

pre-midterm stuff

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**

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

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 ($n \neq 1$):

- (see formula sheet)
- 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

preferably use two-point form
use $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$

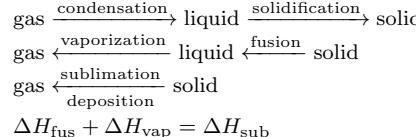
phase equilibrium

phase equilibrium

defn: rate (forward) = rate (reverse)
e.g. vapour liquid equilibrium \implies
 $r_{\text{vap}} = r_{\text{cond}}$

note: phase \neq state of matter

phase changes:



vapour pressure

vapour pressure: pressure of vapour at equilibrium
weak IMF \rightarrow lower T_{bp} \rightarrow higher vapour pressure (more volatile); and **vice versa**

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

evaporation vs. boiling:

- **evaporation:** at surface, any temperature
- **boiling:** throughout liquid, specific temperature (T_{bp})

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

normal boiling point: $P_{\text{vap}} = 1 \text{ atm}$

clausius-clapeyron equation

(see formula sheet)

relates vapour pressure to **temperature**
can be used for **ANY** phase change as long as the right enthalpy is used

non-equilibrium stuff (humidity/saturation)

$$\% \text{ saturation} = \frac{P_A}{P_A^{\text{vap}}(T)} \times 100\%$$

dew point T_{dp} : temperature where humid air reaches saturation
condensation occurs at **100 % saturation**
humidity refers specifically to H_2O

phase diagrams

can be used to get the vapour pressure at a temperature (using the equilibrium lines)

triple point: solid, liquid, gas coexist \rightarrow there can be multiple triple points, but only one is solid-liquid-gas equilibrium

equilibrium line: 2 phases in equilibrium

critical point: point where substance becomes supercritical fluid

supercritical fluid: neither liquid nor gas, but having properties of both

polymorphism: existence of solid in more than one form

note: a substance can phase change at multiple different temperatures or pressures, but at a given P (T), it phase changes at the corresponding T (P).

henry's law

essentially: gas **solubility** in liquid increases with increasing **pressure**

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

use $P_A = H_A x_A$ when constants have units of **pressure**, and working with **mole fractions**

use $C_A = H_A x_A$ when constants have units of **pressure & concentration**, and working with **concentrations**

raoult's law

essentially: adding solute **lowers** the vapour pressure of solvent

$P_A = x_A P_A^{\text{vap}}$ \rightarrow use this if u are given vapour pressures

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

solute and solvent both in vapour and in solution

deviations: positive if total pressure is greater than each individual pure vapour pressure (and vice versa)

colligative properties

defn: properties of solutions that depend on the **RATIO** of solute particles to solvent molecules (NOT type of solute)

vapour pressure lowering

we can use vapour pressure to estimate the **molar mass** of an unknown solid dissolved in a known liquid

$$M_{\text{solid}} = -\frac{M_{\text{liquid}} m_{\text{solid}}}{m_{\text{liquid}}} \left(\frac{P_{\text{liquid}}^{\text{vap}}}{\Delta P_{\text{liquid}}} + 1 \right)$$

b.p. elevation & f.p. depression

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

m is the solute **MOLALITY** (moles solute/kg solvent)!

K_b and K_f are constants, dependent on the **solvent** only

van't hoff factor $i \rightarrow$ for ionic compounds

$i_{\text{min}} = 1$ (pure solid/liquid, no dissociation)

$i_{\text{max}} = \# \text{ of ions}$ (complete dissociation), e.g. 2 for NaCl

$$\% \text{ dissociation} = \frac{i - 1}{i_{\text{max}} - 1} \times 100\%$$

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:

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

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

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_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: $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$

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

current & faraday's law:

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

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

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_{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 $E^\circ = 0 \text{ V}$

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 $R = 8.314 \text{ J/(mol}\cdot\text{K)}$, $T =$ 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: (-)