Chemistry 1250 - Sp22
Solutions for Practice Midterm 3

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1) Use **Combined Gas Law**:

$$\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i}$$

$P_f = 3P_i$ $V_f = 1/2\ V_i$ (Vol dec to 1/2 its initial value)

$$T_f = \frac{P_f V_f}{P_i V_i} T_i = \left(\frac{P_f}{P_i}\right)\left(\frac{V_f}{V_i}\right) T_i$$

$$T_f = \left(\frac{3\ P_i}{P_i}\right)\left(\frac{1/2\ V_i}{V_i}\right) T_i = (3/2)T_i$$

C

2) There are several methods for solving this problem. In all of them you need to know what STP is.

STP => Standard Temp. & Pressure: T = 0°C (273.15K) & P = 1 atm

a) Method 1

To get the volume determine the moles of O_2 and then use IGL (PV=nRT) to get the volume.

Assume 1 L (or just solve for n/V)

$$?\ \text{mol } O_2 = 1.60\text{ g } O_2 \times \frac{1\text{ mol } O_2}{32.00\text{ g } O_2} = 0.050\underline{\mathbf{0}}\text{ mol } O_2$$

$$V = \frac{nRT}{P} = \frac{(0.050\underline{\mathbf{0}}\text{ mol})(0.08206\text{ L•atm/mol•K})\ (273.15\text{ K})}{(1\text{ atm})}$$

$$= 1.1\underline{\mathbf{2}}073\text{ L } O_2$$

$$= 1.12\text{ L } O_2$$

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2) (cont.)

b) Method 2

$$\mathcal{M} = \left(\frac{RT}{P}\right) D \quad \Rightarrow \quad D = \left(\frac{P}{RT}\right)\mathcal{M} \qquad \text{(in g/L)}$$

$$D = \frac{(1\ \text{atm})\ (32.00\ \text{g/mol})}{(0.08206\ \text{L}\bullet\text{atm/mol}\bullet\text{K})\ (273.15\text{K})} = 1.42\underline{\mathbf{7}}6\ \text{g/L}$$

$$V = \frac{m}{D} = \frac{1.60\ \text{g}}{1.42\underline{\mathbf{7}}6\ \text{g/L}} = 1.12\ \text{L}$$

Using dimensional analysis:

$$?\ \text{L} = 1.60\ \text{g} \times \frac{1\text{L}}{1.42\underline{\mathbf{7}}6\ \text{g}} = 1.12\ \text{L}$$

c) Method 3 (only usable at STP)

Molar Volume at STP: $V/n = 22.41\ \text{L/mol}$ (1 mol gas = 22.41 L)

$$?\ \text{L} = 0.050\underline{\mathbf{0}}\ \text{mol} \times \frac{22.41\ \text{L}}{1\ \text{mol}} = 1.12\ \text{L}$$

E

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3) Use Dalton's Law of Partial Pressures,

$$P_{Total} = P_1 + P_2 + P_3 + \bullet\bullet\bullet$$

Each gas acts independently of the other gases and each follows the IGL as does P_{Tot}.

$$P_T = P_{H2} + P_{He}$$

$$P_{He} = P_T - P_{H2} = 3.0 - 0.20 = 2.80\ \text{atm}$$

Want mass of He - find moles first

$$n = \frac{PV}{RT} = \frac{(2.80\ \text{atm})\ (1.0\ \text{L})}{(0.08206\ \text{L}\bullet\text{atm/mol}\bullet\text{K})\ (298.15\ \text{K})} = 0.1\underline{\mathbf{1}}6398\ \text{mol He}$$

$$?\ \text{g He} = 0.1\underline{\mathbf{1}}6398\ \text{mol He} \times \frac{4.00\ \text{g He}}{1\ \text{mol He}} = 0.466\ \text{g} = 0.47\ \text{g He}$$

A

4) Determine molecular formula of a gas given the empirical formula, C_2H_4O, mass & P, V, T data

$MF = (EF)_{\boldsymbol{n}}$ & $MW = \boldsymbol{n} * (EFW)$ (where MW = molecular wt and EFW = empirical formula wt)

$$\boldsymbol{n} = \frac{MW}{EFW} \qquad \& \qquad \mathcal{M} = \frac{\text{mass}}{\text{moles}} \quad \text{(molar mass or molecular wt)}$$

Have mass of 0.345 g, need moles. (Remember, molar mass = g/mol, same as MW.)

P = 0.942 atm; V = 85.0 mL = 0.0850 L; T = 100°C + 273.15 = $37\underline{\mathbf{3}}.15$ K

$$n_{CxHyOz} = \frac{PV}{RT} = \frac{(0.942\ \text{atm})\ (0.0850\ \text{L})}{(0.08206\ \text{L}\bullet\text{atm/mol}\bullet\text{K})\ (37\underline{\mathbf{3}}.15\ \text{K})} = 2.6\underline{\mathbf{1}}48 \times 10^{-3}\ \text{mol}$$

$$\mathcal{M} = \frac{0.345\ \text{g}}{2.6\underline{\mathbf{1}}48 \times 10^{-3}\ \text{mol}} = 13\underline{\mathbf{1}}.93\ \text{g/mol or } 13\underline{\mathbf{1}}.93\ \text{amu}$$

$$EFW_{C2H4O} = 44.05\ \text{amu}$$

$$\boldsymbol{n} = \frac{13\underline{\mathbf{1}}.93\ \text{amu}}{44.05\ \text{amu}} = 2.9951 = 3$$

$$MF = (C_2H_4O)_3 = C_6H_{12}O_3$$

D

5)

Have same # moles of Ne, CO & H_2S in same container. Ne effuses faster than CO because it is lighter than CO. CO effuses faster than H_2S because it is lighter than H_2S. The smaller the molecule the faster its average velocity.

$$u = \left(\frac{3\,RT}{\mathcal{M}}\right)^{1/2} \qquad\qquad r_{eff} \propto u$$

So $r_{eff} \propto 1/(\mathcal{M})^{1/2}$ at constant T ($\mathcal{M}$ = molar mass, i.e. molec. wt.)

So rate of effusion is proportional to $1/(\mathcal{M})^{1/2}$ (inversely prop to $\mathcal{M}^{1/2}$).

$\therefore$ smaller $\mathcal{M}$ => larger r_{eff}

Thus a lighter gas effuses at a faster rater & after a period of time more Ne than CO and more CO than H_2S will escape. Therefore the partial pressures of the gases are in the following order:

$$P_{Ne} < P_{CO} < P_{H2S}$$

C

6) The KE $\propto$ T (in kelvin), **KE** is **<u>directly</u> <u>proportional</u>** to <u>absolute</u> **Temp** (T in kelvin)

The **average velocity** (root-mean-square velocity), u, is **<u>NOT</u>** directly prop. to **T**.

$u \propto T^{1/2}$ (u is proportional to the square root of T)

$$u = \left(\frac{3\,RT}{\mathcal{M}}\right)^{1/2}$$

$\mathcal{M}$ = molar mass (in kg/mol), R = 8.314 J/mol•K, T = temp (K)

$KE_{avg} = 3/2\ RT$ (for 1 mole of gas)

D

7) Want to determine if the gas is behaving ideally or if not is the deviation from ideality a negative or positive deviation since this determines whether the a or b factor in the the **van der Waals** equation is more important (attractive forces or molecular volume):

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

or

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

causes **(+)** deviation	causes **(−)** deviation
$P_m > P_i$	$P_m < P_i$
due to vol of molecules	due to IAF

P_m = measured (real) P; P_i = ideal P

b: corrects for finite molecular volume of real gases (b=0 for an ideal gas)

a: corrects for attractive forces between real molecules (a=0 for an ideal gas)

Thus, larger molecule => larger molecular volume => larger b
stronger AF => larger a

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7) (Cont.)

Real gases behave nearly ideally at high T (where KE is great enough to overcome IAF) and low P (larger container volume, in which case the molecular volume is less important). As the temp dec. and pressure inc. a gas behaves less ideally and approaches its liquefication point. A bigger molecule has larger volume (b value) & would exhibit larger (+) deviations. A molecule with larger "a" value has stronger AF and would exhibit larger (-) deviations.

Can use the data and calculate the ideal pressure, P_i, using the Ideal Gas Law and then use the VDW eqn. to calculate the van der Waals pressure, P_{VW}, which should be closer to the real pressure.

Calulate the ideal pressure

$$P_i = \frac{(1.000 \text{ mol})\ (0.08206 \text{ L•atm/mol•K})\ (273.15 \text{ K})}{(3.000 \text{ L})} = 7.47\underline{\mathbf{1}}56 \text{ atm} = 7.47\underline{\mathbf{2}} \text{ atm}$$

Calulate the VDW pressure

$a = 3.59\ \text{L}^2\text{•atm/mol}^2$ $b = 0.0427$ L/mol

$$P_{VW} = \frac{(1.000 \text{ mol})\ (0.08206 \text{ L•atm/mol•K})\ (273.15 \text{ K})}{\{3.000 \text{ L} - (1.000 \text{ mol})(0.0427 \text{ L/mol}\}} - \frac{(1.000 \text{ mol})^2\ (3.59 \text{ L}^2\text{•atm/mol}^2)}{(3.000 \text{ L})^2}$$

$$= 7.57\underline{\mathbf{9}}44 - 0.39\underline{\mathbf{8}}88$$

$$= 7.18\underline{\mathbf{0}}55 \text{ atm}$$

$P_{VW} < P_i$

This is a **negative deviation** from ideality. A **negative** deviation is caused by **intermolecular attractive forces** (**IAF**), so the IAF are the more important factor under these conditions.

B

8) Can calculate the volume of desired from volume of given by using the volume ratio which is the same as the mole ratio from the balanced equation. You can see this from **Avogadro's Law**:

$$\frac{V_2}{n_2} = \frac{V_1}{n_1} \qquad \text{or} \qquad \frac{n_2}{n_1} = \frac{V_2}{V_1} \qquad \text{vol ratio = mole ratio}$$

$$2\ B_4H_{10}(g) + 11\ O_2(g) \rightarrow 4\ B_2O_3(s) + 10\ H_2O(g)$$

$$?\ \text{L}\ B_4H_{10} = 15.7\ \text{L}\ O_2 \times \frac{2\ \text{L}\ B_4H_{10}}{11\ \text{L}\ O_2} = 2.85\ \text{L}\ B_4H_{10}$$

numbers in this ratio are
coefficients in bal. eqn.

Could use the P, T, V data given to first calculate the moles of O_2 that reacts. Then do a mole-to-mole stoichiometry problem to determine the moles of B_4H_{10} produced from the moles of O_2. Then you could use the moles of B_4H_{10} with the P and T data given to calculate the volume of B_4H_{10}. This is not complicated but certainly more complicated and much more work than above.

A

9) a) T: Viscosity (HF) > Viscosity (HBr)

			HF		HBr
MW:	20	81	LF	<	LF
# e−:	10	36	DD	>	DD
			H-bonds		

The HF and HBr molecules are both polar. The HBr is bigger and has larger LF. The HF molecule is much more polar (due to the very electronegative F atom) and has bigger DD AF. However, HF molecules can form H bonds while HBr can not. Thus, **HF** has **stronger IAF** and a **greater viscosity**.

b) F: b.p.(CH_3OH) > b.p.(CH_3NH_2)

			CH_3OH		CH_3NH_2
MW:	32	31	LF	≈	LF
# e−:	18	18	DD	>	DD
			H-bonds		**H-bonds**

Both molecules are polar and can form H bonds between molecules. The molecules are essentially the same size and have similar LF. The CH_3OH molecules are more polar than the CH_3NH_2 molecules (since an O atom is more electronegative than a N atom) so CH_3OH has greater DD forces. Both molecules can form H bonds. However, H-bonding involving O atoms is stronger than that involving N atoms (again because an O atom is more E.N. than a N atom). Thus **CH_3OH** has **stronger IAF** and a **higher b.p.**

c) T: VP(CO_2) > VP(SO_2)

			CO_2		SO_2
MW:	44	64	LF	≈	LF
# e−:	22	32			DD

SO_2 has **stronger IAF** than the nonpolar CO_2 and thus a **lower vapor pressure**.

d) T: AF(CH_3F) < AF(CH_3OH)

			CH_3F		CH_3OH
MW:	34	32	LF	≈	LF
# e−:	18	18	DD	<	DD
					H-bonds

The CH_3F molecule is polar (tetrahedral but the 4 atoms around C are not identical) and has LF and DD attractive forces (AF). The CH_3OH molecule is polar (tetrahedral but the 4 atoms around C are not identical and it is bent around the O) and has LF, DD and H-bonding between CH_3OH molecules. Thus, **CH_3OH** has **stronger AF** than CH_3F.

e) T: critical temp (H_2O) > critical temp (H_2S)

			H_2O		H_2S
MW:	18	34	LF	<	LF
# e−:	10	18	DD	>	DD
			H-bonds		

The **H-bonding** that occurs between **H_2O** molecules is a **very strong IAF** compared to the other forces and is in addition to the other IAF and is what is the main reason for the higher IAF of H_2O compared to other molecules of approximately same size.

Remember: **Stronger** Att. Forces ⇒ **Lower Vapor Pressure**
Slower rater of **evaporation**

Higher b.p., m.p., sublimation pt.
ΔH_{vap}, ΔH_{fus}, ΔH_{sub},
critical temp., surface tension, viscosity

B (statement B was false - changed to be correct above)

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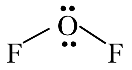
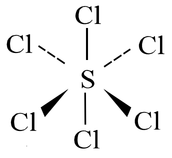
10) Determine if molecules are nonpolar or polar (Draw Lewis Structure and determine shape). Also, remember that in general if there is one or more lone pair of electrons (lpe−) the molecule will be polar. The exceptions to this rule is a linear molecule resulting from 5 e− pairs and a square planar molecule resulting from 6 e− pairs, which can be nonpolar.



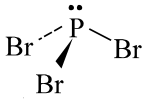
POLAR (around the O atom, just like H_2O. There are lpe− on O.)
Has both LF & DD att. forces

a) SCl_6



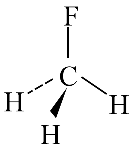
Octahedral
Nonpolar (All 6 atoms around S are indentical.)
LF only

c) PBr_3



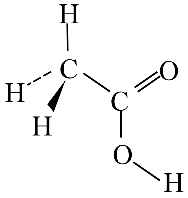
Trigonal pyramidal (like **:**NH_3,**:**NF_3,**:**PH_3, **:**PF_3, etc.)
Polar ; **LF & DD**
(Usually lpe− on central atom ⇒ polar)

c) CH_3F



Tetrahedral (like CH_4, CF_4, SiH_4, $SiCl_4$, etc.)
Polar (all 4 atoms on C are not identical)
LF & DD
(**No** H-bonding; H bonded to C not F)

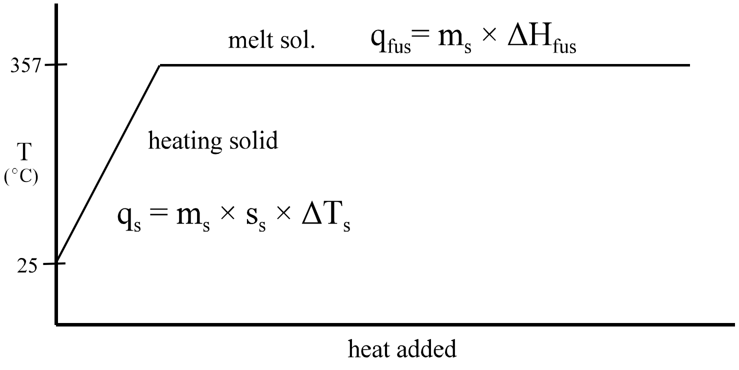
d) CH_3CO_2H



Tetrahedral around CH_3 C atom and trigonal planar around CO_2H C atom.
POLAR (around both C atoms, especially C=O group)
LF, DD, H-bonding (H on OH forms H-bonds)

B

11) Draw a heating curve and label it (makes it easier)



$q = q_{\text{heat solid}} + q_{\text{fusion}}$

$= (m_s \cdot s_s \cdot \Delta T_s) + (m_s \cdot \Delta H_{fus})$

$= [125\text{ g} \cdot 0.138\text{ J/g-°C} \cdot (357 - 25.0)\text{°C}] + (125\text{ g} \cdot 292\text{ J/g})$

= 57**2**7 J + 36**5**00 J = 42**2**27 J = 42.2 kJ

A

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12) For questions 12, it would be helpful to sketch a phase diagram for an imaginary compound (the points are already plotted for you):

triple point = 52 ºC, 0.5 atm

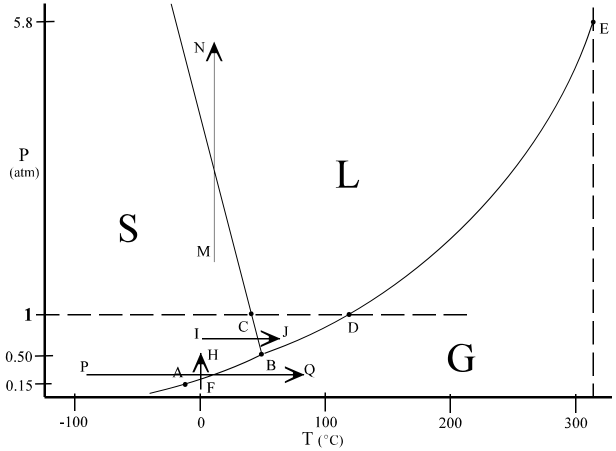
vapor pressure of solid at -15 ºC
= 0.15 atm

normal melting point = 49 ºC

normal boiling point = 118 ºC

critical point = 329 ºC, 5.8 atm

line AB: VP curve for solid (s ⇌ g)
-sublimation curve
line BE: VP curve for liq (ℓ ⇌ g)
-boiling pt. curve
line BC: m.p. curve for solid
(s ⇌ ℓ)



a) T: Line IJ. A phase change occurs going from a solid to a liquid. This is fusion (melting).

b) T: The m.p. curve (line BC, s-ℓ equil.) slopes to the left (has a negative slope) - **m.p.** **dec.** as **Pressure** **inc.** (like H_2O, exception to that of most substances).
- when pressure is supplied you go to the state with a smaller volume.
  - Apply P to solid and get a liquid so the **liquid** has smaller vol., **greater density** (solid is less dense than the liquid)

c) T: The normal melting point is 49 ºC. The s-ℓ equil. line has a negative slope (T dec. as P inc.). The **m.p. dec.** as **P inc.** Thus, the solid **can** be liquefied at temp. less than that of the melting point by applying pressure (inc. P). (See line MN.)

d) F: Line FH. A phase change occurs going from a gas to a solid, **deposition**.

e) T: Line PQ is represents the phase transition of s → g, sublimation.

D

13) cations A in simple cubic (at corners) : 1/8 A cation/corner * 8 coners/uc = 1 A/u.c

cation B at body center: 1 B/u.c

anion X at center of each face : 1/2 X anions/face * 6 faces/uc = 3 X/u.c

ABX_3

A

14) radius, r = 1.247 Å (edge length, ℓ = 2.88 Å = 2.88×10^{-8} cm - see below)
Vol/uc = $\ell^3 = (2.88 \times 10^{-8}\text{ cm})^3$/uc
density = 7.20 g/cm^3
bcc (body-centered cubic) => 2 atoms/uc

Want atomic weight (molar mass) => calc g/mol

$$\ell = \frac{4\,r}{\sqrt{3}} = \frac{4\;(1.247\text{ Å})}{\sqrt{3}} = 2.8798\text{ Å} = 2.880\text{ Å}$$

$$?\frac{\text{g}}{\text{mol}} = \underbrace{\underbrace{\underbrace{\underset{\text{density}}{\frac{7.20\text{ g}}{1\text{ cm}^3}} \times \underset{\text{uc}}{\frac{(2.880 \times 10^{-8}\text{ cm})^3}{\text{uc}}}}_{\text{mass uc}} \times \frac{1\text{ uc}}{2\text{ atoms}}}_{\text{mass per atom}} \times \frac{6.02 \times 10^{23}\text{ atoms}}{1\text{ mol}}}_{\text{mass per mol}}$$

= 51.760 g/mol = 52.0 g/mol (52.0 amu)

C

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15) Which member of the following pairs has **higher m.p.** - look at attractive forces

B **SiC NaCl Mo Al_2O_3**

SiC **covalent network**	or	H_2O molecular

SiC is a covalent network solid which has the diamond structure in which half the C atoms have been replaced by Si atoms - very hard and very high m.p. (solid at room temp) Must break covalent bonds to melt this type of solid
(Group 4A elements form covalent network solids as pure solids and compounds of these elements - C(diamond), C(graphite), Si, Ge, gray Sn & elements close to group 4A - BN (s), SiO_2 (quartz), GeO_2)

H_2O is a molecular solid and forms LF, DD & H-bonds but these are much weaker than covalent bonds
(H_2O is a liquid at room temp.)

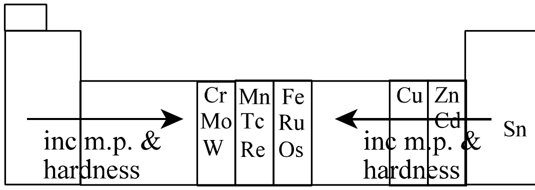
HF molecular	or	**NaCl** **ionic**

NaCl is an ionic solid and has ionic bonds between ions. **Ionic solids** have much **higher m.p.** (400 - 3000°C) than the majority of molecular compounds.

HF is a molecular solid and has LF, DD & H-bonding. Even though HF can form H-bonds these IAF are **NOT** as strong as ionic bonds. HF is a gas at room temp.

Mo metallic	or	Sn metallic

Both are metallic & m.p. inc from both the left and right in the PT toward the middle of the transition elements (has to do with # “valence” e$^-$ in the metal).



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15) (cont.)

Fe_2O_3 ionic or KCl ionic

Ionic Solids - m.p. & hardness (and solubility) depends on Lattice Energy

$$LE \propto \frac{Q^+ Q^-}{d}$$

Q: charge on ion

d: distance between centers of ions & usually determined by adding ionic radii.

The Fe^{3+} has a +3 charge while K^+ has a +1 charge & Fe^{3+} is smaller than K^+

The O^{2-} has a a -2 charge while Cl^- has a −1 charge & O^{2-} is smaller than Cl^-.

∴ Numerator for $Fe_2O_3 \propto |(+3)(-2)| = 6$ & for $KCl \propto |(+1)(-1)| = 1$

so numerator for Fe_2O_3 is 6 times larger than that for KCl

Feso, $r_{(Fe^{3+})} < r_{(K^+)}$ & $r_{(O^{2-})} < r_{(Cl^-)}$ so $d_{(Fe_2O_3)} < d_{(KCl)}$

$\therefore LE_{(Fe_2O_3)} > LE_{(KCl)}$ (mostly based on the charges)

& Fe_2O_3 has higher m.p. (greater LE => higher m.p. Also, generally less soluble.)

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16)

1) T : hcp - ABABAB••• ccp (fcc) - ABCABC•••

Both ccp (same as fcc) and hcp are closest-packed structures. Both have12 nearest neighbors and have the least amount of empty space., 26% empty space (74% space occupied).

2) F: The neighboring molecules in molecular solids are attracted to each other (“held together”) by LF, DD and H-bonds (the atoms within a molecule are held together by covalent bonds). These relatively weak IAF between molecules are the forces broken during phase changes (while the covalent bonds between the atoms within a molecule remain intact).

molecular solids(IAF: LF, DD, H-bonding) generally have the **<u>lowest</u> mp** of the 4 types of solids (-272 to 400°C).

3) **F**: Ionic solids are hard and brittle have very high m.p. (400 - 3000°C). Must break ionic bonds to melt this type of solid. This requires a lot of energy. Ionic solids do **<u>NOT</u> conduct electricity** in the **<u>solid</u>** state (ions or electrons are not free to flow and carry charge). However, the molten substance (liquid state) or solutions of ionic substances do conduct electricity (ions are free to flow and carry the charge).

4) **F**: A fcc structure has 4 atoms/uc and each particle has **12 nearest neighbors** (coordination # of 12).

	sc (pc)	bcc	fcc
# part.	1	2	4
coord #	6	8	12
% empty space	48	32	26
ℓ =	$\frac{4r}{(4)^{1/2}}$	$\frac{4r}{(3)^{1/2}}$	$\frac{4r}{(2)^{1/2}}$

5) T: LiF has the NaCl structure. NaCl has a face-centered lattice structure (Cl^- in a fcc w. Na^+in holes between the Cl^- on the edges and 1 Na^+ in the body center; or Na^+ in fcc w. Cl^- in holes). In this structure, each Na^+ has 6 nearest neighbor (is surrounded by) Cl^- ions and each Cl^- has 6 nearest neighbor (is surrounded by) 6 Na^+ ions. Therefore, since LiF has the NaCl structure each Li^+ has **<u>6</u> nearest neighbor** F^- ions.

<u>E</u> (2, 3 & 4 are False - corrected statements above)

17)

Remember: **"Like Dissolves Like"**

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

Nonpolar solvents dissolve **non**polar solutes

a) Na_2CO_3 in CCl_4 **INSOLUBLE**
ionic molecular
(ionic bonding) (LF only - nonpolar; only C and H in the molecule)

CCl_4 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 CCl_4 the ionic AF between the ions in Na_2CO_3 have to broken and the LF between CCl_4 molecules have to be broken. The only AF that can form between the ions of Na_2CO_3 and nonpolar CCl_4 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 CCl_4.

b) HF in C_2H_5OH
molecular molecular
Polar Polar
(LF, DD, H-bonding) (LF, DD, H-bonding)

H-F: ---- H-OC_2H_5

F-H ----- :OC_2H_5
|
H

Both are polar and form H-bonds between like molecules in the pure substances. So when HF dissolves in C_2H_5OH you are breaking LF, DD and H-bonding between HF molecules and C_2H_5OH molecules and reforming the same AF between solute (HF) and solvent (C_2H_5OH) 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 C_2H_5OH. In addition some of the HF molecules ionize and the resulting ions form ion-dipole AF to the C_2H_5OH molecules.

c) CH_3CN in H_2O
molecular (polar) molecular (polar)
(LF, DD) (LF, DD, H-bonding)

CH_3CN: ----- H-O
|
H

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 H_2O molecules. Forming LF and DD IAF between CH_3CN and H_2O molecules. Also, while CH_3CN can not form H-bonds between solute molecules as a pure substance it can form H-bonds to the H_2O 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 H_2O molecule). Breaking similar AF between solute molecules and between solvent molecules and forming same type of AF between solute and solvent molecules.

******* cont. next page *******

17) (cont.)

d) Br_2 in C_6H_6
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.

NH_4Cl in H_2O
ionic molecular (polar)
(ionic bonding) (LF, DD, H-bonding)

For NH_4Cl to dissolve in H_2O ionic AF have to be broken between NH_4^+ 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 NH_4^+ and Cl^- ions 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

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

D (False)

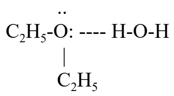
CH_3OH in $CHBr_3$
polar polar

LF & DD AF between CH_3OH & $CHBr_3$. However, these molecules can not form H-bonds to each other in solution. The $CHBr_3$ molecules can not form H-bonds. The H on the C atom in $CHBr_3$ will not form a H-bond to the O atom of CH_3OH and the Br atoms can not form H-bonds to the H atoms on the O of CH_3OH.

(**No H-bonding** between solute and solvent)

a) C_2H_5-O-C_2H_5 in H_2O
polar polar

LF, DD & H-bonding between C_2H_5-O-C_2H_5 & H_2O. Even though C_2H_5-O-C_2H_5 can't form H-bonds in the pure substance (between like molecules) it can form H-bonds between the lone-pair e- on the O and the H atom on the O atom of the H_2O molecules.



C_2H_5-O: ---- H-O-H (with C_2H_5 below the O)

b) $CaCl_2$ in CH_3OH
ionic polar

When $CaCl_2$ dissolves in CH_3OH it dissociates into **ions** which get surrounded by polar CH_3OH molecules (solvated) and form Ion-Dipole AF. The most important AF is Ion-Dipole,

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

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.

c) CH_3NH_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 polar CH_3NH_2 molecules.

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

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

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

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

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

C

20) $\prod = i\,M\,R\,T$, 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 K_2SO_4 at 25°C; $K_2SO_4 \longrightarrow 2\,K^+ + SO_4^{2-}$ $i = 3$

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

b) 0.011 M $FeCl_3$ at 50°C; $FeCl_3 \longrightarrow Fe^{3+} + 3\,Cl^-$ $i = 4$

M_{ions} = 4(0.011 M) = **0.044 M ions** at 50°C

c) 0.011 M $FeCl_3$ at 25°C; $FeCl_3 \longrightarrow Fe^{3+} + 3\,Cl^-$ $i = 3$

M_{ions} = 4(0.011 M) = **0.044 M ions** at 25°C

d) 0.02 M NaCl at 25°C; $NaCl \longrightarrow Na^+ + Cl^-$ $i = 2$

M_{ions} = 2(0.03 M) = **0.04 M ions** at 25°C

e) 0.02 M NaCl at 50°C; $NaCl \longrightarrow Na^+ + Cl^-$ $i = 2$

M_{ions} = 2(0.03 M) = **0.04 M ions** at 50°C

Looking at the solutions at 25°C the 0.011 M $FeCl_3$ (**0.044 M ions**) would have the highest Π.
Looking at the solutions at 50°C the 0.011 M $FeCl_3$ (**0.044 M ions**) would have the higher Π.
Then looking at the two $FeCl_3$ solutions, both have the same conc., 0.011 M $FeCl_3$ (**0.044 M ions**) so the one with the higher T will have the higher osmotic pressure, Π.

<u>B</u>

21) Want the mass of sucrose, $C_{12}H_{22}O_{11}$, that needs to be dissolved in 4.00 x 10^2 g water to produce a solution that boils at 101.36°C. To find the mass of sucrose you first find the moles using the **boiling point elevation** equation to determine molality.

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

i = # ions in the formula for an ionic cmpd or ionizing molecule
= 1 for nonionizing or nondissociating cmpds
$\boldsymbol{m}$ = molality ($i\,m = m_{part}$, molality of particles)

Since $C_{12}H_{22}O_{11}$ is nonionizing $i = 1$. ΔT_b = 101.36°C - 100.00°C = 1.36°C

$$\boldsymbol{m} = \frac{\Delta T_b}{K_b} = \frac{1.36^\circ C}{0.512^\circ C/m} = 2.65625\ m = \frac{2.65625\ mol\ C_{12}H_{22}O_{11}}{kg\ H_2O}$$

$$?\ g = (4.00 \times 10_2)\ g\ H_2O \times \frac{1\ kg\ H_2O}{10^3\ g\ H_2O} \times \frac{2.65625\ mol\ C_{12}H_{22}O_{11}}{kg\ H_2O} \times \frac{342.50\ g\ C_{12}H_{22}O_{11}}{1\ mol\ C_{12}H_{22}O_{11}}$$

= 363.906 g $C_{12}H_{22}O_{11}$

= 364 g $C_{12}H_{22}O_{11}$

<u>D</u>

22) a) T: Volatile substances in an ideal solution follow Raoult's Law:

$$P_A = X_A P_A^0 \quad \text{Raoult's Law}$$

X_A = mole fraction of the volatile substance in the solution
P_A^0 = vapor pressure of pure substance
P_A = vapor pressure due to the substance in the solution.
$P_{solution} = P_{solvent}$ (for a nonvolatile solute - no appreciable vapor pressure)

b) T: The charges on the ions in $CaSO_4$ (Ca^{2+} and SO_4^{2-}) are bigger than those for KCl (K^+ and Cl^-). This means the Ca^{2+} and SO_4^{2-} are more likely to form ion pairs in solution and behave less ideally (stronger attraction due to the larger charges). See Table 13.5 in the text book.

c) T: Vapor pressure lowering. The solute causes the VP to **decrease** compared to the pure solvent. Thus the $VP_{soln} < VP_{solvent}$.

d) T: The VP_{soln} depends on temp, just like that of pure substances. As the temp inc the KE of the particles increases so there are more particles with enough KE able to escape into the vapor phase and thus giving a higher VP.

e) F: Hydrophilic ("water loving") colloid particles have polar or charged groups that allow them to stay dispersed in water. Hydrophobic ("water hating") colloids particles tend to separate from the water and need "help" to stay dispersed (like emulsifying agents).

E

23) 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 [A] changes while [B] is held constant. You have to start with finding n.

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

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

$$\frac{1.60 \times 10^{-3}}{2.00 \times 10^{-4}} = \left(\frac{0.20}{0.20}\right)^m \left(\frac{0.40}{0.20}\right)^n$$

$$8 = (2)^n \qquad n = 3$$

***** cont. next page *****

23) (cont.)

Step 2: determine order, m, with respect to A

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

$$\frac{r_3}{r_1} = \left(\frac{[A]_3}{[A]_1}\right)^m \left(\frac{[B]_3}{[B]_1}\right)^3$$

$$\frac{1.024 \times 10^{-1}}{2.00 \times 10^{-4}} = \left(\frac{0.40}{0.20}\right)^m \left(\frac{0.80}{0.20}\right)^3$$

$$512 = (4)^3\,(2)^m = (64)\,(2)^m \qquad 8 = (2)^m \qquad m = 3$$

The final rate law is:

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

E

24)

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

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

Treat this like any other math equation.

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

Want the conc of C

$$[C] = \left(\frac{r}{k\,[A]^2[B]^{1/2}}\right)^{2/3} = \left(\frac{1.0 \times 10^{-6}\ \text{Ms}^{-1}}{(70.7\ \text{M}^{-3}\text{s}^{-1})\,(0.0100\ \text{M})^2\,(0.0200\ \text{M})^{1/2}}\right)^{2/3}$$

$[C] = 0.010$ M

C

25) A → 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

26) 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, $k = 1.0 \times 10^{-2}\ \text{min}^{-1}$

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

Want time it takes for the reactant to reach 60% of its initial concentration (60% remains). This is the same as stating the time it takes for reaction to be 40% complete (40% of the reactant has reacted).

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

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.

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

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

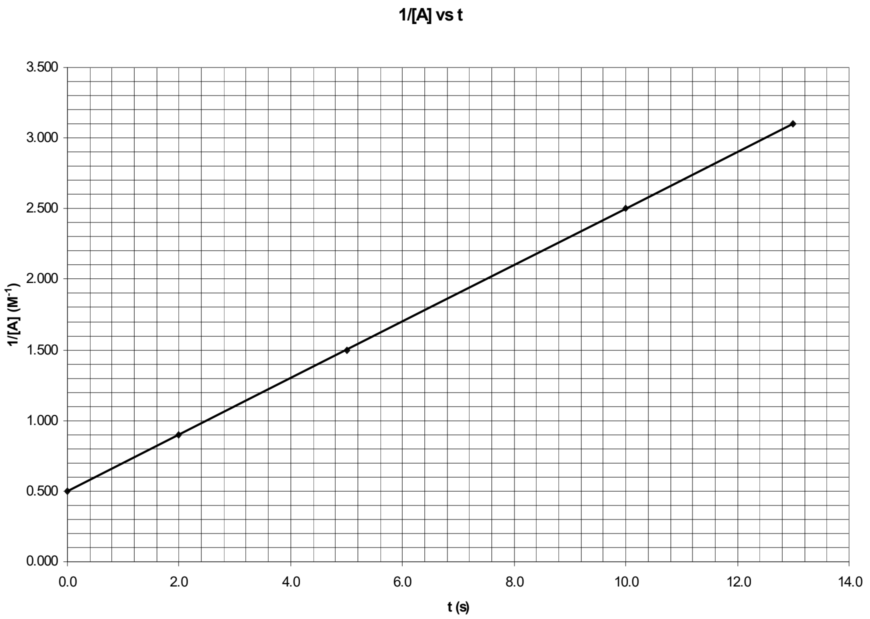
The integrated rate laws for 0 and 2nd order rxn are:

0 order: $[A]_t = -kt + [A]_o$

2nd order: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$

B

27) 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)

2nd order: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$

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

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

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

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

***** cont. next page *****

A

27) (Cont.)

Half-life for 1st order is the only one which is independent of concentration. The half-life is constant as the reaction proceeds. This is not true for reactions with orders other than 1st order.

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

successive half-lifes:

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)

1st-order: successive half-lifes are constant.

0-order: successive half-lifes decrease, cut in half.

2nd-order: successive half-lifes increase, double.

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

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

k_1 T_1 = 20.0°C = 293.15 K

$k_2 = 3\ k_1$ T_2 = 40.0°C = 313.15 K

E_a = ?

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

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

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

C

******* cont. next page *******

28) (cont.)

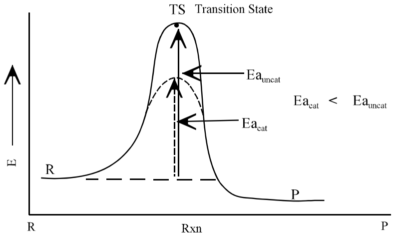
Aside:

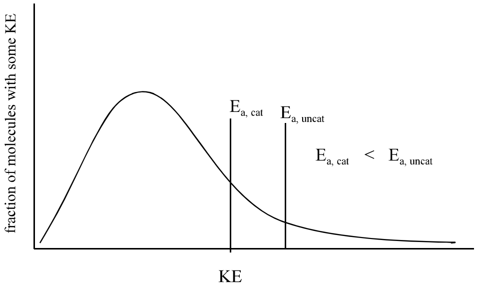
Since it is related to the figure above how are E_a, T and catalyst related to reaction rate?

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.

$k = A e^{-(Ea/RT)}$ 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** ($r \propto k$)





Assuming the frequency factor is the same for different reactions, 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

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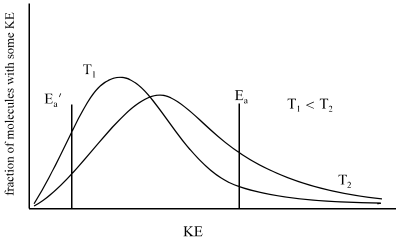
28) (cont.)

You can see how Temperature 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 > E_a and may therefore react



Also, temperature has a bigger effect on the rate constant, k, (and therefore the rate) for reactions with bigger activation energies. That's because for a reaction with a small E_a more molecules are already getting over the barrier (hill) and raising the temp doesn't inc the number of molecules getting over the hill as much as it would for a reaction with a larger E_a. In the figure above, inc temp from T_1 to T_2 inc the number of molecules with KE greater than E_a more for the rxn with E_a than for the rxn with E_a'.

29)

$X + O_2 \longrightarrow XO_2$ (balanced equation)

Mechanism below:

$X + \mathbf{YO_2} \longrightarrow XO + YO$
$XO + YO \longrightarrow XO_2 + Y$
$Y + O_2 + \mathbf{Z} \longrightarrow YO + ZO$
$YO + ZO \longrightarrow \mathbf{YO_2} + \mathbf{Z}$

intermediates: XO, YO, Y, ZO

Appear for the **first time** as a **product** and **used** in **subsequent step** as a **reactant**.

catalysts: $\mathbf{YO_2}$, **Z**

Appear for the **first time** as **reactant** and **reproduced** in **subsequent step** as a **product**.

E

30)

$A_2 + B_2 \rightarrow X + Y$ rate = $k\,[A_2]\,[B_2]/[Y]$ (experimentally determined rate law)

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

a) 2nd step is the slow step

$A_2 \rightleftarrows 2\,A$ (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]

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

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

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

$r = k_2\,[B_2]\,[A]$

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

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

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

b) 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]

*** continued on next page ***

30) (cont.)

$r_1 = r_{-1}$

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

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

c) 2nd step is the slow step

$A_2 \rightleftarrows C + Y$ (fast)

$B_2 + C \rightarrow X$ (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]

$r_1 = r_{-1}$

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

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

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

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

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

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

This agrees w. exp. rate law given - It **IS** the proper mechanism

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---

30) (cont.)

d) 1st step is the slow step

$B_2 \rightarrow 2 B$ (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

e) 2nd step is the slow step

$B_2 \rightleftarrows 2 B$ (fast)

$B \rightarrow C + Y$ (slow)

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

$r = k_2 [B]$ 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

$r = k_2 [B]$

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

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

C

*** continued on next page ***

30) (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.

$A_2 \rightleftarrows 2\,A$ (fast)

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

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

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

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)