Chemistry 1220 - Su17
Solutions for Practice Midterm 1

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1)

Remember: “**Like Dissolves Like**”

Polar solvents **dissolve polar** & **ionic** solutes

Nonpolar solvents dissolve **non**polar solutes

a)	Na_2CO_3 ionic (ionic bonding)	in	C_6H_{12} molecular (LF only - nonpolar; only C and H in the molecule)	**INSOLUBLE**

C_6H_{12} is a NONpolar molecular compound and forms LF only between like molecules in the pure substance. The Na_2CO_3 is an ionic compound with ionic bonding. In order to dissolve Na_2CO_3 in C_6H_{12} the ionic AF between the ions in Na_2CO_3 have to broken and the LF between C_6H_{12} molecules have to be broken. The only AF that can form between the ions of Na_2CO_3 and nonpolar C_6H_{12} molecules is LF. So you are trying to replace very strong ionic AF with very weak LF. This will NOT happen and Na_2CO_3 is **INSOLUBLE** in C_6H_{12}.

b)	CH_3CN molecular Polar (LF, DD)	in	C_2H_5OH molecular Polar (LF, DD, H-bonding)	CH_3CN: ----- $H-OC_2H_5$

CH_3CN is very soluble in C_2H_5OH. Both are polar. Breaking LF and DD between CH_3CN molecules. Breaking LF, DD and H-bonds between C_2H_5OH molecules. Forming LF and DD IAF between CH_3CN and C_2H_5OH molecules. Also, while CH_3CN can not form H-bonds between solute molecules in the pure substance it can form H-bonds to the C_2H_5OH solvent molecules (between the lone-pair e^- on the N atom of a CH_3CN molecule and the H atom on the O of a C_2H_5OH molecule). Breaking similar AF between solute molecules and between solvent molecules and forming same type of AF between solute and solvent molecules.

c)	HF molecular (polar) (LF, DD, H-bonding)	in	H_2O molecular (polar) (LF, DD, H-bonding)	F-H ----- :O-H | H H-F: ---- H-O | H

Both are polar and form H-bonds between like molecules in the pure substances. So when HF dissolves in H_2O you are breaking LF, DD and H-bonding between HF molecules and H_2O molecules and reforming the same AF between solute (HF) and solvent (H_2O) molecules. So replacing AF between like molecules (solute-solute and solvent-solvent) with the same AF between the unlike molecules (solute and solvent). So HF is very soluble in H_2O. In addition some of the HF molecules ionize and the resulting ions form ion-dipole AF to the H_2O molecules.

***** continued on the next page *****

1) (cont.)

d) Br_2 in CCl_4
molecular molecular
(nonpolar - LF only) (nonpolar - LF only)

Both are nonpolar and have only LF between like molecules. So breaking LF between like molecules and reforming LF between unlike (solute-solvent) molecules. Similar AF are being broken and then reformed between solute and solvent molecules.

e) KCl in H_2O
ionic molecular (polar)
(ionic bonding) (LF, DD, H-bonding)

For KCl to dissolve in H_2O ionic AF have to be broken between K^+ and Cl^- ions and LF, DD and H-bonding AF have to be broken between H_2O molecules. Then **ion-dipole** AF are formed between the ions (K^+ and Cl^-) and the H_2O molecules. This is a very strong AF, slightly weaker than ionic bonding but stronger than the H-bonds between H_2O molecules. So forming similar AF between solute and solvent that were broken to separate the solute particles (ions) and solvent molecules (H_2O).

A

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2) Identify the important **solute-solvent** attractions

D (False)

CH_3NH_2 in $CHCl_3$
polar polar

LF & DD AF between CH_3NH_2 & $CHCl_3$. However, these molecules can not form H-bonds to each other in solution. The $CHCl_3$ molecules can not form H-bonds. The H on the $CHCl_3$ will not form an H-bond to the N atom of CH_3NH_2 and the Cl atoms can not form H-bonds to the H atoms on the N of CH_3NH_2.

(**No** H-bonding)

a) CsCl in NH_3
ionic polar

When CsCl dissolves in NH_3 it dissociates into **ions** which get surrounded by NH_3 molecules (solvated) and form Ion-Dipole AF. The most important AF is Ion-Dipole,

$$F_{I\text{-}D} \propto \frac{Q\,\mu}{d^3}$$

Q: charge on ion
μ: dipole moment of solvent molecule
d: distance between centers of ions & usually determined by adding radii of the ion and the molecule.

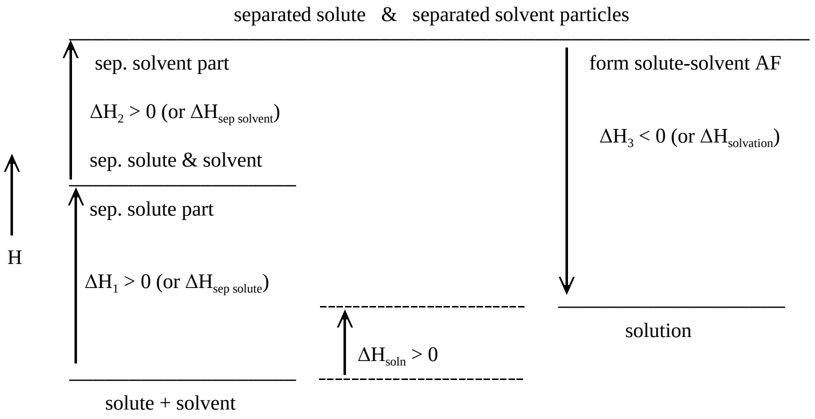
b) CH_3CN in C_2H_5OH
polar polar

LF, DD & H-bonding between CH_3CN & C_2H_5OH. Even though CH_3CN can't form H-bonds in the pure substance (between like molecules) it can form H-bonds between the lone-pair e- on the N and the H atom on the O atom of the C_2H_5OH molecules.

c) CH_2Cl_2 in CCl_4
polar nonpolar

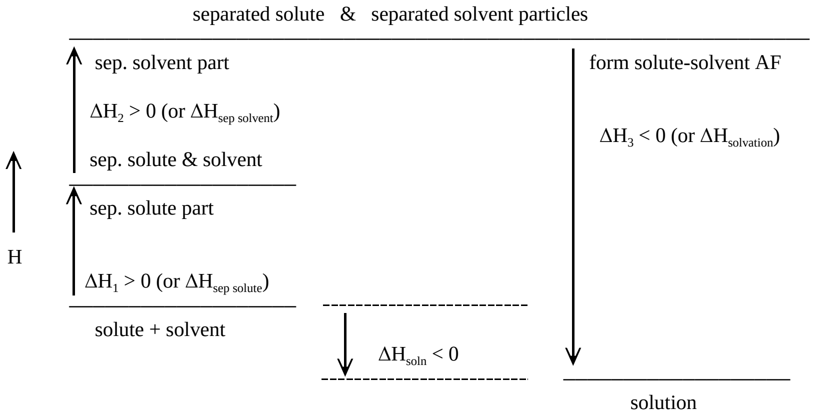
LF only. Since CCl_4 is nonpolar the only AF it can form are LF, either to other CCl_4 molecules or the CH_2Cl_2 molecules.

For 3-5 look at the following diagrams. Remember these pictures.



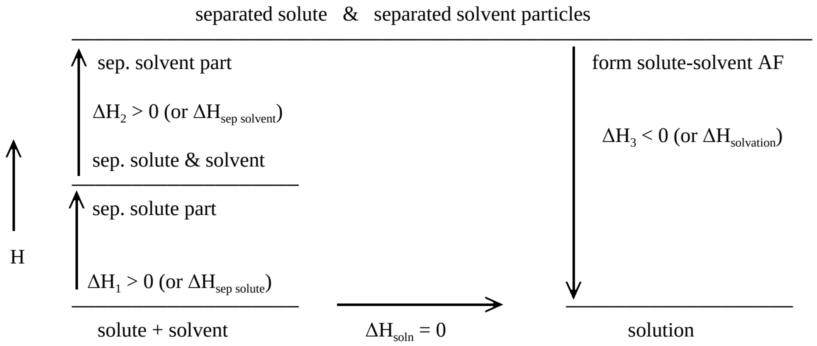
$\Delta H_{\text{soln}} > 0$ (**endothermic**); product (solution) has a higher energy than reactants (solute & solvent).

Attractive forces between solute and solvent (unlike particles) are not as strong as solute-solute and solvent-solvent AF (like particles).



$\Delta H_{\text{soln}} < 0$ (**exothermic**); product (solution) has a lower energy than reactants (solute & solvent).

Attractive forces between solute and solvent (unlike particles) are stronger than solute-solute and solvent-solvent AF (like particles).



$\Delta H_{\text{soln}} = 0$ (**ideal**); product (solution) has same energy as reactants (solute & solvent).

Attractive forces between solute and solvent (unlike particles) are similar to solute-solute and solvent-solvent AF (like particles). Generally, particles with only LF are the most likely to form ideal solutions.

For **ideal** solutions ($\Delta H_{\text{soln}} = 0$) and **endothermic** ($\Delta H_{\text{soln}} > 0$) solutions to form the **change** in **entropy** (disorder) **<u>must</u>** be **positive** ($\Delta S_{\text{soln}} > 0$, **disorder <u>must</u> inc.**). Generally, $\Delta S_{\text{soln}} > 0$ for mixing.

Remember, as given in class:

$\Delta G = \Delta H - T \bullet \Delta S$ and $\Delta G < 0$ (negative) for a spontaneous process
$\Delta G > 0$ (positive) for a nonspontaneous process

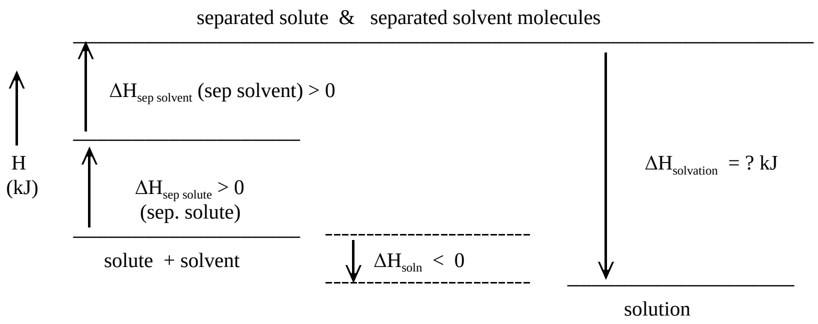
If,

$\Delta H > 0$ (+) or $\Delta H = 0$

then,

<u>MUST</u> have $\Delta S > 0$ (+), **increase** in **disorder**, to have $\Delta G < 0$ (-), at some temperature (i.e. a spontaneous process).

3) ΔH_{soln} = − 10.5 kJ/mol **exo**thermic soln. process (see two previous pages) - releases heat



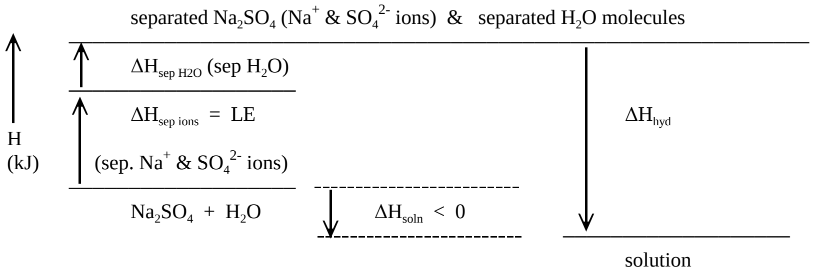
$$\Delta H_{soln} = \Delta H_{sep\ ions} + \Delta H_{sep\ H2O} + \Delta H_{solvation}$$

$$\Delta H_{solvation} = \Delta H_{solutionn} - (\Delta H_{sep.\ solute} + \Delta H_{sep.\ solvent})$$

$$\Delta H_{solvation} = -10.5 - (155.0 + 210.0) = -375.5 \text{ kJ/mol}$$

C

4) ΔH_{soln} < 0 **exo**thermic soln. process (see pp. 3-4 above) - releases heat



$\Delta H_{soln} = \Delta H_{sep\ ions} + \Delta H_{sep\ H2O} + \Delta H_{hyd}$

The **solubility** of Na_2SO_4 **decreases** as **Temp inc**. (30°C: 60g/100 mL H_2O; 100°C: 40g/100 mL H_2O)

This means **added heat** (**inc T**) must cause a **dec** in **solubility** (less solution & more solute + sovent)
- **heat** must be a **product**

Na_2SO_4 (s) + H_2O (ℓ) ⇄ Na_2SO_4 (aq) + **Heat** (heat is product - released)
(actually, 2 Na^+ + SO_4^{2-}) exothermic, ΔH_{soln} < 0)

Add heat, shifts to left (⇐) toward reactns - get less solution

a) T: ΔH_{soln} < 0 , heat is released as a product, exothermic

b) T: get more energy out in solvation (hydration) process when solute-solvent interactions (unlike forces) are **more** favorable (**stronger**) than solute-solute & solvent-solvent interactions (like forces). Solute-solvent AF are stronger. This makes the process exothermic (ΔH_{soln} < 0) which tends to **lead** to a **spontaneous dissolution** process (solution formation).

c) T: Ionic solutes dissolve in H_2O & form **ion-dipole** AF between ions and polar H_2O (solvent).

d) T: ΔH_{soln} < 0 (exothermic) - see above explanations.

e) F: An **inc**. in **entropy** ($\Delta S > 0$) is **NOT** necessary when $\Delta H < 0$.

Remember, $\Delta G_{soln} = \Delta H_{soln} - T \bullet \Delta S_{soln} < 0$ $\Delta G < 0$ (negative) for a spontaneous process

An exothermic soln process, $\Delta H < 0$ (−), tends to **lead** to a **spontaneous dissolution** process (solution formation) since this leads to a neg. ΔG ($\Delta G < 0$). The entropy does not have to increase in this case to make $\Delta G < 0$. You could have a dec in entropy ($\Delta S < 0$) and still get a spontaneous process ($\Delta G < 0$) long as T is low enough (below some temp).

For an **endo**thermic soln process ($\Delta H_{soln} > 0$) & ideal soln process ($\Delta H_{soln} = 0$) an inc. in entropy ($\Delta S_{soln} > 0$, inc. in disorder or randomness) is **necessary** to make $\Delta G_{soln} < 0$ (at “high” temp) (i.e. increase in randomness (disorder) is an important factor for these solutions to form.)

E

5)

See the explanations above on pages 5-6.

a) T: **Solubility** of *most* **ionic** solids **in H_2O <u>inc</u>** w. **<u>inc</u> T**. For most ionic substances dissolving in H_2O the process is endothermic. Use Le Chatelier's Principle to see the effect of temp.

$$\text{ionic solid} + H_2O + \text{heat} \rightleftharpoons \text{solution}$$

Inc. T (add heat), shifts **right** (**<u>away</u>** from **<u>added</u>** heat), forms more solution (**inc solubility**)

b) T: **Solubility** of **gases** in **H_2O <u>inc</u>** w. **<u>inc</u> P** of that gas above the solution. True for all gases. When pressure above a solution is increased more gas molecules are forced into solution. You can see this by looking at Henry's Law:

$$S_g = k_H P_g \quad (S_g = \text{solubility of gas, } k_H = \text{Henry's Law constant, } P_g = \text{pressure of gas})$$

This equation shows that the solubility of a gas increases as it's pressure increases.

c) T: **Solubility** of **solids** or **liquids** in **H_2O** is **<u>NOT</u> affected** by **Pressure**.

d) **F**: **Solubility** of **gases** in **H_2O <u>dec</u>** w. **<u>inc</u> T**. True for ALL gases. For gases dissolving in H_2O the process of dissolution process is **exo**thermic.

<u>exo</u>thermic, $\Delta H_{soln} < 0$ (**heat released** as **<u>product</u>**)

$$\text{Gas} + H_2O \rightleftharpoons \text{Solution} + \text{heat}$$

<u>Inc</u>. **T** (add heat), shifts **left** (**<u>away</u>** from **<u>added</u>** heat), less solution ==> **Solubility <u>Dec</u>**

- rxn shifts to use up added heat and proceeds in the **<u>reverse</u>** direction
  - shifts to left to use up added product - away from what was added (heat).
  As this happens you get less solution and more gas and water (solubility dec).

Can also think of this in terms of kinetic energy and temperature. If T inc the KE inc making it easier for the gas molecules to escape the solution, thus decreasing the solubility.

<u>D</u>

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6) Use mass % as a conversion factor between mass of solute and mass of solution.

$$\text{mass \% } C_6H_{12}O_6 = \frac{\text{mass } C_6H_{12}O_6}{\text{mass solution}} \times 100\% \qquad 5.31 \text{ \% } C_6H_{12}O_6 \implies \frac{5.31 \text{ g } C_6H_{12}O_6}{100 \text{ g solution}}$$

$$? \text{ g } C_6H_{12}O_6 = 0.0109 \text{ mol } C_6H_{12}O_6 \underbrace{\times \frac{180.16 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6}}_{\text{get g of } C_6H_{12}O_6} \underbrace{\times \frac{100 \text{ g soln}}{5.31 \text{ g } C_6H_{12}O_6}}_{\substack{\text{get g of solution} \\ \text{- Use \% as parts} \\ \text{per 100}}}$$

$$= 36.\underline{9}81 \text{ g soln}$$

$$= 37.0 \text{ g soln}$$

<u>C</u>

7) Want mass % of glycerol, $C_3H_8O_3$. For mole fraction we have

$$X_A = \frac{\text{mol substance A}}{\text{total moles}}$$

$$X_{C3H8O3} = \frac{0.258 \text{ mol } C_3H_8O_3}{1 \text{ total mol solution}} \qquad \text{want mass \%:} \quad \frac{\text{mass } C_3H_8O_3}{\text{mass solution}} \text{ x } 100\%$$

Assume 1 mol soln ==> 0.258 mol $C_3H_8O_3$ (assume what's in denominator of given quantity)

Thus, have 1 - 0.258 = 0.742 mol H_2O (mole fractions add to 1)

$$X_{C3H8O3} = 0.258; \qquad X_{H2O} = 0.742$$

$$? \text{ g } C_3H_8O_3 = 0.258 \text{ mol } C_3H_8O_3 \times \frac{92.09 \text{ g } C_3H_8O_3}{1 \text{ mol } C_3H_8O_3} = 23.\underline{\mathbf{7}}59 \text{ g } C_3H_8O_3$$

$$? \text{ g } H_2O = 0.742 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} = 13.\underline{\mathbf{3}}70 \text{ g } H_2O$$

$$\text{mass \% } C_3H_8O_3 = \frac{23.\underline{\mathbf{7}}59 \text{ g } C_3H_8O_3}{23.\underline{\mathbf{7}}59 \text{ g } C_3H_8O_3 + 13.\underline{\mathbf{3}}70 \text{ g } H_2O} \text{ x } 100\% = 63.\underline{\mathbf{9}}8\%$$

$$= 64.\underline{\mathbf{0}}\%$$

B

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8) molality, ***m***, is (mol solute)/(kg solvent)

$$4.26\ \boldsymbol{m}\ (NH_4)_2SO_4 = \frac{4.26 \text{ mol } (NH_4)_2SO_4}{\text{kg solvent}} \qquad \text{Want molarity,} \qquad M = \frac{\text{mol } (NH_4)_2SO_4}{1 \text{ L soln}}$$

Must get mass solute and then mass solution: mass soln = mass solute + mass slovent

Assume 1 kg solvent ==> 4.26 mol $(NH_4)_2SO_4$ (assume what's in denominator of given quantity)

$$? \text{ g } (NH_4)_2SO_4 = 4.26 \text{ mol } (NH_4)_2SO_4 \text{ x } \frac{132.14\text{g } (NH_4)_2SO_4}{1 \text{ mol } (NH_4)_2SO_4} = 562.92 \text{ g } (NH_4)_2SO_4$$

$$? \text{ g } H_2O = 1000 \text{ g } H_2O \quad \text{(assumed 1 kg of } H_2O)$$

$$? \text{ g soln} = 1000 \text{ g } H_2O + 56\underline{\mathbf{2}}.92 \text{ g } (NH_4)_2SO_4 = 156\underline{\mathbf{2}}.92 \text{ g soln}$$

$$? \text{ L soln} = 156\underline{\mathbf{2}}.92 \text{ g soln} \text{ x } \frac{1 \text{ mL soln}}{1.2077 \text{ g soln}} \text{ x } \frac{1 \text{ L soln}}{10^3 \text{ mL soln}} = 1.29\underline{\mathbf{4}}1 \text{ L soln}$$

$$? \frac{\text{mol } (NH_4)_2SO_4}{1 \text{ L soln}} = \frac{4.26 \text{ mol } (NH_4)_2SO_4}{1.2941 \text{ L soln}} = 3.29 \text{ M } (NH_4)_2SO_4$$

E

9) $\prod = i\,M\,R\,T$, where $\prod$ = osmotic pressure

i = # ions in the formula for an ionic cmpd or ionizing molecule
= 1 for nonionizing or nondissociating cmpds

$\prod = M_{part}\,R\,T$

M = molarity ($iM = M_{part}$, molarity of particles)
R = 0.0821L•atm/mol•K; T = temp in kelvin

greater <u>conc</u> of **<u>particles</u>** ==> **greater Π** ; **<u>higher</u> T** ==> **greater Π**

The first thing to do is to calculate the conc of particles in each case and then compare those with the same temp. This is easily done by determining the # particles you get from each compound.

At the same temp the solution with the higher conc of particles will have the higher Π.
For those with the same conc of particles the one with the higher T will have the higher Π.

Do NOT have to actually calculate Π for any of the solutions to do this problem.

a) 0.012 M Na_2SO_4 at 25°C; $(NH_4)_2SO_4 \text{ ---->} 2\,Na^+ + SO_4^{2-}$ $i = 3$

M_{ions} = 3(0.012 M) = **0.036 M ions** at 25°C

b) 0.020 M $AlCl_3$ at 50°C; $AlCl_3 \text{ ---->} Al^{3+} + 3\,Cl^-$ $i = 4$

M_{ions} = 4(0.020 M) = **0.080 M ions** at 50°C

c) 0.020 M $AlCl_3$ at 25°C; $AlCl_3 \text{ ---->} Al^{3+} + 3\,Cl^-$ $i = 3$

M_{ions} = 4(0.020 M) = **0.080 M ions** at 25°C

d) 0.030 M KCl at 25°C; $KCl \text{ ---->} K^+ + Cl^-$ $i = 2$

M_{ions} = 2(0.030 M) = **0.060 M ions** at 25°C

e) 0.030 M KCl at 50°C; $KCl \text{ ---->} K^+ + Cl^-$ $i = 2$

M_{ions} = 2(0.030 M) = **0.060 M ions** at 50°C

Looking at the solutions at 25°C the 0.020 M $AlCl_3$ (**0.080 M ions**) would have the highest Π.
Looking at the solutions at 50°C the 0.020 M $AlCl_3$ (**0.080 M ions**) would have the higher Π.
Then looking at the two $AlCl_3$ solutions, both have the same conc., 0.020 M $AlCl_3$ (**0.080 M ions**) so the one with the higher T will have the higher osmotic pressure, Π.

<u>B</u>

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10) Want mole fractions of two volatile substances in a solution - both will contribute to the vapor pressure above the solution. Assume that both follow Raoult's Law and the gas mixture follows Dalton's of Partial Pressures.

$P_A = X_A\,P_A^o$ $P_B = X_B\,P_B^o$ Raoult's Law

P_A = vapor pressure of A above solution P_B = vapor pressure of B above solution
X_A = mole fraction of A in **liquid phase** X_B = mole fraction of B in **liquid phase**
P_A^o = V.P. of pure A P_B^o = V.P. of pure B

$P_T = P_A + P_B$ Dalton's Law P_T = total vapor pressure above the solution

$P_T = X_A\,P_A^o + X_B\,P_B^o$ for two volatile substances

$P_T = X_{C7H16}\,P_{C7H16}^o + X_{C8H18}\,P_{C8H18}^o$

$X_{C7H16} + X_{C8H18} = 1$ Want X_{C7H16}

$66.31 = (X_{C7H16})\,(91.96 \text{ torr}) + (X_{C8H18})(50.92 \text{ torr})$

$66.31 = (X_{C7H16})\,(91.96 \text{ torr}) + (1 - X_{C7H16})(50.92 \text{ torr})$

$66.31 = (X_{C7H16})\,(91.96 \text{ torr}) + 50.92 \text{ torr} - X_{C7H16}(50.92 \text{ torr})$

$15.39 = (X_{C7H16})\,(41.04 \text{ torr})$

$X_{C7H16} = 0.375$ $X_{C8H18} = 0.625$

<u>B</u>

11) Want MW from boiling point elevation, ΔT_b.

Whenever you want MW think of g/mol: $\text{MW} = \dfrac{\text{mass}}{\text{moles}}$

have mass of 12.0 g, need moles (get from molality)

$\Delta T_b = i\, K_b\, \boldsymbol{m} = \boldsymbol{m}_{\text{part}}\, K_b$ K_b = freezing point depression constant (depends on solvent)

i = 1 for nonelectrolyte (nondissociating- stays as a single particle in solution)

Normal f.p. of H_2O = 100.000 °C b.p. of soln = 100.533 °C K_b = 0.512 °C/m

$$\boldsymbol{m} = \frac{\Delta T_b}{K_b} = \frac{100.533\,^\circ\text{C} - 100.000\,^\circ\text{C}}{0.512\ ^\circ\text{C}/m} = 1.0\underline{\mathbf{4}}10 \text{ molal}$$

$$\text{mol solute} = 0.080\underline{\mathbf{0}} \text{ kg } C_6H_4Cl_2 \times \frac{1.0\underline{\mathbf{4}}10 \text{ mol}}{1 \text{ kg } C_6H_4Cl_2} = 0.083\underline{\mathbf{2}}81 \text{ mol solute}$$

$$\text{MW} = \frac{12.0 \text{ g}}{0.083\underline{\mathbf{2}}81 \text{ mol}} = 14\underline{\mathbf{4}}.09 \text{ g/mol} = 144 \text{ g/mol}$$

B

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12) a) T: Volatile sustances in an ideal solution follow Raoult's Law:

$P_A = X_A P_A^0$ Raoult's Law

X_A = mole fraction of solvent (CH_3OH) in the solution
P_A^0 = vapor pressure of pure solvent
P_A = vapor pressure due to the substance in the solution.

b) T: The Tyndall effect distinguishes a colloidal dispersion (suspensions) from a true solution.

- true soln: particle size ≲ 10 Å
- heterogeneous mixture: particle size > 2000 Å
- colloid: 10 Å ≲ particle size ≲ 2000 Å

In a colloid the particles are large enough to **scatter** **light** - can see a light beam in the colloidal dispersion (Fig. 13.27 & 13.28)

c) T: Hydrophilic ("water loving") colloid particles have polar or charged groups that allow them to stay dispersed in water.

d) **F**: Boiling point elevation. The b.p. of a solution is HIGHER than that of the pure solvent.

e) T: Colligative properties depend on the quantity (concentration) but not the nature (kind or identity) of solute particles. Colligative means "depending on the collection".

D

13) $BrO_3^- + 9\,I^- + 6\,H^+ \longrightarrow 3\,I_3^- + Br^- + 3\,H_2O$

$$\text{rate of rxn} = \frac{1}{1}\left(\frac{-\Delta[BrO_3^-]}{\Delta t}\right) = \frac{1}{9}\left(\frac{-\Delta[I^-]}{\Delta t}\right) = \frac{1}{6}\left(\frac{-\Delta[H^+]}{\Delta t}\right) = \frac{1}{3}\left(\frac{\Delta[I_3^-]}{\Delta t}\right) = \frac{1}{1}\left(\frac{\Delta[Br^-]}{\Delta t}\right) = \frac{1}{3}\left(\frac{\Delta[H_2O]}{\Delta t}\right)$$

relate the rate of reaction to the rates in terms of disappearance of reactants or formation of products by using the reciprocal of the coefficients in the balanced eqn as multiples of the various rates.

$$\frac{1}{6}\left(\frac{-\Delta[H^+]}{\Delta t}\right) = \frac{1}{9}\left(\frac{-\Delta[I^-]}{\Delta t}\right)$$

$$\left(\frac{-\Delta[H^+]}{\Delta t}\right) = \frac{6}{9}\left(\frac{-\Delta[I^-]}{\Delta t}\right) = \frac{6}{9}\,(5.4 \times 10^{-4}\ M/s) = 3.6 \times 10^{-4}\ M/s$$

A

14)

$r = k\,[A]^{3/2}\,[B]^2\,[C]^{1/2}$

3/2 order in A, 2nd order in B, 1/2 order in C

Treat this like any other math equation.

Given the initial rate of reaction, conc of A, B and C.

Want the rate constant, k. Solve the rate law above for k.

$$k = \left(\frac{r}{[A]^{3/2}[B]^2[C]^{1/2}}\right) = \left(\frac{1.0 \times 10^{-6}\ Ms^{-1}}{(0.0100M)^{3/2}(0.0200M)^2(0.0100M)^{1/2}}\right) = 25.0\ M^{-3}s^{-1}$$

B

15) initial rate problem

Write the rate law and use initial rate method to find the order with respect to each substance:

$r = [A]^m\,[B]^n$

You can find the exponents by inspection. However, this isn't the most general way. To find all the exponents, except the "last" one, you need to find reactions in which the concentrations of all substances are held constant except for one substance. You don't have to do this for the last exponent since by that time you will know all the other exponents (i.e. you don't have to look for two reactions in which the conc of all substances, except the one of interest, are held constant). However, this could be difficult to do by inspection.

I am showing the general way of doing these problems. You start by taking the ratio of the rates for two different experiments. This will give the following general relationship that can be used for any set of reactions.

$$\frac{r_i}{r_j} = \frac{[A]_i^m\,[B]_i^n}{[A]_j^m\,[B]_j^n}$$

$$\frac{r_i}{r_j} = \left(\frac{[A]_i}{[A]_j}\right)^m \left(\frac{[B]_i}{[B]_j}\right)^n$$

It doesn't matter which exponent is determined first as long as you can find 2 experiments in which the concentrations of all but one substance are held constant. You will notice that there are no experiments in which [B] changes while [A] is held constant. You have to start with finding m.

Step 1: determine order, m, with respect to A ([B] held constant in exp 1 & 2)

$$\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^m \left(\frac{[B]_2}{[B]_1}\right)^n$$

$$\frac{8.0 \times 10^{-3}}{2.0 \times 10^{-4}} = \left(\frac{0.20}{0.10}\right)^m \left(\frac{0.10}{0.10}\right)^n$$

$$4 = (2)^m \qquad m = 2$$

***** **continued on next page** *****

15) (cont.)

Step 2: determine order, n, with respect to B

No sets of experiments in which A is held constant. That's okay since we know its exponent in the rate law. Just have to make sure [B] changes so we need to use exp 1 & 3 or 2 & 3.

$$\frac{r_3}{r_1} = \left(\frac{[A]_3}{[A]_1}\right)^2 \left(\frac{[B]_3}{[B]_1}\right)^n$$

$$\frac{2.6 \times 10^{-2}}{2.0 \times 10^{-4}} = \left(\frac{0.40}{0.10}\right)^2 \left(\frac{0.20}{0.10}\right)^n$$

$$130 = (4)^2\,(2)^n = (16)\,(2)^n \quad 8.125 = (2)^n$$

$$\log(8.125) = \log 2^n \Rightarrow \log(8.125) = n \log 2 \Rightarrow$$
$$n = (\log 8.125)/(\log 2) \Rightarrow n = 3.02 \Rightarrow n = 3$$

The final rate law is:

$r = [A]^2\,[B]^3$

E

16) $A \longrightarrow B + C$ zero order in A, $r = k[A]^0 = k$

$r = k\,[A]^0 = k$

0 (zero) order in A

The rate is constant as long as there is some reactant and the rate equals the rate constant. Once the reactant goes to zero the rate will be zero.

$r = k = 5.0 \times 10^{-2}$

You can check to see what the conc. is after 5.0 seconds to make sure you still have some reactant left. Use the zero-order integrated rate law.

$[A]_t = -k\,t + [A]_o = -(5.0 \times 10^{-2}\ \text{M/s})(5.0\ \text{s}) + 1.0\ \text{M} = 0.75\ \text{M}$

Since there is still reactant, the rate will be what it was at the start of the reaction (constant).

A

17) Integrated rate law problem.

$r = (1.0 \times 10^{-2}\ \text{min}^{-1})\,[A_2]$ (1st order in A_2)

Need to use 1st-order integrated rate law:

1st order reaction $r = k\,[A_2]$ where, $k = 1.0 \times 10^{-2}\ \text{min}^{-1}$

$$\ln\left(\frac{[A]_t}{[A]_o}\right) = -k\,t \quad \text{or} \quad [A]_t = [A]_o\,e^{-kt} \quad \text{or} \quad \ln[A]_t = -k\,t + \ln[A]_o$$

Want time it takes for $[A_2]$ to decrease to 60% of its initial value (60% remains). This is the same as saying the reaction is 40% complete (means 40% of the reactant has reacted, 60% remains).

$[A_2]_t = 0.60\,[A_2]_o$

Not given $[A_2]_o$ but don't need to have $[A_2]_o$ for a 1st-order reaction. As you see below, the $[A_2]_o$ cancels. If you didn't think to use this form of the equation you can assume a value for $[A]_o$ and it will work out.

$$\ln\left(\frac{[A_2]_t}{[A_2]_o}\right) = -k\,t \qquad \ln\left(\frac{0.60\,[A_2]_o}{[A_2]_o}\right) = -k\,t \qquad \ln(0.60) = -k\,t$$

$\ln(0.60) = -(1.0 \times 10^{-2})\,t$ $t = 5.1 \times 10\ \text{min}$

The integrated rate laws for 0 and 2nd order rxn are:

0 order: $[A]_t = -k\,t + [A]_o$

2nd order: $\dfrac{1}{[A]_t} = k\,t + \dfrac{1}{[A]_o}$

B

18) Integrated rate law problem.

$A \longrightarrow B$

$r = k[A]^2$ (2^{nd} order in A) where, $k = 3.86 \times 10^{-2}\ M^{-1}\ s^{-1}$

Find the conc of A after 74.4 sec., given the initial and rate constant.

Need to use 2^{nd}-order integrated rate law:

$$2^{nd}\text{ order:}\quad \frac{1}{[A]_t} = k\,t + \frac{1}{[A]_o}$$

Given the initial conc: $[A]_o = 0.300\ M$

$$\frac{1}{\mathbf{[A]_t}} = (3.86 \times 10^{-2}\ M^{-1}s^{-1})\ (74.4\ sec) + \frac{1}{0.300\ M}$$

$$\frac{1}{\mathbf{[A]_t}} = 6.2\underline{\mathbf{0}}5\ M^{-1}$$

$\mathbf{[A]_t} = 0.16\underline{\mathbf{1}}15 = 0.161\ M$

A

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19) Second Order

successive half-lifes **decrease** (each is **half** of previous)

(takes shorter & longer time for conc. to dec. by ½ each period)

Half-lives (similar to #50 on Ch 14 extra practice problems handout)

10.0 min, 5.0 min, 2.5 min

Half-lives (similar to #50 on Ch 14 extra practice problems handout)

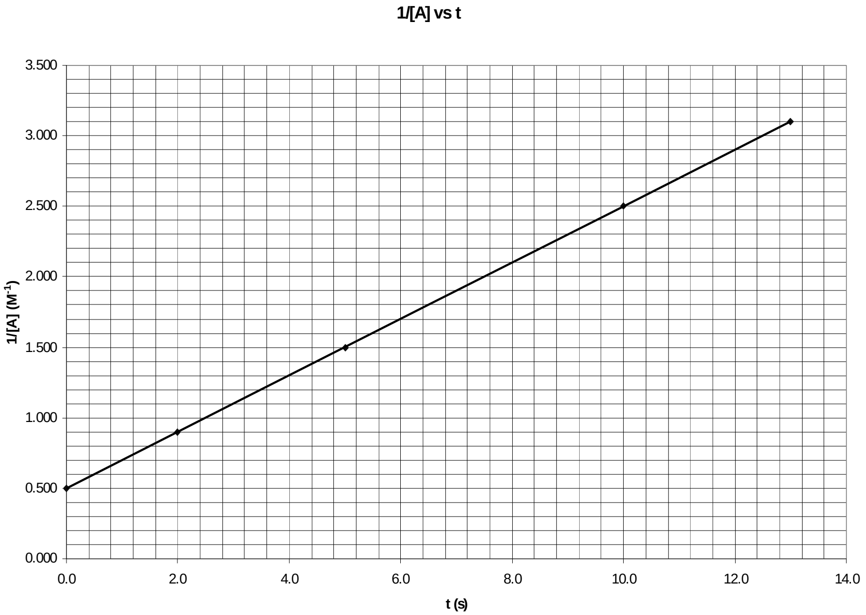
Zero-order	1^{st}-order	2^{nd}-order
$t_{1/2} = \frac{[A]_o}{2\,k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k\,[A]_o}$
DECREASES as rx. proceeds (successive ½-lifes get smaller - ½ previous e.g. $t_{1/2,1} = 40$ s $t_{1/2,2} = 20$ s $t_{1/2,3} = 10$ s)	CONSTANT as rx. proceeds (successive ½-lifes are same e.g. $t_{1/2,1} = 40$ s $t_{1/2,2} = 40$ s $t_{1/2,3} = 40$ s)	INCREASES as rx. proceeds (successive ½-lifes get larger - double e.g. $t_{1/2,1} = 10$ s $t_{1/2,2} = 20$ s $t_{1/2,3} = 40$ s)

Determine the 1^{st} half-life by using the equation for half-life for a 0^{th} order reaction using the first half-life of 10 min and the initial conc. at the beginning of the reaction, 0.10 M.

$$t_{1/2} = \frac{[A]_o}{2\,k};\qquad k = \frac{[A]_o}{2\,t_{1/2}} = \frac{(0.10M)}{2\,(10.0\ min)} = 5.0 \times 10^{-3}\ M\bullet s^{-1}$$

B

20) Find the rate constant, k ($M^{-1}s^{-1}$), from the following plot of 1/[A] vs t



This is the plot for a 2nd order reaction (1/[A] vs t is a straight line - tells you it is 2nd)

$$2^{nd}\text{ order:}\quad \frac{1}{[A]_t} = k\,t + \frac{1}{[A]_o}$$

Equation of a straight line with y = 1/[A], x = t, slope = k, y-intercept = $1/[A]_o$

Slope = k = $(2.100 - 0.900\ M^{-1})/(8.0 - 2.0s) = 0.20\ M^{-1}s^{-1}$

$1/[A]_o$ = y-intercept = $0.500\ M^{-1}$ $[A]_o = 2.00\ M$

$$\text{For } 2^{nd}\text{ order: } t_{1/2,\,1} = \frac{1}{k\,[A]_o} = \frac{1}{(0.20\ M^{-1}s^{-1})(2.00\ M)} = 2.5\ s$$

<u>A</u>

***** see next page *****

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20) (cont.)

Half-lives (similar to #50 on Ch 14 extra practice problems handout)

Zero-order	1st-order	2nd-order
$t_{1/2} = \frac{[A]_o}{2\,k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k\,[A]_o}$
DECREASES as rx. proceeds (successive ½-lifes get smaller - ½ previous e.g. $t_{1/2,1}$ = 40 s $t_{1/2,2}$ = 20 s $t_{1/2,3}$ = 10 s)	CONSTANT as rx. proceeds (successive ½-lifes are same e.g. $t_{1/2,1}$ = 40 s $t_{1/2,2}$ = 40 s $t_{1/2,3}$ = 40 s)	INCREASES as rx. proceeds (successive ½-lifes get larger - double e.g. $t_{1/2,1}$ = 10 s $t_{1/2,2}$ = 20 s $t_{1/2,3}$ = 40 s)

21) The true statements are bolded and the false statements have been corrected.

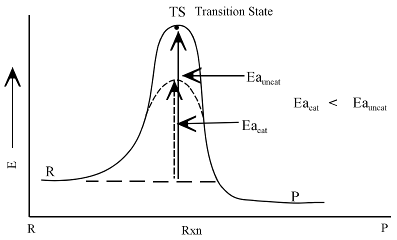
E (1, 3 & 4 are true)

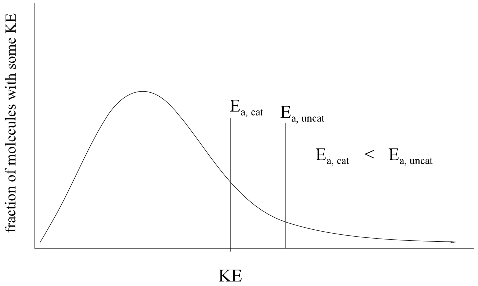
1) **T**: The factors effecting the rate of a reaction are: concentration of reactants (and maybe products), structure of reacting molecules, temperature and the presence of catalysts.

2) F: Catalysts do not shift the equilibrium toward products. **Catalysts speed** up the **rate** at which equilibrium is reached but do **not effect** the **position** of **equilibrium** (i.e. Amounts of reactant and product at equilibrium). **Catalyst inc** rxn **rate** by **lowering Ea** so that at the same temp more molecules have KE > Ea. A catalyst lowers the "hill" (rxn barrier) so it takes less energy to get over (through the transition state, TS). Can use the Arrhenius eqn to see this. The Ea is lowered by the same amount for both the forward and reverse reactions so both speed up by the same amount and thus the position of equilibrium is not affected.

$k = A e^{-(Ea/RT)}$ Arrhenius eqn.

As $\mathbf{E_a}$ **inc**., E_a/RT inc, $e^{-(Ea/RT)}$ dec., **k dec**., **rate dec** ($r \propto k$)
$\mathbf{E_a}$ **dec**., E_a/RT dec, $e^{-(Ea/RT)}$ inc., **k inc**., **rate inc** ($r \propto k$)





The **rate** of a reaction depends **ONLY** on $\mathbf{E_a}$ and not whether a reaction is exothermic or endothermic or how exothermic or endothermic the reaction is. An endothermic reaction will be faster than an exothermic reaction if the E_a for the endothermic reaction is smaller than the E_a for the exothermic reaction.

Reaction 1	Reaction 2
-------------	-------------
$\Delta H = -30$ kJ	$\Delta H = 20$ kJ
$E_a = 20$ kJ	$E_a = 10$ kJ
	faster

***** **continued on next page** *****

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21 (cont.)

3) **T**: Enzymes are catalysts in living organisms. They speed up the reactions in organisms.

4) **T**: Activation energy is required for both exothermic and endothermic reactions.

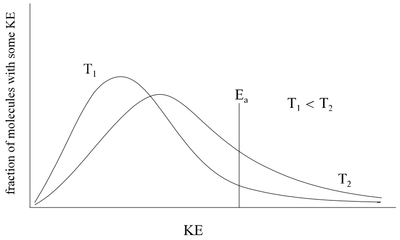
5) F: The concentration of a catalyst (gaseous or in solution) can appear in a rate law. It gets it's biggest effect by lowering the E_a but it's concentration can affect the rate by appearing in the rate law.

Aside: You can see how Temp effects rate by looking at the Arrhenius eqn.

$k = A e^{-(Ea/RT)}$ Arrhenius eqn.

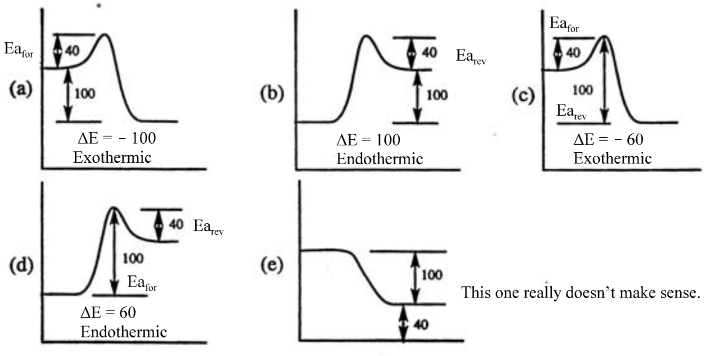
As **T inc**., E_a/RT dec, $e^{-(Ea/RT)}$ inc., **k inc**., **rate inc** ($r \propto k$)
T dec., E_a/RT inc, $e^{-(Ea/RT)}$ dec., **k dec**., **rate dec** ($r \propto k$)

An inc. in T causes an inc. in K.E. so more molecules have KE > Ea and may therefore react



22) The E_a is the activation energy. This is the difference in energy between the reactants and the transition state (the top of the "hill"). The overall energy change, ΔE, is the difference in energy between the products and reactants.

$E_a = 40$ kJ $\Delta E = -100$ kJ   exothermic - products lower in energy than reactants



This one really doesn't make sense.

A

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23)

Find the correct **rate expression** (rate law) from the following mechanism:

$2\,O_3 \rightarrow 3\,O_2$ (balanced equation)

$O_3 \rightleftarrows O_2 + O$ (fast)

$O_3 + O \rightarrow 2\,O_2$ (**slow**)

The rate law is based on step 2 (the **slow** step is the **rate determining** step)

$r = k_2\,[O_3]\,[O]$ can't have an intermediate, [O], in the rate law

Solve for [O] by using the previous fast step. Since the fast step is in equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction.

$r_1 = r_{-1}$

$k_1\,[O_3] = k_{-1}\,[O_2]\,[O]$

$[O] = \frac{k_1}{k_{-1}} \bullet \frac{[O_3]}{[O_2]}$ substitute this expression for [O] into r from step 2

$r = k_2\,[O_3]\,[O]$ -   rate law from above

$$r = k_2\,[O_3]\left\{\frac{k_1}{k_{-1}} \bullet \frac{[O_3]}{[O_2]}\right\}$$

$$r = \left\{\frac{k_2\,k_1}{k_{-1}} \bullet \frac{[O_3]^2}{[O_2]}\right\}$$

$$r = k \bullet \frac{[O_3]^2}{[O_2]}$$

B

24)

$A_2 + B_2 \rightarrow X + Y$ rate = k $[A_2][B_2]^{1/2}$ (experimentally determined rate law)

The rate law is written based on the slow (rate determining) step

a) 1st step is the slow step

$B_2 \rightarrow 2B$ (slow)

$B + A_2 \rightarrow C$ (fast)

$C + B \rightarrow X + Y$ (fast)

$r = k_1 [B_2]$ This does not agree w. exp. rate law given - NOT the proper mechanism

b) 2nd step is the slow step

$A_2 \rightleftarrows C + X$ (fast)

$B_2 + C \rightarrow Y$ (slow)

$r = k_2 [B_2][C]$ C is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [C]

$r_1 = r_{-1}$

$k_1 [A_2] = k_{-1} [C][X]$

$[C] = \frac{k_1}{k_{-1}} \bullet \frac{[A_2]}{[X]}$ substitute this expression for [C] into r from step 2

$r = k_2 [B_2][C]$ - rate law from above

$r = k_2 [B_2] \{\frac{k_1}{k_{-1}} \bullet \frac{[A_2]}{[X]}\}$

$r = \{\frac{k_2 k_1}{k_{-1}}\} \bullet \frac{[B_2][A_2]}{[X]}$

$r = k \frac{[B_2][A_2]}{[X]}$

This does not agree w. exp. rate law given - NOT the proper mechanism

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24) (cont.)

c) 2nd step is the slow step

$A_2 + B_2 \rightleftarrows C$ (fast)

$C \rightarrow X + Y$ (slow)

$r = k_2 [C]$ C is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [C]

$r_1 = r_{-1}$

$k_1 [A_2][B_2] = k_{-1} [C]$

$[C] = (\frac{k_1}{k_{-1}}) [A_2][B_2]$ substitute this expression for [A] into r from step 2

$r = k_2 [C]$

$r = k_2\{(\frac{k_1}{k_{-1}}) [A_2][B_2]\} = (\frac{k_2 k_1}{k_{-1}}) [A_2][B_2] = k [A_2][B_2]$

This does not agree w. exp. rate law given - NOT the proper mechanism

d) 2nd step is the slow step

$A_2 \rightleftarrows 2A$ (fast)

$B_2 + A \rightarrow C$ (slow)

$C + A \rightarrow X + Y$ (fast)

$r = k_2 [B_2][A]$ A is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [A]

$r_{forward,1} = r_{reverse,1}$

$k_1 [A_2] = k_{-1} [A]^2$

$[A] = (\frac{k_1}{k_{-1}})^{1/2} \bullet [A_2]^{1/2}$ substitute this expression for [A] into r from step 2

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24) (cont.)

$r = k_2 [B_2][A]$

$r = k_2 [B_2] \{ (\frac{k_1}{k_{-1}})^{1/2} \bullet [A_2]^{1/2} \}$

$r = k_2 (\frac{k_1}{k_{-1}})^{1/2} [B_2][A_2]^{1/2} = k [B_2][A_2]^{1/2}$

This does not agree w. exp. rate law given - NOT the proper mechanism

e) 2nd step is the slow step

$B_2 \rightleftarrows 2B$ (fast)

$A_2 + B \rightarrow C + X$ (slow)

$B + C \rightarrow Y$ (fast)

$r = k_2 [A_2][B]$ B is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [B]

$r_1 = r_{-1}$

$k_1 [B_2] = k_{-1} [B]^2$

$[B] = (\frac{k_1}{k_{-1}})^{1/2} \bullet [B_2]^{1/2}$ substitute this expression for [B] into r from step 2

$r = k_2 [A_2][B]$

$r = k_2 [A_2] \{ (\frac{k_1}{k_{-1}})^{1/2} \bullet [B_2]^{1/2} \}$

$r = k_2 (\frac{k_1}{k_{-1}})^{1/2} [A_2][B_2]^{1/2} = k [A_2][B_2]^{1/2}$

experimental rate law - correct mechanism

E

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24) (cont.)

Note: Anything that appears in the rate law must appear as a **reactant** in the **slow step** or as a **reactant** and/or **product** in the **fast equilibrium steps** which **precede** the **slow step**.

The fast steps which follow the slow step have no effect on the rate law. They are only there to make sure all steps add up to the balanced equation.

This brings up a good point that makes this type of problem easier to approach.

First look at mech. w. slow step 1 - easy to determine these rate laws (only the reactants in this step will appear in the rate law).

Then look at remaining mech.

To get a rate law with a ½ power (e.g. $[A_2]^{1/2}$) there would need to be the following type of elementary step as a fast step preceding the slow step.

$A_2 \rightleftarrows 2A$ (fast)

$r_{forward,1} = r_{reverse,1}$

$k_1 [A_2] = k_{-1} [A]^2$

$[A] = (\frac{k_1}{k_{-1}})^{1/2} \bullet [A_2]^{1/2}$

Look at (b): Get B_2 in the rate law based on step 2. Then if you look at step 1 you will get something for [C] involving A_2 and X (a product). X will appear in the denominator in the rate law. X does not appear in the rate law. You really shouldn't have to go through the math to see you will wind up with X in the rate law. In order to get a product in the rate law the first step can't be the rate determining step.

Look at (c): B_2 and A_2 will appear in the rate law but not to the ½ power. There is no coefficient in front of C in the balanced equation.

Also, look at the following mechanism: Get C in the rate law based on step 2. Then if you look at step 1 you will get something for [C] involving A and X (a product). X will appear in the denominator in the rate law. You really shouldn't have to go through the math to see you will wind up with X in the rate law. In order to get a product in the rate law the first step can't be the rate determining step.

$A \rightleftarrows C + X$ (fast)

$B + C \rightarrow Y$ (slow)

25) Use Arrhenius equation in its two point form (given on last page).

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{T in KELVIN,} \quad R = 8.314\ \text{J/mol•K}$$

k_1 $T_1 = 20.0\,^\circ\text{C} = 293.15\ \text{K}$

$k_2 = 3\,k_1$ $T_2 = 40.0\,^\circ\text{C} = 313.15\ \text{K}$

$E_a = ?$

$$\ln\left(\frac{3\,k_1}{k_1}\right) = \frac{E_a}{8.314\ \text{J/mol•K}}\left(\frac{1}{293.15\ \text{K}} - \frac{1}{313.15\ \text{K}}\right)$$

$\ln(3) = (2.620 \times 10^{-5}\ \text{J}^{-1}\text{•mol})\,E_a$

$E_a = 4.1924 \times 10^4\ \text{J/mol} = 41.9\ \text{kJ/mol}$

<u>C</u>

26)

$Al_2(SO_3)_3\ (s) + 6\,H^+\ (aq) \rightleftarrows 2\,Al^{3+}\ (aq) + 3\,H_2O\ (\ell) + 3\,SO_2\ (g)$

Pure **solids** and **liquids** do **<u>NOT</u>** appear in the equilibrium constant expression (or in Q).

$$K_c = \frac{[Al^{3+}]^2\,[SO_2]^3}{[H^+]^6}$$

$Al_2(SO_3)_3\ (s)$ & $3\,H_2O\ (\ell)$ do **<u>NOT</u>** appear in K

- gases & aqueous solutes do appear.

While equilibrium constants do not technically have units we can “pretend” they do. In this case what would it be?

$$K_c = (M)^2(M^3)/(M)^6 = (M^{-1})$$

<u>C</u>

27)

At equilibrium:

forward rate = reverse rate

concentrations are constant & $Q_c = K_c$ (equil. constant expression is constant)

The rate constants of the forward and reverse reactions are NOT necessarily equal.

Remember the demo in class involving the aquariums (one empty and one full). Equilibrium was reached when the same amount of water was transferred from one aquarium to the other during the same period of time (**<u>rate of transfer</u>** from one aquarium to the other was **<u>equal</u>**). The amount of water in each aquarium was NOT the same. However, the amounts of water in each aquarium remained constant once equilibrium was reached.

<u>C</u>

28) $BF_3\,(g) \rightleftarrows B(\mathbf{s}) + 3/2\ F_2(g)$

use $K_p = K_c\,(RT)^{\Delta n}$ (Δn = change in moles of **gas**)

$\Delta n = 3/2 - 1 = 1/2$ Do **<u>NOT</u>** include the **solid** (if you do $\Delta n = 3/2$)

$K_c = \dfrac{[F_2]^{3/2}}{[BF_3]}$ $Kp = \dfrac{(P_{F2})^{3/2}}{P_{BF3}}$

R = 0.0821 L•atm/mol•K <u>NOT</u> 8.314 J/mol•K

T = 1100 °C + 273 = 1373 K (**must** be in **<u>kelvin</u>**)

$K_p = 1.56 \times 10^{-51}$

$K_p = K_c\,(RT)^{1/2}$

$K_c = K_p\,(RT)^{-1/2}$

$= (1.56 \times 10^{-51})\,\{(0.0821)\,(1373)\}^{-1/2}$

$K_c = 1.47 \times 10^{-52}$

<u>D</u>

29)

(1) $CH_4(g) + H_2O(g) \rightleftarrows CO(g) + 3\,H_2(g)$

$$K_1 = \frac{[CO]\,[H_2]^3}{[CH_4]\,[H_2O]} = 2.55 \times 10$$

(2) $2\,CO(g) + 6\,H_2(g) \rightleftarrows 2\,CH_4(g) + 2\,H_2O(g)$

$$K_2 = \frac{[CH_4]^2\,[H_2O]^2}{[CO]^2\,[H_2]^6}$$

Rx 2 is the reverse of rx 1 and then multiplied by 2

K_{rev} for rev. rx is $1/K_{for}$ (reciprocal of K_{for} for the forward rx)

Also, when multiply a rxn by some factor the K for the new rxn is equal to original K raised to the factor the rxn was multiplied by (multiplying by -1 reverses the rxn)

$$K_2 = K_1^{-2} = 1/K^2 = (2.55 \times 10)^{-2} = 1.5\underline{\mathbf{3}}78 \times 10^{-3} = 1.54 \times 10^{-3}$$

D

Proof

$aA + bB \rightleftarrows xX + yY$

$$K_1 = \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b}$$

Multiply by n

$(a\bullet n)\,A + (b\bullet n)\,B \rightleftarrows (x\bullet n)\,X + (y\bullet n)\,Y$

$$K_2 = \frac{[X]^{xn}\,[Y]^{yn}}{[A]^{an}\,[B]^{bn}} = \left(\frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b}\right)^n = K_1^n$$

Multiply by -1 reverses rxn.

$-aA + -bB \rightleftarrows -xX + -yY$

want (+) coeff - like in math switch reactants & products to other sides

$xX + yY \rightleftarrows aA + bB$

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29) (cont.)

When you add reactions together to get another reaction the K for the overall reaction equals the K's from the added reactions multiplied together.

Rxn 1 + Rxn 2 = Rxn 3

$K_1 * K_2 = K_3$

Proof

(1) $aA + bB \rightleftarrows xX + yY$ and (2) $cC + dD \rightleftarrows rR + sS$

$$K_1 = \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b} \qquad K_2 = \frac{[R]^r\,[S]^s}{[C]^c\,[D]^d}$$

Add the two equations (reactions) to get a third equation (reaction)

$aA + bB + cC + dD \rightleftarrows xX + yY + rR + sS$

$$K_3 = \frac{[X]^x\,[Y]^y\,[R]^r\,[S]^s}{[A]^a\,[B]^b\,[C]^c\,[D]^d} = \left(\frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b}\right) * \left(\frac{[R]^r\,[S]^s}{[C]^c\,[D]^d}\right)$$

$K_3 = K_1 * K_2$

30) Determine reaction quotient, Q, and compare to K.

Q = K system at equlibirium

Q < K not at equilibrium - not enough product & too much reactant
shifts to **__right__** (------>) **toward __product__** to reach equil. (when Q = K)

Q > K not at equilibrium - too much product & not enough reactant
shifts to **__left__** (<------) **toward __reactant__** to reach equil. (when Q = K)

$CO_2(g) + C(s) \rightleftarrows 2\,CO(g)$

$$K_c = \frac{[CO]^2}{[CO_2]} = \frac{(0.312)^2}{(0.100)} = 0.97\underline{\mathbf{3}}44 = 0.973 \text{ (to 3 s.f.)}$$

$Q_c = 0.973 \quad K_c = 1.17$

$Q_c < K_c$

∴ rxn is **__NOT__** at **equilibrium**: Too much reactant and not enough product so the reaction shifts to the **__right__** **toward product** (**forward** direction)

__A__

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31)

For temperature changes you treat heat as a reactant or product. Also, changes in temperature are the only changes that cause a numerical change in the equilibrium constant, K.

__Remember__:

ΔH < 0 (-); **__exo__**thermic; **heat** is a **__product__**
- inc T (add heat, a product), shift left (K dec)
- dec T (remove heat, a product), shift right (K inc)

ΔH > 0 (+); **__endo__**thermic; **heat** is a **__reactant__**
- inc T (add heat, a reactant), shift right (K inc)
- dec T (remove heat, a reactant), shift left (K dec)

ΔH < 0	ΔH > 0
T ↑, ←, K ↓	T ↑, →, K ↑
T ↓, →, K ↑	T ↓, ←, K ↓
T & K move in opposite direction	T & K move in same direction
__Product__ favored by **__LOW__ T**	**__Product__** favored by **__HIGH__ T**

__Dec__. **__Temp__**. (__remove__ __heat__) rxn shifts **__left__** - if **__remove__** a **__reactant__** (heat) shift **__left__** (**toward __reactants__**).

1) **heat** + $CO_2(g)$ + C(**s**) $\rightleftarrows$ 2 CO(g) ΔH = 172.5 kJ <----------

2) $N_2(g)$ + $3\,H_2(g)$ $\rightleftarrows$ $2\,NH_3(g)$ + **heat** ΔH = -91.8 kJ ---------->

3) CO(g) + $2H_2(g)$ $\rightleftarrows$ $CH_3OH(g)$ + **heat** ΔH = -21.7 kJ ---------->

4) **heat** + $N_2(g)$ + $O_2(g)$ $\rightleftarrows$ 2 NO(g) ΔH = 181 kJ <----------

5) **heat** + $2\,H_2O(g)$ $\rightleftarrows$ $2\,H_2(g)$ + $O_2(g)$ ΔH = 484.6 kJ <----------

__C__ (1, 4, 5)

32)

Want **product** formation **favored** (shift **right**) by **high P AND low T**

When changes in P and T are applied at the same time do temp. part first (easier than P changes).

Low T, favors **product** (shifts **right**) for **EXO**thermic (**$\Delta H < 0$**)

Only (1), (3) & (5) are **exo**thermic ($\Delta H < 0$). Only need to apply pressure rule to these reactions. However, I will do them all.

High P favors **fewer** moles **gas**

High **P** Low **T**

2 mol gas 3 mol gas

<------ 1) $2\ NO_2(g) \rightleftarrows N_2(g) + 2\ O_2(g)$ + **heat** ΔH = - 66.4 kJ -------->

1 mol gas 2 mol gas

<------ 2) **heat** + $CO_2(g) + C(\mathbf{s}) \rightleftarrows 2\ CO(g)$ ΔH = 172.5 kJ <--------

2 mol gas 2 mol gas

NC 3) $H_2(g) + I_2(g) \rightleftarrows 2\ HI(g)$ + **heat** ΔH = - 9.4 kJ -------->

2 mol gas 2 mol gas

NC 4) **heat** + $N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$ ΔH = 181 kJ <--------

4 mol gas 2 mol gas

------> 5) $CO(g) + 3\ H_2(g) \rightleftarrows CH_4(g) + H_2O(g)$ + **heat** ΔH = - 206.2 kJ -------->

Only # 5 has **BOTH T** and **P** shifting **toward product**.

E

33)

Reactant	**Product**	**Shift**
Add	Remove	Right
Remove	Add	Left

Move **AWAY** from what is **ADDED**

Move **TOWARD** what is **REMOVED**

NOTE: **K** remains **constant** (**Q changes**) for changes in conc. & pressure (numerical value of K changes only for temp. changes)

***** **continued on next page** *****

33) (cont.)

NOTE: Adding or Removing **Pure SOLIDS** of **LIQUIDS** (as long as some is present) does **NOT affect** the equil. (adding water to an aqueous rxn involving water can cause an affect due to dilution - changing the conc. of aqueous substances).

This is because the conc. of pure solids and liquids are essentially constant and do **NOT** appear in K (or Q).

You can see how Le Chatelier's Principle works by looking at the following:

Changing conc. changes the value or the **reaction quotient**, **Q**. We can see how it changes and compare it to K (qualitatively) to see which way the reaction shifts. See example below.

When the reaction is at equilibrium Q = K.

For example: **Remove** a **reactant**: (conc. of reactant dec.)

$Q = \frac{[P]}{[R]\downarrow}$ denominator dec, so **Q inc** and Q **>** K (too much prod, not enough react to be at equil.)

rx must **shift** to **left** to make Q = K again (inc. denominator & dec. numerator)

Shift **left** to make **more reactant** and **use product** to **reestablish** a **new equil**. (in which conc & amounts of reactants and products will be different than in the original equil. but the value of K will be the same).

1) $CO_2(g) + C(\mathbf{s}) \rightleftarrows 2\ CO(g)$ **add** $CO_2(g)$, **reactant**, $Q = \frac{[P]}{[R]\uparrow}$, Q < K, shift **right**

2) $CO(g) + 3\ H_2(g) \rightleftarrows CH_4(g) + H_2O(g)$ **remove** CO(g), **reactant**, $Q = \frac{[P]}{[R]\downarrow}$, Q > K, shift **left**

3) $2\ CO_2(g) \rightleftarrows 2\ CO(g) + O_2(g)$ **add** CO(g), **product**, $Q = \frac{[P]\uparrow}{[R]}$, Q > K, shift **left**

4) $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$ **add** $N_2(g)$, **reactant**, $Q = \frac{[P]}{[R]\uparrow}$, Q < K, shift **right**

5) $CO(g) + 2\ H_2(g) \rightleftarrows CH_3OH(\ell)$ **remove** $CH_3OH(\ell)$, **liquid** product, **NO shift**

B (1 & 4)

34) The Haber process is the reaction of N_2 and H_2 to form NH_3 It is one of the most used industrial processes worldwide. It is used to make NH3 for the use in fertilizers and explosives. The reaction is exothermic ($\Delta H = -92$ kJ/mol) with a large equilibrium constant ($K = 3.8 \times 10^8$) at 25°C.

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g) + \textbf{heat} \quad (\textbf{exo}\text{thermic})$$

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = 3.8 \times 10^8 \text{ (at } 25^\circ\text{C)}$$

1) T: **Raise** **T**, **add** **heat** ==> add product ==> shift **left**, **less product** (NH_3)

changing **temp**., **changes** value of **K**

shift **left** (reverse) ==> **dec**. **product** (inc. reactant)

$$K = \frac{[\text{Product}]\ \downarrow}{[\text{Reactant}]\ \uparrow} \qquad \textbf{K dec}$$

Remember:

Exothermic rxn ($\Delta H < 0$) **Low** **T** favors **products** (High T favors reactants)

T ↑ K ↓ and T ↓ K ↑

Endothermic rxn ($\Delta H > 0$) **High** **T** favors **products** (Low T favors reactants)

T ↑ K ↑ and T ↓ K ↓

2) F: Catalysts speed up the reaction (this part is true) but do NOT change the position of equilibrium (just reach equilibrium faster).

3) F: Raising the total pressure by adding a non-reactive (inert) gas (such as He in this case) does not affect the partial pressures of the gases in the equilibrium so it has no effect on the equilibrium. When we speak of pressure changes these are changes due to volume changes.

4) T: In order for the reaction (balanced eqn) to be a single step mechanism 4 molecules (1 N_2 and 3 H_2) would have to collide simultaneously. This won't happen. Termolecular reactions (3 molecules colliding) are rare (low probability of 3 things colliding at the same time) so 4 molecules colliding simultaneously would be nearly impossible.

5) T: Decreasing the volume (inc. pressure) at constant temp. will cause the reaction to shift to the side with fewer moles of gas. There are 4 moles of gaseous reactants and 2 moles of gaseous product so the reaction will shift to the right (toward the product) and thus result in more NH_3.

D (1, 4, 5)

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35)

Set up an equilibrium table (in molarity). Initially 1.000 mol of C is placed in a 2.000 L flask to give an initial concentration 0.5000 M for C. The reaction is allowed to reach equilibrium and 0.7500 mol of C remains (0.3750 M).

	2 A	+ B	⇄ 2 C	
initial	0.00	0.00	0.5000	(1.000 mol/2.000 L)
change	+ 2x	+ x	- 2x	
equil	2x	x	0.5000 - 2x	

At equilibrium [C] = 0.5000 - 2x = 0.3750 M

2x = 0.1250

x = 0.06250 M

$$K = \frac{[C]^2}{[A]^2\,[B]} = \frac{(0.5000 - 2x)^2}{(2x)^2\,(x)} = \frac{(0.3750)^2}{(0.1250)^2\,(0.06250)} = 1440 = 1.440 \times 10^2$$

E

36) Set up an equilibrium table (in molarity): $[A]_o = [B]_o = 5.00$ mol/10.00 L = 0.500 M

	A	+ B	⇄ 2 C
initial	0.500	0.500	0.00
change	- x	- x	+ 2x
equil	0.500 - x	0.500 - x	2x

$$K = \frac{[C]^2}{[A]\,[B]} = \frac{(2x)^2}{(0.500 - x)\,(0.500 - x)} = \frac{(2x)^2}{(0.500 - x)^2} = 11\underline{\mathbf{0}}$$

$$\frac{(2x)^2}{(0.500 - x)^2} = 11\underline{\mathbf{0}} \quad \text{perfect square (take square root of both sides)}$$

$$\frac{(2x)}{(0.500 - x)} = (11\underline{\mathbf{0}})^{1/2} = 10.\underline{\mathbf{4}}88$$

$2x = (10.\underline{\mathbf{4}}88)\,(0.500 - x)$; $2x = 5.2\underline{\mathbf{4}}4 - (10.\underline{\mathbf{4}}88)\,x$; $x = 0.41\underline{\mathbf{9}}9 = 0.420$ M

$[A] = [B] = 0.500 - x = 0.500 - 0.420 = 0.080$ M; $[C] = 2x = 0.840$ M

A (0.080, 0.840)