are first order with rate constants k_1 and k_2 respectively.

Rate of formation of B: $d[B]/dt = k_1[A] - k_2[B]$

Rate of formation of C: $d[C]/dt = k_2[B]$

The concentration of B will rise and then fall. The time at which [B] is maximum depends on the ratio k_1/k_2.

c) Parallel Reactions

A → B (rate constant k_1) and A → C (rate constant k_2). Both are first order with respect to A.

Overall rate of disappearance of A = $(k_1 + k_2)[A]$

The ratio of products formed is determined by the ratio of rate constants: $[B]/[C] = k_1/k_2$.

6. TEMPERATURE DEPENDENCE OF RATE CONSTANT AND ARRHENIUS EQUATION

The rate of most chemical reactions increases significantly with temperature.

The **Arrhenius Equation** quantitatively relates the rate constant (k) to temperature (T):

$$\mathbf{k = A\, e^{-E_a/RT}}$$

Where:

- **k** is the rate constant.
- **A** is the **pre-exponential factor** or frequency factor (related to the frequency of collisions and their orientation).
- **E_a** is the **activation energy** (the minimum energy required for a reaction to occur, typically in J/mol or kJ/mol).
- **R** is the ideal gas constant (8.314 J/mol·K).
- **T** is the absolute temperature (in Kelvin).

The linearized form of the Arrhenius equation is useful for graphical determination of E_a and A:

$\ln(k) = \ln(A) - E_a / (RT)$

This is in the form of $y = mx + c$, where $y = \ln(k)$, $x = 1/T$, $m = -E_a/R$, and $c = \ln(A)$.

For two different temperatures (T_1 and T_2) and their corresponding rate constants (k_1 and k_2):

$\ln(k_2 / k_1) = (E_a / R) * (1/T_1 - 1/T_2)$

NUMERICAL PROBLEMS

Problem 1: Order and Rate Law

For the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, initial rate data are given:

Experiment	[NO] (M)	$[O_2]$ (M)	Initial Rate (M/s)
1	0.010	0.010	2.5×10^{-5}
2	0.020	0.010	10.0×10^{-5}
3	0.010	0.020	5.0×10^{-5}

Determine:

1. The rate law for the reaction.
2. The overall order of the reaction.
3. The rate constant, k, with correct units.
4. The initial rate when [NO] = 0.015 M and $[O_2]$ = 0.015 M.

Hint: Use ratios of rates from different experiments to find partial orders.

Problem 2: First-Order Reaction - Integrated Rate Law

The decomposition of N_2O_5 is a first-order reaction: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. At 45°C, the rate constant is $k = 3.7 \times 10^{-3}\ s^{-1}$.

If the initial concentration of N_2O_5 is 0.10 M, what is its concentration after 5.0 minutes?

Hint: Use the integrated rate law for a first-order reaction.

Problem 3: First-Order Reaction - Half-life

For the decomposition of N_2O_5 at 45°C, $k = 3.7 \times 10^{-3}\ s^{-1}$.

Calculate the half-life of this reaction.

Hint: Use the half-life formula for a first-order reaction.

Problem 4: Second-Order Reaction - Rate Constant

The reaction between NO and Cl_2 is: $NO(g) + Cl_2(g) \rightarrow NOCl(g) + Cl(g)$. It is found to be second order overall and first order with respect to both NO and Cl_2. The rate law is $\text{Rate} = k[NO][Cl_2]$.

In one experiment, $[NO] = 0.050$ M and $[Cl_2] = 0.030$ M, and the rate was measured to be 1.1×10^{-3} M/s.

Calculate the rate constant, k.

Hint: Rearrange the rate law to solve for k.

Problem 5: Arrhenius Equation

The rate constant for a particular reaction is $0.050\ s^{-1}$ at 25°C and $0.15\ s^{-1}$ at 40°C.

Calculate:

1. The activation energy (E_a) for the reaction in kJ/mol.
2. The pre-exponential factor (A).

Hint: Use the two-point form of the Arrhenius equation to find E_a first. Then use one of the data points and the calculated E_a to find A.