Chemistry 1250 - Sp22
Solutions for Practice Midterm 2

1)

$$4\,Al_2O_3(s) + 9\,Fe(s) \longrightarrow 3\,Fe_3O_4(s) + 8\,Al(s) \qquad \Delta H° = +3347.6 \text{ kJ}$$

$\Delta H_{rxn} > 0$ **endo**thermic, energy is **absorbed** from the surroundings (required)
Think of heat as a reactant (required). It might feel cold to the touch.

$\Delta H_{rxn} < 0$ **exo**thermic, energy is **released** to the surroundings (given off)
Think of heat as a product (produced or given off). It might feel hot to the touch.

A thermometer in the **calorimeter** registered an **<u>decrease</u>** in **temperature**. That means the **surroundings** is **<u>losing</u> heat**. That means the **system <u>gained</u> heat**. Thus the process of is **endothermic**.

For the above reaction, $\Delta H_{soln} > 0$ since the reaction is <u>**endo**thermic</u> and **heat** is **released**.

$\Delta H_{rxn} = H_{final} - H_{initial}$

Since $\Delta H_{rxn} < 0$, $H_{products} < H_{reactants}$

Thus, **products** have **<u>higher</u> heat content than** the **reactants**

The rxn. is carried out at **constant volume** (bomb calorimeter) so the **heat** is **equal** to **internal energy**.

$\Delta H = q_p$ enthalpy is heat at constant pressure

$\Delta E = q_v$ internal energy is heat at constant <u>volume</u>

<u>E</u>

2) heat stoichiometry problem

$$2\ C_2H_2\ (g)\ +\ 5\ O_2\ (g)\ \longrightarrow\ 4\ CO_2\ (g)\ +\ 2\ H_2O\ (g)\qquad \Delta H\ =\ -302\ \text{kcal}$$

This is an exothermic rx ($\Delta H < 0$) and 302 kcal of heat are released (as product) per mole of rxn (i.e. for eqn. with quantities as written)

2 mol C_2H_2 = 302 kcal released
5 mol O_2 = 302 kcal released
4 mol CO_2 = 302 kcal released
2 mol H_2O = 302 kcal released

$$?\ \text{kcal}\ =\ 208\ \text{g}\ C_2H_2\ \times\ \frac{1\ \text{mol}\ C_2H_2}{26.04\ \text{g}\ C_2H_2}\ \times\ \frac{302\ \text{kcal}}{2\ \text{mol}\ C_2H_2}$$

$= 12\underline{\mathbf{0}}6.14$ kcal

$= 1.2\underline{\mathbf{1}} \times 10^3$ kcal

$1.2\underline{\mathbf{1}} \times 10^3$ kcal is produced by combustion of 208 g C_2H_2

C

3)

Standard Enthalpy (heat) of Formation: Change in enthalpy for a reaction which forms ONE mole of a compound from its elements with all substances in their standard states.

$$\Delta H_f^\circ$$

Standard state: pure form at atmospheric pressure (and some temperature of interest). A specific temp. is NOT part of the definition. Thus, for H_2O at 1 atm and 25 °C it's standard state would be a liquid. For H_2O at 1 atm and 110 °C it's standard state would be a gas.

The only reaction given which produces 1 mole of a substance in its standard state from it's elements is

b) $1/2\ N_2(g)\ +\ O_2(g)\ \rightarrow\ NO_2(g)$

Note: You may see fractions in these balanced eqns. for ΔH_f°

B

4)

For calorimetry problems you should know what heat capacity, C, is and how molar heat capacity, C_m, and specific heat, C_s, are related to it and how they all related to heat transfer and temperature change.

Heat Capacity: The amount of heat required to raise the temperature of a substance by 1 °C. Often used when you don't have pure or uniform substances (such as a styrofoam cup in exp 6). This is an extensive property (depends on how much is present, how big the cup is).

$$C\ =\ q/\Delta T$$

Molar Heat Capacity: Heat Capacity of one mole of a substance (heat cap. per mol). The amount of heat required to raise the temp. of 1 g of a substance by 1 °C. This is most often used for a pure substance and is an intensive property (while the heat added is extensive).

$$C_m\ =\ C/\text{mol}$$

Specific Heat: Heat Capacity of one gram of a substance (heat cap. per gram). The amount of heat required to raise the temp. of 1 g of a substance by 1 °C. This is most often used for a pure substance and is an intensive property (while the heat added is extensive).

$$C_s\ =\ C/\text{gram}$$

This problem is very similar to what you did in experiment 6 in lab except the problem assumes no heat is lost to the calorimeter (it has a heat capacity of zero). Heat was gained by the H_2O since it's temp. increased (from 23.4 °C to 24.9 °C) and heat was lost by the metal since it's temp. decreases (from 99.7 °C to 25.0 °C).

$q\ =\ m\ \times\ C_s\ \times\ \Delta T$ Heat = (mass) · (specific heat) · (temperature change)

$q_{\text{gained by H2O}}\ =\ -\ q_{\text{lost by nickel}}$

$C_s\ = 4.184$ J/g·°C (the specific heat of H_2O to 4 s.f. - from the first sentence)

$q_{H2O}\ =\ m \cdot C_s \cdot \Delta T\ =\ 150.0\ \text{g}\ \times\ (4.184\ \text{J/g}\cdot{}^\circ\text{C})\ \times\ (24.9\ {}^\circ\text{C} - 23.4\ {}^\circ\text{C})$

$q_{H2O}\ =\ 9\underline{\mathbf{4}}1.4$ J (2 s.f. since 25.0 − 23.5 = 1.54, 2 s.f.)

$q_{metal}\ =\ -\ 9\underline{\mathbf{4}}1.4\ \text{J}$ & $q_{metal}\ =\ m \cdot C_s \cdot \Delta T$

$-\ 9\underline{\mathbf{4}}1.4\ \text{J}\ =\ (28.2\ \text{g}) \bullet C_{s,metal} \bullet (24.9\ {}^\circ\text{C} - 99.7\ {}^\circ\text{C})\ =\ (-21\underline{\mathbf{0}}9.36\ \text{g}\bullet{}^\circ\text{C}) \bullet C_{s,metal}$

$C_{s,metal}\ =\ -\ 9\underline{\mathbf{4}}1.4\ \text{J}\ /\ (-21\underline{\mathbf{0}}9.36\ \text{g}\bullet{}^\circ\text{C})\ =\ 0.4\underline{\mathbf{4}}62\ \text{J/g}\cdot{}^\circ\text{C}$ (technically only 2 s.f.)

A

5)

Use ΔH_f° to determine the ΔH_{rxn}. Based on Hess's Law.

$$\Delta H^{o} = \sum_{\text{products}} \mathbf{n}\, H^{0}_{f,\ \text{products}} - \sum_{\text{reactants}} \mathbf{m}\, H^{0}_{f,\ \text{reactants}}$$

$$3\ H_2S(g) + 2\ HNO_3(\ell) \longrightarrow 2\ NO(g) + 4\ H_2O(\ell) + 3\ S\ (s)$$

H_2S (g) ΔH_f° = -20.6 kJ/mol
$HNO_3(\ell)$ ΔH_f° = -174.1 kJ/mol
NO(g) ΔH_f° = 90.25 kJ/mol
H_2O (ℓ) ΔH_f° = -285.6 kJ/mol

$$\Delta H^\circ = [(2\text{ mol})(90.25\text{ kJ/mol}) + (4\text{ mol})(-285.6\text{ kJ/mol}) + (3\text{ mol})(0\text{ kJ/mol})] - [(3\text{ mol})(-20.6\text{ kJ/mol}) + (2\text{ mol})(-174.1\text{ kJ/mol})]$$

$$= [-961.9\text{ kJ}] - [-410\text{ kJ}]$$

$$= -551.9\text{ kJ}$$

B

6) Hess's Law problem

Want ΔH_{rxn} for a reaction given ΔH_{rxn} for other reactions.

$B_2H_6(g) + 6\ Cl_2(g) \longrightarrow 2\ BCl_3(g) + 6\ HCl(g)$ ΔH_{rxn} = **?**

1a) $BCl_3(g) + 3\ H_2O\ (\ell) \rightarrow H_3BO_3(g) + 3\ HCl(g)$ ΔH = - 112.5 kJ

2a) $B_2H_6(g) + 6\ H_2O\ (\ell) \rightarrow 2\ H_3BO_3(g) + 6\ H_2(g)$ ΔH = - 493.4 kJ

3a) $1/2\ Cl_2(g) + 1/2\ H_2(g) \rightarrow HCl(g)$ ΔH = - 92.3 kJ

Remember:

1) If you multiply an eqn. by some factor the ΔH gets multiplied by that factor.

2) If you reverse an eqn. it simply changes the sign of ΔH.

$$\Delta H_{reverse} = -\Delta H_{forward}$$

To get the reverse of a reaction you multiply everything by −1, the coefficients and ΔH. Your coefficients in the balanced eqn. would all be negative. To get rid of the negative signs you simple turn the whole eqn. around (reverse it), just like in a math eqn. So in reality, this is #1 using a −1 as the multiplying factor.

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

6) (cont.)

1) Need BCl_3 as a product and need a coeff. of 2 (2 BCl_3). Can take eqn. **1a**, **reverse** it and **multiply** it by **2** (multiply by −2).

1b) $2\ H_3BO_3(g) + 6\ HCl(g) \rightarrow 2\ BCl_3(g) + 6\ H_2O\ (\ell)$ $\quad \Delta H_{1b} = -2\ (-\ 112.5\text{ kJ}) = +\ 225\text{ kJ}$

2) Need 1 B_2H_6 molecule as a reactant. Use eqn **2a as is**.

2b) $B_2H_6(g) + 6\ H_2O\ (\ell) \rightarrow 2\ H_3BO_3(g) + 6\ H_2(g)$ $\quad \Delta H_{2b} = -\ 493.4\text{ kJ}$

3) Need 6 Cl_2 molecule as a reactant. Take eqn **3a** and **multiply** it by **12**. Also, need 12 HCl as product to cancel the 6 HCl as a reactant from 1(b) & 6 H_2 as a reactant to cancel 6 H_2 as a product from 2(b).

3b) $6\ Cl_2(g) + 6\ H_2(g) \rightarrow 12\ HCl(g)$ $\quad \Delta H_{3b} = 6\ (-\ 92.3\text{ kJ}) = -\ 553.8\text{ kJ}$

Add the eqns. and delH values:

1b) $2\ H_3BO_3(g) + 6\ HCl(g) \rightarrow 2\ BCl_3(g) + 6\ H_2O\ (\ell)$ $\quad \Delta H_{1b} = -2\ (-\ 112.5\text{ kJ}) = +\ 225\text{ kJ}$

2b) $B_2H_6(g) + 6\ H_2O\ (\ell) \rightarrow 2\ H_3BO_3(g) + 6\ H_2(g)$ $\quad \Delta H_{2b} = -\ 493.4\text{ kJ}$

3b) $6\ Cl_2(g) + 6\ H_2(g) \rightarrow 12\ HCl(g)$ $\quad \Delta H_{3b} = 12\ (-\ 92.3\text{ kJ}) = -\ 1107.6\text{ kJ}$

$$2\ H_3BO_3(g) + 6\ HCl(g) + B_2H_6(g) + 6\ H_2O\ (\ell) + 6\ Cl_2(g) + 6\ H_2(g) \rightarrow$$
$$2\ BCl_3(g) + 6\ H_2O\ (\ell) + 2\ H_3BO_3(g) + 6\ H_2(g) + 6\ HCl(g)$$

$$\Delta H_{rxn} = \Delta H_{1b} + \Delta H_{2b} + \Delta H_{3b}$$

Cancel things in eqn. which are the same on both sides, combine same things which appear on the same side and add ΔH values:

$B_2H_6(g) + 6\ Cl_2(g) \longrightarrow 2\ BCl_3(g) + 6\ HCl(g)$ (desired eqn.)

$$\Delta H_{rxn} = (+\ 225\text{ kJ}) + (-\ 493.4\text{ kJ}) + (-\ 1107.6\text{ kJ})$$
$$= -\ 1376\text{ kJ}$$

A

7)

The rules for the values for the quantum numbers are given in section 6.5 (and 6.7 concerning the spin q.n.).

$n = 1, 2, 3, \ldots, \infty$ (integer values starting at 1) principal quantum number (shell number)

$\ell = 0, 1, 2, \ldots, (n-1)$ angular momentum (azimuthal) q.n. (subshell q.n. and defines shape of orbitals w/in a subshell)

$m_\ell = -\ell, \ldots, 0, \ldots, +\ell$ (values increase by 1) magnetic q.n. (describes orientation of orbital in space - orbitals are degenerate unless in an applied magnetic field)

$m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ (only one with non-integer values) spin magnetic q.n. (electrons “spin” around an axis, only has two directions of spin, “up” or “down”)

Correct q.n.:

For (2) when $n = 4$ and $\ell = 2$ the possible values of m_ℓ are $m_\ell = -2, -1, 0, 1, 2$

For (3) when $n = 6$ and $\ell = 4$ the possible values of m_ℓ are $m_\ell = -4, -3, -2, -1, 0, 1, 2, 3, 4$

Incorrect q.n.:

For (1) when $n = 3$ and $\ell = 0$ is okay but the possible values of m_ℓ is $m_\ell = 0$ (can’t be -1)

For (4) when $n = 2$ and $\ell = 0, 1$ (can’t have $\ell = 2$ when $n = 2$)

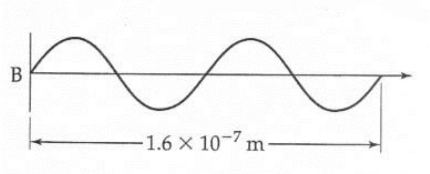
For (5) can’t have $m_s = 0$ (only $+\frac{1}{2}$ and $-\frac{1}{2}$)

A (2 and 3)

8)

The frequency of radiation is related to wavelength,

$$\nu = \frac{c}{\lambda}$$



The figure shows the distance between TWO wavelengths. Two wavelengths have a distance of 1.6×10^{-7} m. Thus, the a single wavelength is 8.0×10^{-8} m.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{8.0 \times 10^{-8}\ \text{m}} = 3.\underline{7}5 \times 10^{15}\ \text{s}^{-1} = 3.8 \times 10^{15}\ \text{Hz}$$

$$E = h\nu = \frac{h\,c}{\lambda} \qquad h = \text{Planck's constant} = 6.626 \times 10^{-34}\ \text{J}\bullet\text{s}$$

$$E = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})\ (3.\underline{7}5 \times 10^{15}\ \text{s}^{-1}) = 2.\underline{\mathbf{4}}8475 \times 10^{-18}\ \text{J} = 2.5 \times 10^{-18}\ \text{J}$$

E

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9)

The frequency and wavelength are related through the following eqn.

$$c = \lambda\nu$$

c = speed of light, λ = wavelength ν = frequency

This eqn. shows that wavelength and frequency are inversely proportional (when one is large the other is small).

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{5.89 \times 10^{-7}\ \text{m}} = 5.09 \times 10^{14}\ \text{s}^{-1}$$

A

10)

a) T: According the Heisenberg uncertainty principle there is a fundamental limitation on how precisely one can simultaneously measure both the location (x) and momentum (mv) of an object. According to this principle the uncertainty in the position times the uncertainty in the momentum is given by the following formula:

$$\Delta x \bullet \Delta p \geq h/4\pi$$

x = position
p = momentum (m•v, m = mass, v = velocity)
h = Planck's constant

b) T: Lower energy orbitals are always filled with electrons first to give the ground state (lowest energy state).

c) F: When filling degenerate orbitals (such as the three p orbitals in a p-subshell) each orbital is singly occupied, with the same spin for each electron, before electron pairing occurs. This is Hund's rule: "for degenerate orbitals, the lowest energy is attained when the number of electrons having the same spin is maximized". This can only occur when the electrons are added one a time to each orbital until all the orbitals in the subshell have one electron (all with the same spin) before the electrons are paired up (two in an orbital).

d) F: The energy levels for the subshells in a shell are different (not degenerate) in multi-electron atoms (e.g. the 2s is lower in energy than the 2p). This is due to the fact the multiple electrons interact with each other and the nucleus. This causes the energies of the subshells to be different. The orbitals within a subshell are still degenerate (have the same energy, e.g. the three 2p orbitals have the same energy). The orbitals will split (have different energies) in the presence of an external magnetic field.

E (More than one statement, © and (d), were incorrect. They've been fixed above.)

11)

For energy changes in a hydrogen atom we have the following eqn.,

$$\Delta E_{Hydrogen} = -(hcR_H)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\Delta E_{Hydrogen} = -(2.18 \times 10^{-18}\ J)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\Delta E_{Hydrogen} = -(hcR_H)\ (1/n_f^2 - 1/n_i^2)$$

For a transition from $n_i = 4$ to $n_f = 1$,

$$\Delta E_{Hydrogen} = -(hcR_H)\ (1/n_f^2 - 1/n_i^2)$$

$$= -(hcR_H)\ (1/1^2 - 1/4^2) = -\mathbf{15/16}\ (hcR_H)$$

This is negative because this is the energy change for an electron falling to a lower energy level which releases energy in the form of a photon. While this is negative, the energy of the photon would be positive.

D

12) **[Xe] 6s^1 4f^{14} 5d^9** or **[Xe] 4f^{14} 5d^9 6s^1**

If the # e− is ≤ # e− in a half-filled subshell, then;
the number of unpaired e− = the number of e− in the subshell.
If the # e− is > half filled (or filled), then;
# of unpaired e− = (the maximum # of e− in the subshell) - (the # of e− present in the subshell).

There are 0 unpaired e− in the 4f, 1 unpaired e− in the 5d & 1 unpaired e− in the 6s. This gives a total of 2 unpaired e−.

↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿ ↿
4f **5d** **6s**

B (2 unpaired e$^-$)

13) Use the periodic table to get the electron configurations. Remember, for the shorthand notation you use the noble gas from the previous period in square brackets to signify the core electrons and just show the subshells and electrons outside the core.

Correct ones:

2) Sn: [Kr] $5s^2\ 4d^{10}\ 5p^2$
3) Fe^{2+}: [Ar]$3d^6$ (Electrons come out of 4s first, then 3d.)
5) Au: [Xe] $6s^1\ 4f^{14}\ 5d^{10}$ (Exception like Cu)

Incorrect ones:

1) Ti: [Ar] $4s^2\ 4d^2$ ==> [Ar] $4s^2\ 3d^2$ (The d orbitals filled are the (n-1)d)
4) In: [Kr] $5s^2\ 4d^{10}\ 5p^3$ ==> [Kr] $5s^2\ 4d^{10}\ 5p^1$ (First element in p-block, 1 electron in p.)

D (2, 3, 5)

14) (see periodic trends in ch 7)

For (c): The radius of $_{31}$Ga is **greater** than $_{33}$As. Size increases from right to left across a period.

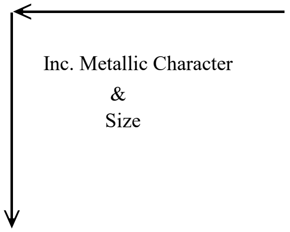
For b) The ionic radius of S^{2-} is **greater** than Ca^{2+}.

S^{2-} & Ca^{2+} are isoelectronic (they have the same number of e− and look like Ar). In an isoelectronic series, anions are bigger than cations. The cations have more protons and the same # e− as the anions so "extra" protons pull the e^- in closer.

C

15) Again, look at the periodic table:

Pb Sb As Se Br



B

16) The following is the proportionality eqn. for LE and it's dependence on charge and distance:

$$LE \propto \frac{Q_1 Q_2}{d}$$

Q = charges on ions d = distance between cation and anion (sum of ionic radii)

This eqn. shows the **LE** is **proportional** to the **charges** on the ions. The bigger the charges the greater the LE. (Use the magnitude, absolute value, of the charges).

The eqn also shows the **LE** is **<u>inversely</u> proportional** to the **distance between** the **charges**. The smaller the distance (the smaller the ions) the greater the LE.

The numerator is more important then the denominator. (i.e. has a bigger effect).

LiF: +1 on Li^+ and −1 on F^-
KBr: +1 on K^+ and −1 on Br^-
CaO +2 on Ca^{2+} and −2 on O^{2-}
CaS +2 on Ca^{2+} and −2 on S^{2-}
AlN +3 on Al^{3+} and −3 on N^{3-}

The AlN has +3/-3 charges so it's numerator is much larger than CaO and CaS with +2/-2 charges which as a much larger numerator than LiF and KBr. Based on this one would expect the LE for AlN would be the greatest and that for the CaO and CaS to be next and the LiF and KBr to be the least (but not the same) since the charges are only +1 and -1.

How about the sizes of the ions? Since two of the cations are isoelectronic they increase in size $Ca^{2+} < K^+$. Al^{3+} would be smaller than the two former cations. The F^-, O^{2-} and N^{3-} are also isoelectronic so they inc. in size $F^- < O^{2-} < N^{3-}$. The Br^- and S^{2-} are larger than the other anions nad Br- is larger than S^{2-}. The LE inc. as the ions get smaller.

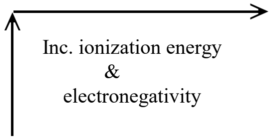
We would expect the AlN to have the greatest LE.

We would expect the **KBr** to have the **smallest LE** (smallest charges and larger ions)

<u>B</u>

17)

Simply look at the electronegativities of the atoms. Remember, **EN <u>increases</u> bottom** to **top** and **left** to **right** in the periodic table.



Also remember the ordering of a number of the most used atoms and the fact there is a big drop in EN going from the 2nd row to the 3rd row and then from the 3rd row down the EN decreases but not by much.

Since all the molecules are binary compounds involving H and one other atom one would expect the most polar bond to be the one involving the most EN atom attached to the H atom. F is the most electronegative of the elements in the answers (P < S < N < O < F). Thus, one would expect HF to have the most polar bond. The P is the least EN of the elements in the answers so one would expect **PH_3** to have the **<u>least</u> polar bonds**.

<u>D</u>

18) SeO_3^{2-}

Se (6A) O (6A) −2 chg

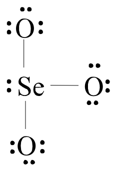
1) A = 1(6e−) + 3(6e−) + (2e−) = 26 val e−

2) Draw skeleton structure. The more EN O atoms attached to Se. This accounts for 6 e$^-$.

3) Put 6 e$^-$ on each O to fulfill octet. This uses 18 e$^-$.

4) # e$^-$ left = 26 e$^-$ - (6 e$^-$ + 18 e$^-$) = 2 e$^-$
The 2e- go on the Se to fulfill octet on Se.

FC should add up to give overall chg., in this case -2 (as they do) and the more negative FC's are on the more electronegative atoms. Also, the absolute values add up to 2.



The structure in (d) is the correct structure for it conforming to the octet rule.

Trigonal pyramidal, angles of **approx.** 109.5°

C

19) NO_2^-

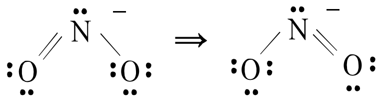
N (5A) O (6A) −1 chg

1) A = 1(5e−) + 2(6e−) + (1e−) = 18 val e−

2) Draw skeleton structure. The more EN O atoms attached to N. This accounts for 4 e$^-$.

3) Put 6 e$^-$ on each O to fulfill octet. This uses 12 e$^-$.

4) # e$^-$ left = 18 e$^-$ - (4 e$^-$ + 12 e$^-$) = 2 e$^-$
2 more e- to put on N. However, this still would not give an octet on N. Must move a pair from an O atom to form double bond between N and O. There are 2 oxygen atoms for which you could do this. Thus the double bond could be drawn in 2 different positions leading to 2 resonance structures.



2 resonance structures (double bond can be in 1 of the 2 different positions)
Bent, angles of **approx.** 120°

To fulfill the octet rule on nitrogen there has to be a double bond between the N and an O atom. The double bond could be drawn in 2 different positions leading to 2 resonance structures. The double bond isn't moving or flipping back and forth between the two regions. There aren't two separate molecules. The two bonds are identical (have the same bond length and electron distribution). There's simply no easy way to draw one single Lewis Structure for this molecule. What it represents is that the "extra" pair of electrons represented in the double bond is actually being shared equally in both regions (actually shared by all three atoms in a molecular orbital which spans all three atoms). It's like the "extra" bond is shared equally to give a bond order of 1.5.

B

20)

Formal Charge on the atoms in SCN^-

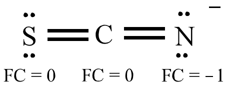
Divide e$^-$ in bonds equally between atoms
(each atom gets ½ the e$^-$ involved in the bond).

lpe$^-$ assigned to the atom they're on.

Subtract this total from the valence e$^-$ on the atom.

Ex: For S: 6 - (4 + 2) = 0
For C: 4 - (4) = 0
For N: 5 - (4 + 2) = −1

FC should add up to give overall chg., in this case −1 (as they do)



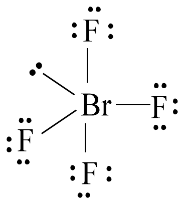
E

21) BrF_4^+

Br: 7A F: 7A
Br F

1) A = 1(7e-) + 4(7e-) - (1e-) = 34 val e−

2) Draw skeleton structure. The more EN F atoms attached to Br. This accounts for 10 e$^-$.



Bromine is in the middle

3) Put 6 e$^-$ on each F to fulfill octet. This uses 24 e$^-$.

4) # e$^-$ left = 34 e$^-$ - (8 e$^-$ + 24 e$^-$) = 2 e$^-$
These go on the Br atom. This gives 10 e- on the Br atom, more than an octet.

Br has 4 bonds & 1 lpe$^-$ in this case since it is in the middle (when halogens are on the outside they have only 1 bond, F is always on the outside, never in the middle)

The ED geometry around the Br is trigonal bipyramidal and the molecular geometry is seesaw with bond angles of ~ 90° and ~ 120°.

A (1 lone pair of electrons on the Br)

22)

PF_5 and BCl_3

There are several instances when the “octet” rule (noble gas rule) is not obeyed.

There are cases when there is less than an octet and there’s an even number of electrons.
This occurs for **Be** (group 2A) and **B** and **Al** (group 3A).

Be gets only 4 e^- around it and forms 2 bonds (group 2A)

B and Al get only 6 e^- around them and form 3 bonds (group 3A)

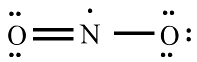
$\bullet\text{Be}\bullet$ $\bullet\overset{\bullet}{\text{B}}\bullet$ (Al like B since they are in the same group, 3A)

2 bonds 3 bonds
4 e^- 6 e^-

There’s also the cases when an atom can get more than an octet of electrons. This occurs for atoms from the 3rd row down. It does NOT occur for atoms in row 2. Examples are PF_5 (10 e^-), SF_4 (10 e^-), ClF_3 (10 e^-), XeF_2 (10 e^-), SF_6 (12 e^-), BrF_5 (12 e^-), XeF_4 (12 e^-) and others.

There are some systems with an odd # of electrons. These will not get an octet on one of the atoms and there will be an unpaired electron. This occurs most often with Nitrogen containing compounds (group 5A).

> NO_2 has 17 valence electrons and it winds up with an unpaired e^- in the molecule and it’s usually shown on the N atom.



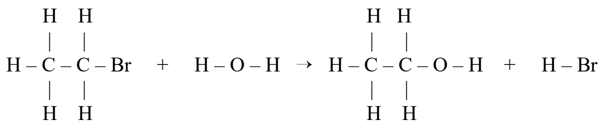
Hydrogen does not get an octet of electrons around it. It can only get 2 e^- around it (so it looks like He). However, it conforms to the “octet” rule (“noble gas” rule) since it winds up looking like He, a noble gas, with a complete valence shell.

D (2 and 4)

23)

Use bond enthalpies to determine the ΔH_{rxn}. You will see bond enthalpies as BE(bond) or D(bond).

$$\Delta H = \sum BE_{broken} - \sum BE_{formed}$$



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Br + H-O-H \rightarrow H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H + H-Br$$

C - H = 414 kJ
H - Br = 366 kJ
C - C = 348 kJ

C - Br = 276 kJ
C - O = 358 kJ
O - H = 463 kJ

$$\Delta H^\circ = [(5)\,D(C-H) + (1)\,D(C-C) + (1)\,D(C-Br) + (2)\,D(O-H)] - [(5)\,D(C-H) + (1)\,D(C-C) + (1)\,D(C-O) + (1)\,D(O-H) + (1)\,D(H-Br)]$$

$$\Delta H^\circ = [(5)(414\text{ kJ}) + (1)(348\text{ kJ}) + (1)(276\text{ kJ}) + (2)(463\text{ kJ})] - [(5)(414\text{ kJ}) + (1)(348\text{ kJ}) + (1)(358\text{ kJ}) + (1)(463\text{ kJ}) + (1)(366\text{ kJ})]$$

$$= [3620\text{ kJ}] - [3605\text{ kJ}]$$

$$= +15\text{ kJ}$$

There is an easier way to do this. Since the C-C and C-H bonds being broken are also being reformed you can ignore them (they simply cancel out in the end). The same for one of the O-H bonds.

$$\Delta H^\circ = [(1)\,D(C-Br) + (1)\,D(O-H)] - [(1)\,D(C-O) + (1)\,D(H-Br)]$$

$$\Delta H^\circ = [(1)(276\text{ kJ}) + (1)(463\text{ kJ})] - [(1)(358\text{ kJ}) + (1)(366\text{ kJ})]$$

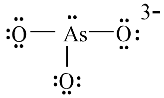
$$= +15\text{ kJ}$$

D

24) AsO_3^{3-}

As: 6A O: 6A
As O 3e−
1) A = 1(5e-) + 3(6e-) + (3e-) = 26 val e−

2) Draw skeleton structure. The more EN O atoms attached to As. This accounts for 6 e^-.



As is in the middle

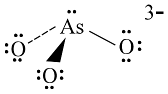
3) Put 6 e^- on each O to fulfill octet. This uses 18 e^-.

4) # e^- left = 26 e^- - (6 e^- + 18 e^-) = 2 e^-
These go on the As atom to fulfill octet.

As has 3 bonds & 1 lpe^- in this case since it is in the middle

O has 1 bond & 3 lpe^- (Oxygen and other group 6A elements usually have 2 bonds and 2 lpe^- or 1 bond 3 lpe^-, particularly when surrounding another atom, like Cl, Br, I, N and S)

Shape and bond angle



3 atoms (bonds) & 1 lpe^- on arsenic
trigonal pyramidal, angles of ≈ or < 109.5°

There are 4 “things” around As (3 O’s and 1 lpe^-). These 4 “things” arrange themselves in a tetrahedral structure (electron-pair geometry) around As and bond angles start out at 109.5°. However, since all 4 things on As are **not** identical the O – As – O angles are ≈ 109.5° but not exactly 109.5°. Three atoms and 1 lpe^- on As gives a **trigonal pyramidal** shape around the As with bond angles of ≈ 109.5°. Ignore the lpe^- when giving the molecular shape.

E

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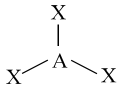
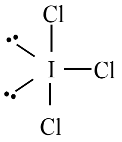
25) BF_3 & SO_3

In order for a molecule to be **trigonal planar** there must be **3 atoms** surrounding the central atom. (**NO lpe^-**)

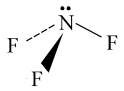


trigonal planar: 3 atoms surrounding A and no lpe^-
angle = 120° (if all surrounding atoms are identical)

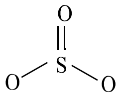
*1) BF_3
3 atoms and no lpe^- (3 things total)
trigonal planar
angle = 120° (exactly)
Nonpolar



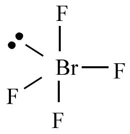
2) NF_3
3 atoms and 1 lpe^- on N (4 things total)
trigonal pyramidal
angle ≈ 109.5 °
Polar



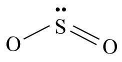
*3) SO_3
3 atoms and no lpe^- on S (3 things total)
trigonal planar
angle = 120° (exactly)
Nonpolar



4) BrF_4^+
4 atoms and 1 lpe^- (5 things total)
Seesaw
angle ≈ 90° and ≈ 120°
Polar



5) SO_2
2 atoms and 1 lpe^- on S (3 things total)
bent
angle ≈120°
Polar



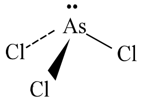
B (only 1 & 3, BF_3 & SO_3, is trigonal planar)

26)

1) $AsCl_3$

trigonal pyramidal: 4 things around As and they are not all identical (3 Cl and **1 lpe$^-$**) lpe$^-$ on As (≈ 109.5° angles)

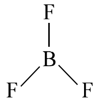
Polar (like $:NH_3$, $:NF_3$, $:PH_3$, $:PF_3$, etc.)



*2) BF_3

trigonal planar (120° angles, exactly) 3 things around B and **<u>all</u> identical** (and no lpe$^-$)

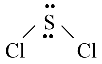
Nonpolar (like BH_3, BF_3, $AlCl_3$ etc.)



3) SCl_2

bent: 4 things around Se and not all identical (2 H and **2 lpe$^-$**) lpe$^-$ on O (≈ 109.5° angles)

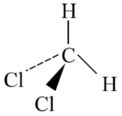
Polar (like $H_2\ddot{O}:$, $H_2\ddot{S}:$, etc.)



4) CH_2Cl_2

tetrahedral (≈109.5° angles) all 4 atoms on C are **<u>not</u>** identical

Polar (like $CHCl_3$, CH_3Cl, CH_2F_2, ect.)



*5) CO_2

linear (180° angles) the 2 atoms on C are **identical**

$O=C=O$

Nonpolar (as is CS_2)

<u>Note</u>: The symmetric shapes (linear, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral and square planar) are the only ones that can give nonpolar. For linear, trigonal planar and tetrahedral all surrounding atoms have to be identical to each other for the molecule to be nonpolar.

For $SiHF_3$ (#5) all surrounding atoms are **<u>NOT</u> identical** so the molecule is **<u>polar</u>**.

Also, the molecules (1 & 3) with **lpe$^-$** are **polar**. Generally, if there are 1 or more lpe$^-$ on the central atom, the molecule will be polar (at least for molecular shapes coming from ED geometries involving 2, 3 or 4 ED). The exceptions to this are for the linear molecular geometry arising from the trigonal bipyramidal ED geometry and the square planar molecular geometry arising from the octahedral ED geometry. These can be nonpolar if all the atoms surrounding the central atom are identical.

<u>C</u> (2 & 5 are **NON**polar)

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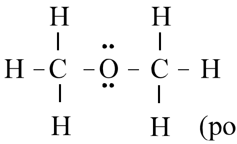
27)



$H_3C-\ddot{\underset{\cdot\cdot}{O}}-CH_3$ (polar)

Shape around:

C atoms: **tetrahedral** - 4 atoms attached to the C atoms and no lone pairs, bond angles around C are ~109.5° and it is polar around the C atoms.

O atom: **bent** - 2 atoms and 2 lone pairs of electrons on the O atom. Since the electron-pair arrangement around the O atom is tetrahedral but all 4 things on the O atom are not identical the molecule will have a bond angle (C-O-C) of ~109.5° and it will be polar around the O atom. Around the O atom it looks like H_2O but with both of the H atoms replaced with CH_3- groups.

<u>E</u>

28) sp^3 sp^3 sp sp sp^3 sp^3 sp^2 sp sp^2
CH_2 - CH - C ≡ C - CH_2 - CH_2 - CH = C = CH_2
| |
CH = CH
sp^2 sp^2

For carbon atoms with one double bond the carbon forms 3 ***sp^2*** hybrid orbitals each with a *p* orbital remaining. The ***sp^2*** orbitals form a σ bond with hydrogen and/or with carbon atoms (total of 3 σ bonds). The fourth bond between the carbon atoms results from a side-by-side overlap of the *p* orbitals of each carbon atom to form one pi (π) bond. A carbon atom with a triple bond forms 2 ***sp*** hybrid orbitals and has two *p* orbitals remaining for the π bonds. The molecule above has 4 ***sp^3***, 4 ***sp^2*** and 3 ***sp*** hybridized C atoms.

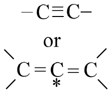
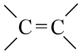
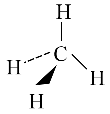
The molecule above has 3 double bonds. The double-bonded C atoms in the ring each have only 1 double bond to them so there are 2 ***sp^2*** hybridized carbon atoms (Remember, each "normal" double bond has 2 ***sp^2*** hybridized carbon atoms; see exception below). There are 2 more double bonds. The C atom on the right end has only 1 double bond to it so it is ***sp^2*** hybridized. The 3rd carbon from the right has only 1 double bond to it so it is ***sp^2*** hybridized. That's a total of 4 ***sp^2*** hybridized C atoms. Normally C atoms with double bonds are ***sp^2*** hybridized. However, there is an **exception** when a **C atom** has **2 double bonds** to it (the 2nd carbon from the right). In this case the C atom is ***sp*** hybridized (see below). **Tripled bonded carbons** are ***sp*** hybridized.

− C ≡ C − sp hybrid carbon atoms

\ * / * /
C = C = C sp hybrid carbon atom (= C = in middle, = C is *sp*^{2})
/ \ \

\ /
C = C *sp*^{2} hybridized carbon (2 single bonds and double bond to carbon)
/ \

|
−C − *sp*^{3} (4 single bonds)

	2 things attached to a central atom	sp hybridization linear, 180°
	3 things attached to a central atom	sp^2 hybridization trigonal planar, 120°
	4 things attached to a central atom	sp^3 hybridization tetrahedral, 109.5°

C (3 sp hybridized C atoms)

29) **sp^3** hybrid orbitals give an overall tetrahedral geometry with angles of 109.5°. When an atom has 4 things around it the atom generally is using **sp^3** hybrid orbitals for bonding. The **trigonal pyramidal** shape arises when an atom is bonded to 3 other atoms and has 1 lpe$^-$ on it (4 things total). An example is **:**NH_3. The N atom is sp^3 hybridized and uses three of the hybrid orbitals to form the bonds to the H atoms and 1 sp^3 hybrid orbital is used for the lpe$^-$ on the N atom.

sp	linear, 180°
sp^2	trigonal planar, 120° (molecular shapes: trigonal planar, bent)
sp^3	tetrahedral, 109.5° (molecular shapes: tetrahedral, trigonal pyramidal, bent)

C

30)

Bond order: Essentially the number of bonds between two atoms. While this is in the section dealing with molecular-orbital diagrams I went over it in class. You don't need MO diagrams to determine this for simple molecules.

	BO		
Single bond:	1	longest bonds	weakest bonds
Double bond:	2		
Triple bond:	3	shortest bonds	strongest bonds

C ≡ C most likely the shortest bond since it has a triple bond.

E