

Name

KEN #1

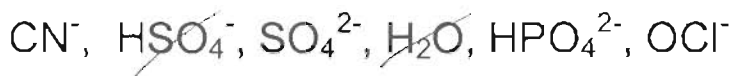
General instructions:

1. Don't panic! Write down what you know and what you need to figure out. Think about all relevant equalities. Make sure to keep track of units. Check your answer and see if it makes sense! Some questions are easier than others, so make sure you look all the questions over.
2. **Remember the honor system.** No notes, books, stored information in calculators, or external help is allowed.
3. Use the space provided for answers. The back of pages can be used as scrap paper. **Show work for partial credit!** Write legibly!
4. There are **120 total points** on this exam. Questions are numbered and parts of questions are lettered. Numbers in parentheses indicate the point value of the question. If you can not get an answer to a prior part of a question, make up a number and carry on with it. You will not be penalized twice for an incorrect answer.
5. Use significant figures where appropriate.
6. This exam has 14 pages. If you are missing a page, now would be a good time to tell me about it.

The last two pages have useful information on them!

MEAN	74.8	(62.3%)
MEDIAN	74	(61.7%)
SD	16	(13.4%)
HIGH	105	

1. (5) Rank the following in order of increasing base strength:



	K_b
CN^-	1.6×10^{-5}
SO_4^{2-}	8.3×10^{-13}
HPO_4^{2-}	1.6×10^{-7}
OCl^-	2.9×10^{-7}

2. (10 points) In order to study an enzyme from an alien life form that has acidic blood, you prepare 1.0 liter of a 100.0 mM acetate buffer at pH 5.0.

A) What is the pH following the addition of 50.0 ml of 0.50 M NaOH?

$$5 = 4.74 + \log \frac{A^-}{HA} \quad 0.26 = \log \frac{A^-}{HA}$$

$$\frac{[A^-]}{[HA]} = 1.82 = \frac{x}{100-x}$$

$$182 - 1.82x = x$$

$$182 = 2.82x$$

$$x = 64.53$$

$$[A^-]_0 = 64.54 \quad [HA]_0 = 35.46$$

$$[A^-] = 89.54 \quad [HA] = 10.46$$

$$\text{pH} = 4.74 + \log \frac{89.54}{10.46}$$

$$= \underline{\underline{5.67}}$$

$$[A^-] = 64.54$$

$$[HA] = 35.46$$

B) What is the pH following the addition of 50.0 ml of 0.50 M HCl?

$$[A^-]_0 = 64.54 \quad [HA]_0 = 35.46$$

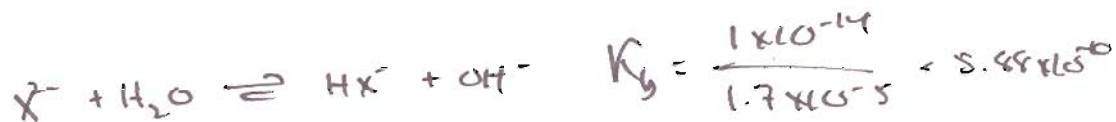
$$[A^-] = 39.54 \quad [HA] = 60.46$$

$$\text{pH} = 4.74 + \log \frac{39.54}{60.46} = \underline{\underline{4.56}}$$

3. (15 points) From the acid spraying nasal organ of the same alien, you isolate an unknown strong acid that appears to be diprotic (assume the formula H_2X). You determine that K_{a1} for this acid is "really large" and that K_{a2} for the acid is 1.7×10^{-5} . In order to study this acid, you titrate 1.0 liter of it (this is a really big alien!) with 100.0 mM NaOH. If the pH of the acid is initially 1.3, determine the pH after adding the following volumes of NaOH:

- A) 125.0 ml $\overset{OH^-}{12.5 \text{ mmol}}$ $\overset{H^+}{37.5} / 1.125 = 33.3 \text{ mM}$ pH 1.48
- B) 250.0 ml 25.0 mmol $25 / 1250 = 20 \text{ mM}$ pH 1.70
- C) 500.0 ml 50.0 mmol ONLY HX^- LEFT pH 3.1
- D) 750.0 ml 75.0 mmol $\rightarrow 1/2 \text{ EQUIV} \therefore \text{pH} = \text{p}K_{a2}$ pH 4.77
- E) 1000.0 ml 100 mmol $\rightarrow \text{EQUIV POINT ONLY } X^{2-}$ pH 8.58
- F) 1250.0 ml 125 mmol $\rightarrow \text{EXCESS } OH^-$ 25 mmol pH 12.05
- pH = 1.3
 $[H^+]_0 = 10^{-1.3}$
 $= 50. \text{ ~~mmol~~ mM}$
 $\therefore 50 \text{ mmol}$
 $\therefore 100 \text{ mmol } H^+$

$$1.7 \times 10^{-5} = \frac{x^2}{50 / 1.5 - x} = \frac{x^2}{3.33 \times 10^{-2} - x} \quad x = 7.5 \times 10^{-7} \quad \text{pH } 3.1$$



$$5.88 \times 10^{-10} = \frac{x^2}{\frac{50}{2000} - x} = \frac{x^2}{2.5 \times 10^{-2} - x}$$

$$\frac{25 \text{ mmol } OH^-}{2250 \text{ ml}} = .011 \text{ M}$$

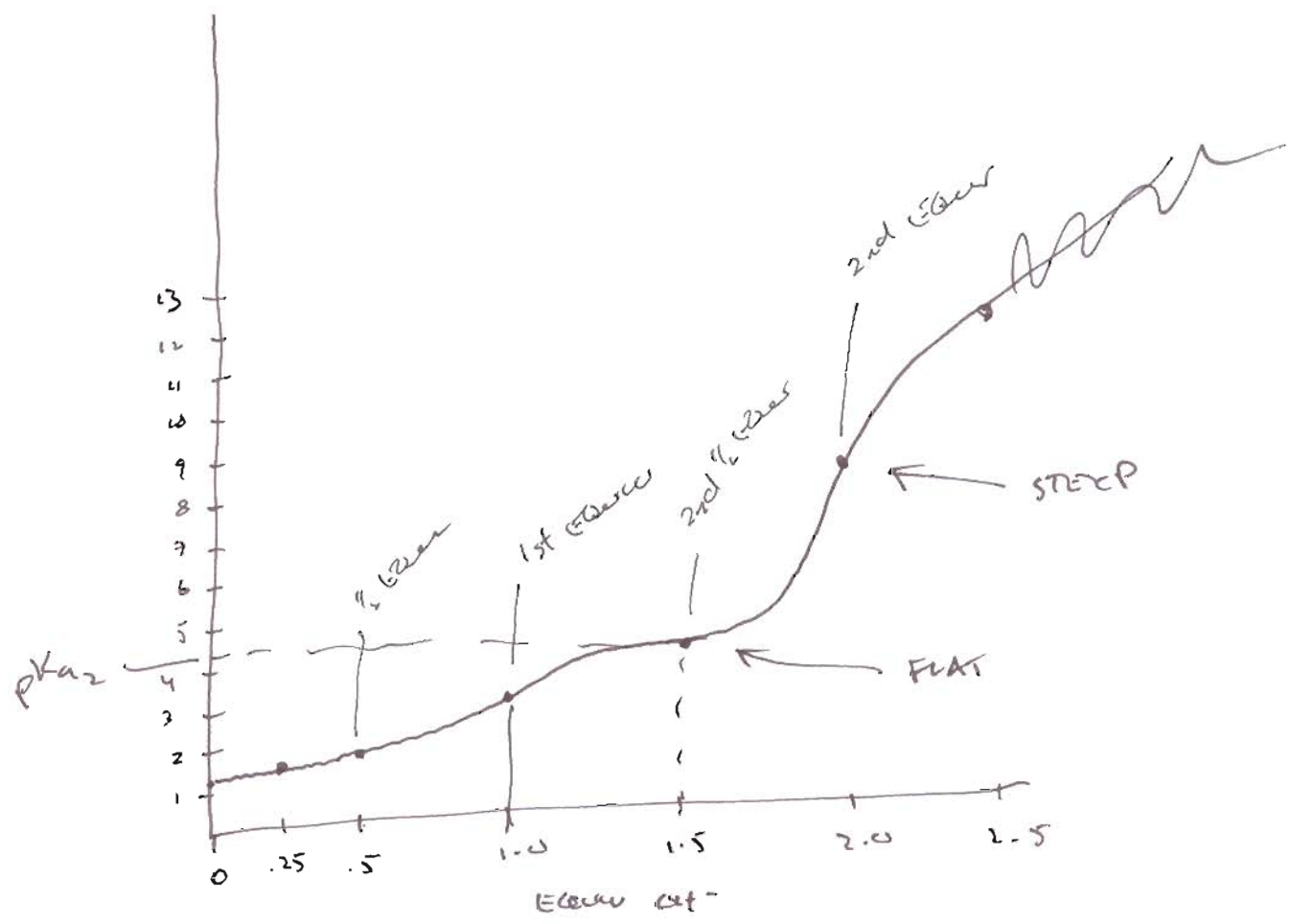
$$\text{pOH} = 1.95$$

$$\text{pH} = 12.05$$

$$\text{pOH} = 5.42$$

$$\text{pH} = 8.58$$

G) Sketch the titration curve for the experiment above. Indicate the important points on the curve.



4. (15 points) Determine the pH of the following solutions:

A) 1.0×10^{-3} M HNO_3

$\text{pH} = 3$ STRONG ACID

B) 1.0×10^{-10} M HCN

WEAK ACID, USE K_a
 $6.2 \times 10^{-10} = \frac{x^2}{1 \times 10^{-2} - x}$

$\text{pH} = 5.6$
 $x = 2.49 \times 10^{-6}$
 ~~$x = 7.87 \times 10^{-7}$~~

C) $2.0 \times 10^{-7} \text{ M HCl}$

DILUTE STRONG ACIDS SO H^+ FROM H_2O WILL BE SIGNIFICANT

$$2 \times 10^{-7} < [\text{H}^+] < 3 \times 10^{-7}$$

$$[\text{H}^+] = 2 \times 10^{-7} + \frac{1 \times 10^{-14}}{[\text{H}^+]}$$

$$[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-] \quad \text{CHARGE BALANCE}$$

$$[\text{H}^+] = 2.41 \times 10^{-7}$$

$$[\text{OH}^-] = \frac{1 \times 10^{-14}}{[\text{H}^+]} \quad K_w \text{ EQUATION}$$

$$\text{pH} = 6.62$$

D) $3.0 \times 10^{-10} \text{ M H}_2\text{SO}_4$

VERY DILUTE, SO $\text{pH} = 7.0$

E) 100.0 mM NH_3

WEAK BASE

$$K_b = \frac{1 \times 10^{-4}}{5.6 \times 10^{-10}} = 1.79 \times 10^{-5}$$

$$x = [\text{OH}^-] = 1.34 \times 10^{-3}$$

$$\text{pOH} = 2.87$$

$$\text{pH} = 14 - \text{pOH} = 11.13$$

$$= \frac{x^2}{0.1 - x} \quad \leftarrow \text{IGNORE } x$$

5. (5) What is the pH of 50.0 mM NaH_2PO_4 ? How is the pH affected by increasing the concentration to 500.0 mM? Explain your answer.

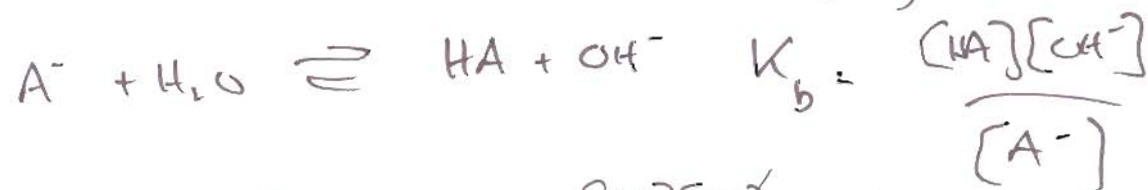
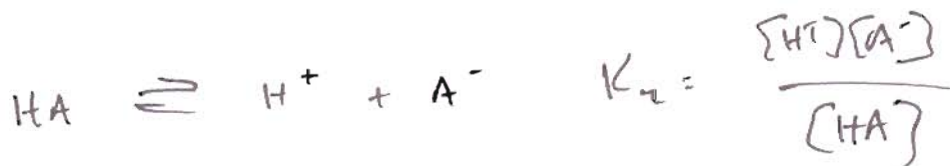
DOMINANT EQUILIBRIUM:



AS RATIOS OF CONCENTRATIONS ARE ALWAYS EQUAL, pH DOES NOT DEPEND ON CONCENTRATION!

$$\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} = 4.67 \quad \text{AT ALL pH'S}$$

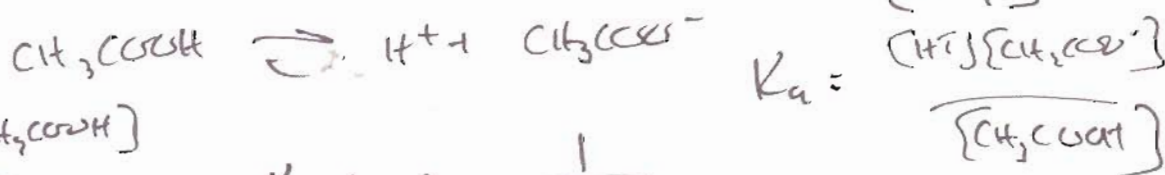
6. (5) Write down the chemical equilibrium equation for a generic weak acid (HA) and a generic base (A^-). Now, show how the K_a expression for the first reaction and the K_b expression for the second reaction can be combined to form an expression for K_w .



$$K_a \cdot K_b = \frac{[H^+][A^-]}{[HA]} \cdot \frac{[HA][OH^-]}{[A^-]}$$

$$= [H^+][OH^-] = K_w$$

7. (5) When NH_4CH_3COO is dissolved in water, what is the dominant equilibrium reaction taking place and what is its equilibrium constant (K)?



$$K = \frac{[NH_3][CH_3COOH]}{[NH_4^+][CH_3COO^-]} = K_a(NH_4^+) \times \frac{1}{K_b(CH_3COOH)}$$

$$= 5.6 \times 10^{-10} \times \frac{1}{1.8 \times 10^{-5}} = 3.11 \times 10^{-5}$$

8. (5) Show how one obtains the Henderson-Hasselbalch equation from the expression for K_a ?

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad [H^+] = K_a \frac{[HA]}{[A^-]}$$

$$-\log [H^+] = -\log \left(K_a \frac{[HA]}{[A^-]} \right) = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

9. (10) $Zn(OH)_2$ is only slightly soluble ($K_{sp} = 1.9 \times 10^{-17}$) in pure water.

A) What is the solubility of $Zn(OH)_2$? What is the solubility of $Zn(OH)_2$ in a solution buffered at pH 6.0?



$$K_{sp} = 1.9 \times 10^{-17} = \underbrace{[Zn^{2+}]}_x \underbrace{[OH^-]}_{2x}^2$$

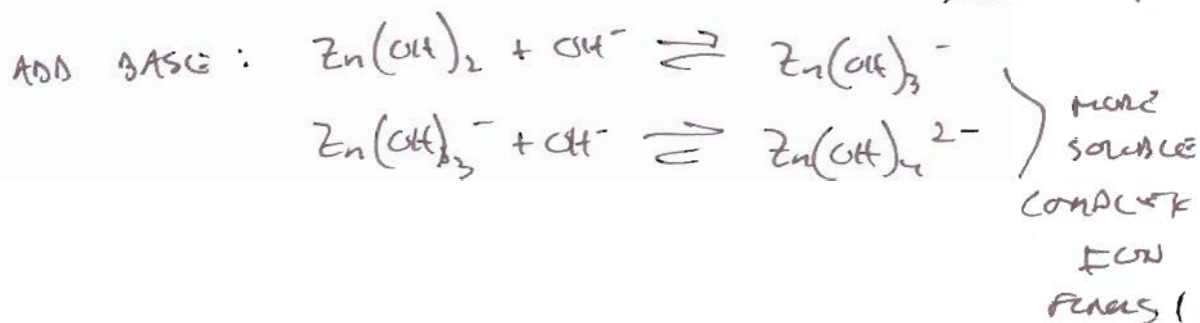
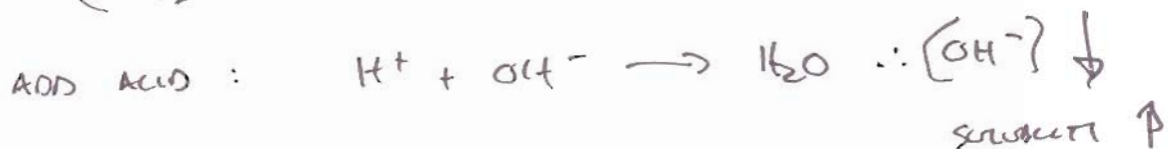
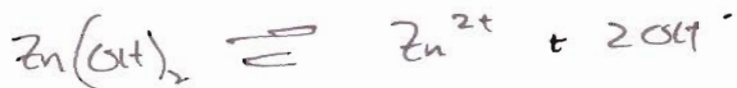
At pH 6, $[OH^-] = 1 \times 10^{-8} M$

$$1.9 \times 10^{-17} = 4x^3$$

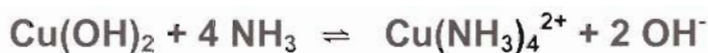
$$1.9 \times 10^{-17} = x (1 \times 10^{-8})^2 \quad x = \underline{1.68 \times 10^{-6} M} \quad \begin{array}{l} \text{PSDE} \\ \text{H}_2O \end{array}$$

$$x = \underline{1.9 \times 10^{-1} M} \text{ @ pH 6.0}$$

B) Explain why the solubility of $Zn(OH)_2$ increases upon addition of either a strong acid or a strong base.



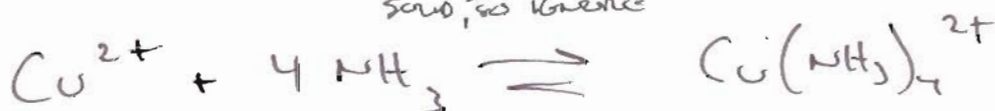
10. (5) If the K_{sp} for $Cu(OH)_2$ is 1.6×10^{-19} and the K for the reaction shown below is 1.6×10^{-6} , what is the K for the formation of the complex ion $Cu(NH_3)_4^{2+}$.



$$K_{sp} \quad 1.6 \times 10^{-19} = [Cu^{2+}][OH^-]^2$$

$$K \quad 1.6 \times 10^{-6} = \frac{[Cu(NH_3)_4^{2+}][OH^-]^2}{[Cu(OH)_2][NH_3]^4}$$

solubility constant



$$K = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = K \times \frac{1}{K_{sp}}$$

$$= 1 \times 10^{13} !!$$

11. (10) If 0.50 moles of an ideal gas at 1.00 atm and 273 K expands against an external pressure of 0.10 atm until the gas pressure reaches 0.20 atm and the temperature reaches 210 K, calculate the work, heat change, ΔE and ΔH of the process.

INITIAL: $n = 0.5 \text{ mole}$

$P_i = 1.00 \text{ atm}$

$T_i = 273 \text{ K}$

$V_i = \frac{nRT}{P} = \frac{(0.5)(0.08206)(273)}{1}$

$= 11.2 \text{ L}$

FINAL: $n = 0.5$

$P_f = 0.2 \text{ atm}$

$T_f = 210 \text{ K}$

$V_f = 43.1 \text{ L}$

WORK IS AGAINST EXTERNAL PRESSURE!

$w = -P_{\text{ext}} \Delta V = (0.10)(43.1 - 11.2) = -3.19 \text{ L}\cdot\text{atm} = \underline{\underline{-323.1 \text{ J}}}$

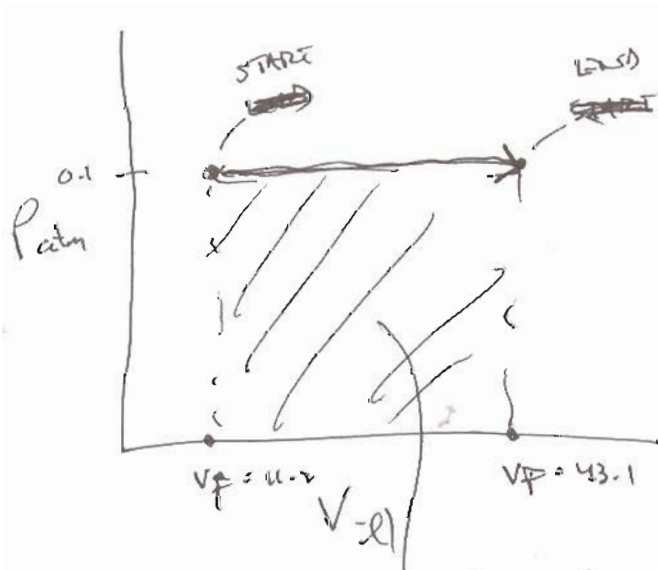
$\Delta E = n C_v \Delta T = (0.5) \left(\frac{3}{2} R\right) (-63) = -393 \text{ J} \left(\frac{-3.98 \text{ L}\cdot\text{atm}}{1 \text{ L}\cdot\text{atm}}\right)$

$\Delta H = n C_p \Delta T = (0.5) \left(\frac{5}{2} R\right) (-63) = -655 \text{ J} \left(\frac{-6.47 \text{ L}\cdot\text{atm}}{1 \text{ L}\cdot\text{atm}}\right)$

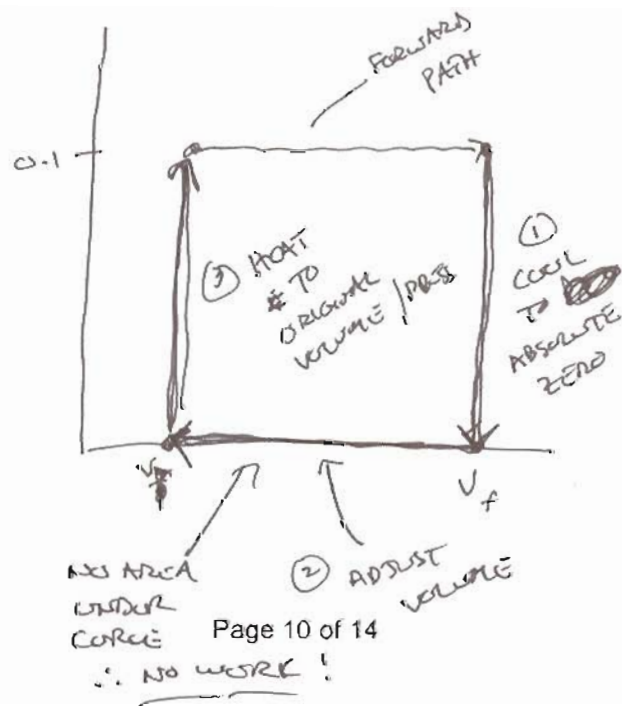
$\Delta E = q + w \therefore q = \Delta E - w = -393 \text{ J} - (-323.1 \text{ J})$

$= -70 \text{ J}$

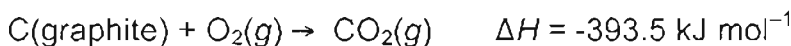
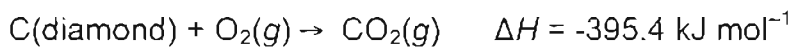
12. (5) Draw a PV diagram for the process described above. Now, draw a hypothetical pathway that returns the system to its initial state but requires no work. Describe the substeps of this return pathway.



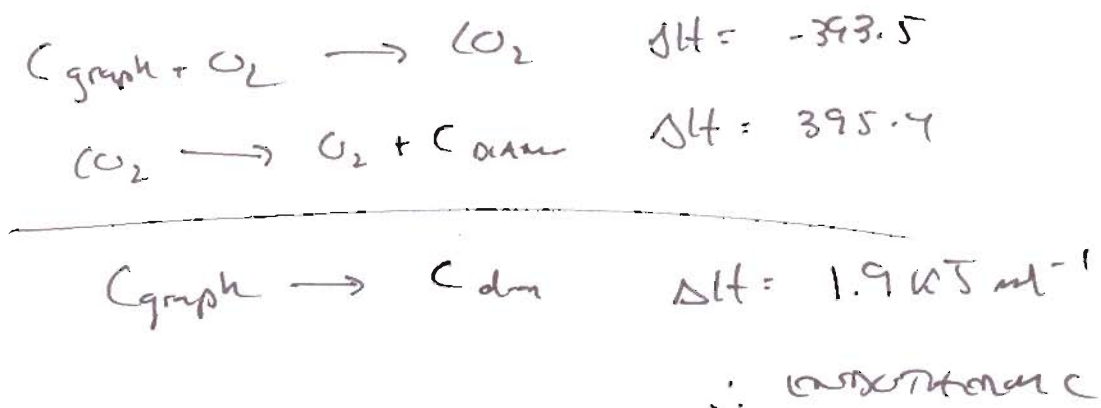
IF YOU USE P_{sys} 'S WORK DOES NOT WORK OUT!



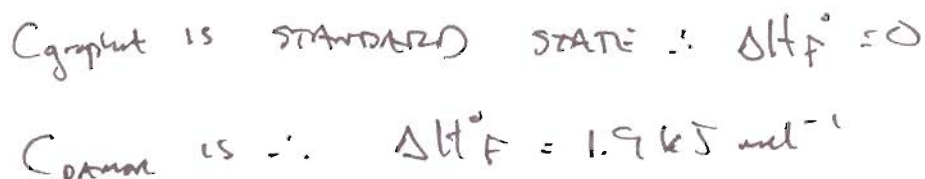
13. (10) Like anything containing carbon, both graphite and diamond can be burned in the presence of oxygen as shown below:



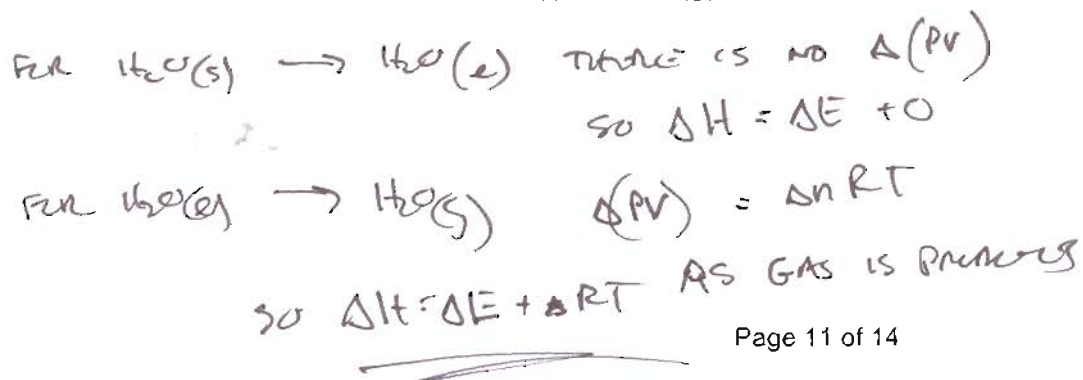
A) Given these data, is the conversion of graphite to diamond endothermic or exothermic?



B) What is the standard molar enthalpy of formation of diamond and of graphite?



14. (5) Explain why ΔH and ΔE are equal for the phase transition (at constant T) of $\text{H}_2\text{O}(\text{s})$ to $\text{H}_2\text{O}(\text{l})$ and *not* equal for the constant T phase transition of $\text{H}_2\text{O}(\text{l})$ to $\text{H}_2\text{O}(\text{g})$.



15. (10) The exothermic reaction that forms NaCl is $\text{Na(s)} + 1/2 \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$. If this is done in the presence of water, the water will heat up. If we use this reaction in a portable water heater that needs to heat 250.0 ml of water from 70°F (21°C) to 200°F (93°C), how many moles of Na(s) and Cl₂(g) should be used? For NaCl(s), $\Delta H_f^\circ = -411.15 \text{ kJ mol}^{-1}$, and the molar heat capacity of liquid water is $C_p = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

want $\Delta T = 72^\circ\text{C}$

$$250 \text{ ml H}_2\text{O} \times \frac{1 \text{ g H}_2\text{O}}{1 \text{ ml H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}}$$

$$= 13.9 \text{ mol H}_2\text{O}$$

want $\Delta E = (75.3 \text{ J K}^{-1} \text{ mol}^{-1})(13.9 \text{ mol})(72 \text{ K})$

$$= \underline{\underline{75.36 \text{ kJ}}}$$

$$\# \text{ mol NaCl} = 75.36 \text{ kJ} \times \frac{1 \text{ mol}}{411.15 \text{ kJ}}$$

$$= 0.183 \text{ mol NaCl}$$

$$\therefore 0.183 \text{ mol Na}$$

$$0.92 \text{ mol Cl}_2$$