FIRST EXAM

Closed book, one page of notes allowed.

Answer all questions. Please state any additional assumptions you made, and show all work.
        You are welcome to use a graphical method of solution if it is appropriate.

> Miscellaneous Information:
>   R = 1.987 cal/mole°K = 8.314 J/mole°K
>   Absolute zero = -273.15°C
>   1 joule = 0.239 calories
>   540 calories = 1 Big Mac

1.   (50%) What is the pH of a $10^{-2.00}$ M solution of Sodium fluoride (NaF)?
      Calculate this for each of the three conditions below (obviously, the ionic
      strength will never be zero for this solution, but let's assume the ideal case for
      part "a" and "b" anyway).

            a. 25°C, I = 0
            b. 100°C, I = 0
            c. 25°C, I = 0.25

Preferred Approach
- recognize that this is a simple base problem
- then adopt an appropriate set of assumptions, and solve for [H+]
- finally correct pKa (and pK_w) for temperature, ionic strength, and repeat
- check assumptions

a. 25°C, I = 0

                Assume a weak base: [F⁻] >> [HF]

$$\left[OH^-\right]= \sqrt{K_b C + K_w}$$

if the pK_a for HF/F (at 25° C and I=0) is 3.2, then the pK_b is 14-3.2 or 10.8

$$\left[OH^-\right]= \sqrt{10^{-10.8}10^{-2.00}+10^{-14}} = 4.105x10^{-7}$$

$$\left[H^+\right]= K_w \Big/ \left[OH^-\right] = 10^{-14} \Big/ 10^{-6.39} = 10^{-7.61}$$

Check Assumptions:

$$[F^-] >> [HF] \quad \text{or:} \quad \frac{[F^-]}{[HF]} >> 1$$

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$\frac{[F^-]}{[HF]} = \frac{K_a}{[H^+]} = \frac{10^{-3.2}}{10^{-7.61}} = 10^{+4.4}, \quad \text{YES!!!}$$

b. 100°C, I = 0

determine enthalpy change for the HF dissociation reaction:
$$HF = H^+ + F^-$$
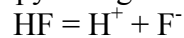
$$\begin{aligned}
^\Delta H^o &= \sum v_i \, ^\Delta H_f^o \\
&= ^\Delta H_{F^-}^o + ^\Delta H_{H^+}^o - ^\Delta H_{HF}^o \\
&= -80.15 + 0 - (-77.23) \\
&= -2.92 \, Kcal / mole
\end{aligned}$$

then re-estimate K_a

$$\log \frac{K_2}{K_1} = \frac{^\Delta H^o (T_2 - T_1)}{2.303 RT_2 T_1}$$

$$\begin{aligned}
\log \frac{K_{100}}{K_{25}} &= \frac{-2.92 Kcal / mole (373.15 - 298.15)}{2.303 (1.987 x 10^{-3} \, Kcal / mole) 373.15 (298.15)} \\
&= -0.430 \\
\log K_{100} &= \log K_{25} - 0.430 \\
&= -3.2 - 0.430 \\
&= -3.63
\end{aligned}$$

$$K_{100} = 2.34 \text{ x } 10^{-4}$$

Do the same for K_w

$$^{\Delta}H^{o} = \sum v_i \, ^{\Delta}H^{o}_f$$
$$= ^{\Delta}H^{o}_{OH^-} + ^{\Delta}H^{o}_{H^+} - ^{\Delta}H^{o}_{H2O}$$
$$= -54.957 + 0 - (-68.317)$$
$$= 13.36 \, Kcal/mole$$

then re-estimate K_w

$$\log \frac{K_2}{K_1} = \frac{^{\Delta}H^o(T_2 - T_1)}{2.303 R T_2 T_1}$$

$$\log \frac{K_{100}}{K_{25}} = \frac{-13.36 Kcal/mole(373.15 - 298.15)}{2.303(1.987 x 10^{-3} Kcal/mole)373.15(298.15)}$$

$$= 1.97$$

$$\log K_{100} = \log K_{25} + 1.97$$
$$= -14 + 1.97$$
$$= -12.03$$

$$Kw_{100} = 9.29 \times 10^{-13}$$

and now:

As before, assume a weak base: $[F^-] \gg [HF]$

$$[OH^-] = \sqrt{K_b C + K_w}$$

if the pK_a for HF/F (at 100° C and I=0) is 3.63, then the pK_b is 14-3.63 or 10.37

$$[OH^-] = \sqrt{10^{-10.37} 10^{-2.00} + 10^{-12.03}} = 6.36 x 10^{-6} = 10^{-5.20}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-12.03}}{10^{-5.20}} = 10^{-6.84}$$

pH = 6.84

Check Assumptions:

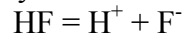$$[F^-] \gg [HF] \text{ or: } \frac{[F^-]}{[HF]} \gg 1$$

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

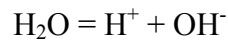$$\frac{[F^-]}{[HF]} = \frac{K_a}{[H^+]} = \frac{10^{-3.63}}{10^{-6.84}} = 10^{+3.21}, \quad \text{YES!!!}$$

If you had not adjusted K_w for the higher temperature, you would have calcuated that pH=7.82.

c. 25°C, I = 0.25

determine activity coefficients for the species in the reaction:
$$HF = H^+ + F^-$$
And for
$$H_2O = H^+ + OH^-$$
For this level, use the simple Davies equation for the charged species, and assume no change in the activity of theuncharged species:

$$\log f - 0.5(z)^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$$

so:

$$\log f_{F^-} = \log f_{H^+} = \log f_{OH^-} - 0.5(1)^2\left(\frac{\sqrt{0.25}}{1+\sqrt{0.25}} - 0.2(0.25)\right) = -0.142$$

$$f_{F^-} = f_{H^+} = f_{OH^-} = 0.722$$

then re-estimate K_a and K_w under this condition, i.e., the conditional K's

$$^C K_a = K_a \frac{\gamma_{HF}}{\gamma_{H^+}\gamma_{F^-}}$$

$$= 10^{-3.2}\frac{1}{0.722x0.722}$$

$$= 1.2x10^{-3}$$

$$= 10^{-2.92}$$

and:

$$^{C}K_w = K_w \frac{\gamma_{H_2O}}{\gamma_{H^+}\gamma_{OH^-}}$$

$$= 10^{-14} \frac{1}{0.722x0.722}$$

$$= 1.92x10^{-14}$$

$$= 10^{-13.72}$$

and now:

As before, assume a weak base: $[F^-] \gg [HF]$

$$[OH^-] = \sqrt{K_b C + K_w}$$

if the pK_a for HF/F (at 25° C and I=0.25) is 2.92, then the pK_b is 13.72-2.92 or 10.80

$$[OH^-] = \sqrt{10^{-10.80}10^{-2.00} + 10^{-13.72}} = 4.22x10^{-7} = 10^{-6.38}$$

$$[H^+] = K_w \Big/ [OH^-] = 10^{-13.72} \Big/ 10^{-6.38} = 10^{-7.34}$$

now we must recognize that pH is related to proton activity not concentration

$$pH = -\log\{H^+\} = -\log(f_{H^+}[H^+]) = -\log(0.722x10^{-7.34})$$

pH = 7.48

Check Assumptions:

$$[F^-] \gg [HF] \text{ or: } \frac{[F^-]}{[HF]} \gg 1$$

$$^{c}K_a = \frac{[H^+][F^-]}{[HF]}$$

$$\frac{[F^-]}{[HF]} = \frac{^{c}K_a}{[H^+]} = \frac{10^{-2.92}}{10^{-7.34}} = 10^{+4.42}, \quad \text{YES!!!}$$

2. (40%) What is the complete composition of a 1-liter volume of water containing 10^{-2} M of ammonium bisulfide (NH$_4$HS)? Approximate values ($\pm$ 0.2 log units) will suffice.

Approach

- prepare a logC vs pH diagram for ammonia system (C_T=0.01 M) and the acetic acid system (C_T = 0.01M) superimposed over it.
- write the PBE and find a solution
- read off concentrations from the graph

This is a good problem for the graphical solution (no acid/base conjugates added, nor any strong acids or bases). The first task is then to prepare the species lines on our usual log C vs pH axes (see below)

Recall that we're adding ammonium cation (NH$_4^+$) and the partially deprotonated bisulfide (HS$^-$). These are simple solutions of two unrelated acids/bases. Therefore we don't have any acid/conjugate base mixtures, nor do we have an acids or bases that have been partly titrated with a strong acid or base. This means we are free to use the PBE, and in fact, should use the PBE (an ENE won't give us a "clean" or identifiable intersection).
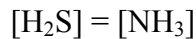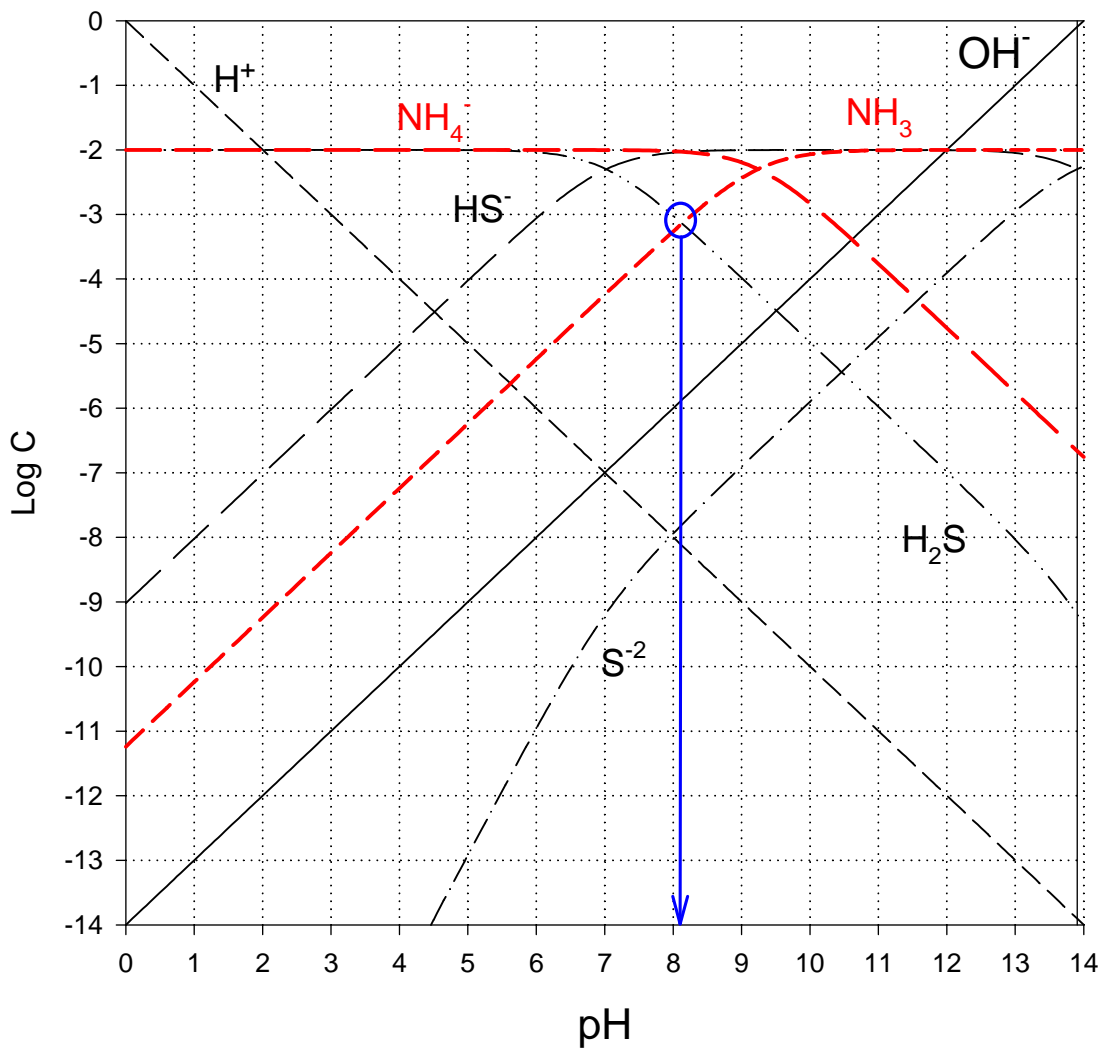
Thus, the PBE is:

$$[H_2S] + [H^+] = [OH^-] + [NH_3] + [S^{-2}]$$

And if we presume that H+ and OH- are insignificant, we get:

$$[H_2S] = [NH_3] + [S^{-2}]$$

And going a step further we might presume that the sulfide is small as well. This gives us the PBE intersection

$$[H_2S] = [NH_3]$$

$pH \approx 8.15$ $[H^+] \approx 7.1 \times 10^{-9}$
$\log [H_2S] \approx -3.15$ $[H_2S] \approx 7.0 \times 10^{-4}$
$\log [HS^-] \approx -2.0$ $[HS^-] \approx 1 \times 10^{-2}$
$\log [S^{-2}] \approx -7.8$ $[S^{-2}] \approx 2 \times 10^{-8}$
$\log [NH_4^+] \approx -2.0$ $[NH_4^+] \approx 1 \times 10^{-2}$
$\log [NH_3] \approx -3.1$ $[NH_3] \approx 8 \times 10^{-4}$
$\log [OH^-] \approx -5.85$ $[OH^-] \approx 1.4 \times 10^{-6}$

Check assumptions:
$[H_2S] >> [H^+]$
$10^{-3.15} >> 10^{-8.15}$, YES

$[NH_3] >> [OH^-]$
$10^{-3.1} >> 10^{-5.85}$, again YES

3. **(10%) True/False.** Mark each one of the following statements with either a "T" or an "F".

a. __T__ Water is an amphoteric substance.

b. __F__ A nano gram is equivalent to one-thousanths of a milligram.

c. __T__ The third most common gas in the atmosphere is argon

d. __T__ Non-carbonate hardness only exists in waters with alkalinities less than than their total hardness.

e. __T__ Mass defects are directly proportional to nuclear binding energy

f. __T__ The Guntelberg Approximation says that activity coefficients are dependent on charge and ionic strength, but not on ion size.

g. __F__ The reactivity of neutral species is unaffected by changes in ionic strength.

h. __F__ Increases in ionic strength cause a increase in the pKa of an acid, if the fully-protonated form of the acid is an uncharged species.

i. __T__ The standard assumption used for calculating the pH of buffer solutions is that $[H+]$ and $[OH-]$ are negligible.

j. __T__ The value of α_0 plus α_1 must always equal unity for a monoprotic acid.

Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

NAME	FORMULA	pK_a
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7 STRONG
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3 (&2) ACIDS
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-0
Hydronium ion	$H_3O^+ = H^+ + H_2O$	**0**
Trichloroacetic acid	$CCl_3COOH = H^+ + CCl_3COO^-$	0.70
Iodic acid	$HIO_3 = H^+ + IO_3^-$	0.8
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15 (&7.2,12.3)
o-Phthalic acid	$C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$	2.89 (&5.51)
Citric acid	$C_3H_5O(COOH)_3 = H^+ + C_3H_5O(COOH)_2COO^-$	3.14 (&4.77,6.4)
Hydrofluoric acid	$HF = H^+ + F^-$	3.2
Aspartic acid	$C_2H_6N(COOH)_2 = H^+ + C_2H_6N(COOH)COO^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.06 (&9.92)
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.48 (&9.32)
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Propionic acid	$C_2H_5COOH = H^+ + C_2H_5COO^-$	4.87
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35 (&10.33)
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02 (&13.9)
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Boric acid	$B(OH)_3 + H_2O = H^+ + B(OH)_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
p-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.32
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
m-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.92
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Bisulfide ion	$HS^- = H^+ + S^{-2}$	13.9
Water	$H_2O = H^+ + OH^-$	**14.00**
Ammonia	$NH_3 = H^+ + NH_2^-$	23
Methane	$CH_4 = H^+ + CH_3^-$	34

Species	$\Delta \overline{H}_f^o$ kcal/mole	$\Delta \overline{G}_f^o$ kcal/mole
$Ca^{+2}(aq)$	-129.77	-132.18
$CaCO_3(s)$, calcite	-288.45	-269.78
CaO (s)	-151.9	-144.4
$C(s)$, graphite	0	0
$CO_2(g)$	-94.05	-94.26
$CO_2(aq)$	-98.69	-92.31
CH_4 (g)	-17.889	-12.140
H_2CO_3 (aq)	-167.0	-149.00
HCO_3^- (aq)	-165.18	-140.31
CO_3^{-2} (aq)	-161.63	-126.22
CH_3COO^-, acetate	-116.84	-89.0
H^+ (aq)	0	0
H_2 (g)	0	0
HF (aq)	-77.23	-71.63
F^- (aq)	-80.15	-67.28
Fe^{+2} (aq)	-21.0	-20.30
Fe^{+3} (aq)	-11.4	-2.52
$Fe(OH)_3$ (s)	-197.0	-166.0
NO_3^- (aq)	-49.372	-26.43
NH_3 (g)	-11.04	-3.976
NH_3 (aq)	-19.32	-6.37
NH_4^+ (aq)	-31.74	-19.00
HNO_3 (aq)	-49.372	-26.41
O_2 (aq)	-3.9	3.93
O_2 (g)	0	0
OH^- (aq)	-54.957	-37.595
H_2O (g)	-57.7979	-54.6357
H_2O (l)	-68.3174	-56.690
PO_4^{-3} (aq)	-305.30	-243.50
HPO_4^{-2} (aq)	-308.81	-260.34
$H_2PO_4^-$ (aq)	-309.82	-270.17
H_3PO_4 (aq)	-307.90	-273.08
SO_4^{-2}	-216.90	-177.34
HS^- (aq)	-4.22	3.01
$H_2S(g)$	-4.815	-7.892
$H_2S(aq)$	-9.4	-6.54