

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**

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

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 ($n \neq 1$):

- (see formula sheet)

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

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

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

$\text{rate}_{\text{vap}} = \text{rate}_{\text{cond}}$

note: phase \neq state of matter

phase changes:

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

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

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

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

vapour pressure

vapour pressure: pressure of vapour at equilibrium

weak IMF \rightarrow lower $T_{\text{bp}} \rightarrow$ 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)

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

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

chemical equilibrium

chemical equilibrium: at equilibrium, forward rate = reverse rate
concentrations at equilibrium stay constant, but the reaction is **still going on**

equilibrium constants

depends on **temperature ONLY**

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

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

for pressure use units of **bar**, and $R = 0.08314$ L·bar/(mol·K)

only include aqueous and gaseous species, **do NOT include pure liquids and solids relationship:**

$$K_P = K_c(RT)^{\Delta n} \quad \text{or} \quad K_c = K_P(RT)^{-\Delta n}$$

where $\Delta n = (c + d) - (a + b)$
magnitude of K :

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

properties of equilibrium constants

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

equilibrium constant calculations

usually use ICE table approach

reaction quotient

same formula as K but use the data at ANY point (not necessarily equilibrium)

direction of change:

- $Q_c < K_c$: reactants excess, forward reaction
- $Q_c > K_c$: products excess, reverse reaction

le chatelier's principle

concentration changes

- add reactant: forward reaction, more products
- add product: reverse reaction, more reactants

volume/pressure changes

if there're SAME number of gas molecules on both sides, changing volume/pressure does NOT affect equilibrium

recall: when T is constant, $V \propto \frac{1}{P}$

- reduce volume (increase pressure): shifts towards side with fewer gas molecules
- increase volume (decrease pressure): shifts towards side with more gas molecules

temperature changes

- endothermic ($\Delta H > 0$): $T \uparrow$, K increases, shifts to products, and vice versa
- exothermic ($\Delta H < 0$): $T \uparrow$, K decreases, shifts to reactants, and vice versa;

determine K at a certain temperature (two point form) \rightarrow **van't hoff equation** (see formula sheet)

adding solids, liquids or inert gases does NOT affect equilibrium, **unless it causes a change of concentration, P, T or V**

when one or multiple changes occur and you're unsure which way the reaction will go, use Q!

electrochemistry

oxidation states & redox reactions

rules for assigning OS:

- free element: OS = 0 (e.g. H_2 , O_2)
- monatomic ion: OS = charge (e.g. Na^+)
- sum of OS in neutral species = 0
- sum of OS in polyatomic ion = charge
- H is generally +1, O is generally -2
- others *USUALLY* just go check group number

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
- oxidation: OS increases, loses electrons
- reducing agent: stuff that gets oxidized
- oxidizing agent: stuff that gets reduced

notes: to become redox rxn, there needs to be a reduction and an oxidation (OS changes)

balancing redox rxns:

1. write separate half-reactions for oxidation and reduction
2. balance all atoms except H, O
3. balance O with H_2O
4. balance H with H^+
5. balance charges with e^-
6. multiply & add half-rxns to cancel e^-
7. for basic: add OH^- equal to H^+ to each side, simplify (combine H^+ and OH^- to form H_2O)

galvanic cell & faraday's law

galvanic cell: spontaneous redox rxns \rightarrow electrical energy

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:

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

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

current efficiency:

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

standard cell potential

standard conditions: 1.0 M for dissolved species, 1 bar for gases, $25^\circ C$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ > 0$$

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

non-standard conditions \rightarrow nernst equation (see formula sheet)

$$\text{nernst @ } 25^\circ C: E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q$$

concentration cell: same material at anode and cathode. **higher concentration** acts as **cathode**, $E_{\text{cell}} = 0$

general 3 first steps for galvanic cell problems

1. identify oxidation and reduction half-reactions using the reduction potentials
2. add them up (with same # of e^-) to get overall reaction
3. calculate E_{cell}

nernst at equilibrium

battery dies when:

- equilibrium is reached ($E_{\text{cell}} = 0$, $Q = K$)

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

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

- the LR runs out (not in equilibrium)

electrochemical 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 (negative): e^- are freed by the oxidation half-reaction
 - electrolytic (positive): e^- are withdrawn from electrode
- cathode: always reduction.
 - galvanic (positive): e^- are removed by the reduction half-reaction
 - electrolytic (negative): e^- are forced onto electrode