

### Temp Conversion

$$T(K) = T(^{\circ}C) + 273.15$$

$$T(^{\circ}F) = 1.8 T(^{\circ}C) + 32$$

$$0^{\circ}C = 273.15K$$

$$Avogadro \# = 6.022E23$$

Mole Formula != Emp Formula

**Percentage yield** is the ratio of the actual yield to the theoretical yield multiplied by 100%.

**Molar Mass = Density \* Molar Volume**

$$\rho = \frac{m}{V} : \left( \frac{g}{L} \right)$$

$$M = \rho \frac{22.4 L}{mol} : \left( \frac{g}{L} \frac{L}{mol} = \frac{g}{mol} \right)$$

**Dalton's Law of Partial Pressures**

$$P = P_A + P_B = (n_A + n_B) \frac{RT}{V} = n \frac{RT}{V}$$

$$\frac{P_A}{P} = \frac{n_A}{n_A + n_B} = y_A$$

### KMT

- Gas particles move constant, random, straight-line motion
- Lots of space
- There are no intermolecular forces
- energy of the entire gas remains constant – molecular collisions are elastic

### Kinetic theory Momentum

$$P = \frac{1}{3} m \bar{u}^2 \frac{N}{V}$$

$$u_{rms} = \sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}}$$

$$u_{mp} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$

$$u_{av} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

### Real Gases

$$\frac{PV_m}{RT} = Z$$

Compressibility factor:  $0.1 < Z < 1.5$ .

### Van Der Waals

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$PV_m^3 - (bP + RT)V_m^2 + aV_m - ab = 0$$

### Vapor Pressure

- At **phase equilibrium** there is no net conversion of one phase to the other – equilibrium is a dynamic process

### Antoine's Equation

(T is abs Temp, Others are constants)

$$\log P_{vap} = A - \frac{B}{C + T}$$

### Enthalpy

$\Delta H > 0$ , **Endothermic**

$\Delta H < 0$ , **Exothermic**

$\Delta H_{vap}/\Delta H$  on order of KJ/mol

**CCE** ( $\Delta H$  could be for other transitions)

$$\ln \left[ \frac{P_{vap2}}{P_{vap1}} \right] = \frac{\Delta H_{vap}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

### Solutions

- Ideal solutions** are the ones where solvent and solute do not to interact with each other – similar to ideal gases

$$x_i = \frac{n_i}{n_1 + n_2 + \dots + n_n} = \frac{n_i}{\sum_{j=1}^n n_j}$$

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

### Henry's Law

$$P_i = k_i x_i$$

### Raoult's law

- For binary, liquid/liquid solutions:

$$P = P_1 + P_2 = x_1 P_{vap,1} + x_2 P_{vap,2}$$

$$= x_1 P_{vap,1} + (1 - x_1) P_{vap,2}$$

In general:  $P_{vap,liquid} \gg P_{vap,solid}$

**Boiling occurs when  $P_{vap} > P_{atm}$**

### Vapor Pressure Lowering

$$\Delta P_l = P - P_{vap,1} = x_1 P_{vap,1} - P_{vap,1}$$

$$= -x_2 P_{vap,1}$$

### BP Ele

$$\Delta T_b = i K_b m$$

**Molality (m)**

$i$  – Van't Hoff's constant

$1 < i < \text{total dissociation}$

### FP Depr

$$\Delta T_f = -i K_f m$$

### Diffusion towards

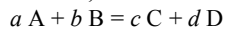
**Osmotic Pressure** (Semi-Permeable MB)

$$\pi = cRT = \frac{n_2}{V} RT$$

### Equilibrium

@ Eqm,  $R_{forward} = R_{reverse}$

**For RX,**



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$K_c = C @ T_1$$

$$K_c = K_p \times RT^{a+b-c-d}$$

$$K_p = K_c \times RT^{-a-b+c+d}$$

**Reaction Quotient Q** determines direction of reaction.

### Le Chatelier's Principle

A system will react to minimize the impact of a disturbed equilibrium.

**Changing equilibrium** conditions **WILL affect Yield**, but adding **catalysts don't**.

### Electrochemistry

Reduced – ox. agent, gained e-, O.S.--

Oxidized– red. agent, lost e-, O.S.++

### Oxidation States

- Group 1 metals (**Li, Na, K, Rb, Cs, Fr**) have **O.S. = +1**
- Group 2 metals (**Be, Mg, Ca, Sr, Ba, Ra**) have **O.S. = +2**
- F** has **O.S. = -1**
- Cl, Br, I, At** have **O.S. = -1** except when combined **with oxygen and other halogens**
- H** has **O.S. = +1**, except when bonded to **metals when its O.S. = -1** (LiH, for instance)
- O** has **O.S. = -2** except for **peroxides** ( $H_2O_2$  and  $N_2O_2$  where **O.S. = -1** for O) or when combine **with F** ( $OF_2$  where **O.S. = +2** for O)
- In **binary compounds with metals**:
- group 17 elements (**F, Cl, Br, I, At**) have **O.S. = -1**
- group 16 elements (**O, S, Se, Te, Po**) have **O.S. = -2**
- group 15 elements (**N, P, As, Sb, Bi**) have **O.S. = -3**

### Balance Redox Equations:

- Balance O atoms by adding  $H_2O$
- Balance of H atoms:
  - Acid: Add  $H^+$  to the hydrogen-deficient side
  - Base: Add  $H_2O$  to the hydrogen-deficient side and  $OH^-$  to the other side

### Galvanic Cells

- Oxidation @ anode. e- flow from anode to cathode.**
- Reduction @ cathode. e- flow to cathode, it is pos.**  $= - (1 - x_1) P_{vap}$
- The **salt bridge permits ions to diffuse** from one side to the other forcing e- to flow through wire
- The ammeter measures the magnitude of the electrical current. A voltmeter could also be used to measure the cell's voltage.
- e- flow from the anode to the cathode. Ions in solution are free to flow in any direction.**
- A schematic representation of this galvanic cell is: **Cu|Cu<sup>2+</sup>||Ag<sup>+</sup>|Ag**.
- These **electrodes are called active** since they dissolve (Cu) or form (Ag) during the reaction.

### Definitions

$$I = \frac{Q}{t} \left[ \frac{\text{coulombs}}{\text{second}} = \text{ampere (A)} \right]$$

$$n = \frac{It}{F} = \frac{\text{total charge passing the circuit}}{\text{charge of a mole of electrons}}$$

### Standard State:

- 1.0 M of dissolved (i.e. 0.5M NaCl)
- 1 atm pressure
- Most stable form at 25 °C for solids

**Nernst Equation** (n - # e- in equation)

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log_{10} Q$$

**Concentration Cells** allow uses the fact that

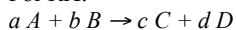
$$E_{\text{cell}} = -\frac{0.0592}{n} \log_{10} Q \neq 0V$$

@ **Equilibrium**,  $0 = E_{\text{cell}}^0 - \frac{RT}{nF} \ln K_c$

**No salt-bridge is needed for Electrolytic cells.**

**Rate Laws**

For RX:



$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

**Differential Rate Law**

$$r = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n[B]^m$$

**0<sup>th</sup> Order:**

$$[A] = -kt + [A]_0$$

**1<sup>st</sup> Order:**

$$\ln[A] = -kt + \ln[A]_0$$

**2<sup>nd</sup> Order:**

$$-\frac{d[A]}{dt} = k[A]^2$$

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k \int_0^t dt$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

**Half-Life of RXs**

**0<sup>th</sup> Order**

$$t_{1/2} = [A]_0 / 2k$$

**1<sup>st</sup> Order:**

$$t_{1/2} = \ln 2 / k \text{ (Indep of } [A]_0 \text{)}$$

**2<sup>nd</sup> Order:**

$$t_{1/2} = 1 / k[A]_0$$

Use Intgrd. Rate Laws, guess 1, 2, 3, 0, 0.5

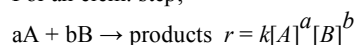
**Activation Energy**

**Arrhenius Law** (k - rate constant) ~ CCE

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

**RX Mechanisms: unimole, bimole, termoleWW**

For an elem. step,



**RDS** - slowest step that is the bottle-neck, it has the **highest activation En.**

**Approx. Method 1:**

**r<sub>forward</sub> = r<sub>reverse</sub>** (only valid for fast equilibrium); then substitute to eliminate intermediates.

**Steady-State Approx.:**

**Rate of intermediate production = Rate of intermediate consumption**; then substitute to eliminate intermediates.

**Catalysts** provide alt. reaction pathway with lower  $E_a$ . **Catalysts** may be consumed but is always present at end.

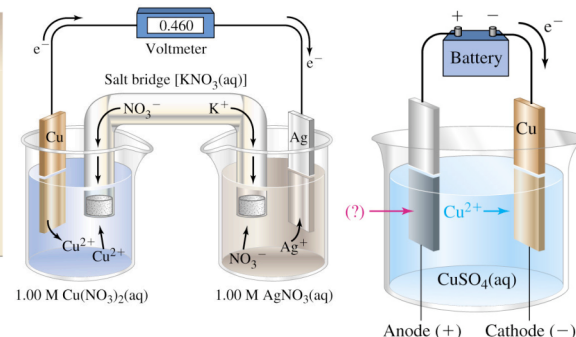
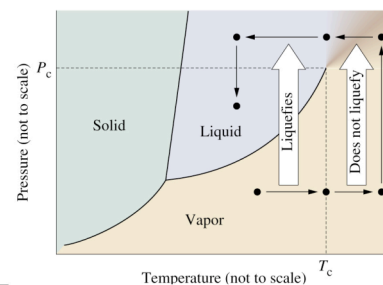
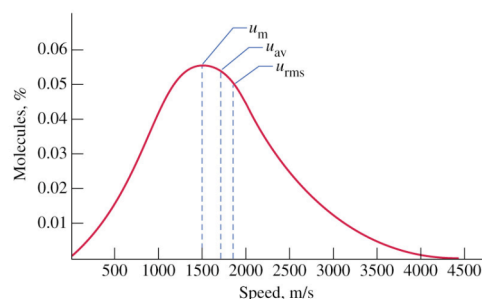


**Heterogeneous Catalysts**  
**Adsorption** of reagents on the catalyst surface

- **Diffusion of reagents on the catalyst surface**
- **Reaction on an active site to form products**
- **De-adsorption** of the product into the gas or liquid phase

**Enzymes bind via Lock-n-Key method.**

If **[substrate] too high**, all **active sites filled**, so RX rate is **0<sup>th</sup> order** wrt. [substrate], **otherwise 1<sup>st</sup> order** wrt. [substrate].



**Examples**

**1. PV = nRT**

Two containers (volume  $V_1$  and  $V_2$ ) are connected by a capillary tube of negligible volume. The containers are filled with  $H_2$  initially at  $T_1 = 0^\circ C$  and  $P_1 = 1 \text{ atm}$ . The temperature of  $V_2$  is suddenly increased to  $T_2 = 100^\circ C$ , while  $V_1$  is maintained at  $T_1 = 0^\circ C$ . After equilibrium is reached, the pressure in the two vessels is equal to  $P_f = 1.2176 \text{ atm}$ . What is the ratio of  $V_1$  to  $V_2$ ?

**Basis:** Total volume of  $H_2$  is  $(V_1 + V_2)$  at  $T_1 = 0^\circ C$  and  $P_1 = 1 \text{ atm}$ .

**By conservation of mass, the total number of moles of  $H_2$  in the vessel is constant**

**After the temperature of  $V_2$  is increased to  $100^\circ C$  and the equilibrium pressure of  $1.2176 \text{ atm}$  is reached, the total number of moles of  $H_2$  is still**

**the same. Rearranging this equation gives:**  $\frac{V_1}{V_2} = \frac{\frac{P_f \cdot T_1}{P_1 \cdot T_2} - 1}{1 - \frac{P_f \cdot T_1}{P_1 \cdot T_2}} = 0.49955$  **The ratio of  $V_1:V_2$  is equal to 0.49955**

**2. Tripple Point**

A one-component phase diagram has a single critical point above which the liquid phase does not exist. **TRUE**

**3. Vapor Pressure**

The vapour pressure of benzene ( $C_6H_6$ ) at  $25^\circ C$  is  $94.7 \text{ mmHg}$ . After  $1.00 \text{ g}$  of benzene is injected into a  $10 \text{ L}$  container held at  $25^\circ C$ , what is the partial pressure of benzene in the bulb and how many grams remain as liquid?

**Check if  $P$  for one gram of  $C_6H_6$  is greater than  $94.7 \text{ mmHg}$ . If is, then the extra amount stays as liquid.**

**4. Vapor Pressure**

In some areas, the winter snow sublimates into the air without melting. Use the heat of sublimation and the vapour pressure of ice at  $0^\circ C$  to determine how low the partial pressure of water vapour in air above ice at  $-20^\circ C$  must be for ice to sublime.

**For ice to sublime,  $P_{H_2O} < P_{\text{vap}H_2O}$  @  $-20^\circ C$**