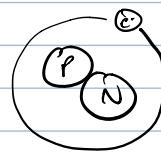


# MATTER & CHEMICAL COMPOUNDS

- Atom: smallest unit of matter that has properties



⇒ Different shells

↳ Recall valence shells! If same # of  $e^-$  in valence shell, then similar properties

- Atomic number: # of protons

- Same # of  $e^-$  if neutral atom

- Isotope: atoms of same protons but diff. # of neutrons

- Atomic mass = # of protons + # of neutrons

- Ex:// Chlorine has number 17, mass is 35.45 u. # of neutrons?

$$\therefore \text{# of neutrons} = 35 - 17 = 18 \text{ neutrons}$$

We know that 75.8%  $^{35}\text{Cl}$  and 24.2%  $^{37}\text{Cl}$ .

↳  $35 \times 0.758 + 37 \times 0.242 = 35.45$  ! ⇒ This is why atomic mass is not integer

- Ex:// As has 107.868 u.  $^{109}\text{As}$  has 108.905 u at 48.16%. What is u of  $^{107}\text{As}$ .

$$107.868 = 0.4816 \cdot 108.905 + (1 - 0.4816) \cdot x$$

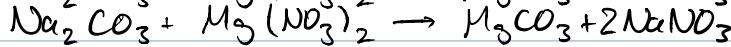
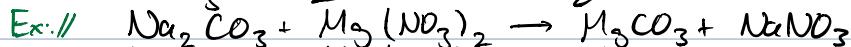
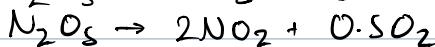
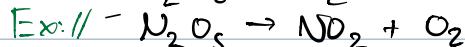
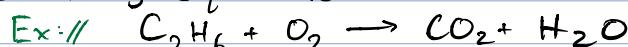
$$x = \frac{107.868 - 0.4816 \cdot 108.905}{(1 - 0.4816)}$$
$$= 106.905$$

## UNIT 1: STOICHIOMETRY

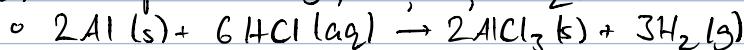
### Chemical Reactions & Mole Concept

- Conservation of Atoms: total # of atoms in reaction stays constant

- Balancing equations:



- Indicate phase: (s), (l), (s), (aq) ⇒ dissolved in water



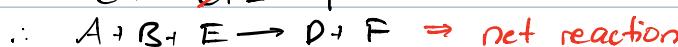
- Multiple reactions:

- Ex:// Consider natural gas w/ 70% methane and 30% ethane being combusted with oxygen to form carbon dioxide and water

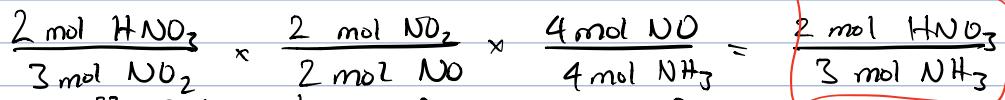
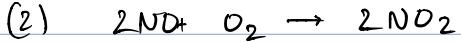
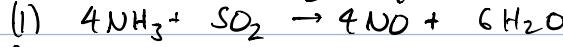


Adding is wrong b/c it assumes  $[\text{CH}_4] = [\text{C}_2\text{H}_6]$ . Never combine!

- If sequential, then you can combine



Ex:// How many molecules of nitric acid ( $\text{HNO}_3$ ) can be produced from each molecule of ammonia using the following sequence



- Mole:  $6.022 \times 10^{23}$ . Defined by # of atoms in 12 g of  $^{12}\text{C}$

- o Atomic mass on periodic table: g/mol of element

- o Ratio of moles of compound to element is equal to ratio of compound to element

Ex://  $\text{CH}_4$

- ↳ 1 molecule of  $\text{CH}_4$  has 1 carbon + 4 hydrogen

- 1 mol of  $\text{CH}_4$  has 1 mol carbon  $\rightarrow$  4 mol hydrogen

- o Applies to equations too!

Ex:// Bees release 1.0 mg of  $\text{C}_7\text{H}_{14}\text{O}_2$ . How many moles released?

Molar mass:

$$\begin{aligned} M_{\text{IA}} &= 7M_{\text{C}} + 14M_{\text{H}} + 2M_{\text{O}} \\ &= 130.18 \text{ g/mol} \end{aligned}$$

Converting to moles:

$$1.0 \times 10^{-6} \text{ g} \times \frac{\text{mol}}{130.18 \text{ g}} = 7.7 \times 10^{-9} \text{ mol IA}$$

- Concept check:

$$\begin{aligned} 5.0 \text{ L} \times \frac{15.5 \text{ g}}{0.1 \text{ L}} \times \frac{\text{mol}}{64500 \text{ g}} \times \frac{4 \text{ mol Fe}}{1 \text{ mol Hc}} \times \frac{55.845 \text{ g}}{1 \text{ mol Fe}} \\ = 2.7 \text{ g Fe} \end{aligned}$$

- Concept check: # of atoms in 1.0 lb-mol of  $^{12}\text{C}$

$$\begin{aligned} 1.0 \text{ lb-mol } ^{12}\text{C} \times \frac{12 \text{ lb}}{1 \text{ lb-mol}} \times \frac{1 \text{ kg}}{2.20462 \text{ lb}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \\ = 2.7 \times 10^{26} \text{ atoms.} \end{aligned}$$

## Composition of Compounds and Mixtures

- Molar fraction: molar fraction of A =  $\frac{n_A}{n_T} = \frac{n_A}{\sum n_i}$

- o Molar percentage: molar fraction  $\rightarrow \%$

- Mass fraction: same as molar fraction but mass

- o Mass percentage: same as molar % but mass

Ex:// A natural gas is composed of 70 mol-%  $\text{CH}_4$  and 30 mol-%  $\text{C}_2\text{H}_6$ . What are the mass percentages.

$$M_{\text{CH}_4} = 16.0426 \text{ g/mol}$$

$$M_{\text{C}_2\text{H}_6} = 30.0694 \text{ g/mol}$$

Assume 1 mol in entirety of system.

$$0.7 \text{ mol CH}_4 = 11.23 \text{ g}$$

$$0.3 \text{ mol C}_2\text{H}_6 = 9.02 \text{ g}$$

$$\therefore \text{Mass \% of CH}_4 = \frac{11.23}{11.23 + 9.02} = 55.45\%$$

$$\text{Mass \% of C}_2\text{H}_6 = 44.55\%$$

Ex://  $\text{PDX}$  contains 16.22% C, 2.72% H, 37.84% N, 43.22% O by mass. Molar ratio is 220:1mol.

Find empirical and molecular formula of  $\text{PDX}$ .

$$0.1622 \text{ g C} = 0.0135 \text{ mol C}$$

$$0.0272 \text{ g H} = 0.02698 \text{ mol H}$$

$$0.3788 \text{ g N} = 0.02701 \text{ mol N}$$

$$0.4322 \text{ g O} = 0.02701 \text{ mol O}$$



Molar mass of empirical:  $74.0206 \text{ g/mol}$

Multiplicator:  $220 / 74.0206 \approx 3x$



- Average molar mass: Used in mixtures

$$\text{Avg molar mass} = \frac{\text{total mass}}{\text{total moles}}$$

o Can also take weighted average of individual molar mass

o Ex:// For natural gas problem:

$$\textcircled{1}: \frac{\text{Methane} \cdot n_{\text{methane}}}{\text{Methane} + n_{\text{methane}}} = \frac{0.7(\text{Methane}) \cdot 0.3(\text{Methane})}{1} = 20.251 \text{ g/mol}$$

$$\textcircled{2} \quad 0.7(\text{Methane}) + 0.3(\text{Methane}) = 20.251 \text{ g/mol}$$

o Ex:// Dry air has avg. molar mass of  $28.85 \text{ g/mol}$ . Assuming air only has  $\text{O}_2$  and  $\text{N}_2$  gases, determine mass + mole fraction of air.

$$28.85 = x_{\text{O}_2} (31.998 \text{ g/mol}) + (1-x_{\text{O}_2}) (28.014 \text{ g/mol})$$

$$28.85 = 31.998 x_{\text{O}_2} + 28.014 - 28.014 x_{\text{O}_2}$$

$$0.836 = 3.984 x_{\text{O}_2}$$

$$x_{\text{O}_2} = 0.209$$

$$x_{\text{N}_2} = 0.790 \quad \} \text{Mole fractions.}$$

Convert to mass fraction:

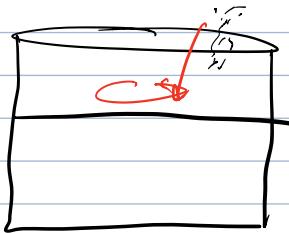
$$\text{O}_2: 0.209 \text{ mol} \times 31.998 \text{ g/mol} = 6.714 \text{ g O}_2$$

$$\text{N}_2: 0.709 \text{ mol} \times 28.014 \text{ g/mol} = 22.13106 \text{ g N}_2$$

$$\therefore \text{mass fraction O}_2 = \frac{6.714}{6.714 + 22.13106} = 0.232$$

$$\therefore \text{mass fraction N}_2 = 1 - \text{mass fraction of O}_2 = 0.767$$

- Solution:



- Process of dissolving: solute dispersed in solvent

solute (①)  $\xrightarrow{\text{solution}}$  solvent (②)

amount of ① < amount of ②

o Covalent molecules disperse, ionic compounds dissociate into ions

o Molarity: solute/solution

$$C = \frac{\text{amount of solute in mol}}{\text{volume of solution in L}} \quad [\text{mol/L}]$$

o Can use weight instead (notated w/w), or volume (v/v) or weight of solute  $\rightarrow$  volume of solution (w/v)

$$C \text{ (w/w)} = \frac{\text{mass of solute}}{\text{mass of solution}}$$

o Molarity: solute/solvent

o Small concentrations: ppm or ppb

o Ex:// 13200 ppb is how many times bigger than 0.01 ms/L (ppb in mass)?

Convert  $0.01 \frac{\text{ms}}{\text{L}} \rightarrow \text{ppb}$

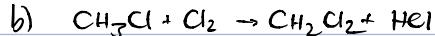
$$\frac{0.01 \text{ ms}}{\text{L}} = \frac{0.01 \times 10^{-3} \text{ s}}{1000 \text{ s}} = \frac{1 \times 10^{-5}}{10^3} = \frac{1 \times 10^{-5} \times 10^6}{10^3 \times 10^6} = \frac{10}{10^9} = 10 \text{ ppb}$$

∴ 13200 is 1320 times bigger than 0.01 ms/L

## Stoichiometry Calculations

### - Yield:

- Actual yield: amount of product formed (either mass or moles) from experiment
- Theoretical yield: max amount of product that could have been formed based on equation
- Why is theoretical > actual: equilibrium, time, side reaction, loss of product
- Fractional yield:  $\frac{\text{actual yield}}{\text{theoretical yield}}$
- Percentage yield = fractional yield × 100
- Ex:// Consider following reactions. Each reaction has 92% yield. 112 g of CH<sub>4</sub> and excess Cl<sub>2</sub>, how many grams of CH<sub>2</sub>Cl<sub>2</sub> is formed?



$$\text{mol CH}_4 = 112 \text{ g} \div 16.0426 \text{ g/mol} = 6.98 \text{ mol}$$

$$\therefore \text{Theoretical yield of CH}_3\text{Cl} = 6.98 \text{ mol}$$

$$\text{Actual yield} = 6.98 \times 0.92 = 6.42 \text{ mol}$$

$$\text{Theoretical yield of CH}_2\text{Cl}_2 = 6.42 \text{ mol}$$

$$\text{Actual yield} = 6.42 \times 0.92 = 5.91 \text{ mol}$$

$$\text{mass CH}_2\text{Cl}_2 = 5.91 \text{ mol} \times 84.9328 \text{ g/mol} = 501 \text{ g}$$

### - Limiting and excess reactants:

- Limiting reactant: reactant that runs out first (determines yield). All other reactants are excess
- To determine limiting reactant: just compare # of moles (# of actual moles ÷ # of theoretical ⇒ see which one has smaller ratio).
- Also can look at ratios between compounds to determine

- Ex:// 2H<sub>2</sub> + O<sub>2</sub> → 2H<sub>2</sub>O. 4g of H<sub>2</sub> and 16g of O<sub>2</sub>. Identify limiting reactant and theoretical yield of water in grams.

Converting to moles:

$$4 \text{ g H}_2 \times \frac{\text{mol H}_2}{2 \times 1.0079 \text{ g}} = 1.98 \text{ mol}$$

$$16 \text{ g O}_2 \times \frac{\text{mol O}_2}{2 \times 15.999 \text{ g}} = 0.50 \text{ mol} \Rightarrow \text{Limiting blk if this is limiting, it only needs 1.0 mol of H}_2!$$

Yield:

$$0.50 \text{ mol O}_2 \times \frac{2 \text{ mol H}_2\text{O}}{\text{mol O}_2} = 1.000 \text{ mol H}_2\text{O} \times \frac{18.01482 \text{ g}}{\text{mol H}_2\text{O}} = 18.02 \text{ g}$$

- Ex:// Fe<sub>2</sub>O<sub>3</sub> + 3CO → 2Fe + 3CO<sub>2</sub>. 433.2 g Fe<sub>2</sub>O<sub>3</sub> w/ 255.3 g CO yields 284.3 g Fe. Calculate theoretical yield and percentage yield of iron.

Converting to moles:

$$433.2 \text{ g Fe}_2\text{O}_3 \times \frac{\text{mol}}{159.687 \text{ g}} = 2.712 \text{ mol Fe}_2\text{O}_3$$

$$255.3 \text{ g CO} \times \frac{\text{mol}}{28.01 \text{ g}} = 9.11 \text{ mol CO}$$

{ Fe<sub>2</sub>O<sub>3</sub> is limiting

∴ Theoretical yield:

$$2.712 \text{ mol Fe}_2\text{O}_3 \times \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} \times \frac{55.845 \text{ g}}{\text{mol Fe}} = 302.99 \text{ g Fe}$$

$$\therefore \text{yield} = \frac{254.3}{202.99} = 83.9\%$$

- Percentage excess: % by which excess reactant exceeds stoich amount.

- Ex:// Methane is combusted in 150% excess oxygen. How much oxygen should be supplied for each mol  $\text{CH}_4$ ?



$$2 \times 1.5 = 3 \Rightarrow \text{excess needed.}$$

2 moles needed ~~anyways~~

$$\therefore \text{Total} = 2 + 3 = 5 \text{ mol O}_2$$

- Conversion: reactant  $\rightarrow$  product

- Atom economy:  $\frac{\text{mass of all product}}{\text{mass of all reactant}}$

Assume 100% yield, no excess reactant considered

## UNIT 2: STATES OF MATTER

### Molecular Nature of Gases and Gas Pressure

- Gas postulates: composed of large # of molecules & molecules separated by large distances and undergo ceaseless motion

- Collisions cause gas molecules to have random speed + direction and behave like spheres undergoing perfectly elastic collisions

- Pressure of gas:  $P = \frac{F_{\text{wall}}}{A_{\text{wall}}} = \frac{Nmv_x^2}{V}$

- Some issues to resolve:

1. We need to use average speed:  $v_x^2 \Rightarrow \overline{v_x^2}$

2. Need to consider speed from all directions:

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

Avg. sum:  $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$

$$\therefore \overline{v^2} = 3\overline{v_x^2}$$

Define  $c^2$  as the mean square molecular speed

$$c^2 = 3\overline{v_x^2}$$

$$\therefore \overline{v_x^2} = \frac{1}{3}c^2$$

$$\therefore PV = Nm \frac{1}{3}c^2$$

$$PV = nM \frac{1}{3}c^2 \Rightarrow N = \frac{m}{M} n \underset{\substack{\text{mass} \\ \text{# of moles}}}{\underset{\substack{\text{molar mass}}}{\underset{\text{# of moles}}{\underset{\text{mass}}{\times}}}} \quad \text{# of moles}$$

### Ideal Gas Law and Applications

- Ideal gas law:  $PV = nRT \Rightarrow T \text{ in K!}$

- Comparing with derived formula above:

$$PV = \frac{1}{3}Mc^2$$

$$T = \frac{Mc^2}{3R}$$

$$T = \frac{2}{3R} \left( \frac{1}{2} Mc^2 \right) = \frac{2 \overline{E_k}}{3R}$$

- Temperature: average translational kinetic energy

- Type of gas has no impact

- Ex:// He and  $\text{N}_2$  put in chamber s.t. equal # of moles, pressure, volume + temperature. Which has greater average speed?

$$\cancel{\frac{1}{2} M_{\text{He}} c_{\text{He}}^2} = \cancel{\frac{1}{2} M_{\text{N}_2} c_{\text{N}_2}^2}$$

$$4c_{\text{He}}^2 = 28c_{\text{N}_2}^2$$

$$C_{N_2} = \frac{1}{57} C_{He}$$

$$C_{N_2} = 0.37 C_{He} \Rightarrow He \text{ is faster}$$

- Ex:// He and N<sub>2</sub> in same vessels (V same) at same temperature. He must have higher speed than all molecules of N<sub>2</sub>.

False! Avg. speed is higher!

- Ex:// Gas has density of 2.56 g/L at 22.8°C and 1 atm. Molar mass?

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

assumed

↓

$$M = \frac{mRT}{PV}$$

$$V = 1 \text{ L}, T = 295.95 \text{ K}, R = 0.082058, m = \rho V = 2.56 \text{ g}$$

$$\therefore M = \frac{2.56 \times 0.082058}{1 \text{ atm} \times 1 \text{ L}} \approx 295.95$$

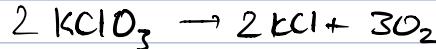
We can use density instead!

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

$$P = \frac{\frac{m}{M} RT}{V} = \frac{\rho RT}{M}$$

- Ex:// 3.87 g sample of KCl and KClO<sub>3</sub> is decomposed. 119 mL of O<sub>2</sub> produced at 0°C and 0.98692 atm. % by mass of KClO<sub>3</sub> in original mixture?



1) Finding # of moles:

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{0.98692 \times 0.119}{0.082057 \times 273.15} = 0.05 \text{ mol O}_2$$

2) Mol of KClO<sub>3</sub>

$$0.05 \text{ mol} \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} = 0.033 \text{ mol KClO}_3$$

3) Mass pct

$$0.033 \text{ mol KClO}_3 \times \frac{122.55 \text{ g}}{\text{mol}} = 0.4283$$

$$\therefore \text{mass} = \frac{0.4283}{2.57 \text{ g}} \times 100 = 12.0\%$$

- Standard conditions:

◦ STP: 0°C + 100 kPa

◦ SATP: 25°C + 100 kPa

◦ NTP: 20°C + 1 atm

- Ex:// Inflate tire to 35.0 psi at 30°C. Pressure if temp at -20.0°C?

$$35 \text{ psi} = 2.38 \text{ atm}$$

$$V = 1 \text{ L}$$

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{2.38 \times 1}{0.082057 \times 302.15} = 0.0957 \text{ mol}$$

Winter:

$$P = \frac{nRT}{V} = \frac{0.0957 \text{ mol} \times 0.082057 \times 252.15 \text{ K}}{1 \text{ L}} = 1.99 \text{ atm}$$

~ 29.22 psi

Better way of solving:

$$\begin{array}{l} \textcircled{1} \quad P_1 V = n_1 R T_1 \\ \textcircled{2} \quad P_2 V = n_2 R T_2 \end{array} \Rightarrow \frac{\textcircled{1}}{\textcircled{2}} \Rightarrow \frac{P_1}{P_2} = \frac{T_1}{T_2} \Rightarrow \boxed{29.2 \text{ psi}}$$

↳ Use ratio method if looking at CHANGE

## Mixtures of Gases

- Partial pressure: pressure that a gas exerts if it was the only gas in the system

$$P_T = \frac{n_T R T}{V} = \frac{(n_A + n_B) R T}{V} = \frac{n_A R T}{V} + \frac{n_B R T}{V} = P_A + P_B$$

- Mixtures of gases can only have 1 temperature:  $T = T_A = T_B$

- Dalton's law:  $P_T = P_A + P_B + P_C + \dots$

o We can use this principle to show:

$$\frac{n_1}{n_T} = \frac{P_1}{P_T} !! \Rightarrow \text{In other words, gases obey stoichiometry!}$$

- Ex:// 3 cylinders (5L, 4L, 3L) connected by closed valves. 5L cylinder contains oxygen at 2.51 atm, 4L contains nitrogen at 0.792 atm and 3L cylinder contains argon at 1.23 atm. Total pressure after mixing?

Temperature  $\rightarrow$  # of moles stay constant  $\Rightarrow$  using  $P_1 V_1 = P_2 V_2$

$$P_{1, O_2} V_{1, O_2} = P_{2, O_2} V_{2, O_2}$$

$$P_{2, O_2} = \frac{2.51 \times 5}{12} = 1.05 \text{ atm}$$

$$\therefore P_{2, N_2} = \frac{0.792 \times 4}{12} = 0.264 \text{ atm}$$

$$P_{2, Ar} = \frac{1.23 \times 3}{12} = 0.3075 \text{ atm}$$

$$\left. \begin{array}{l} \\ \\ \end{array} \right\} P_T = 1.62 \text{ atm}$$

- Ex://  $C_2H_4 + H_2 \rightarrow C_2H_6$ .  $n_{H_2} > n_{C_2H_4}$ . Mixture pressure = 82 mmHg. After reaction, pressure is 34 mmHg in same vol. + temp. Mole fraction of  $C_2H_6$ ?

First mixture:  $C_2H_4 + H_2$  # of moles of  $C_2H_4$  and  $C_2H_6$  are same.

Second mixture:  $H_2 + C_2H_6$

$$\textcircled{1} \quad P_{C_2H_4} + P_{H_2} + P_{H_2 \text{ excess}} = 82 \text{ mmHg}$$

$$\textcircled{2} \quad P_{C_2H_6} + P_{H_2 \text{ excess}} = 34 \text{ mmHg}$$

↓

$$\textcircled{1} \quad 2P_{C_2H_4} + P_{H_2 \text{ excess}} = 82$$

$$\textcircled{2} \quad P_{C_2H_4} + P_{H_2 \text{ excess}} = 34 \text{ mmHg}$$

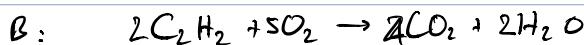
$$\therefore P_{C_2H_4} = 18 \text{ mmHg}$$

$$\therefore \frac{P_{C_2H_4}}{P_{\text{total}}} = \frac{18}{82} = 0.34$$

1. Split excess reactants into reacted and unreacted

2. Use stoich to show equality of partial pressures

- Ex://  $CH_4 + C_2H_2$  occupy vol. @ 63 mmHg. Combusted to form  $CO_2 + H_2O$ .  $PCO_2 = 96 \text{ Hz}$ . Original mole fraction of methane?



Pressure equations:

$$P_{CH_4} + P_{C_2H_2} = 63 \text{ mmHg} \quad \textcircled{1}$$

For every mol  $CH_4$ , 1 mol  $CO_2$ . 1 mol  $C_2H_2 \rightarrow 2 \text{ mol } CO_2$

$$P_{CO_2} = 96 \text{ mmHg}$$

$$P_{CO_2, CH_4} + P_{CO_2, C_2H_2} = 96$$

$$P_{CH_4} + 2P_{C_2H_2} = 96 \quad \textcircled{2}$$

$$\therefore P_{C_2H_2} = 33 \text{ mmHg} \Rightarrow \text{Mole fraction of } CH_4:$$

$$P_{CH_4} = 30 \text{ mmHg} \quad 30 \div 63 = 0.46$$

- This can be extended to partial volumes:  $V_T = V_A + V_B + V_C$

o Although gases take up volume of whole container, often expressed by vol-% ( $\frac{V_A}{V_T} \times 100$ )

$$\text{ppmv} = \frac{V_A}{V_T} \times 10^6 \quad \text{ppb} = \frac{V_A}{V_T} \times 10^9$$

o Note:  $\frac{V_A}{V_T} = \frac{n_A}{n_T}$  just like pressure.

## Intermolecular Forces, Condensed States and Temperature

- Recall that bond dipoles are created due to differing electronegativities of atoms

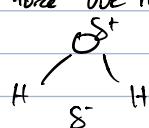
- o If bond dipoles cancel out, it is non-polar. Otherwise, it can create molecular dipoles/polar molecules
- o Polar molecules attract and repulse each other, which is not captured in ideal gas law

- Instantaneous dipoles can be created in molecules due to random movement of electrons

- Dipole-induced dipole interactions: polar attracts non-polar (polar in this case could also result from instant dipoles)

- o London dispersion forces are forces from this

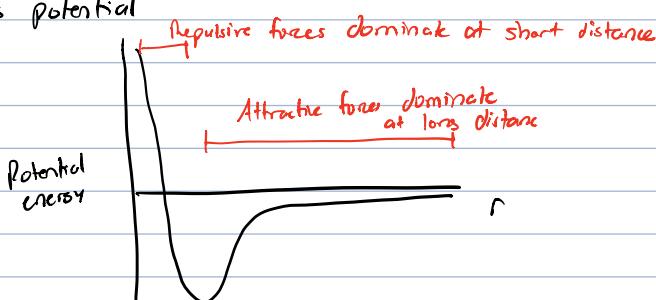
- Hydrogen bonds: strong intermolecular force due to bonds w/ H and extremely electronegative atoms (N, O, F)



o Really strong force

- Repulsive forces: appear if molecules become too close

o Lennard Jones potential



o Gas molecules will attract like oscillating springs b/c of this, esp. if slow

- These IMF are more prevalent if molecules are slow and packed together (high pressure, low temp.)

- Van der Waals equation: used in non-ideal scenarios.

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \rightarrow \text{Accounts for molecular forces}$$

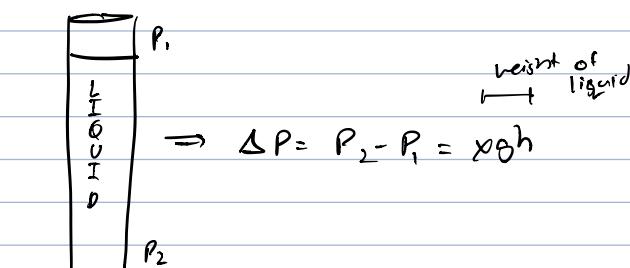
molar volume      Value of molecule

o Use this formula to determine impact on ideal nature of molecule if a factor changes

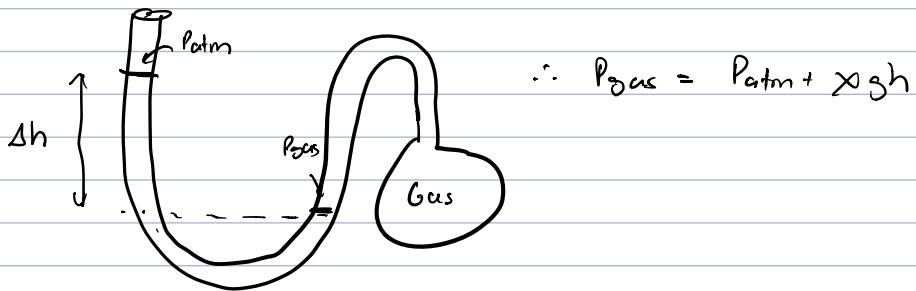
- Both van der Waals and ideal gas law cannot account for extremely low pressures

- Condensed states (liquids + solids) don't have such elegant ideal states b/c we cannot ignore IMF

o Liquids: much more dense  $\Rightarrow$  lower energy. Repulsive forces makes them incompressible



- Remember: pressure in a fluid is same at all horizontal points



- Solids: molecules oscillate b/c IMF is strong
    - ▷ If regular, repeating order  $\Rightarrow$  crystallic. Else: amorphous
    - ▷ Incompressible
  - Different types based on bonds: molecular (pure), covalent, ionic and metallic

### - Temperature:

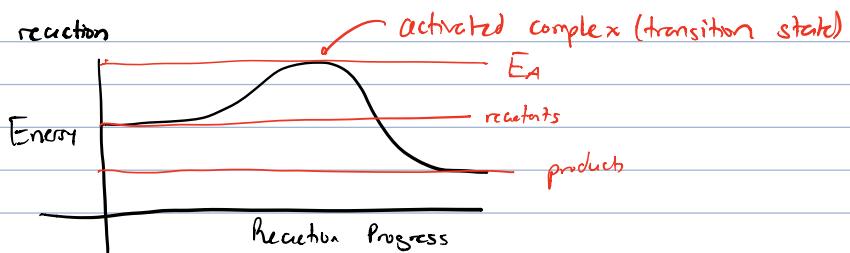
- Heat is not a property of a system. It is due to energy transfer!
  - Thermal equilibrium: no spontaneous transfer of thermal energy

## RATE OF REACTIONS

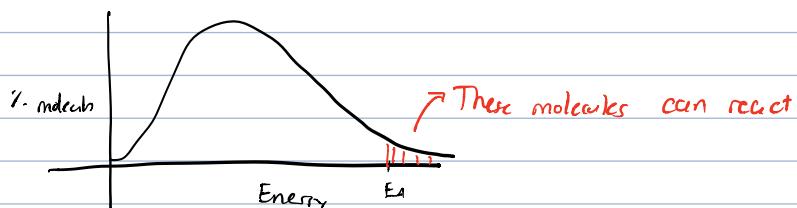
## Collision Theory and Measuring Reaction Rates

- Chemical reactions require bonds to be broken and new bonds to form
  - 3 key requirements:
    1. Molecular collisions
    2. Activation energy: reactant molecules must collide w/ sufficient energy to break bonds
      - Average activation energy: minimum combined energy that particles must have for reaction
    3. Collision orientation:

### - Energy vs. reaction



- From Maxwell-Boltzmann distribution



- If we increase temp, more molecules will have the sufficient energy → faster reaction
  - Catalysts decrease activation energy barrier → more molecules can react
    - Does this by providing alternative activated complex

- Exothermic reaction:  $\Delta H_{\text{products}} - \Delta H_{\text{reactants}} < 0$

- Other words: more energy released forming bonds than energy required to break bonds
  - This release of energy can help other molecules overcome activation energy (eg. fire)

- 4 main factors affect reaction rate:

1. Increase reactant concentration: increases collisions

2. Reaction temperature: faster collisions w/ more molecules above Ea

3. Catalysts: facilitates creation of alternative activated complexes that have lower EA

P Do not change as a result of reaction

4. Physical nature of reactants: greater surface area / liquid + gas state increase reaction rate

## - Measuring reaction

- Given some reaction  $A + BC \rightarrow AB + C$  and  $[A]$  decreases by  $\xi$ , then:

$$C_A(\Delta t) = C_{A_0} - \xi \Rightarrow n_A(\Delta t) = n_{A_0} - \xi V$$

$$\therefore \text{Rate of reaction for } A: \frac{n_{A_0} - n_A(\Delta t)}{0 - \Delta t} = - \frac{\xi V}{\Delta t}$$

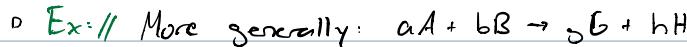
Volumetric rate of reaction A:

$$\dot{R}_A = \frac{C_{A_0} - C_A(\Delta t)}{0 - \Delta t} = - \frac{\xi}{\Delta t}$$

- Reaction rates follow stoichiometric ratios



$$\dot{R}_A = \dot{R}_{BC} = - \dot{R}_{AB} = - \dot{R}_C$$



$$-\frac{\dot{R}_A}{a} = -\frac{\dot{R}_B}{b} = \frac{\dot{R}_C}{c} = \frac{\dot{R}_D}{d} = \dot{R}$$

- Reaction rate slows down as reaction progresses b/c conc.  $\downarrow$

- Reaction will stop if either limiting reactant exhausted or reaches equilibrium w/ reverse reaction

## Dependence of Reaction Rate on Concentration

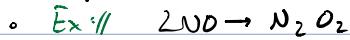
- We can relate reaction rate to reactant molar concentrations

$$\dot{R} = k C_A^m C_B^n \dots$$

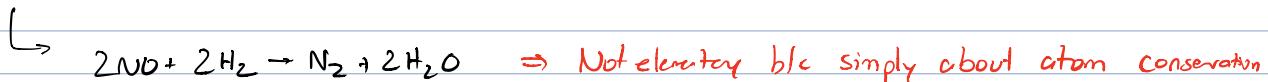
- $k$  is reaction rate constant,  $m$  is order of reaction w.r.t A and  $n$  is order of reaction w.r.t B
- $k$  dependent on reaction, catalysts + temperature. reaction rate  $\propto k$
- $m$  and  $n$  (exponents) sum to overall reaction order. Obtained experimentally + not related to stoich
- Zero order: reactant conc. has no impact on rate
- First order:  $n \times \text{conc.} \Rightarrow n \times \text{rate}$
- Second order:  $n \times \text{conc.} \Rightarrow n^2 \times \text{rate}$

- Elementary reaction: 1/more reactants react directly to form products w/ single step + transition state

- Exponents in reaction rate are equal to stoich coefficients for elementary reactions



} elementary reactions



- Method of initial rates: series of reactions w/ one reactant changing concentrations. Compare to find exp.



Experiment	$C_A$	$C_B$	$C_C$	Rate (M/s)
1	1.6	1.6	1	$\dot{R}_1$
2	0.8	1.6	1	$\dot{R}_2 = \frac{1}{2} \dot{R}_1$
3	0.8	0.8	1	$\dot{R}_3 = \frac{1}{4} \dot{R}_1$
4	1.6	1.6	0.5	$\dot{R}_4 = 16 \dot{R}_1$
5	0.8	0.8	0.5	$\dot{R}_5$

Remember:  $\dot{R} = k C_A^m C_B^n C_C^p$

- ① Compare experiments where only 1 reactant conc. changed

$$1: \frac{\dot{R}_1}{\dot{R}_2} = \frac{1}{2} = \frac{k \cdot 0.8^m \cdot 1.6^n \cdot 1^p}{k \cdot 1.6^m \cdot 1.6^n \cdot 1^p} = \left(\frac{1}{2}\right)^m$$

$$\therefore m = 1$$

$$2: \frac{\dot{R}_2}{\dot{R}_3} = 4 = \frac{k \cdot 0.8^m \cdot 1.6^n \cdot 1^p}{k \cdot 0.8^m \cdot 0.8^n \cdot 1^p} = 2^n$$

$$\therefore n = 2$$

- ② Use algebra to find remaining exponents.

$$\frac{P_A}{P_A} = \dots \Rightarrow p = -1$$

- Integrated rate laws: if only 1 reactant limiting  $\Rightarrow P_A = -k C_A^m$

- Limiting compound controls rate of entire reaction

- Integration leads to following:

- Order of 0  $\Rightarrow C_A(t) = -kt + C_{A_0}$

- Order of 1  $\Rightarrow \ln(C_A(t)) = -kt + \ln C_{A_0}$

- Order of 2  $\Rightarrow \frac{1}{C_A(t)} = kt + \frac{1}{C_{A_0}}$

- Solving integrated rates problems

- Identity order: transform graph to  $\ln(C_A(t))$  or  $\frac{1}{C_A(t)}$  + see if reaction rate is straight line.  $k$  = slope!

- Initial rate: use general rate law ( $k C_A^m$ )

- Concentration at time ( $t$ ): simply use concentration as function of time formulas

- Half-life: time it takes for  $1/2$  of reactant to be consumed or  $C_A(t_{1/2}) = \frac{1}{2} C_{A_0}$

- 0 order:  $t_{1/2} = \frac{C_{A_0}}{2k}$

- 1 order:  $t_{1/2} = \frac{\ln 2}{k}$   $\Rightarrow$  Does not depend on concentration!

- 2nd order:  $t_{1/2} = \frac{1}{k C_{A_0}}$

- Tip: use apparent reaction rate constants ( $k' = k C_A^m$ )

- Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \xrightarrow{\text{activation energy (J/mol)}} \text{Temp. (K)} + \text{gas constant}$$

- Ex:// First order reaction  $A \rightarrow$  products has  $t_{1/2} = 46.2$  min at  $28^\circ\text{C}$  and 2.6 min at  $102^\circ\text{C}$

a) Activation energy of reaction

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{-\ln\left(\frac{\ln 2}{2 \cdot t_{1/2,1}}\right)}{\ln\left(\frac{\ln 2}{2 \cdot t_{1/2,2}}\right)}$$

Solve for  $E_a$

b) What temperature would  $t_{1/2} = t_2$

Use above equation but now  $E_a$  solved and  $T_2$  unknown

## PHASE EQUILIBRIUM

### Phase Transitions, Phase Equilibrium and Vapor Pressure

- Phase: region of space where state of aggregation (organization of atoms) and chem. comp. is uniform

- Just b/c in same state doesn't mean in same phase (e.g. different ice crystal structures  $\Rightarrow$  polymorphism)

- Phase transition: matter changes from one phase to another  $\leftarrow$  temp. / pressure.

- Molecules transfer energy via heat until thermal equilibrium

- As molecules gain/lose energy, intermolecular bonds are broken or formed, causing change of state

- Condensation: molecular IMF  $\uparrow \rightarrow$  physical bonds created, releasing energy  $\rightarrow$  bond kept in liquid state  $\rightarrow$  energy int.

- Vaporization: IMF  $\downarrow \rightarrow$  bond broken, requiring energy from condensate

- Enthalpy of vaporization / condensation: amount of energy needed to keep liquid temp. constant when quantity vaporized/condensed

$$\Delta H_{\text{vap}} = H_{\text{vapour}} - H_{\text{liquid}} = -\Delta H_{\text{cond}}$$

Ex://  $\Delta H_{\text{vap}} = 44.01 \text{ kJ/mol}$  for water at  $25^\circ\text{C}$  + 1 atm

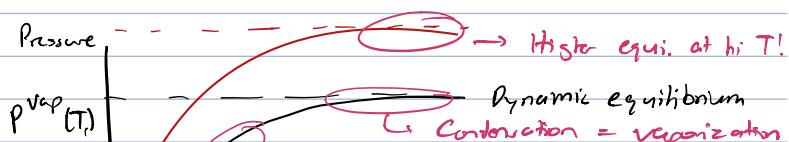
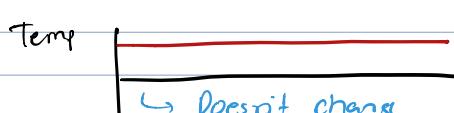


- Stronger IMF requires more energy

- Higher temp  $\rightarrow \downarrow \Delta H$

- Surface-level molecules vaporize first  $\Rightarrow$  rate of vaporization  $\propto$  area of liquid-vapour interface

- Closed system:



b/c energy doesn't leave!

→ Condensation starts  
→ Initial vaporization from most energetic

Time

Time

- Vapor pressure:  $P_{\text{vap}}$  is pressure exerted by vapor in equilibrium w/ liquid in closed sys. @ given temp.

- $P_{\text{vap}} \propto T$ : more molecules can vaporize
- $P_{\text{vap}} \propto \frac{1}{\Delta H_{\text{vap}}}$ : molecules need more energy to vaporize if more IMF
- Volatile substances have high  $P_{\text{vap}}$

- Boiling: unlike evaporation which is surface level, boiling is vaporization in entire liquid  $\Rightarrow$  bubbles

- Boiling point ( $T_{\text{bp}}$ ):  $P_{\text{vap}} = P_{\text{atm}}$
- Normal boiling point:  $P_{\text{vap}} = 1 \text{ atm}$ .

• Higher altitudes  $\rightarrow$  lower pressure  $\rightarrow$  lower temp needed for  $P_{\text{vap}} = P_{\text{atm}}$

- Clausius-Clapeyron equation:  $P_{\text{vap}} \leftrightarrow T$

$$\ln P_{\text{vap}} = -A \left( \frac{1}{T} \right) + B$$

$$\therefore A = \frac{\Delta H_{\text{vap}}}{R}$$

• B: eliminate by comparing  $P_1^{\text{vap}}$  and  $P_2^{\text{vap}}$

$$\therefore \ln \left( \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} \right) = - \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

o Ex:// Pressure cooker releases at 2 atm. Volume is 6 L and contains liquid + vapor  $\text{H}_2\text{O}$

c) What is temp. when valve first opens

We know  $\text{H}_2\text{O}$  boils at  $100^\circ\text{C} \Rightarrow P_{\text{vap}} = 1 \text{ atm}$  at  $373.15 \text{ K}$

$$\therefore \ln \left( \frac{2}{1} \right) = - \frac{44. \times 10^3 \text{ J}}{8.314} \left( \frac{1}{T_2} - \frac{1}{373.15} \right)$$

$$\therefore T_2 = 119^\circ\text{C}$$

b) Minimum amount of water needed if 200 g of water still left when valve first opens.

$$V_{\text{liquid}} + V_{\text{vapor}} = 6.0 \text{ L}$$

$$200 \text{ g of liquid} = 0.2 \text{ L} \text{ (using density of } 1 \text{ g/mL})$$

$$\therefore V_{\text{vapor}} = 5.8 \text{ L}$$

$$\therefore m_{\text{vapor}} = \frac{P V M}{R T} = 6.5 \text{ g}$$

$$\therefore \text{Add } 200 + 6.5 = 206.5 \text{ g of water.}$$

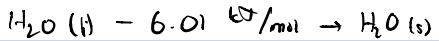
c) Fraction of total water mass is vapor phase.

$$\frac{6.5}{206.5} = 3.1\%$$

- Solid  $\leftrightarrow$  liquid involves melting point (either melting / fusion)

• Enthalpy of fusion (solidification): amount of energy needed to keep solid at constant temp. due to change in phase  
 $\Delta H_{\text{fus}} = H_{\text{liquid}} - H_{\text{solid}}$

o Ex:// If  $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$  for  $\text{H}_2\text{O}$  at  $0^\circ\text{C} + 1 \text{ atm}$



o Since not completely destroying all IMF, requires much less energy than vaporization

- Solid  $\rightarrow$  vapor called sublimation. Vapor  $\rightarrow$  solid: deposition

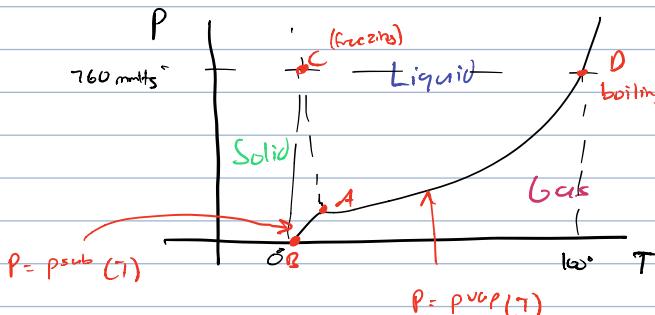
- $\Delta H_{\text{sub}} = H_{\text{vapor}} - H_{\text{solid}}$   
=  $(H_{\text{vapor}} - H_{\text{liquid}}) + (H_{\text{liquid}} - H_{\text{solid}})$   
=  $\Delta H_{\text{vap}} + \Delta H_{\text{fus}}$

o Sublimation pressures: like vapor pressures but much smaller b/c IMF much stronger so less volatile

o Can use Clausius-Clapeyron to calculate by subbing  $\Delta H_{\text{sub}}$  for  $\Delta H_{\text{vap}}$

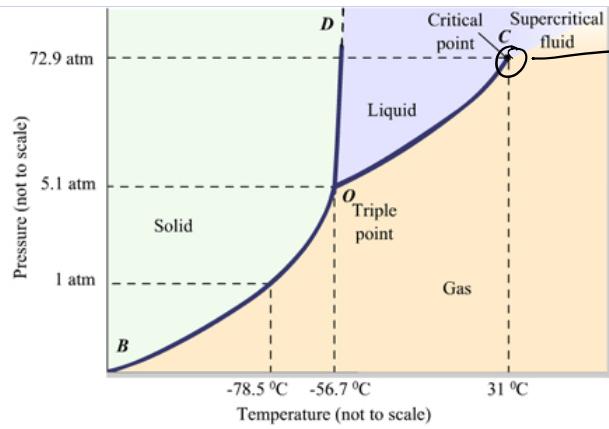


# Phase diagram (P vs. T) of water



A: all three states exist

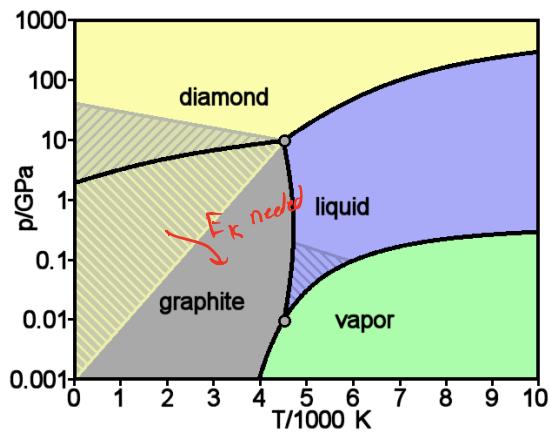
- In this example, note that increasing pressure can melt ice! This is because of water's unique density prop.
- $\text{CO}_2$  phase diagram:



Highest temperature which pure substance can exist

Supercritical fluid: vapor + liquid mixed

- Carbon phase diagram



Diamond is unstable at STP but requires a lot of kinetic energy to convert to graphite

## Henry's Law and Raoult's Law

- Gasses sometimes dissolve into liquids

- Temp  $\uparrow \rightarrow$  solubility  $\downarrow$
- Pressure  $\uparrow \rightarrow$  solubility  $\uparrow$

- Henry's Law: concentration of soluble gas + partial pressure of gas above liquid

$$P_A = x_A H_A$$

or

$$C_A = k_A P_A$$

- $x_A$  is mole fraction of gas in liquid.  $H_A / k_A$  are constants dependent on units, temp. + solute-solvent
- Applies to gas/liquid equilibrium when  $x_A$  close to 0.

- Ex:// How much  $\text{O}_2 + \text{N}_2$  dissolved in 250 mL  $\text{H}_2\text{O}$  at 20°C dry at 758 mmHg + humidity @ 70%  
Determine concentration of  $\text{O}_2 + \text{N}_2$  in mg/L.

Dry air is 79 mol %  $\text{N}_2$  21 mol %  $\text{O}_2$ . At 20°C:  $P_{\text{H}_2\text{O}}^{\text{vap}} = 17.5 \text{ mmHg}$ ,  $H_{\text{O}_2} = 9.01 \times 10^4 \text{ atm}$ ,  $H_{\text{N}_2} = 8.01$

## ① Determine partial pressures

$$P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}^{\text{vap}} \cdot 0.7 = 0.7 \times 17.5 \text{ mm Hg} = 12.25 \text{ mm Hg} \Rightarrow \text{Need to find } P_{\text{dry air}} = P_{\text{H}_2\text{O}}$$

$$P_{\text{dry air}} = 760 \text{ mm Hg} - 12.25 \text{ mm Hg} \\ = 747.75 \text{ mm Hg}$$

$$P_{\text{N}_2} = 747.75 \text{ mm Hg} \times 0.79 = 589.14 \text{ mm Hg}$$

$$P_{\text{O}_2} = 747.75 \text{ mm Hg} \times 0.21 = 156.61 \text{ mm Hg}$$

$\Rightarrow$  Need to adjust  $P_{\text{dry air}}$  + take out wet air

## ② Finding mole fractions:

$$P_{\text{NO}_2} = x_{\text{NO}_2} \cdot P_{\text{NO}_2}$$

$$\therefore x_{\text{NO}_2} = (589.14 \div 760 \text{ mm Hg}) \div 8.04 \times 10^{-6} \\ = 9.69 \times 10^{-6} \text{ mol NO}_2 / \text{mol}$$

$$\text{Similarly: } x_{\text{O}_2} = 5.19 \times 10^{-6} \text{ mol O}_2 / \text{mol}$$

## ③ Finding correct concentrations

mol solution  $\sim$  mol  $\text{H}_2\text{O}$

Do stoich + unit analysis

- Ex:1 What mass of  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$  needs to be added to 18.9 L of ale at 20°C to achieve carbonation of 1.5 volumes? Bottled in 330 mL bottles, pressure in 20 mL headspace?

$$\text{At } 20^\circ\text{C, } P_{\text{CO}_2} = 0.192 \times 10^4 \text{ atm.}$$

① Desired amount of  $\text{CO}_2$  in ale

$$18.9 \text{ L ale} \times \frac{1.5 \text{ L CO}_2}{1 \text{ L ale}} = 28.35 \text{ L CO}_2$$

$$n_{\text{CO}_2} = \frac{PV}{RT} = 1.265 \text{ mol CO}_2$$

Product from either saturation or glucose

## ② # of moles dissolved by saturation (Henry's Law)

$$P_{\text{CO}_2} = x_{\text{CO}_2} \cdot P_{\text{CO}_2} \quad \rightarrow P_{\text{CO}_2} = 1 \text{ atm} \\ \therefore x_{\text{CO}_2} = 7.09 \times 10^{-4} \frac{\text{mol CO}_2}{\text{mol sol.}}$$

Finding # of moles dissolved due to saturation

$$18.9 \text{ L} \times \frac{1000 \text{ g}}{\text{L}} \times \frac{\text{mol}}{18 \text{ g}} \times \frac{7.09 \times 10^{-4} \text{ mol CO}_2}{\text{mol}} = 0.739 \text{ mol CO}_2$$

This means that 0.739 mol  $\text{CO}_2$  from saturation and  $(1.265 - 0.739)$  mol  $\text{CO}_2$  from glucose

## ③ Using stoich to find glucose required

## ④ Pressure in headspace

$$\text{Moles of CO}_2 \text{ in each bottle: } \frac{1.265 \text{ mol CO}_2}{11.9 \text{ L}} \times 330 \text{ mL} = 0.0221 \text{ mol CO}_2$$

$$n_{\text{CO}_2} = n_{\text{gas CO}_2} + n_{\text{CO}_2, \text{liquid}} \\ = \frac{P_{\text{CO}_2} V_{\text{CO}_2}}{RT} + \frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} n_{\text{liquid}}$$

Solve for  $P_{\text{CO}_2}$

- Raoult's Law: multiple liquid + gas components

$$\gamma_A P = P_A = x_A P_A^{\text{vap}} \quad \gamma_A = \text{mole fraction in vapour phase}$$

- Ex:11 Benzene + toluene in solution.  $P_{\text{benzene}}^{\text{vap}} = 86.35 \text{ kPa}$ .  $P_{\text{toluene}}^{\text{vap}} = 32.58 \text{ kPa}$ . Mole fraction of benzene in liquid is 0.4.

## a) Partial pressures above solution?

$$P_{\text{benzene}} = 0.4 \times 86.35 \text{ kPa}$$

$$= 39.54 \text{ kPa}$$

$$\begin{aligned} P_{\text{toluene}} &= 0.6 \times 32.58 \text{ kPa} \\ &= 19.548 \text{ kPa} \end{aligned}$$

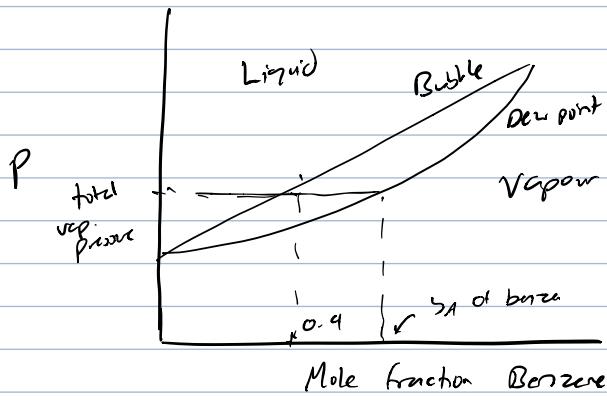
b) Total vapour pressure:

$$P_{\text{tot}} = P_{\text{benzene}} + P_{\text{toluene}} = 54.01 \text{ kPa}$$

c) Composition:

64% benzene, 36.14% toluene

Given a phase diagram



- Bubble point curve:  $P_{\text{total}} = x_A [P_A^{\text{vap}} - P_B^{\text{vap}}] + P_B^{\text{vap}}$

o Straight line fit in example problem

o Bubble point is composition of liquid at given pressure, dew point is composition of gas

- Ideal solutions: barely any difference in component interactions  $\Rightarrow$  Henry's Law applies

- If non-ideal, laws only apply if solution dilute

o Raoult's Law applies well if component in question is in great excess + linear dependence holds for minority component, which is Henry's Law line  $\Rightarrow$  slope = Henry constant

## Colligative Properties

- If solution has volatile solvent but non-volatile solute (e.g. water + salt)  $\Rightarrow$  exhibits colligative prop.

- Consider components A and B (non-volatile):

$$P_{\text{pure solvent}} = P_A^{\text{vap}}$$

$$P_{\text{soln}} = x_A P_A^{\text{vap}}$$

$$\therefore \Delta P = P_{\text{soln}} - P_{\text{pure}}$$

$$= (x_A - 1) P_A^{\text{vap}}$$

$$= -x_B P_A^{\text{vap}}$$

+ osmotic press.

o Observed vapour pressure decreases if non-volatile substance added  $\Rightarrow$  elevation of BP, depression of freezing

- Ex: // 20g of non-volatile substance added to 100g H<sub>2</sub>O @ 25°C. Vapor pressure of pure H<sub>2</sub>O = 23.76 mmHg.

Vapor pressure of solution is 22.91 mmHg. Molar mass of solute?

$$\Delta P = -x_{\text{solute}} P_{\text{solvent}}^{\text{vap}}$$

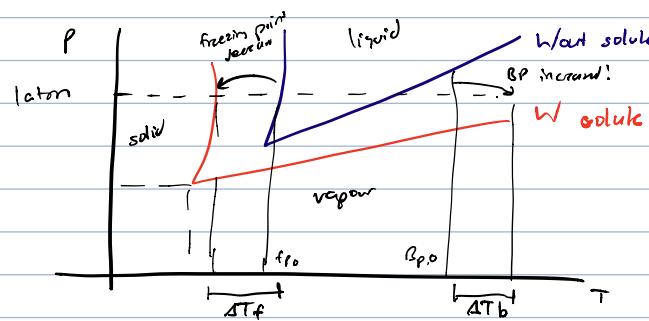
$$x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$= \frac{m_{\text{solute}} / M_{\text{solute}}}{m_{\text{sol}} / M_{\text{sol}} + m_{\text{solv}} / M_{\text{solv}}}$$

$$\therefore \frac{\Delta P}{P_{\text{vap}}^{\text{sol}}} = -1 - \frac{m_{\text{solvent}} / M_{\text{solvent}}}{m_{\text{solute}} / M_{\text{solute}}}$$

Solve for M<sub>solute</sub>

- If vapor pressure lowered, higher temp. needed for  $P_{\text{vap}} = P_{\text{atm}} \Rightarrow$  higher boiling point



$$\Delta T_b = K_b m, \Delta T_f = -K_f m$$

□  $K_b + K_f \Rightarrow$  constants that only depend on solvent

□ m: moles of solute / kg of solvent

$$K_b = \frac{R T_{Bp,0}^2 M_{\text{solute}}}{1000 \Delta H_{\text{vap}}} \quad K_f = \frac{R T_{fp,0}^2 M_{\text{solute}}}{1000 \Delta H_{\text{fus}}}$$

- Ex:// Soln I prepared by dissolving 0.1150 g of solute ( $M_{\text{solute}} = 110.1 \text{ g/mol}$ ) in 100 g of solvent ( $M_{\text{solute}} = 99.1 \text{ g/mol}$ ). Solution has FP 0.11°C below pure solvent. Soln II prepared with 0.4660 g of solute ( $M_{\text{solute}} = \text{unknown}$ ) in 95.6 g of same solvent w/ 0.49°C depression observed. Determine molecular weight of second solute +  $\Delta H_{\text{fus}}$  of solvent. Mp of pure solvent: -8.00°C

① Find  $K_f$ :

$$\Delta T_f = -K_f m_I$$

$$m_I = \frac{0.115 \text{ g}}{100 \text{ g solv.}} \times \frac{1000 \text{ g solv.}}{1 \text{ kg solv.}} \times \frac{\text{mol solute}}{110.1 \text{ g solute}} = 0.04678$$

$$\therefore K_f = -\frac{\Delta T_f}{m_I} = -\frac{-0.49^\circ\text{C}}{0.04678} = 8.76^\circ\text{C} \cdot \text{kg/mol}$$

② Molality of soln II:

Since same solvent,  $K_f$  above will be useful

$$m_{II} = -\frac{\Delta T_f, II}{K_f} = -\frac{-0.49}{8.76} = 0.05594 \frac{\text{mol solv.}}{\text{kg solut}}$$

③ Calculating molar mass.

$$M_{\text{solute}} = \frac{1 \text{ kg solut}}{0.05594 \text{ mol solute}} \times \frac{0.4660 \text{ g solute}}{95.6 \text{ g solut}} \times \frac{1000 \text{ g solut}}{1 \text{ kg solut}} \\ = 83.4 \text{ g/mol}$$

④ Find  $\Delta H_{\text{fus}}$ :

$$K_f = \frac{R T_{fp,0}^2 \cdot M_{\text{solute}}}{1000 \cdot \Delta H_{\text{fus}}}$$

$$\Delta H_{\text{fus}} = \frac{R T_{fp,0}^2 \cdot M_{\text{solute}}}{1000 \cdot K_f} \\ = \frac{8.314 \times (273.15 - 8)^2 (99.1 \text{ g/mol})}{1000 \cdot 8.76} \\ = 6.4 \text{ kJ/mol}$$

- If solute dissociates, actual molality is much higher

◦ Effect on BP increase / FP depression is multiplying m w/ i (van't Hoff factor)

$$\Delta T_b = i K_b m$$

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

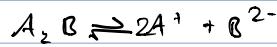
◦ Magnitude of van't Hoff:

1) Degree of dissociation: moles of ion in soln / mol of solut ( $i_{\text{ideal}} = 2$ )

2) II association: more ion  $\Rightarrow$  less independent.  $\therefore i \propto \frac{1}{[\text{ion}]}$

$$i = \frac{\text{moles of particles}}{\text{moles of compound}}$$

- Ex:// Freezing point formed by dissolving 0.01 mol  $A_2B$  in 1000g of  $H_2O$  is  $-0.0241^\circ C$ . Estimate degree of dissociation.



$$K_f \text{ for water} = 1.86^\circ C \cdot \text{kg/mol}$$

- ① Determine  $i$ :

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

$$0.0241 = i \cdot 1.86 \cdot \frac{0.01}{1 \text{ kg}}$$

$$i = 1.3$$

- ② Determining dissociation:

Since  $i$  is not 1 but not 3 (fully dissociates),  $A_2B$  partially dissociates. Let  $\alpha$  be fraction of  $A_2B$  that dissociates.



Initial	1	0	0
Change	$-\alpha$	$+2\alpha$	$\alpha$
Total	$1-\alpha$	$2\alpha$	$\alpha$

$$\therefore \text{Total mols of particles: } 1-\alpha + 2\alpha + \alpha = i$$

$$1 + 2\alpha = i$$

$$\therefore \alpha = \frac{i-1}{2} = 0.15$$

$\therefore$  15% of  $A_2B$  dissociates.

## REACTION EQUILIBRIUM

### Chemical Equilibrium and Equilibrium Constants

- Equilibrium constant:  $aA + bB \rightleftharpoons cC + dD$ . Constant:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \Rightarrow \text{concentrations at equilibrium}$$

◦ Independent of initial concentration

- Ex://  $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ . At equilibrium, 2 L flask contains 4.93g  $PCl_3$ , 9.63g  $Cl_2$ , and 13.35g  $PCl_5$ . Find  $K_c$

- ① Find concentrations

$$[PCl_3] = \frac{4.93/137.373}{22} = 0.018 \text{ M} \quad [Cl_2] = \frac{9.63/70.906}{2} = 0.07 \text{ M} \quad [PCl_5] = \frac{13.35/208.239}{2} = 0.03 \text{ M}$$

- ② Calculate  $K_c$

$$K_c = \frac{[PCl_5]}{[Cl_2][PCl_3]} = \frac{0.03}{0.018 \cdot 0.07} = 26.3$$

- If we have pressures + gases, use:

$$K_p = \frac{(P_C)^c (P_O)^d}{(P_A)^a (P_B)^b} \rightarrow \text{partial pressure at equilibrium}$$

- Relationship between  $K_p$  and  $K_c$

$$K_c = K_p (RT)^{-\Delta n} \quad \text{where } \Delta n = \sum \text{product coeff.} - \sum \text{reactant coeff.}$$

$$\hookrightarrow 0.08374 \frac{\text{bar}}{\text{mol} \cdot \text{K}}$$

- Ex://  $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$ .  $K_c = 26.3$ . Find  $K_p$  at  $250^\circ\text{C}$

$$K_p = \frac{K_c}{(RT)^{\Delta n}} = \frac{26.3}{(0.08314 \cdot (273.15 + 250))} = 0.605$$

- Heterogeneous reactions: components in different phases

- Don't include pure liquids/solids in equilibrium constant

- Generalized equilibrium constant:

$$K = \frac{\alpha_c^c \alpha_d^d}{\alpha_a^a \alpha_b^b}$$

where:

$$\alpha = \gamma \frac{c}{c^\circ} \text{ for aqueous components where } c^\circ \text{ is } 1 \text{ mol/L}$$

$$\alpha = \gamma \frac{P}{P^\circ} \text{ for aqueous components where } P^\circ \text{ is 1 bar}$$

$$\alpha = 1 \text{ for pure solids + liquids, } \gamma = 1 \text{ for ideal gas + solutions}$$

- Always use mol/L for  $K_c$  and bar for  $K_p$

- Very large  $K \Rightarrow$  goes to completion. Small  $K \Rightarrow$  does not occur

- Equilibrium can be reached but often not observable b/c reaction rate is slow.

## Properties and Calculations of Equilibrium Constants

- Relationships:

- If reaction multiplied by constant, equilibrium const. raised to power of constant

$$K_1 = \frac{a_B}{a_A} \quad A \rightleftharpoons B \Rightarrow K_2 = (K_1)^c$$

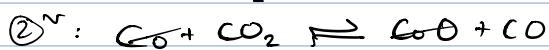
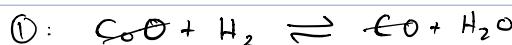
- Reverse of reaction is inverse of equilibrium const.

$$K_1 = \frac{a_B}{a_A} \quad B \rightleftharpoons A \Rightarrow K_2 = \frac{1}{K_1}$$

- If two chemically reactions added, overall eq. const. is product of individual const.



What is constant for



$$\therefore K_{p3} = K_{p1} \cdot \frac{1}{K_{p2}} =$$

- ICE table

- Steps:

1. Write initial amount of each reactant  $\rightarrow$  product

2. Assume change of  $x$  for 1 species

3. Use stoich to find changes for other species

4. Determine equilibrium in terms of  $x$

5. Write equilibrium expression

- Ex://  $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$ .  $K_c = 1.2 \times 10^3$ . Initially, 0.01 mol each  $\text{CO} + \text{Cl}_2$  placed in 10L container. Equilibrium conc. of  $\text{COCl}_2$ ?

① ICE

CO	Cl <sub>2</sub>	CO Cl <sub>2</sub>
0.01	0.01	0
-x	-x	x
0.01-x	0.01-x	x

② Equilibrium:

$$1.2 \times 10^2 = \frac{x}{10} \times \frac{10^2}{(0.01-x)^2}$$

$$1.2 \times 10^2 = \frac{10x}{(0.01-x)^2}$$

$$1.2 \times 10^2 (0.01-x)^2 = x$$

$$1.2 \times 10^2 (0.01^2 - 0.02x + x^2) = x$$

$$x = 0.000413, 0.00242$$

0.00242 is too high (conc. of CO + Cl<sub>2</sub> < 0)

$$\therefore x = 0.000413$$

$$\therefore [\text{COCl}_2] = \frac{0.000413}{10} = 4.1 \times 10^{-4} \text{ M}$$

Ex:// H<sub>2</sub> + I<sub>2</sub>  $\rightleftharpoons$  2HI. 0.005 M H<sub>2</sub> and 0.0125 M I<sub>2</sub>. Equilibrium conc. of I<sub>2</sub> is 0.0072. What is K<sub>c</sub>?

① ICE

H <sub>2</sub>	I <sub>2</sub>	HI
0.005	0.0125	0
-x	-x	+2x
0.005-x	0.0125-x	2x

} Assumed base of 1 L

② Solve for x:

$$0.0125-x = 0.0072$$

$$x = 0.00476 \text{ M}$$

③ K<sub>c</sub>:

$$K_c = \frac{2(0.00476)}{(0.005-x)(0.0125-x)} = 53.8$$

Ex:// 2CaSO<sub>4</sub>  $\rightleftharpoons$  2CaO<sub>(s)</sub> + 2SO<sub>2</sub><sub>(g)</sub> + O<sub>2</sub><sub>(g)</sub>. Only CaO<sub>(s)</sub> present at first. K<sub>p</sub>? P<sub>T</sub> = 0.04608 bar

$$K_p = (P_{SO_2})^2 P_{O_2}$$

$$0.04608 = P_{SO_2} + P_{O_2}$$

$$\text{From stoich} \Rightarrow P_{SO_2} = 2P_{O_2}$$

$$\therefore 0.04608 = 3P_{O_2}$$

$$\therefore P_{O_2, eq} = \frac{0.04608}{3} = 0.01536 \text{ bar}$$

$$\therefore P_{SO_2, eq} = 2 \times 0.01536 = 0.3072$$

K<sub>p</sub> eq:

$$K_p = (0.3072)^2 (0.01536) = 1.45 \times 10^{-5}$$

Ex:// CH<sub>4</sub> + H<sub>2</sub>O  $\rightleftharpoons$  CO + 3H<sub>2</sub>. K<sub>p</sub> = 26.6. 6 mol steam + 6 mol CH<sub>4</sub>. Mole fraction of H<sub>2</sub>?

$$K_p = \frac{P_{CO} \cdot (P_{H_2})^3}{P_{CH_4} \cdot P_{H_2O}} = 26.6$$

$$\frac{(y_{CO} P_{total}) \cdot (y_{H_2} P_{total})^3}{(y_{CH_4} P_{total}) \cdot (y_{H_2O} P_{total})} \Rightarrow \frac{y_{CO} y_{H_2}^3}{y_{CH_4} y_{H_2O}} \cdot P_{total}^2 = 26.6$$

ICE:

CH <sub>4</sub>	H <sub>2</sub> O	CO	H <sub>2</sub>
3	6	0	0
-x	-x	x	3x
7-x	6-x	2	3x

$$n_{\text{total}} = 9+2x$$

From  $K_p$ :

$$\frac{\left(\frac{x}{9+2x}\right) \left(\frac{3x}{9+2x}\right)^3}{\left(\frac{3-x}{9+2x}\right) \left(\frac{6-x}{9+2x}\right)} = 26.6$$

$$x = 1.28 \Rightarrow y_{H_2} = \frac{3(1.28)}{9+2(1.28)} = 73 \text{ y.}$$

### Net Direction of Chemical Change

- Reaction quotient ( $Q$ ): If  $aA + bB \rightleftharpoons cC + dD$

$$Q = \frac{a_c^c a_d^d}{a_A^a a_B^b} \Rightarrow a \text{ is activity of species at } \underline{\text{any}} \text{ point in time}$$

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

$$Q_p = \frac{P_c^c P_d^d}{P_A^a P_B^b}$$

- Reaction quotient approaches equilibrium constant as  $t \rightarrow \infty$

- Generally, if  $Q < K$ , reaction is forward.  $Q > K$ , reaction is backward

- Ex: //  $K_c = 280$  for  $2SO_2 + O_2 \rightleftharpoons 2SO_3$ .  $[SO_2] = 0.025$ ,  $[O_2] = 0.035$ ,  $[SO_3] = 0.096$ . Net direction?

① Calculate  $Q$ :

$$Q = \frac{[SO_3]^2}{[SO_2]^2 \cdot [O_2]} = \frac{0.096^2}{0.025^2 \cdot 0.035} = 96.73$$

② Compare with  $K$ .

Since  $Q < K$ , reaction is forward.

- Ex: //  $NO_2 + CO \rightleftharpoons NO + CO_2$ .  $NO_2$  is brown.  $P_{NO_2} = P_{CO} = 3.4 \text{ bar}$ ,  $P_{NO} = P_{CO_2} = 1.4 \text{ bar} \Rightarrow$  brown fades.

What should  $K_p$  be?

① Determine reaction direction

Brown color  $\downarrow \Rightarrow$  reaction is forward  $\Rightarrow Q < K_p$

② Determine  $Q$ :

$$Q_p = \frac{P_{NO} P_{CO_2}}{P_{NO_2} P_{CO}} = \left(\frac{1.4}{3.4}\right)^2 = 0.169$$

③ Condition:

$$Q < K_p$$

$$0.17 < K_p$$

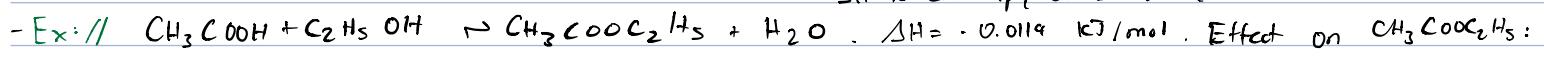
- Le Chatelier's Principle: if system @ equilibrium + subjected to change, system attains new equilibrium to offset impact of change

- o Change in concentration:  $Q$  changes  $\rightarrow$  reaction moves back/forward to new equilibrium ( $Q = K$ )
- o Change in volume:  $Q \propto V^{-A-n}$ . All concentrations affected, but depending on powers, some affected more
- o Pressure change: adding inert gas has no impact
- o Temperature: equilibrium constant will change  $\Rightarrow$  use energy as term in reaction + use same principles

- Van't Hoff equation: used to estimate  $K_p(T_2)$  if  $K_p(T_1)$  known.

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow T \text{ in Kelvin}$$

$$R: 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$



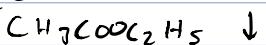
a) Adding  $\text{CH}_3\text{COOH}$ :



b) Adding  $\text{CH}_2\text{H}_5\text{OH}$ :



c) Adding  $\text{H}_2\text{O}$ :



d) Increasing reaction temp:



e) Increase pressure:

No effect



a) Decreasing temp:



b) Adding inert gas @ constant volume

No effect

c) Removing 90% of solid  $\text{I}$ :

$\text{HI} \uparrow \Rightarrow$  Wrong: solid has no impact on equilibrium

d) Decreasing volume:

$$Q = \frac{[\text{H}_2]}{[\text{HI}]^2} = V \downarrow, Q \uparrow \Rightarrow \text{HI} \downarrow$$

e) Adding inert gas at constant pressure.

Basically increasing volume

$$\therefore \text{HI} \uparrow$$

If volume changes, direction is to direction that

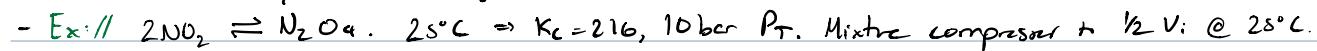
- a)  $V \uparrow \rightarrow \text{gas mol} \uparrow$
- b)  $V \downarrow \rightarrow \text{gas mol} \downarrow$



1) High pressure by decreasing volume  $\Rightarrow$  side of fewer mol. favored

2) low temp b/c exothermic

3) Always remove  $\text{NH}_3$



a) Initial mole fraction of  $\text{NO}_2$

①  $K_p$ :

$$K_p = K_c (RT)^{\Delta n}$$

$$= 8.71$$

$$8.71 = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} + P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2} = 10 \text{ bar}$$

② Find partial pressure values.

$$\text{Let } x = P_{\text{NO}_2}$$

$$\therefore P_{\text{N}_2\text{O}_4} = 10 - x$$

$$\therefore 8.71 = \frac{10 - x}{x^2}$$

$$\therefore x = 1.016$$

③ Find mole fraction:

$$\gamma_{\text{NO}_2} = \frac{x}{10} = 0.102$$

b) Total pressure at new equilibrium

By Le Chatelier  $\Rightarrow$  reaction should go forward.

By Ideal Gas Law  $\Rightarrow V/2 \Rightarrow P \times 2$

ICE:

	$2\text{NO}_2$	$\rightarrow$	$\text{N}_2\text{O}_4$
P <sub>i</sub>	1.016		8.984
P <sub>after</sub>	2.082		17.968
C	-2x		+2
E	2.082 - 2x		17.968 + 2x

Solve using equilibrium constant:

$$\frac{17.968 + 2x}{(2.082 - 2x)^2} = 8.71$$

$$\therefore x = \{0.292, 1.265\}$$

$$x = 0.292$$

$$\therefore P_T = (2.082 - 2 \times 0.292) + (17.968 + 0.292)$$

$$= 19.7 \text{ bar}$$

c) Mole fraction of  $\text{NO}_2$

$$\frac{2.082 - 2(0.292)}{19.7} = 0.0785$$

## ELECTROCHEMICAL SYSTEMS

### Oxidation States and Redox Reactions

- For an ionic compound, O.S. = charge of each ion

- Rules:

- O.S. of any free element (not bound) is zero
- Monatomic ion O.S. = charge of ion ( $\text{Cl}^-$  has O.S. of -1,  $\text{Cu}^{2+}$  has O.S. of 2)
- Sum of oxidation states should equal overall charge of entity

- From periodic table:

- Alkali metals have O.S. of 1
- Alkaline metals have O.S. of 2
- Halogen have O.S. of -1
- Group 16 (O, S, ...) has O.S. of -2
- Group 15 (N, P, ...) has O.S. of -3

- Ex://  $\text{MgBr}_2$

$$\begin{array}{l} \text{O.S. of Mg} = 2 \\ \text{O.S. of Br} = -1 \end{array} \quad \left. \begin{array}{l} \text{Total} = 2 + 2(-1) = 0 \end{array} \right. \checkmark$$

- Ex://  $\text{MnO}_4^-$

$$\text{Total} = \text{O.S. Mn} + 4 \text{ O.S. O} = -1$$

$$\text{O.S. Mn} + 4(-2) = -1$$

$$\therefore \text{O.S. Mn} = 7$$

- Exceptions:

- If hydrogen with some metal, then O.S. = -1
- If oxygen in a peroxide, then O.S. = -1

- Oxidation states can be fractional

- Redox reactions:

- Consider  $\text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$  or oxidizing agent
  - $\therefore \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$   $\Rightarrow$  Copper is reduced, (reduction half reaction)
  - $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$   $\Rightarrow$  Oxygen is oxidized (oxidation half rxn)

o Memory trick: LEO goes GER

o  $\therefore$  Reduction if O.S.  $\downarrow$  by gain of  $\text{e}^-$ , oxidation if O.S.  $\uparrow$  if loss of  $\text{e}^-$

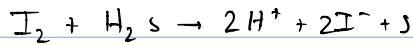
o To determine if a reaction is a redox reaction, determine if O.S. of species changes

- Balancing redox reactions requires balancing of all species, including  $\text{e}^-$  (balance charge)

Ex://

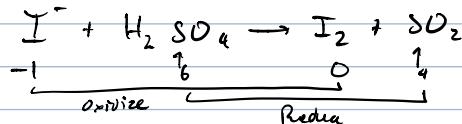


Balance H + I



Steps: Balance  $I^- + H_2 SO_4 \rightarrow I_2 + SO_2$

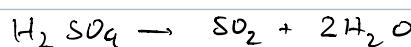
1. Identify oxidation + reduction half reactions by comparing O.S. states



2. Balance all atoms except hydrogen + oxygen



3. Balance oxygen by adding water



4. Balance hydrogen by adding hydrogen ions



5. Balance charge via  $e^-$



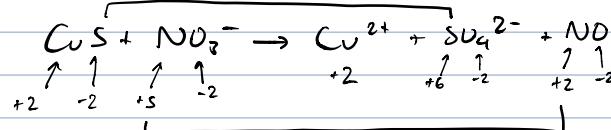
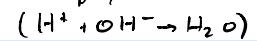
6. Multiply reaction to make sure right amount (equal) # of  $e^-$  transferred

7. Add

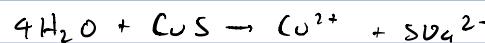


8. If reaction in basic environment, add equal # of  $OH^-$  to each side of eqn + simplify

Ex:// Balance  $CuS + NO_3^- \rightarrow Cu^{2+} + SO_4^{2-} + NO$



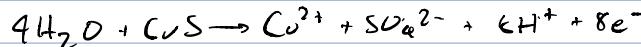
Balancing oxygen:



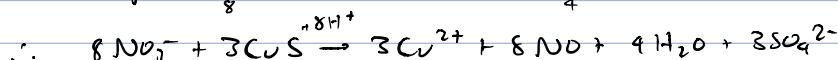
Balancing hydrogen:



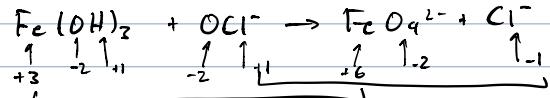
Balancing charge:



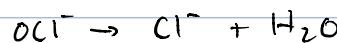
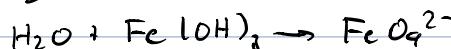
Adding:



Ex://  $Fe(OH)_3 + OCl^- \rightarrow FeO_4^{2-} + Cl^-$



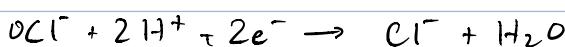
## Balancing oxygen:



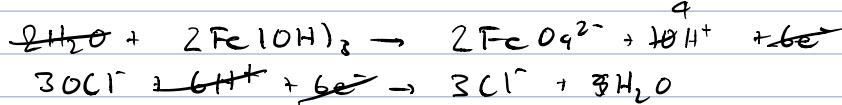
## Balancing by oxygen



## Balancing charge:



Address:

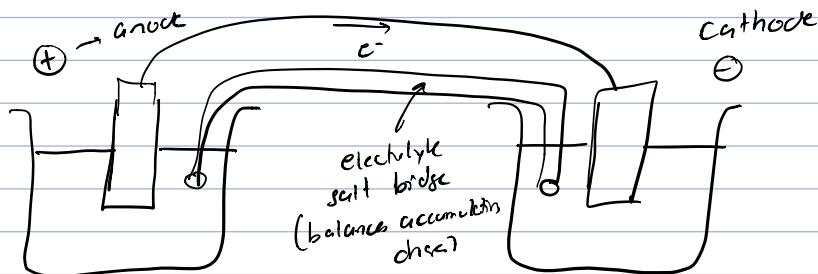


Add  $\text{OH}^-$

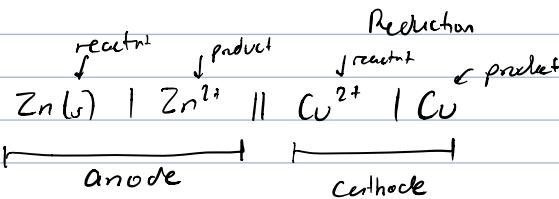


## The Galvanic Cell and Faraday's Law

- Galvanic cell: uses redox reactions to power itself



### Oxidation

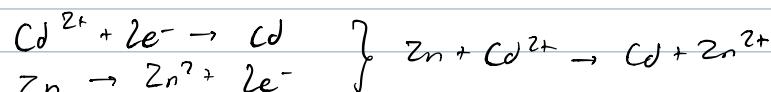


- Faraday's Law:  $Q = F n$  where  $Q$  is charge in circuit,  $F$  is Faraday's constant and  $n$  is # of e<sup>-</sup>

$$\therefore I = \frac{Q}{t} = \frac{Fm}{t}$$

- Ex:// Cadmium cathode in  $\text{CdSO}_4$  solution and zinc anode in zinc Sulphate solution.

a) Write balanced reaction:



b) Current  $I$  flows for  $t$  hours. Charge has passed?

$$\rho = Th \approx 3600$$

c) Change in mass of zinc electrode

$$n = \frac{Q}{F} = \frac{3600 \text{ IAh}}{F}$$

$$\therefore n_{\text{Zn}} = \frac{1800 \text{ IAh}}{F} \times M_{\text{Zn}}$$

d) Change in mass of Cd electrode

$$n_{\text{Cd}} = \frac{1800 \text{ IAh}}{F} \times M_{\text{Cd}}$$

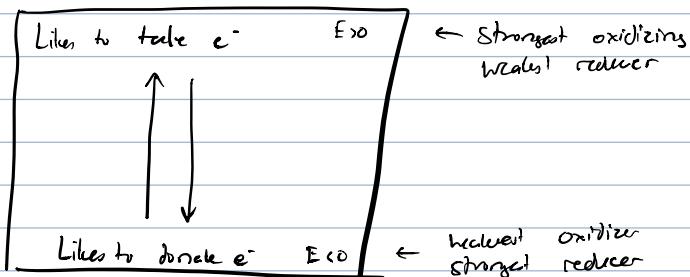
### Standard Cell Potential and the Nernst Equation

- Standard state of electrode: 1.0 M for all dissolved species, 1 bar pressure for gas, 25°C

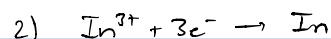
- How to determine cell potential:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

o Use table of reduction potentials



- Ex:// Zn in  $\text{Zn}(\text{NO}_3)_2$  solution + In in  $\text{In}(\text{NO}_3)_3$  solution. Cell voltage is 0.425 V and In plate out



a) Balanced equation:



b) Standard potential for  $\text{In}^{3+}$  reduction

$$E = E_{\text{cathode}} - E_{\text{anode}}$$

$$0.427 = E - (-0.763)$$

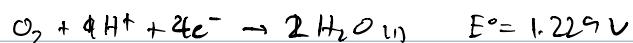
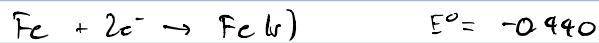
$$E = -0.336 \text{ V}$$

- Reactions happen spontaneously if  $E > 0$

- In a mixture, we are optimizing for  $E$ , so want greatest separation of two half-reactions

- Corrosion: formation of oxides on metal when exposed to  $\text{H}_2\text{O}/\text{O}_2$

o Ex:// Iron rust:



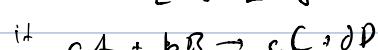
∴ Reaction potentials are favored

- Nernst equation: allows us to determine cell potential given concentrations at particular moment

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q \quad \begin{matrix} E^{\circ}: \text{standard cell potential} \\ T: \text{temp.} \end{matrix}$$

$$R: 8.314 - \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\text{Here: } Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$



F: faraday's constant

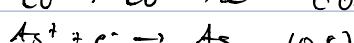
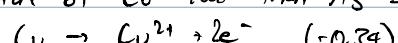
Q: reaction quotient

n = # of electrons transferred

o Ex:// 0.02 M  $\text{Ag}^+$  w/ Ag electrode + 0.05 M  $\text{Cu}^{2+}$  solution w/ Cu electrode.

a) Which electrode positive:

Standard potential of Cu lower than Ag so



b) Cell potential standard:

$$E^\circ = 0.8 - 0.39 = 0.46 \text{ V}$$

c) Cell potential at given conditions



$$\therefore \alpha = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\therefore E_{\text{cell}} = 0.46 - \frac{8.314 \times 298.15}{2 \cdot F} \ln \frac{0.05}{0.022} = 0.04 \text{ V}$$

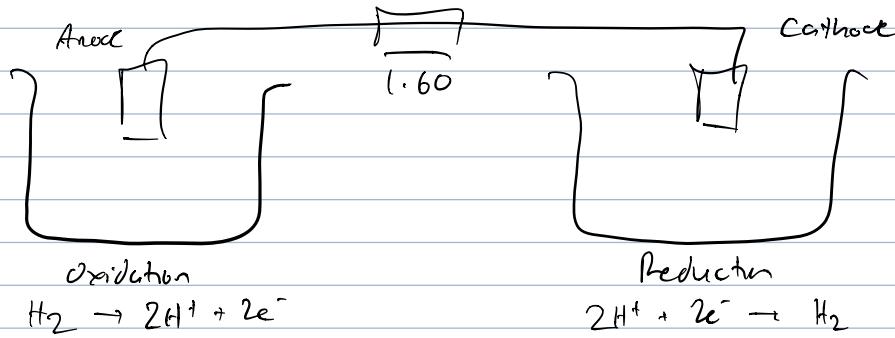
- Concentration cell: anode + cathode are same, so  $e^-$  flow from low conc. to high conc.

◦ Opposite if involving negative ions

$$- \text{pH} = -\log_{10} [\text{H}^+]$$

- Ex:// 2 H-H ion half-cells connected at 25°C. One half cell has pH of 1.0, other pH is unknown. Measured voltage  $\rightarrow 0.16 \text{ V}$  and electrode at half-cell w/ known pH  $> 0$ .

a) Is concentration of  $\text{H}^+$  greater or lesser in unknown container?



If reaction occurs spont., then  $[\text{H}^+]$  in anode  $< [\text{H}^+]$  in cathode

b) What is unknown pH?

$$\begin{aligned} E_{\text{cell}} &= E^\circ - \frac{2.3026 R T}{n F} \log_{10} \alpha \\ &= E^\circ - \frac{2.3026 R T}{2 F} \log_{10} \frac{[\text{H}^+]_{\text{anode}}^2}{[\text{H}^+]_{\text{cathode}}^2} \quad \left. \begin{array}{l} 2\text{H}^+_{\text{cathode}} \rightarrow 2\text{H}^+_{\text{anode}} \\ E^\circ = 0 \text{ since H is standard} \end{array} \right. \\ &= - \frac{2.3026 R T}{2 F} \log_{10} \frac{[\text{H}^+]_{\text{anode}}^2}{[\text{H}^+]_{\text{cathode}}^2} \\ & \quad \text{, Solve.} \end{aligned}$$

### Nernst Equation @ Equilibrium

- Spontaneous cell:  $E_{\text{cell}} > 0$

◦ As reaction continues,  $\alpha \rightarrow 0$ ,  $\ln \alpha \rightarrow 0 \Rightarrow E_{\text{cell}} \rightarrow 0$  (equilibrium)

◦ Thus:

$$0 = E^\circ_{\text{cell}} - \frac{R T}{n F} \ln K$$

◦ Ex:// Cell has 2 compartments. One is Co electrode in 1 L of 0.1 M  $\text{Co}^{2+}$ , other is Ni in 4 L of 1.0 M  $\text{Ni}^{2+}$ . Equilibrium of  $\text{Co}^{2+}$  at 25°C?



$$\therefore E^\circ_{\text{cell}} = \frac{RT}{nF} \ln k$$

$$\frac{nF \cdot E^\circ}{RT} = \ln k$$

Using ICE:

$$\begin{array}{ccc}
 \text{Ni}^{2+} & \text{Cu}^{2+} & \\
 4.0 \text{ mol} & 6.1 \text{ mol} & \left. \begin{array}{c} \\ \end{array} \right\} \\
 -x & +x & \\
 4-x \text{ mol} & 0.1+x \text{ mol} & \left. \begin{array}{c} k = \frac{0.1+x}{1} \\ \frac{4-x}{4} \end{array} \right\}
 \end{array}$$

Plug and solve for  $x$ :  $2.7 \text{ mol}$

$$[\text{Cu}^{2+}] = 2.8 \text{ M}$$

- May be non-spontaneous because electrode at anode consumed

- Ex:// 2  $\text{Cu}|\text{Cu}^{2+}$  half-cells with 2 L electrolyte at  $[\text{Cu}^{2+}] = 1.0 \text{ M}$  and 60 g Cu electrode. Other has 1.0 L of  $[\text{Cu}^{2+}] = 0.01 \text{ M}$  and 30 g Cu electrode. What is situation if cell is dead?

Concentration cell  $\Rightarrow E^\circ_{\text{cell}} = 0$

$$\therefore E_{\text{cell}} = -\frac{RT}{nF} \ln \frac{[\text{Cu}^{2+}]_{\text{cathode}}}{[\text{Cu}^{2+}]_{\text{anode}}}$$

Could be dead if equilibrium concentrations equal. Checking via ICE

$$\begin{array}{ccc}
 \text{Cu}^{2+} & \text{Cu}^{2+} & \\
 2 & 0.01 & \\
 -x & +x & \\
 2-x & 0.01+x & 
 \end{array}$$

$$\therefore 0 = -\frac{RT}{nF} \ln \frac{2(0.01+x)}{2-x}$$

$$\therefore x = 0.66 \text{ mol}$$

$$\text{Mass: } 0.66 \text{ mol Cu} = 42 \text{ g}$$

$\hookrightarrow$  42 g dissolves at anode but anode has only 30 g  $\Rightarrow$  anode must have dissolved

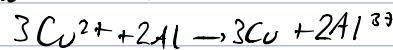
- Can find K at equilibrium:

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

- Ex:// Should displacement of  $\text{Cu}^{2+}$  by Al go to completion?

If completion  $\Rightarrow K_c \gg 10^{10}$

We need to find  $K_c$  for



$$\therefore E^\circ_{\text{cell}} = 2.016 \text{ V}$$

Find  $K_c$ :

$$K_c = \exp \left( \frac{E^\circ_{\text{cell}} nF}{RT} \right)$$

$$= e^{2.016} > 10^{10} \Rightarrow \text{goes to completion}$$

- Electrolytic cell: must provide energy for non-spontaneous reaction to occur

o Usage: car batteries/recharging, Li batteries, electrorefining (impure to pure electrode)

o Ex:// Coin is 2.5 g with 97.5% Zn by mass and 2.5% Cu by mass. How long to coat Zn?

$$\text{Amount to coat: } 2.5 \text{ g} \times 0.025 = 0.0625 \text{ g}$$

$$\hookrightarrow \text{Mol. } 0.06258 \times \frac{\text{mol}}{62.5968} = 9.84 \times 10^{-4} \text{ mol}$$

Electrons h coat:

$$9.84 \times 10^{-4} \times \frac{2 \text{ mole}^-}{1 \text{ mol Cu}} = 0.00197 \text{ mole}^-$$

Charge:

$$1.967 \times 10^{-9} \times \frac{96485 \text{ C}}{\text{mol e}^-} =$$

Rate of 0.1 C/s  $\therefore$

$$189.79 \text{ C} \times \frac{\text{s}}{0.1 \text{ C}} \times \frac{\text{min}}{60 \text{ s}} = 31.6 \text{ min}$$

- Ex:// Cell operates at 2.5V and produces 1T of  $\text{Cl}_2$  / hr when 2500 kJ supplied. Efficiency?

$$\text{Current} = 2500 \text{ kW} \div 2.5 = 100 \text{ kA}$$

# of  $e^-$ :

$$n = \frac{I \times 3600}{F} = 37311 \text{ mol e}^-$$

Amount of  $\text{Cl}_2$ :



$$\therefore 37311 \text{ mol Cl}_2$$

$$\text{Mass: } 37311 \times 70.9066 \text{ g} = 2695631 \text{ g} = 2695.631 \text{ kg}$$

$\therefore$  Efficiency:

$$\frac{1000}{2695.631} = 37.8\%$$