Chemical Kinetics Formula Sheet

Rate of Reaction

1. **Rate of Reaction Definitions**
    - Average rate = $-\Delta[R]/\Delta t = +\Delta[P]/\Delta t$
    - Instantaneous rate = $-d[R]/dt = +d[P]/dt$
    - Rate = $k[A]^a[B]^b[C]^c$ (Rate law)
    - Units of rate = mol L^{-1} s^{-1}
2. **Reaction Rate Relations**
    - For reaction: $aA + bB \rightarrow cC + dD$
    - Rate = $-(1/a)(d[A]/dt) = -(1/b)(d[B]/dt) = (1/c)(d[C]/dt) = (1/d)(d[D]/dt)$

Rate Constants

1. **Units of Rate Constant (k)**
    - For zero order: mol L^{-1} s^{-1}
    - For first order: s^{-1}
    - For second order: L mol^{-1} s^{-1}
    - General: (mol/L)^(1-n) s^{-1} (where n is order)
2. **Arrhenius Equation**
    - $k = Ae^{(-Ea/RT)}$
    - $\ln k = \ln A - Ea/RT$
    - $\log k = \log A - Ea/2.303RT$
    - $k_2/k_1 = e^{[-(Ea/R)(1/T_2 - 1/T_1)]}$

Integrated Rate Laws

1. **Zero Order Reaction**
    - $[A]t = [A]_0 - kt$
    - $t_1/_2 = [A]_0/2k$
    - Graph: [A] vs t is linear with slope = -k
2. **First Order Reaction**
    - $\ln[A]t = \ln[A]_0 - kt$
    - $[A]t = [A]_0e^{-kt}$
    - $t_1/_2 = 0.693/k$ (ln 2/k)
    - Graph: ln[A] vs t is linear with slope = -k
3. **Second Order Reaction**
    - $1/[A]t = 1/[A]_0 + kt$
    - $t_1/_2 = 1/k[A]_0$
    - Graph: 1/[A] vs t is linear with slope = k

Half-Life Relations

1. **General Half-Life Formula**
   - For nth order: $t_1/_2 \propto [A]_0$^(n-1)
   - For zero order: $t_1/_2 \propto [A]_0$
   - For first order: $t_1/_2$ is constant
   - For second order: $t_1/_2 \propto 1/[A]_0$

Complex Reactions

1. **Parallel Reactions**
   - Total rate = $k_1[A] + k_2[A]$
   - keff = $k_1 + k_2$
2. **Consecutive Reactions**
   - A → B → C
   - Rate of formation of B = $k_1[A] - k_2[B]$
   - Rate of formation of C = $k_2[B]$
3. **Opposing Reactions**
   - For $A \rightleftharpoons B$
   - At equilibrium: $k_1[A]eq = k_2[B]eq$
   - Keq = k_1/k_2

Temperature Dependence

1. **Temperature Coefficient**
   - $\gamma = k_2/k_1$ for $\Delta T = 10°C$
   - Usually between 2 to 3 for most reactions
2. **Activation Energy Relations**
   - ΔH = Ea - RT (for exothermic)
   - ΔH = Ea + RT (for endothermic)
   - Ea(forward) - Ea(backward) = ΔH

Collision Theory

1. **Rate Expression**
   - Rate = ZPe^(-Ea/RT)
   - Z = Collision frequency
   - P = Steric factor
   - e^(-Ea/RT) = Boltzmann factor

Pseudo First Order Reactions

- When [B] >> [A], Rate = k[A]^1[B]^1 becomes Rate = k'[A]^1
- Where k' = k[B] (k' is pseudo first order rate constant)

Important Points for JEE Advanced

1. **Steady State Approximation**
   - Rate of formation = Rate of consumption
   - Used for intermediate species in complex reactions
2. **Effect of Catalyst**
   - Decreases Ea equally for forward and backward reactions
   - Does not affect ΔH or equilibrium constant
   - Provides alternate reaction pathway
3. **Surface Area Effects**
   - Rate ∝ Surface area (for heterogeneous catalysis)
   - Important for solid-gas and solid-liquid reactions
4. **Important Relations**
   - Slope of ln k vs 1/T plot = -Ea/R
   - Slope of log k vs 1/T plot = -Ea/2.303R
   - For every 10°C rise in temperature, rate approximately doubles
   - $\ln(k_2/k_1) = -(Ea/R)(1/T_2 - 1/T_1)$
5. **Temperature Coefficient**
   - Temperature coefficient (γ) = k_2/k_1 (for ΔT = 10°C)
   - For most reactions: $2 < \gamma < 3$
   - Higher Ea → Higher temperature coefficient

Catalysis and Catalysts

1. **Effect on Reaction Parameters**
   - Decreases activation energy (Ea)
   - Provides alternate reaction pathway
   - Does not change:
     - ΔH (enthalpy of reaction)
     - ΔG (Gibbs free energy)
     - Equilibrium constant (K)
     - Position of equilibrium
     - Final composition of mixture
2. **Types of Catalysis**
   - **Homogeneous Catalysis**
     - Catalyst in same phase as reactants
     - Example: NO in oxidation of SO_2
     - Rate ∝ [Catalyst]
   - **Heterogeneous Catalysis**
     - Catalyst in different phase from reactants
     - Rate ∝ Surface area of catalyst
     - Examples: Pt in Contact Process, Fe in Haber Process
3. **Catalyst Characteristics**
   - **Activity**
     - Measured by % conversion
     - Depends on strength of intermediate complex
   - **Selectivity**

        - Ability to direct reaction to desired products
        - Example: Ni in hydrogenation of alkynes vs alkenes

4. **Catalyst Poisoning**
    - Deactivation of catalyst by impurities
    - Common poisons: As, Pb, CO (for Pt catalysts)
    - Prevention requires pure reactants
5. **Promoters**
    - Substances that increase catalyst activity
    - Example: Mo in Fe catalyst for Haber process
    - Small quantities significantly enhance activity
6. **Energy Profile Diagrams**
    - Shows lower Ea path with catalyst
    - Multiple peaks possible for multi-step mechanisms
    - Energy of reactants and products unchanged