

pre-midterm stuff

fundamentals

ΔT conversion factor: $\frac{1K}{1.8F}$ & $\frac{1^\circ C}{1^\circ F}$

molality: $m = \frac{\text{mol solute}}{\text{kg solvent}}$

ppm and ppb:

$$y_i = \text{ppm}_i \times 10^{-6} = \text{ppb}_i \times 10^{-9}$$

gases

ideal: $PV = nRT$; $\rho = \frac{PM}{RT}$

real: van der waals equation

- ideal behavior at high T, low P

manometer: $P = \rho gh$. watch units!

intermolecular forces

strength: H-bond > Dipole-Dipole > LDF

- LDF: all molecules. \uparrow strength with size/mass (polarizability)
- H-bond: H bonded to N, O, F

limiting reactant (LR)

1. balance rxn
2. calculate n for all reactants
3. divide them by coefficients and find min

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 ($\frac{\text{mol}}{\text{L}\cdot\text{s}}$)

positive for products, negative for 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

(see formula sheet)

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

phase equilibrium

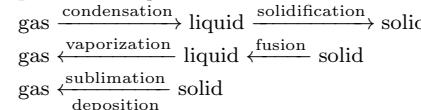
phase equilibrium

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:



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

vapour pressure

vapour pressure: pressure of vapour at equilibrium

weak IMF \rightarrow lower T_{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, use $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$)

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 $C_A = k_A P_A$ 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 ($x_{\text{soln}} > 0.98$)

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

(see formula sheet)

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

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

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

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

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

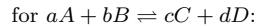
$$\% \text{ dissociation} = \frac{i - 1}{i_{\max} - 1} \times 100\%$$

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**



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

for pressure use units of **bar**, and $R = 0.08314 \text{ L}\cdot\text{bar}/(\text{mol}\cdot\text{K})$

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

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

inert gas addition:

- @ const. **volume**: P_{total} increases, but P_i unchanged \rightarrow **NO shift**.
- @ const. **pressure**: V_{total} increases, P_i decreases \rightarrow shifts to **more gas moles**.

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

electrochemistry

use $n = \# \text{ electrons transferred}$,
 $R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$

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

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

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}

find best oxidizing/reducing agent

best oxid. agent: choose highest E°

best redu. agent: choose lowest E°

ernst at equilibrium

battery dies when:

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

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

if $K > e^{10}$ or $K < e^{-10}$, the rxn approx. fully goes in the right/left direction

- 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

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

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 **ernst equation** (see formula sheet)