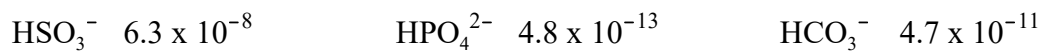


Name _____ KEY _____ Rec. TA/time _____

1. (3 pts) Given the following K_a values, determine which species is the **strongest base**. **Explain!**



Remember:

Larger $K_a \implies$ smaller $\text{p}K_a \implies$ stronger acid \implies weaker conj. base

Larger $K_b \implies$ smaller $\text{p}K_b \implies$ stronger base \implies weaker conj. acid

For a conj. Acid-Base pair:

$$K_a \times K_b = K_w \qquad \text{and} \qquad \text{p}K_a + \text{p}K_b = \text{p}K_w$$

$$K_a = 6.3 \times 10^{-8} \qquad K_b = 1.6 \times 10^{-7}$$

$$K_a = 4.8 \times 10^{-13} \qquad K_b = 2.1 \times 10^{-2}$$

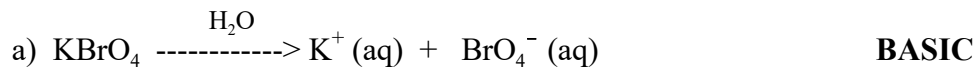
$$K_a = 4.7 \times 10^{-11} \qquad K_b = 2.1 \times 10^{-4}$$

HSO_3^- strongest acid (largest K_a) \implies weakest conj. base, SO_3^{2-} (smallest K_b)

HPO_4^{2-} weakest acid (smallest K_a) \implies **strongest conj. base, PO_4^{3-}** (largest K_b)

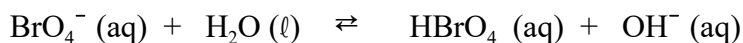
2. (2 pts) Would you expect the following solutions to be acidic, neutral, or basic? **Explain or show work!**

In general: cations => acidic soln (except group 1A & 2A {Ca²⁺, Sr²⁺, Ba²⁺} cations - give neutral)
anions => basic soln (except conj. bases of strong acids; Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₃⁻, ClO₄⁻ are neutral
HSO₄⁻ is acidic)
Also, for most amphoteric anions (like HCO₃⁻, HSO₃⁻, H₂PO₄⁻, etc.) you can't tell if it's basic or acidic w/o doing calculations)



K⁺ : group 1A cation ("conj. acid" of a strong base, KOH, and does not act as an acid) - neutral

BrO₄⁻ is conj. base of a weak acid, HBrO₄, & acts as a **weak base**



Cl⁻ : conj. base of a strong acid, HCl & does not act as a base - neutral

Pb²⁺ : metal cation - causes soln to be **acidic**

3. (8 pts) What is the **pH** of a 0.30 M NaCHO₂ solution at 25°C? (HCHO₂: K_a = 1.8 x 10⁻⁴, at 25°C) (Show the ICE table, state any assumptions made and check your percent error.) Explain or show work!

Hydrolysis problem (salt solution- ions reacting with H₂O to make the soln acidic or basic)

GENERALLY:

Cations - acidic (except group 1A & 2A {Ca²⁺, Sr²⁺, Ba²⁺} cations which are neutral)

Anions - basic (except conj. base of strong acids: Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₃⁻, ClO₄⁻ are neutral
HSO₄⁻ is acidic)

NaCHO₂ -----> Na⁺ + CHO₂⁻ (this is the first step in a salt soln problem - what ions are present?)

Neutral Basic Solution will be basic.

CHO₂⁻ is conj base of weak acid HCHO₂ - base equil problem - **Use ICE (equil.) table** (in Molarity)

	CHO ₂ ⁻	+	H ₂ O	⇌	HCHO ₂	+	OH ⁻	(Na ⁺ is neutral so ignore it)
initial	0.30				0		0	
change	- x				+ x		+ x	
equil	0.30 - x				x		x	

Find the pH of the solution - need the K_b for CHO₂⁻

For a conj. acid base pair : K_a • K_b = K_w = 1.0 x 10⁻¹⁴ & pK_a + pK_b = pK_w = 14.00

$$K_b = \frac{[\text{HCHO}_2][\text{OH}^-]}{[\text{CHO}_2^-]} = \frac{x^2}{0.30 - x} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.55 \times 10^{-11}$$

Assume 0.30 >> x, so (0.30 - x) ≈ 0.30 $\frac{x^2}{0.30} = 5.55 \times 10^{-11}$; x = [OH⁻] = 4.082 x 10⁻⁶
(0.0014% error)

% error = $\frac{4.082 \times 10^{-6}}{0.30} \times 100\% = 0.0014\%$ error (very good assumption that "x" was small)

pOH = -log(4.082 x 10⁻⁶) = 5.39 (2 s.f.)

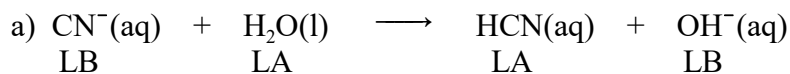
pH = 14.00 - 5.39 = 8.61 (2 s.f.)

or [H⁺] = $\frac{1.0 \times 10^{-14}}{4.082 \times 10^{-6}} = 2.449 \times 10^{-9}$

pH = -log(2.449 x 10⁻⁹) = 8.61

Note: The number of sig. fig. in pH and pOH is to the right of the decimal point. While the 2.96 for pOH above appears to have "3" sig. fig. in reality it only has 2, the digits to the right of the decimal. The "2" in the 2.96 comes from the power of 10 in the [OH⁻].

4. (2 pts) Identify the Lewis acid and Lewis base in the following reactions. **Explain!**



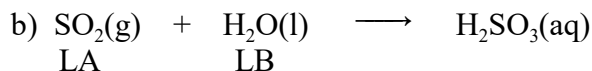
Lewis Acid : e^- pair acceptor (something that is electron deficient: H^+ is technically the Lewis Acid)

Lewis Base : e^- pair donor (something with a lone-pair of electrons - does not have to have a negative chg)

Bronsted-Lowry theory involves a proton transfer from an acid to a base. The H^+ literally is pulled off the acid by the base (the H^+ is transferred, actually moves, from the acid to the base).

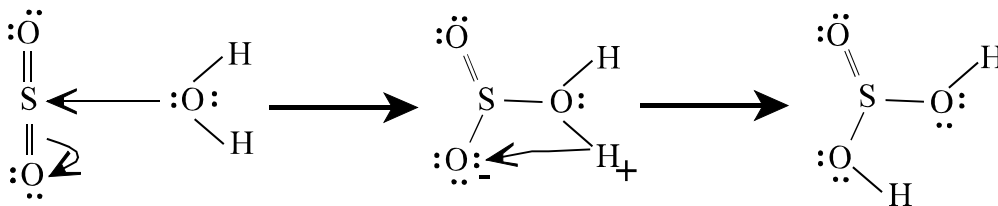
In Lewis theory the e^- pair does not actually move from one atom to another. Instead the LA combines with the LB and in so doing the LA is accepting a pair of e^- from the LB (the LB is donating the e^- pair) to form a new bond between the two. A good example is the reaction between BF_3 with NH_3 . The BF_3 molecule is overall e^- deficient (even though there's electrons on the F atoms the B has only 6 e^- around it making it and the molecule e^- deficient). The NH_3 has an e^- pair on the N. Thus, the N atom in NH_3 can donate the e^- pair to the B in the BF_3 to form a new bond and new molecule, $\text{H}_3\text{N}-\text{BF}_3$.

The CN^- would also be considered a B-L base and the H_2O would be a B-L acid. Remember, Arrhenius acids and bases are B-L acids and bases and B-L acids and bases are Lewis acids and bases. However, it doesn't necessarily go the other way.



Lewis Acid : e^- pair acceptor (something that is electron deficient: the S is "electron deficient" - double bonded to the O atoms)

Lewis Base : e^- pair donor (something with a lone-pair of electrons - like O atom)



5. (3 pts) Calculate the ΔS (J/mol•K) of fusion for a compound which melts at $-183.0\text{ }^{\circ}\text{C}$. The heat of fusion is 2.86 kJ/mole.

Given the $\Delta H^{\circ}_{\text{fus}}$ and the melting point determine $\Delta S^{\circ}_{\text{fus}}$.

Fusion, melting, (phase change) is an equilibrium process

$$\Delta G^{\circ} = \Delta H^{\circ} - T \cdot \Delta S^{\circ} = 0 \quad (\text{constant } T, \text{ standard state conditions})$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ}}{T} = \frac{2.86 \text{ kJ/mol}}{90.15 \text{ K}} = 0.031724 \text{ kJ/mol}\cdot\text{K}$$

$$\Delta S^{\circ} = 0.031724 \text{ kJ/mol}\cdot\text{K}$$

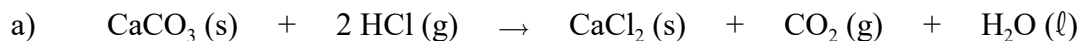
$$\Delta S^{\circ} = 31.7 \text{ J/mol}\cdot\text{K}$$

This applies to any phase change.

NOTE:

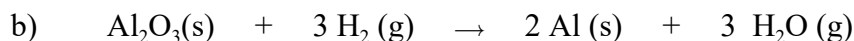
The temp. in Celsius is given to the first decimal place so you should be adding 273.15 and NOT 273. Adding just 273 often won't make a difference but it can.

6. (4 pts) Predict the **sign** of ΔS of the system **or** if it's **approximately zero** for the following reactions and **explain** your choices.



$\Delta S < 0 (-)$ The number of moles of gas is decreasing. Generally speaking, when the number of moles of gas decreases in a reaction that leads to an decrease in entropy and ΔS is negative. There's also a liquid being formed which is less ordered than a solid but since the liquid is H_2O it is more ordered than most liquids due to hydrogen bonding. This makes ΔS more negative than it would be if a different (less ordered) liquid formed.

$$\Delta S = - 78.2 \text{ J/K (calc. from } S^\circ \text{ values)}$$



$\Delta S > 0 (+)$ The number of moles of gas is on each side is the same and there is solid on each side (doesn't matter that much that there are 2 moles of solid in the products compared to 1 mole in the reactants). In this case, I would expect someone to say the change in entropy is small and approx. zero. It would likely be a positive number (inc. in entropy) due to the fact the bent H_2O molecule has many more rotational and vibrational degrees of freedom than the linear H_2 and thus H_2O many more microstates.

$$\Delta S = + 178.8 \text{ J/K (calc. from } S^\circ \text{ values)}$$

The following generally cause an inc. in entropy:

Inc # gas particles.

solid \rightarrow liquid \rightarrow gas (phase changes require energy when going to a more disordered state).

Forming a solution ($\Delta S_{\text{soln}} > 0$ usually, mixing generally leads to more disorder, but not always.).

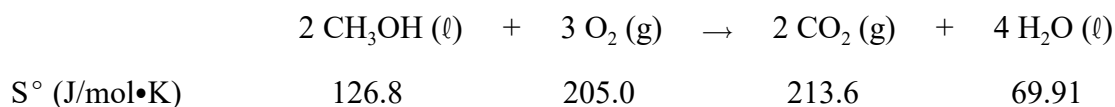
Inc. V (mainly for gases) - more room for the molecules to move around in, more positions for the gas molecules, more microstates.

Inc. Temp (molecular speeds are more spread out and molecules move around more randomly, more microstates.).

Molecules with more atoms generally have more disorder (greater number of vibrational degrees of freedom).

Inc. with inc. molar mass.

7. (5 pts) Determine the entropy of reaction (ΔS°) (in J/mol-K) for the following reaction at 25 °C.



$$\Delta S^\circ = \sum_{\text{products}} n S_{\text{products}}^\circ - \sum_{\text{reactants}} m S_{\text{reactants}}^\circ$$

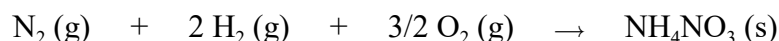
$$\begin{aligned}
 \Delta S^\circ &= [(2 \text{ mol})(213.6 \text{ J/mol}\cdot\text{K}) + (4 \text{ mol})(69.91 \text{ J/mol}\cdot\text{K})] - \\
 &\quad [(2 \text{ mol})(126.8 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})] \\
 &= [706.84 \text{ J/K}] - [868.6 \text{ J/K}]
 \end{aligned}$$

$$= -161.8 \text{ J/K}$$

(A fairly large neg ΔS° , as you might expect; 3 mol gas \rightarrow 2 mol gas and H_2O is more ordered than CH_3OH since H_2O forms more H-bonds per molecule and has fewer degrees of freedom.)

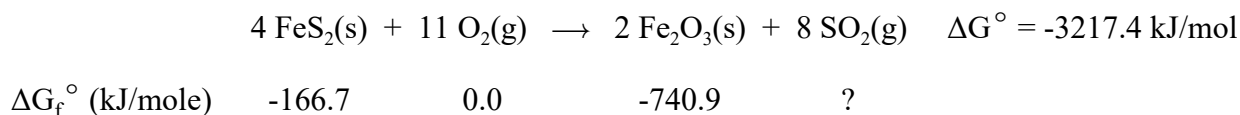
8. (3 pts) Write the reaction for the formation of $\text{NH}_4\text{NO}_3 (\text{s})$ which corresponds to ΔH_f° and ΔG_f° **and** explain why you've written it the way you have.

ΔH_f° and ΔG_f° for a substance correspond to the formation of 1 mole of the substance from its elements in their standard states at a given temp. of interest.



Note: On the right there is only 1 mole of 1 substances. On the left there are only elements. For the elements in this reaction their standard states at 25 °C are the gas state (i.e. they exist as gases at 1 atm and 25 °C). The temp of 25 °C is not part of the standard state definition but is our reference temp.

9. (3 pts) Given $\Delta G^\circ = -3217.4 \text{ kJ/mol}$ and the listed ΔG_f° values calculate ΔG_f° for $\text{SO}_2(\text{g})$.



$$\Delta G^\circ = \sum_{\text{products}} n \mathbf{G}_f^\circ - \sum_{\text{reactants}} m \mathbf{G}_f^\circ$$

$$\Delta G^\circ = [(2 \text{ mol})(\Delta G_f^\circ (\text{Fe}_2\text{O}_3(\text{s}))) + (8 \text{ mol})(\Delta G_f^\circ (\text{SO}_2(\text{g})))] - [(4 \text{ mol})(\Delta G_f^\circ (\text{FeS}_2(\text{s}))) - (11 \text{ mol})(\Delta G_f^\circ (\text{O}_2(\text{g})))]$$

$$\Delta G^\circ = [(2 \text{ mol})(-740.9 \text{ kJ/mol}) + (8 \text{ mol})(x)] - [(4 \text{ mol})(-166.7 \text{ kJ/mol}) - (11 \text{ mol})(0.0 \text{ kJ/mol})]$$

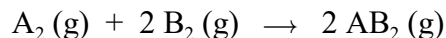
$$-3217.4 \text{ kJ} = [-1481.8 \text{ kJ} + 8x] - [-666.8 \text{ kJ}]$$

$$8x = -2402.4 \text{ kJ}$$

$$x = -300.3 \text{ kJ}$$

$$\Delta G_f^\circ (\text{SO}_2(\text{g})) = -300.3 \text{ kJ}$$

10. (5 pts) For the following reaction ΔH° is -150.5 kJ/mol , ΔS° is $-293.1 \text{ J/K}\cdot\text{mol}$ at 25°C . Assuming these don't change with temperature what is the value of ΔG° (kJ/mol) at 141.0°C ?



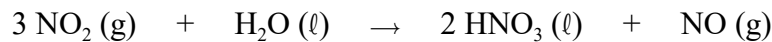
Assume ΔH° and ΔS° are constant over this temperature range. They do change with temp. but the change is fairly small and much smaller than the variation of ΔG° with temp. The ΔG° given has no bearing on the problem.

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$$

$$= (-150.5 \text{ kJ/mol}) - (414.15 \text{ K}) \cdot (-0.2931 \text{ kJ/mol}\cdot\text{K})$$

$$= -29.112 = -29.1 \text{ kJ/mol}$$

11. (13 pts) Given $\Delta H^\circ = -71.75 \text{ kJ}$ and $\Delta S^\circ = -268.0 \text{ J/mol}\cdot\text{K}$ for the following reaction at 25°C ,



a) (2 pts) Calculate the ΔG° of the reaction at 25°C . Is the reaction spontaneous or nonspontaneous at this temperature under standard state conditions? **Show all work and explain.**

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

T in kelvin; ΔS° converted to kJ/K

$$= -71.75 \text{ kJ} - (298.15 \text{ K})(-0.2680 \text{ kJ/K})$$

$$= +8.15 \text{ kJ}$$

$$\Delta G^\circ > 0$$

NONspontaneous under standard conditions
(nonspont. to products, but small so significant amounts of reactants and products at equil.)

$$\Delta H^\circ < 0 \quad \text{and} \quad \Delta S^\circ < 0 \quad \text{so rxn is **spont** at "**low**" temp}$$

(becomes more spont as temp dec and less spont as temp inc.)

b) (4 pts) If the reaction is nonspontaneous, at what temperature would it be spontaneous. If the reaction is spontaneous, at what temperature would it be nonspontaneous. If the reaction will always be spontaneous at all temperatures or never be spontaneous at any temperature state that. **Show ALL work & explain!**

Rxn. is NONspont. at $T = 25^\circ\text{C}$. At what temp will it become spont., i.e. at what temp will $\Delta G^\circ < 0$

$$\Delta H^\circ < 0 \quad \text{and} \quad \Delta S^\circ < 0 \quad \text{so rxn is **spont** at "**low**" temp}$$

(becomes more spont as temp dec and less spont as temp inc.)

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ < 0$$

$$\Delta H^\circ < T \Delta S^\circ$$

$$-71.75 \text{ kJ} < T (-0.2680 \text{ kJ/K})$$

$$\frac{-71.75 \text{ kJ}}{-0.2680 \text{ kJ/K}} > T \quad \text{(Remember, when multiply or divide by a negative number an inequality } (<, >) \text{ flips } (>, <))$$

$$T < 267.72 \text{ K}$$

$$T < 267.7^\circ\text{C}$$

(becomes spont. at temp below this)
(becomes more spont as temp dec)

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

11. (Cont.)

c) (2 pts) What is the equilibrium constant at 25 °C? **Show all work and explain.**

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\Delta G^\circ/RT = -(8.15 \times 10^3 \text{ J})/\{(8.314 \text{ J/K})(298.15 \text{ K})\} = -3.28785 \text{ (3 s.f.)}$$

$$K = e^{-3.28785} = 3.73 \times 10^{-2} \text{ (fairly small but not extremely small - mostly reactants at equilibrium, but not "only" reactants. This is more likely appreciable amounts of reactants and products at equil.)}$$

d) (1 pt) This ΔG° and K corresponds to an equilibrium that is: (choose one from below & explain)

- 1) closer to products
- 2) closer to reactants
- 3) **midway between reactants and products (significant amounts of both at equilibrium)**

ΔG° positive but small. Since $K < 1$ the reaction lies toward reactant. However, the ΔG° and K are small so there's significant amount of reactants and products at equil.)

e) (4 pts) Is the reaction spontaneous or nonspontaneous at 25 °C when the pressures of NO_2 and NO are 2.50 atm and 0.50 atm, respectively? **Show all work and explain.**

$$\Delta G = \Delta G^\circ + RT \ln(Q) \quad \text{T in kelvin; R converted to kJ/K}$$

$$Q = \frac{P_{\text{NO}}}{(P_{\text{NO}_2})^3} = \frac{0.50}{(2.50)^3} = 0.032$$

$$\begin{aligned} \Delta G &= 8.15 \text{ kJ} + (8.314 \times 10^{-3} \text{ kJ/K})(298.15 \text{ K}) \ln(0.032) \\ &= 8.15 \text{ kJ} - 8.532 \text{ kJ} \\ &= -0.38 \text{ kJ} \end{aligned}$$

$\Delta G < 0$ **spontaneous** under these pressure and temperature conditions