

# rates of reaction

## collision theory

**conditions for rxn:** collide + sufficient  $E_a$  + correct orientation

**catalyst:**

- increases rate via **lower  $E_a$  path**
- participates but **not altered** by rxn
- does **not appear** in overall rxn
- does **NOT** change equilibrium

**factors affecting rxn rate:**

- concentration of reactants
- temperature
- presence of **catalysts**
- physical nature of reactants

$E_p$  **diagrams:** enthalpy of reactants and products are **FIXED** regardless of catalyst presence.

## reaction rates

must be determined **experimentally**

rxn rate can get the rate of change of single species using **mole ratio**

$$\dot{R} = -\frac{\dot{R}_A}{a} \implies \dot{R}_A = -a \times \dot{R}$$

unit:  $M/s$  ( $\frac{mol}{L \cdot s}$ )

**positive 4 products, negative 4 reactants**

## rate laws

relates rate to **concentration** of reactants

## differential

for  $aA + bB \rightarrow$  products:

$$\dot{R} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = k[A]^m[B]^n$$

- $m$ : order w.r.t. A ;  $n$ : order w.r.t. B
- $m + n$ : overall order
- $k$ : rate constant (only changes with T)

**note:** exponents  $\neq$  coefficients

## integrated & half-life

for  $aA \rightarrow$  products:

**zero-order:**

- $[A] = -akt + [A]_0$
- unit of  $k$ :  $M/s$

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

**first-order:**

- $\ln[A] = -akt + \ln[A]_0$
- unit of  $k$ :  $1/s$

$$t_{1/2} = \frac{\ln 2}{ak}$$

**second-order:**

- $\frac{1}{[A]} = akt + \frac{1}{[A]_0}$

- unit of  $k$ :  $1/(M \cdot s)$

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

**n-order ( $n \neq 1$ ):**

$$\frac{1}{[A]^{n-1}} = (n-1)akt + \frac{1}{[A]_0^{n-1}}$$

- unit of  $k$ :  $\frac{1}{M^{n-1} \cdot s}$

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

## arrhenius equation

**two-point form:**

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

- $R$  is (8.314 J/(mol · K))

# phase equilibrium

## phase transitions & vapour pressure

**phase:** region where state of aggregation and chemical composition are uniform. **note:** phase  $\neq$  state of matter

**phase transition:** matter changes from one phase to another due to temperature/pressure changes

**vaporization:** molecules pass from liquid surface to vapour state

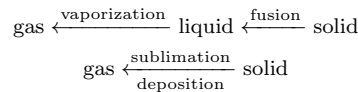
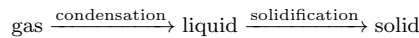
**condensation:** molecules pass from vapour to liquid state

**enthalpy of vaporization:**

$$\Delta H_{\text{vap}} = H_{\text{vapour}} - H_{\text{liquid}} = -\Delta H_{\text{condensation}}$$

stronger intermolecular forces  $\rightarrow$  higher  $\Delta H_{\text{vap}}$

**phase change relationships:**



$$\Delta H_{\text{fus}} + \Delta H_{\text{vap}} = \Delta H_{\text{sub}}$$

**phase equilibrium:** no net conversion between phases. at equilibrium: vaporization rate = condensation rate

**vapour pressure:** pressure at equilibrium. weak intermolecular forces  $\rightarrow$  high vapour pressure (volatile). strong intermolecular forces  $\rightarrow$  low vapour pressure (non-volatile)

$$P_{\text{vap}} = f(T, \text{type of liquid})$$

**evaporation vs. boiling:**

- evaporation: at surface, any temperature
- boiling: throughout liquid, specific temperature where  $P_{\text{vap}} = P_{\text{atm}}$

**boiling point:** temperature where  $P_{\text{vap}}(T_{\text{bp}}) = P$ . normal boiling point:  $P_{\text{vap}} = 1$  atm

higher molecular mass  $\rightarrow$  higher polarizability  $\rightarrow$  stronger IMF  $\rightarrow$  higher bp. exceptions:  $\text{H}_2\text{O}$ , HF,  $\text{NH}_3$  (hydrogen bonding)

## clausius-clapeyron equation

$$\ln P = -A \left( \frac{1}{T} \right) + B$$

where  $A = \frac{\Delta H_{\text{vap}}}{R}$ ,  $R = 8.314 \text{ J/(mol}\cdot\text{K)}$

**two-point form:**

$$\ln \left( \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} \right) = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

plot  $\ln P_{\text{vap}}$  vs.  $\frac{1}{T}$ : slope =  $-\frac{\Delta H_{\text{vap}}}{R}$

**relative humidity:**

$$\%RH = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^{\text{vap}}(T)} \times 100\%$$

**dew point:** temperature where humid air reaches saturation

## phase diagrams

**phase diagram:** shows regions where phases are in equilibrium (T vs. P)

**critical point:** no phase boundary between liquid/vapour,  $\Delta H_{\text{vap}} = 0$ , above critical T only gas exists

**supercritical fluid:** properties of both gas and liquid (e.g., supercritical  $\text{CO}_2$  for decaffeinated coffee)

**triple point:** solid, liquid, gas coexist

## henry's law & raoult's law

**solution:** homogeneous mixture. solvent: largest amount. solute: smaller amount

**concentrations:**

- mole fraction:  $x_i = \frac{n_i}{\sum n_j}$
- molarity:  $M = \frac{\text{moles solute}}{\text{L solution}}$  (temp dependent)
- molality:  $m = \frac{\text{moles solute}}{\text{kg solvent}}$

**ideal solution:**  $\Delta H_{\text{soln}} = 0$ , similar forces between all components

**nonideal solution:**  $\Delta H_{\text{soln}} \neq 0$

**henry's law:** gas solubility increases with pressure

$$P_A = H_A x_A \quad \text{or} \quad C_A = k_A P_A$$

where  $H_A$  or  $k_A$  = henry's constant (depends on solute/solvent pair and temperature)

**raoult's law:** solute lowers vapour pressure of solvent

$$P_A = x_A P_A^{\text{vap}}$$

for binary ideal solution:

$$P_{\text{total}} = x_A P_A^{\text{vap}} + x_B P_B^{\text{vap}}$$

applies to ideal solutions or dilute solutions ( $x_{\text{soln}} > 0.98$ )

**deviations:**

- positive:  $P_{\text{total}} > P_{\text{ideal}}$  (weaker unlike interactions)
- negative:  $P_{\text{total}} < P_{\text{ideal}}$  (stronger unlike interactions)

## colligative properties

depend on ratio of solute particles to solvent molecules: (1) vapour pressure lowering, (2) boiling point elevation, (3) freezing point depression, (4) osmotic pressure

$$\Delta P_{\text{solvent}} = -x_{\text{solute}} P_{\text{solvent}}^{\text{vap}}$$

$$\Delta T_{\text{bp}} = i K_b m \quad \Delta T_{\text{fp}} = -i K_f m$$

**van't hoff factor  $i$ :** particles per formula unit. min:  $i = 1$ ; max: number of ions ( $\text{NaCl} \rightarrow 2$ ,  $\text{Pb}(\text{NO}_3)_2 \rightarrow 3$ ).  $i \rightarrow$  max as dilutes

# chemical equilibrium

## equilibrium constants

**chemical equilibrium:** at equilibrium, forward rate = reverse rate  
for  $aA + bB \rightleftharpoons cC + dD$ :

**equilibrium constant  $K_c$ :**

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where  $[ ]$  = equilibrium concentration in mol/L.  
 $K_c$  is constant at given temperature, independent of initial concentrations

**equilibrium constant  $K_P$ :**

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

partial pressures at equilibrium, use units of bar.  $K_P$  is constant at given temperature

**relationship:**

$$K_P = K_c(RT)^{\Delta n} \quad \text{where} \quad \Delta n = (c+d) - (a+b)$$

$$R = 0.08314 \text{ L}\cdot\text{bar}/(\text{mol}\cdot\text{K})$$

**heterogeneous reactions:** pure liquids and solids are **not included** in equilibrium constant expressions

**magnitude of  $K$ :**

- $K > 10^{10}$ : reaction goes to completion
- $K < 10^{-10}$ : reaction does not occur forward
- $10^{-10} < K < 10^{10}$ : equilibrium calculation needed

## properties of equilibrium constants

- multiply reaction by constant  $\rightarrow$  raise  $K$  to that power
- reverse reaction:  $K_{\text{reverse}} = \frac{1}{K_{\text{forward}}}$
- add reactions: multiply equilibrium constants

## reaction quotient & direction

**reaction quotient  $Q$ :**

$$Q_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad Q_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

calculated same as  $K$  but system doesn't need to be at equilibrium

**direction of change:**

- $Q_c < K_c$ : reactants in excess, forward reaction
- $Q_c = K_c$ : at equilibrium
- $Q_c > K_c$ : products in excess, reverse reaction

## le chatelier's principle

system responds to change by attaining new equilibrium that partially offsets the change  
**change in concentration:**

- add reactant:  $Q_c < K_c$ , forward reaction, more products
- add product:  $Q_c > K_c$ , reverse reaction, more reactants

**change in volume:** reduce volume  $\rightarrow$  shifts towards side with fewer gas molecules. effect negligible for condensed phases

**change in pressure:**

- add/remove gas: affects equilibrium
- change volume: affects equilibrium if gas present
- add inert gas at constant volume: no effect (partial pressures unchanged)

**change in temperature:**

- endothermic ( $\Delta H > 0$ ):  $T \uparrow \rightarrow K \uparrow \rightarrow$  shifts to products
- exothermic ( $\Delta H < 0$ ):  $T \uparrow \rightarrow K \downarrow \rightarrow$  shifts to reactants
- reaction shifts away from "energy term" as temperature increases

**van't hoff equation:**

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

estimate  $K$  at different temperature.  
clausius-clapeyron is special case where  $K$  = vapour pressure

# electrochemistry

## oxidation states & redox reactions

**oxidation state (OS):** charge atom would have if all bonds were ionic. not measurable, conceptual tool

**rules for assigning OS:**

- free element: OS = 0
- monatomic ion: OS = charge
- sum of OS in neutral species = 0
- sum of OS in ion = charge
- H, group 1: +1; group 2: +2; halogens: -1; group 16: -2; group 15: -3

**exceptions:** H is -1 in hydrides (e.g., LiH); O is -1 in peroxides (e.g., H<sub>2</sub>O<sub>2</sub>)

**redox reactions:**

- reduction: OS decreases, gains electrons. oxidizing agent causes oxidation
- oxidation: OS increases, loses electrons. reducing agent causes reduction

**balancing redox:**

- write separate half-reactions
- balance atoms except H, O
- balance O with H<sub>2</sub>O
- balance H with H<sup>+</sup>
- balance charges with e<sup>-</sup>
- add half-reactions to cancel e<sup>-</sup>
- for basic: add OH<sup>-</sup> equal to H<sup>+</sup> to each side, simplify

## galvanic cell & faraday's law

**galvanic cell:** derives electrical energy from spontaneous redox reactions

notation: Zn(s)|Zn<sup>2+</sup>(aq)||Cu<sup>2+</sup>(aq)|Cu(s)

**anode (oxidation):** lower potential, electrons flow from anode. **cathode (reduction):** higher potential, electrons flow to cathode

**current & faraday's law:**

$$I = \frac{Q}{t} \quad \text{units: } A = C/s$$

$$Q = nF \quad n = \frac{It}{F} = \frac{It}{F}$$

where  $F = 96,485 \text{ C/mol}$  (charge of 1 mole of electrons),  $n$  = moles of electrons

**applications:** from moles of electrons, determine moles of substance produced/consumed at electrode

**current efficiency:**

$$\eta = \frac{\text{charge used}}{\text{charge supplied}} \times 100\% = \frac{\text{actual mass}}{\text{theoretical mass}} \times 100\%$$

## standard cell potential & nernst equation

**cell potential  $E_{\text{cell}}$ :** electrical potential difference (voltage) between electrodes in V (J/C)

**standard state:** 1.0 M for dissolved species, 1 bar for gases, 25°C

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

standard:  $2\text{H}^{+}(aq) + 2e^{-} \rightarrow \text{H}_2(g)$  with  $E^{\circ} = 0 \text{ V}$

**spontaneous direction:** electrons travel from low to high potential. higher  $E^{\circ}$  gets reduced (cathode).  $E_{\text{cell}}^{\circ} > 0$  for spontaneous

**nernst equation:**

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

where  $R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$ ,  $T$  = temperature (K),  $F = 96,485 \text{ C/mol}$ ,  $Q$  = reaction quotient (aq: M, gas: bar),  $n$  = electrons transferred  
**at 25°C:**

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

**concentration cell:** same material at anode and cathode. higher concentration acts as cathode

## nernst at equilibrium & electrolytic cells

**at equilibrium:**  $E_{\text{cell}} = 0$ ,  $Q = K$

$$0 = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln K$$

$$K = \exp\left(\frac{E_{\text{cell}}^{\circ} nF}{RT}\right)$$

use to determine equilibrium constants with galvanic cells

**galvanic vs. electrolytic:**

- galvanic: derives electrical energy from spontaneous redox ( $E_{\text{cell}} > 0$ )
- electrolytic: uses electrical energy to promote non-spontaneous reaction ( $E_{\text{cell}} < 0$ )

**electrochemical cells:**

- anode: always oxidation. galvanic: (-); electrolytic: (+)
- cathode: always reduction. galvanic: (+); electrolytic: (-)