CEE 680 27 October 2009

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. (30%) Calculate the pH for a 1-liter volume of pure water at 80°C to which you have dissolved 10^{-3} moles of H_2S. The temperature of the final solution is at 80°C. Be accurate in your calculations (better than a graphical intersection, but not necessarily needing an exact solution)

determine enthalpy change for the reaction:

$H_2S = H^+ + HS^-$

$$
\begin{aligned}
{}^{\Delta}H^o &= \sum \nu_i {}^{\Delta}H_f^o \\
&= {}^{\Delta}H^o_{HS^-} + {}^{\Delta}H^o_{H^+} - {}^{\Delta}H^o_{H_2S} \\
&= -4.22 - (-9.4) \\
&= 5.18 Kcal/mole
\end{aligned}
$$

then re-estimate K_a

$$
\begin{aligned}
\log \frac{K_2}{K_1} &= \frac{{}^{\Delta}H^o (T_2 - T_1)}{2.303 R T_2 T_1} \\
\log \frac{K_{80}}{K_{25}} &= \frac{5.18 Kcal/mole (353.15 - 298.15)}{2.303 (1.987 x 10^{-3} Kcal/mole) 353.15 (298.15)} \\
&= 0.5913 \\
\log K_{80} &= \log K_{25} + 1.6294 \\
&= -7.02 + 0.5913 \\
&= -6.43
\end{aligned}
$$

Or:

$K_{80} = 3.73 \times 10^{-7}$

Now make the acidic solution assumption

$$[H^+] \approx \frac{-K_a + \sqrt{K_a^2 + 4K_aC}}{2}$$

$$\begin{aligned}[H^+] &= \frac{-K_a + \sqrt{K_a^2 + 4K_aC}}{2} \\ &= \frac{-10^{-6.43} + \sqrt{(10^{-6.43})^2 + 4x10^{-6.43}10^{-3}}}{2} \\ &= 1.912x10^{-5}\end{aligned}$$

pH = 4.7185

now check assumptions

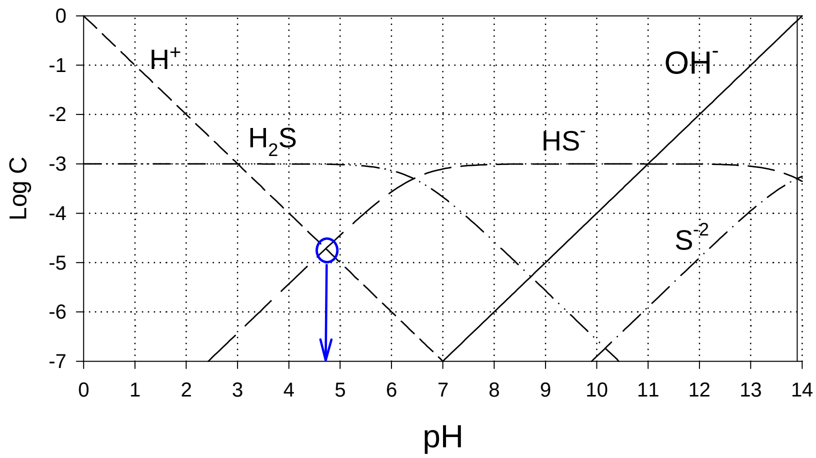
or a weak acid and acidic solution assumption

$$[H^+] \approx \sqrt{K_aC}$$

$$\begin{aligned}[H^+] &= \sqrt{K_aC} \\ &= \sqrt{10^{-6.43}10^{-3}} \\ &= \sqrt{10^{-9.43}} \\ &= 10^{-4.7144} \\ &= 1.9304x10^{-5}\end{aligned}$$

pH = 4.7144

now check assumptions



2. (65%) Determine the complete composition of a 1-liter volume of water to which you have added

   a. 10^{-3} M of Sodium Bicarbonate ($NaHCO_3$), and 10^{-2} M of Phenol (C_6H_5OH)

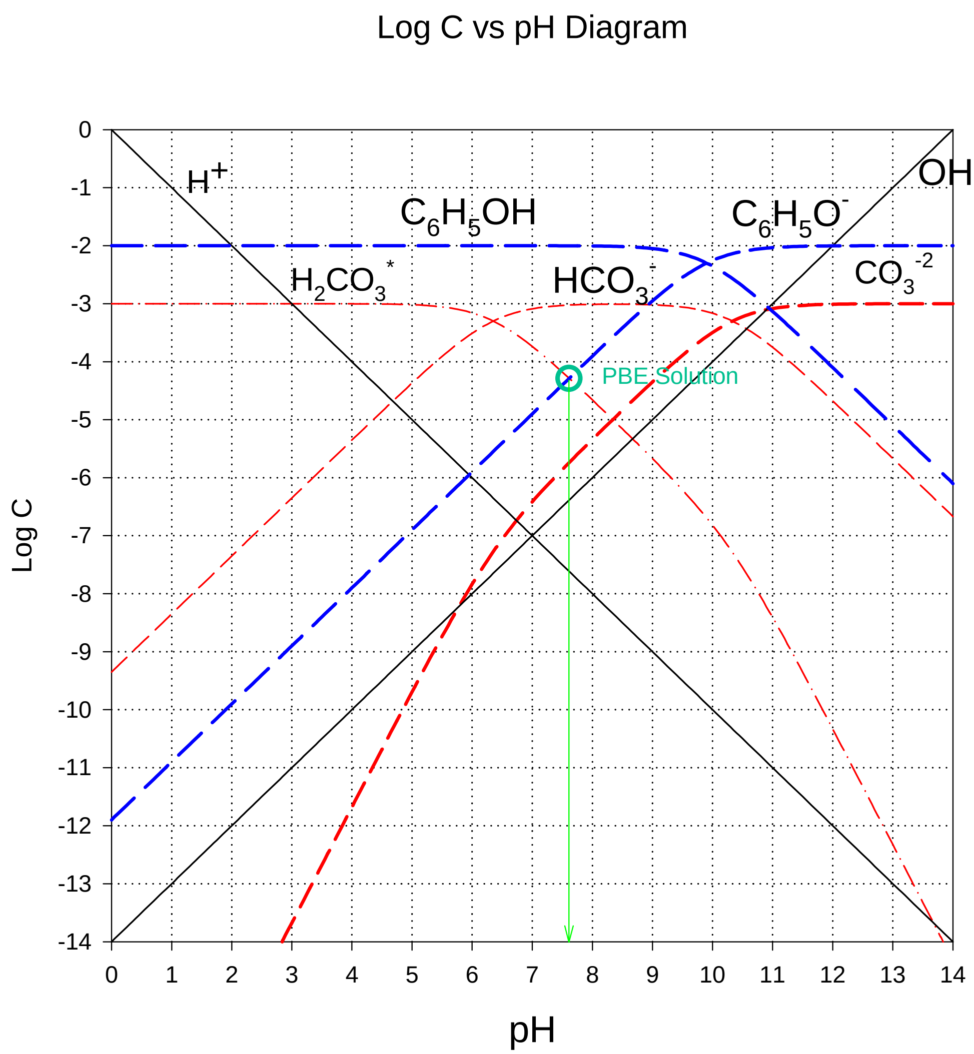
   b. 10^{-3} M of sodium hydroxide (NaOH), and 10^{-3} M of sodium dihydrogen phosphate (NaH_2PO_4)

   Approximate values (± 0.2 log units) will suffice.

Approach: part a

- prepare a logC vs pH diagram for carbonate system (C_T=0.001 M) and the fluoride 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 bicarbonate (HCO_3^-) and the protonated phenol. 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:

$$[H_2CO_3] + [H^+] = [OH^-] + [CO_3^{-2}] + [C_6H_5O^-]$$

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

$$[H_2CO_3] = [CO_3^{-2}] + [C_6H_5O^-]$$

And recognizing that carbonate will be small

$$[H_2CO_3] = [C_6H_5O^-]$$

pH ≈ 7.6

log $[C_6H_5OH] \approx -2.0$	$[C_6H_5OH] \approx 1 \times 10^{-2}$
log $[C_6H_5O^-] \approx -4.2$	$[C_6H_5O^-] \approx 6.3 \times 10^{-5}$
log $[H_2CO_3] \approx -4.2$	$[H_2CO_3] \approx 6.3 \times 10^{-5}$
log $[HCO_3^-] \approx -3.0$	$[HCO_3^-] \approx 1 \times 10^{-3}$
log $[CO_3^{-2}] \approx -5.7$	$[CO_3^{-2}] \approx 2 \times 10^{-6}$
log $[OH^-] \approx -6.4$	$[OH^-] \approx 4 \times 10^{-7}$
log $[Na^+] = -3.0$	$[Na+] = 1 \times 10^{-3}$

Check assumptions:

$[H_2CO_3] >> [H^+]$
$10^{-4.2} >> 10^{-7.6}$, YES

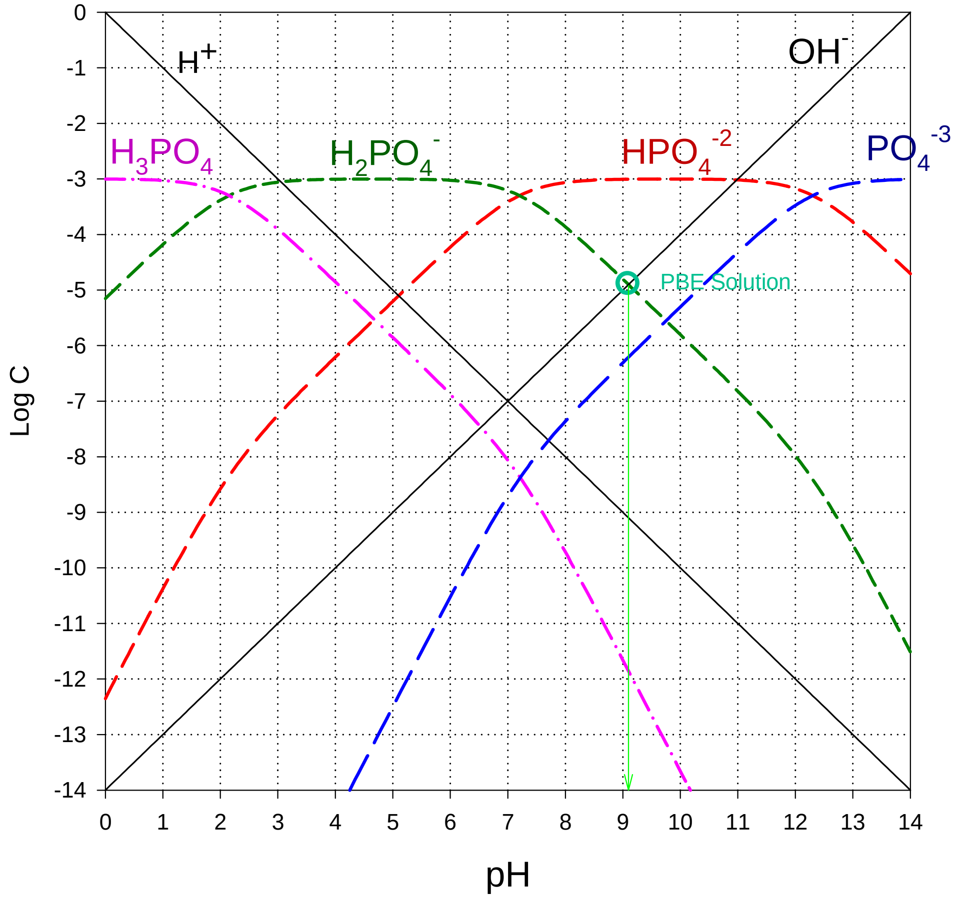
$[C_6H_5O^-] >> [OH^-]$
$10^{-4.2} >> 10^{-6.4}$, again YES

$[C_6H_5O^-] >> [CO_3^{-2}]$
$10^{-4.2} >> 10^{-5.7}$, again YES

Approach: part b

* recognize that this is essentially a titration where you've ended up with a pure Na_2HPO_4 solution
* prepare a logC vs pH diagram for the phosphate system ($C_T = 10^{-2.5}$ M).
* write the PBE and find a solution
* read off concentrations from the graph

Again, 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 the monhydrogen phosphate (HPO_4^{-2}) which is produced by partial titration of the dihydrogen phosphate. This is simple solution of an pure ampholyte. Therefore we don't have any acid/conjugate base mixtures. 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:

$$2[H_3PO_4] + [H_2PO_4^-] + [H^+] = [OH^-] + [PO_4^{-3}]$$

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

$$2[H_3PO_4] + [H_2PO_4^-] = [PO_4^{-3}]$$

And recognizing that the extreme pH species are likely to be small

$$[H_2PO_4^-] = [PO_4^{-3}]$$

But at this pH, its clear that hydroxide isn't small, so the following intersection is most important:

$$[H_2PO_4^-] = [OH^-]$$

pH ≈ 9.1	$[H^+] \approx 8 \times 10^{-10}$
$\log [H_3PO_4] \approx -11.9$	$[H_3PO_4] \approx 1.3 \times 10^{-12}$
$\log [H_2PO_4^-] \approx -4.9$	$[H_2PO_4^-] \approx 1.3 \times 10^{-5}$
$\log [HPO_4^{-2}] \approx -3$	$[HPO_4^{-2}] \approx 1 \times 10^{-3}$
$\log [PO_4^{-3}] \approx -6.2$	$[PO_4^{-3}] \approx 6.3 \times 10^{-7}$
$\log [OH^-] \approx -4.9$	$[OH^-] \approx 1.3 \times 10^{-5}$

Check assumptions:

$[H_2PO_4^-] >> [H^+]$
$10^{-4.9} >> 10^{-9.1}$, YES

$[H_2PO_4^-] >> 2[H_3PO_4]$
$10^{-4.9} >> 10^{-11.6}$, YES

and

$[OH^-] >> [PO_4^{-3}]$
$10^{-4.9} >> 10^{-6.2}$, YES

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

a. **T** Water has an unusually high boiling point based on its molecular weight.

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

c. **F** The third most common gas in the atmosphere is carbon dioxide

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 strenth, but not on ion size.

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

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

i. **F** The standard assumption used for calculating the pH of buffer solutions is that all positive ions are negligible.

j. **F** The value of α_o plus α_1 must always equal unity for a diprotic 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
$CaC0_3$(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
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