1 Calculating Rate of Reaction

The rate of reaction for a reaction of the form:

$$a\,A + b\,B \rightarrow \text{Products}$$

is calculated as:

$$\text{Rate} = k \cdot [A]^a \cdot [B]^b$$

where: - k is the rate coefficient (from the modified Arrhenius equation). - $[A], [B]$ are the number densities of the reactants. - The exponents a and b are the stoichiometric coefficients of the reactants.

1.1 Key Assumptions & Simplifications

- Elementary Reactions: Assumption: The reaction occurs in a single step (no intermediates). Justification: For elementary reactions, the reaction order equals the stoichiometric coefficient (from collision theory). Example:
$$2\,OH \rightarrow H_2O + O \quad \Rightarrow \quad \text{Rate} = k[OH]^2$$
- Irreversible Reactions: Assumption: The reverse reaction is negligible. Justification: Simplifies rate laws by ignoring product concentrations. Can do as we treat the forward and backward as separate reactions.
- No Third-Body Dependence: Assumption: Reactions like $H_2 + M \rightarrow 2H + M$ are treated as elementary (ignoring $[M]$ if it's in excess). Justification: In high-pressure systems, $[M]$ is constant and folded into k.
- No Fractional/Complex Orders: Assumption: Orders are integers matching stoichiometry. Limitation: Non-elementary reactions (e.g., chain mechanisms) may have fractional orders. If empirical data is unavailable, this is the best guess.

1.2 When Assumptions Break Down

- Third-Body Reactions: If M is not in excess, explicitly include $[M]$ in the rate law:
$$\text{Rate} = k[H_2][M]$$
- Non-Elementary Reactions: For complex mechanisms (e.g., combustion), use measured orders or mechanistic approximations (e.g., steady-state analysis).

Also assumed pressure-independent reactions.