Chemistry 4A F'00, Exam II
October 23, 2000
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Problems

1.	(15)	10	4.	(15)	~~6~~ 10
2.	(15)	8	5.	(15)	1+10 ⑪
3.	(25)	13	6.	(15)	8

TOTAL EXAM SCORE (100) ______

Rules:

- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, Conversion Factors included

1. (5+5+5 points) Use the data from Oxtoby Table 7.3 copied below, together with your knowledge of thermodynamics to answer the following:

Average Bond Enthalpies

	Molar Enthalpy of Atomization (kJ mol⁻¹)	Bond Enthalpy (kJ mol⁻¹)								
		H—	C—	C=	C≡	N—	N=	N≡	O—	O=
H	218.0	436	413			391			463	
C	716.7	413	348	615	812	292	615	891	351	728
N	472.7	391	292	615	891	161	418	945		
O	249.2	463	351	728					139	498
S	278.8	339	259	477						
F	79.0	565	441			270			185	
Cl	121.7	432	328			200			203	
Br	111.9	366	276							
I	106.8	299	240							

a) Calculate the bond enthalpy for the Cl-Cl bond in $Cl_{2(g)}$, which is the standard state for chlorine.

121.7 kJ/mol to atomize Cl_2

3/5

b) A suggested reaction for the removal of $^{\bullet}CF_3$ radicals in the atmosphere is:

C-F broke C-H broke

$$^{\bullet}CF_{3\,(g)} + CH_{4\,(g)} \rightarrow HF_{(g)} + {}^{\bullet}CH_3CF_{2\,(g)}$$

C-C made H-F made

Calculate ΔH for this reaction. Is it exothermic or endothermic?

− Products + reactants

(C-C) + (H-F) −(C-F) −(C-H)

348 563 441 413 = 57 = pos = endothermic

3/5

6

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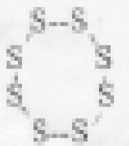
c) The standard state of sulfur is a solid consisting of S_8 molecules with the sulfur atoms joined in an 8-membered ring.



Estimate the average S--S bond enthalpy. (You may ignore the weak intermolecular interactions in the solid.)

278.8 kJ/mol = ΔH atomization

8 bonds/mol = 34.85 kJ/bond

35

+4/5

4

13

2. (5+5+5 points)

$R = 8.3\ J\ K^{-1}mol^{-1} = 0.082\ L\text{-}atm\text{-}K^{-1}mol^{-1}$

Data for H_2O at 298K

	ΔH_f^0 ($kJmol^{-1}$)	S^0 ($JK^{-1}mol^{-1}$)	ΔG_f^0 $kJmol^{-1}$	C_p ($JK^{-1}mol^{-1}$)
$H_2O_{(g)}$	-241.82	188.72	-228.59	35.58
$H_2O_{(l)}$	-285.83	69.91	-237.18	75.29

At the normal boiling point of water, 373K, ΔH^0_{vap} is 40.66 $kJmol^{-1}$.

Assuming ideal gas behavior:

a) Calculate ΔE^0 and w for converting 1 mole of liquid water to vapor at 373K

$q_P = \Delta H$

$\Delta E = q_P + w$

$nC_p\,\Delta T \quad + \quad P\Delta V$

$V_o = 0$

$V_f = \frac{nRT}{P}$

$40.66\ (+)\ \frac{30.6 \times 101.325\ J/L\,atm}{1000\ J/kJ}$

~~2.2×10^{-4}~~

30.6 L

43.76 kJ/mol

3/5

b) calculate the equilibrium vapor pressure of water at 298K.

~~44.01 kJ/mol~~

0/5

c) Calculate ΔH^0_{vap} for water at 298K

$H_{prod} - H_{reac}$

$H_f\ H_2O_g - H_f\ H_2O_L$

$-241.82 - (-285.83) = 44.01\ kJ/mol$

5/5

8

13

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3. (25 points) A 60g sample of hydrogen bromide, $HBr_{(g)}$, MW 80.9, at 300K and occupying 50.0L is first expanded isothermally and reversibly to a volume such that, when it is heated reversibly at constant volume to 500K, the final pressure is the same as the initial pressure. Using C_p ($HBr_{(g)}$) = 29.1 $JK^{-1}mol^{-1}$, calculate ΔE, q, w, ΔH, and ΔS for the entire process beginning to end. Assume HBr is an ideal gas under these conditions.

$\frac{60g\ HBr}{81g/mol} = .741$

$\Delta E_{isot} = 0$ Δ

500

$\Delta E_{heat} = q_v = nc_v\Delta T$

.36atm -

$q = nc_v\Delta T + (-w)$

$.7407\,(29.1 - 8.3145)\,(200k)$

$P\Delta V = nRT\ln\frac{V_2}{V_1}$ 3.079 kJ =

$84.41 = V_2$

$\Delta V = 34.41$

967.5 J

$nC_p\Delta T = \Delta H$

$.7407\,(29.1$

Answers/units:

ΔE = 3.079 kJ +5

q = 4.096 kJ +5

~~w = .967.5 J~~ → no work shown

~~ΔH = 4.31 kJ~~ → no work shown

~~ΔS = 8.092 J~~

8. 4.096

$\Delta S = \frac{q_{rev}}{T}$ +2

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4. (5+5+5 points) Ocean water at 298K contains 0.01M Ca^{2+} and the K_{sp} for $CaCO_3$ dissolution is $9x10^{-7}$ M^2.

a) The ocean is saturated in $CaCO_{3\,(s)}$. What is the concentration of CO_3^{2-} in the ocean.

$K_{sp\,CaCO_3} = [Ca][CO_3] = 9 \times 10^{-7}$ ✓

$[CO_3^{2-}] = [CaCO_3] + [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$

.01 M Ca^{2+}

$[.01]M\ [CO_3^{2-}] = 9 \times 10^{-7}$

$9 \times 10^{-5} = [CO_3^{2-}]$ ✓

5

b) The K_{sp} for $CaSO_{4(s)}$ is $2.4x10^{-5}$ M^2. How many grams of Na_2SO_4 will dissolve in a liter of ocean water.

already has Na^+ but okay.

$2.4 \times 10^{-5} = [Ca][SO_4]$ ✓

$[.01]$

$2.4 \times 10^{-3} = [SO_4]$ ✓ mole

times molecular weight (Na_2SO_4)

.3409 g Na_2SO_4 ✓

4

c) If the same number of moles of H_2SO_4 were added to ocean water would $CaSO_4$ precipitate? Why? Why not? yes, because the water would then be supersaturated in the SO_4^{2-} ion and be forced to compensate.

INCONSISTENT.

0

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5. (3+2+2+8 points)

a) Write expression for the equilibrium constant for the following reactions:

dissolution of $Ca(OH)_2$
the 3rd acid ionization constant of Phosphoric acid (H_3PO_4)
reaction of Hemoglobin in the presence of H^+, O_2 and CO_2

$$k_{sp} = \frac{[Ca^{2+}][OH^-]^2}{[Ca(OH)_2]} \quad X$$

$$k: P\ HPO_4^{2-} = \frac{[H_3O]^+[PO_4^{3-}]}{[HPO_4^{2-}]} \quad ✓$$

$$k = \frac{[Hemo\,H^+]\cdot[Hemo\,O_2][Hemo\,CO_2]}{[Hemo][H^+][O_2][CO_2]} \quad X$$

①

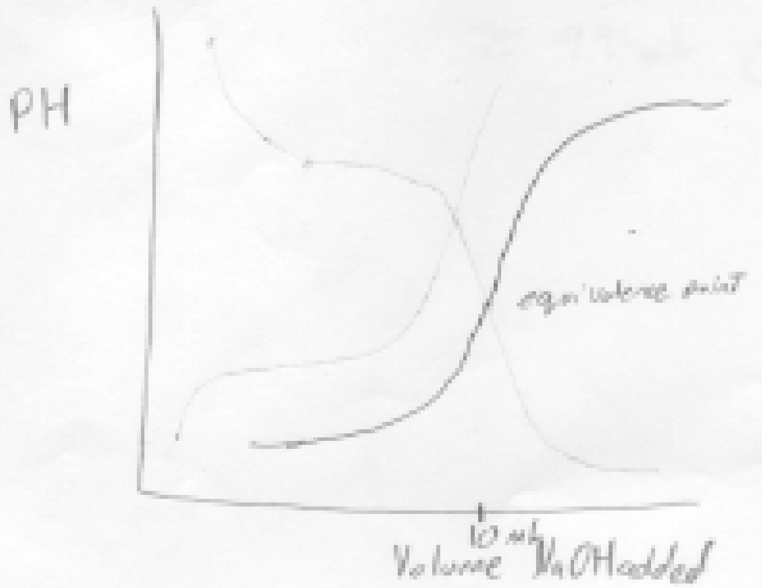
b) Which solution is a better buffer? (circle your answer)

0.01M $NaHCO_3$ with 0.01 M Na_2CO_3 or [✓ 0.1M $NaHCO_3$ with 0.1M Na_2CO_3] +2

c) Which solution is a better buffer? (circle your answer)

0.03M NaOH with 0.1 M H_3PO_4 or [✓ 0.1M NaOH with 0.03M H_3PO_4] 0

d) Sketch a titration curve for a 10ml aliquot of a formic acid buffer 0.01M HCOOH with 0.01M NaHCOO using 0.01M NaOH as the titrant. Label the axes. What is the volume of NaOH at the equivalence point?



8/8

8/15

.5

6. (8+5+2 points) a) A student dissolves 0.5000 g of an unknown sulfate salt in water and adds excess $BaCl_2$. The mixture is digested until all the $BaSO_4$ present has precipitated out. The precipitate is collected on a Gooch crucible with an initial mass 14.5687 g; when the dry product and crucible are weighed the mass is determined to be 15.1285 g. A calorimetry experiment using the metal of the same unknown cation yields a specific heat capacity of roughly 0.22 J/ g °C. What is the molecular weight (to four significant digits) and identity of the unknown metal?

$.5_g\ X_ySO_4 \rightarrow (14.5687_g - 15.1285_g)\ BaSO_4$

.5598 ~~.4407~~$_g$ $BaSO_4$ ✓

$.5_g$

265.0978 g/mol unk

g/mol $BaSO_4$ (233.392)

2.3985×10^{-3} ✓

~~1.9861~~ $\times 10^{-3}$ g/mol $BaSO_4$ = moles X_ySO_4

− g/mol (SO_4)

112.4016 g/mol

~~169.03~~ g/mol X_y

Cd

8/8

b) If 1.000 g of the metal is placed at the bottom of a beaker of water which is then acidified while trapping the gas produced, what is the equivalent mass of hydrogen gas evolved?

$nH^+_{(aq)} + M^0_{(s)} \rightarrow M^{n+}_{(aq)} + n/2\ H_{2\ (g)}$

8.896×10^{-3} moles X

4.4483×10^{-3} moles $H_{2(g)}$

9/5

c) If the experiment is carried out in a lab at 1.000 atm and 25 C, neglecting the vapor pressure of water, will a 25mL graduated cylinder be large enough to contain the gas produced?

4.4483×10^{-3} moles $H_{2(g)}$ × 22.4 L/mol$_g$ @ STP

.09964 L

≈ 99.6 mL No

9/2