rates of reaction

collision theory

conditions for reaction:

- molecules must **collide**
- molecules must collide with **sufficient energy** (activation energy E_a)
- molecules must collide in **correct orientation**

activation energy: reactant molecules must achieve E_a before reaction can occur

catalyst:

- increases rate by providing **lower activation energy path**
- participates but **not altered** by reaction
- does **not appear** in overall reaction
- avoids high temperature needed for high E_a reactions

factors affecting rate:

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

measuring reaction rates

rate of reaction $\dot{R}$: units M/s ($\frac{mol}{L \cdot s}$)

for $aA + bB \rightarrow cC + dD$:

$$\dot{R} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

instantaneous rate: $\frac{d[A]}{dt}$ = slope of tangent on $[A]$ vs. time plot

rates must be determined **experimentally**

differential rate laws

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 (function of temperature)

note: exponents $(m, n) \neq$ stoichiometric coefficients (a, b)

method of initial rates: determines instantaneous rate at beginning before concentrations change significantly

integrated rate laws

for $aA \rightarrow$ products:

zero-order:

- $[A] = -akt + [A]_0$
- plot: $[A]$ vs. time, slope $= -ak$
- units of k: M/s
- $t_{1/2} = \frac{[A]_0}{2ak}$

first-order:

- $\ln[A] = -akt + \ln[A]_0$
- plot: $\ln[A]$ vs. time, slope $= -ak$
- units of k: $1/s$
- $t_{1/2} = \frac{\ln 2}{ak}$

second-order:

- $\frac{1}{[A]} = akt + \frac{1}{[A]_0}$
- plot: $\frac{1}{[A]}$ vs. time, slope $= ak$
- units of k: $1/(M \cdot s)$
- $t_{1/2} = \frac{1}{ak[A]_0}$

arrhenius equation

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

where:

- A: pre-exponential factor
- E_a: activation energy (J/mol)
- R: gas constant (8.314 J/(mol $\cdot$ K))
- T: temperature (K)

linear form:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

plot $\ln k$ vs. $\frac{1}{T}$: slope $= -\frac{E_a}{R}$

two-point form:

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

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

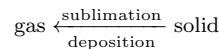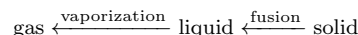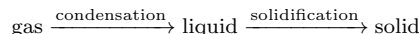**vaporization:** molecules pass from liquid surface to vapour state

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 ΔH_{vap}

phase change relationships:

$$\text{gas} \xrightarrow{\text{condensation}} \text{liquid} \xrightarrow{\text{solidification}} \text{solid}$$

$$\text{gas} \xleftarrow{\text{vaporization}} \text{liquid} \xleftarrow{\text{fusion}} \text{solid}$$

$$\text{gas} \xleftarrow[\text{deposition}]{\text{sublimation}} \text{solid}$$

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

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: H_2O, HF, NH_3 (hydrogen bonding)

clausius-clapeyron equation

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

where $A = \frac{\Delta H_{\text{vap}}}{R}$, $R = 8.314$ J/(mol·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:

$$\%RH = \frac{P_{H_2O}}{P_{H_2O}^{\text{vap}}(T)} \times 100\%$$

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 CO_2 for decaffeinated coffee)

triple point: solid, liquid, gas coexist

CO_2: triple point 5.1 atm, -56.7°C; critical point 72.9 atm, 31°C

H_2O: polymorphism (ice I, II, III, V, VI, VII); solid-liquid boundary has negative slope (ice less dense than water); triple point 0.006 atm, 0.01°C

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 ($x_{\text{solv}} > 0.98$)

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

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

$$\Delta T_{\text{bp}} = iK_b m \quad \Delta T_{\text{fp}} = -iK_f m$$

water: $K_b = 0.512$, $K_f = 1.86$ K·kg/mol. K_b, K_f depend only on solvent, m = molality

van't hoff factor i: particles per formula unit. min: $i = 1$; max: number of ions (NaCl $\rightarrow$ 2, Pb(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:
$K_P = K_c(RT)^{\Delta n}$ where $\Delta n = (c+d)-(a+b)$
$R = 0.08314$ L·bar/(mol·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_2O_2)
redox reactions:

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

balancing redox:

1. write separate half-reactions
2. balance atoms except H, O
3. balance O with H_2O
4. balance H with H^+
5. balance charges with e^-
6. add half-reactions to cancel e^-
7. for basic: add OH^- equal to H^+ to each side, simplify

galvanic cell & faraday's law

galvanic cell: derives electrical energy from spontaneous redox reactions
notation: $\text{Zn}(s)|\text{Zn}^{2+}(aq)||\text{Cu}^{2+}(aq)|\text{Cu}(s)$
anode (oxidation): lower potential, electrons flow from anode. **cathode (reduction):** higher potential, electrons flow to cathode
current & faraday's law:

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

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

where $F = 96,485$ 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_{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: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ with $E^{\circ} = 0$ V
spontaneous direction: electrons travel from low to high potential. higher E° 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 $R = 8.314$ J/(mol·K), $T = $ temperature (K), $F = 96,485$ 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: ($-$)