

# pre-midterm stuff

## fundamentals

**ΔT conversion:**  $\frac{1K}{1.8F}$  and  $\frac{1^{\circ}C}{1^{\circ}F}$

**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. ↑ strength with size/mass (polarizability)
- H-bond:** H bonded to N, O, F

## 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**

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

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

**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

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

# phase equilibrium

## phase equilibrium

**defn:** rate (forward) = rate (reverse)

e.g. vapour liquid equilibrium  $\Rightarrow$

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

**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  $\xleftarrow{\text{sublimation}}$  solid  
 $\xrightarrow{\text{deposition}}$

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

## 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 ( $T_{\text{bp}}$ )

**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  $T_{\text{dp}}$ :** temperature where humid air reaches saturation

condensation occurs at **100 % saturation**

humidity refers specifically to  $\text{H}_2\text{O}$

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

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)

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.  $\text{H}_2$ ,  $\text{O}_2$ )
- monatomic ion: OS = charge (e.g.  $\text{Na}^+$ )
- 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.,  $\text{H}_2\text{O}_2$ )

**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  $\text{H}_2\text{O}$
4. balance H with  $\text{H}^+$
5. balance charges with  $e^-$
6. multiply & add half-rxns to cancel  $e^-$
7. for basic: add  $\text{OH}^-$  equal to  $\text{H}^+$  to each side, simplify (combine  $\text{H}^+$  and  $\text{OH}^-$  to form  $\text{H}_2\text{O}$ )

## galvanic cell & faraday's law

**galvanic cell:** spontaneous redox rxns  $\rightarrow$  electrical energy

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:**

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

where  $F = 96,485 \text{ C/mol}$  (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,  $25^\circ\text{C}$

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

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

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

in the nernst equation use  $n$  = # of electrons transferred,  $R = 8.314 \text{ L}\cdot\text{J}/(\text{mol}\cdot\text{K})$

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

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

## 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  $E_{\text{cell}}$

## nernst at equilibrium

battery dies when:

- equilibrium is reached ( $E_{\text{cell}} = 0$ ,  $Q = K$ )  
$$0 = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln K \Rightarrow K = \exp\left(\frac{E_{\text{cell}}^\circ nF}{RT}\right)$$

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