

## 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)
- 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  $\implies$

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

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

**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 hof 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;

K changes with temperature  $\rightarrow$  **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

**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<sub>2</sub>O<sub>2</sub>)

**redox reactions:**

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

**balancing redox:**

- write separate half-reactions
- balance atoms except H, O
- balance O with H<sub>2</sub>O
- balance H with H<sup>+</sup>
- balance charges with e<sup>-</sup>
- add half-reactions to cancel e<sup>-</sup>
- for basic: add OH<sup>-</sup> equal to H<sup>+</sup> to each side, simplify

## galvanic cell & faraday's law

**galvanic cell:** derives electrical energy from spontaneous redox reactions

notation: Zn(s)|Zn<sup>2+</sup>(aq)||Cu<sup>2+</sup>(aq)|Cu(s)

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

**current & faraday's law:**

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

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

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  $E_{\text{cell}}$ :** 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  $E^{\circ}$  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: (-)