

**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:

$$R = 1.987 \text{ cal/mole}^\circ\text{K} = 8.314 \text{ J/mole}^\circ\text{K}$$

$$\text{Absolute zero} = -273.15^\circ\text{C}$$

$$1 \text{ joule} = 0.239 \text{ calories}$$

$$1230 \text{ calories} = 1 \text{ Triple Whopper}$$

1. (50%) You have been asked to prepare a buffer at pH 5.30. The choices are an acetate buffer with a  $C_T$  of 5mM and carbonate buffer with a  $C_T$  of 8 mM. Which of the two will have a higher buffer intensity at the desired pH (i.e., at pH 5.30) under each of the following conditions? In answering this please show the calculated buffer intensity for both under each condition. Assume a closed system.
  - a.  $25^\circ\text{C}$ ,  $I = 0$
  - b.  $100^\circ\text{C}$ ,  $I = 0$

**Preferred Approach**

- recognize that this is a simple buffer intensity problem once you have the correct pKa's
- for part "b" you must correct pKa (and  $pK_w$ ) for temperature, and repeat

**a.  $25^\circ\text{C}$ ,  $I = 0$** 

first calculate for the acetate buffer

recall that for a monoprotic acid, the buffer intensity is calculated from:

$$\beta \approx 2.303 \left( [OH^-] + [H^+] + C_T \alpha_0 \alpha_1 \right)$$

and since this is a buffer problem, we can normally drop the hydroxide and hydrogen ion terms:

$$\beta \approx 2.303(C_T \alpha_0 \alpha_1)$$

and substituting in for the alphas, we get:

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{1 + \frac{K_1}{[H^+]}} \right) \left( \frac{1}{\frac{[H^+]}{K_1} + 1} \right) \right)$$

and for the particular pH of 5.3, this reduces to:

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{1 + \frac{10^{-4.75}}{10^{-5.3}}} \right) \left( \frac{1}{\frac{10^{-5.3}}{10^{-4.75}} + 1} \right) \right)$$

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{1 + 10^{+0.55}} \right) \left( \frac{1}{10^{-0.55} + 1} \right) \right)$$

$$\begin{aligned} \beta &\approx 2.303 C_T (0.2198 * 0.7801) \\ &\approx 0.395 C_T \end{aligned}$$

So that at 5 mM  $C_T$ , we have:

$$\beta \approx 0.395(5 \times 10^{-3}) \approx 0.00198$$

next for the carbonate buffer

recall that for a diprotic acid, the buffer intensity is calculated from:

$$\beta \approx 2.303([OH^-] + [H^+] + C_T \alpha_0 \alpha_1 + C_T \alpha_1 \alpha_2)$$

and since the pH is closest to the first pK, we can drop the second alpha term as well as the hydroxide and hydrogen ion terms:

$$\beta \approx 2.303(C_T \alpha_0 \alpha_1)$$

and substituting in for the alphas, we get:

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} \right) \left( \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}} \right) \right)$$

and since  $[H^+] \gg K_2$ , then we can simplify:

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{1 + \frac{K_1}{[H^+]}} \right) \left( \frac{1}{\frac{[H^+]}{K_1} + 1} \right) \right)$$

and for the particular pH of 5.3, this reduces to:

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{1 + \frac{10^{-6.35}}{10^{-5.3}}} \right) \left( \frac{1}{\frac{10^{-5.3}}{10^{-6.35}} + 1} \right) \right)$$

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{1 + 10^{-1.05}} \right) \left( \frac{1}{10^{+1.05} + 1} \right) \right)$$

$$\beta \approx 2.303 C_T (0.9182 * 0.0818)$$

$$\approx 0.173 C_T$$

So that at 8 mM  $C_T$ , we have:

$$\beta \approx 0.173(8 \times 10^{-3}) \approx 0.00138$$

So, at 0.00198, **the acetate buffer is stronger than the carbonate buffer**

### b. 100°C, I = 0

determine enthalpy change for the important dissociation reactions. First the acetate reaction:

$$\begin{aligned} \text{CH}_3\text{COOH} &= \text{H}^+ + \text{CH}_3\text{COO}^- \\ \Delta H^\circ &= \sum v_i \Delta H_f^\circ \\ &= \Delta H_{\text{CH}_3\text{COO}^-}^\circ + \Delta H_{\text{H}^+}^\circ - \Delta H_{\text{CH}_3\text{COOH}}^\circ \\ &= -116.84 + 0 - (-116.79) \\ &= -0.05 \text{ Kcal / mole} \end{aligned}$$

then re-estimate  $K_a$

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ (T_2 - T_1)}{2.303RT_2T_1}$$

$$\log \frac{K_{100}}{K_{25}} = \frac{-0.05 \text{ Kcal / mole} (373.15 - 298.15)}{2.303(1.987 \times 10^{-3} \text{ Kcal / mole}) 373.15 (298.15)}$$

$$= -0.00708$$

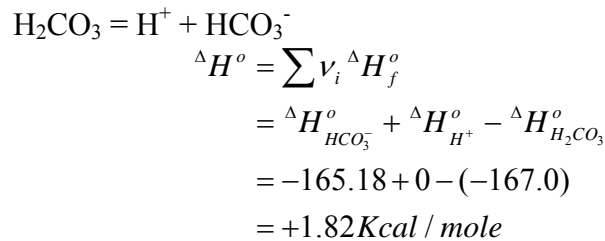
$$\log K_{100} = \log K_{25} - 0.00708$$

$$= -4.75 - 0.01$$

$$= -4.76$$

$$K_{100} = 1.75 \times 10^{-5}$$

Now the carbonate reaction (note that only the  $K_1$  is needed)



then re-estimate  $K_a$

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ (T_2 - T_1)}{2.303RT_2T_1}$$

$$\log \frac{K_{100}}{K_{25}} = \frac{1.82 \text{ Kcal / mole} (373.15 - 298.15)}{2.303(1.987 \times 10^{-3} \text{ Kcal / mole}) 373.15 (298.15)}$$

$$= +0.268$$

$$\log K_{100} = \log K_{25} + 0.268$$

$$= -6.35 + 0.268$$

$$= -6.08$$

$$K_{100} = 8.28 \times 10^{-7}$$

Do the same for  $K_w$

$$\begin{aligned}
\Delta H^\circ &= \sum v_i \Delta H_f^\circ \\
&= \Delta H_{OH^-}^\circ + \Delta H_{H^+}^\circ - \Delta H_{H_2O}^\circ \\
&= -54.957 + 0 - (-68.317) \\
&= 13.36 \text{ Kcal / mole}
\end{aligned}$$

then re-estimate  $K_w$

$$\begin{aligned}
\log \frac{K_2}{K_1} &= \frac{\Delta H^\circ (T_2 - T_1)}{2.303 RT_2 T_1} \\
\log \frac{K_{100}}{K_{25}} &= \frac{-13.36 \text{ Kcal / mole} (373.15 - 298.15)}{2.303 (1.987 \times 10^{-3} \text{ Kcal / mole}) 373.15 (298.15)} \\
&= 1.97 \\
\log K_{100} &= \log K_{25} + 1.97 \\
&= -14 + 1.97 \\
&= -12.03
\end{aligned}$$

$$K_{w100} = 9.29 \times 10^{-13}$$

and now:

follow method in part "a"  
this time it's the Carbonate that has the higher Beta.  
(0.0025 vs 0.0020)

2. (40%) What is the complete composition of a 1-liter volume of water containing  $10^{-2}$  M of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and  $10^{-2}$  M of sodium bisulfide ( $\text{NaHS}$ )? 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 ( $C_T = 0.01\text{M}$ ) 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 ( $\text{NH}_4^+$ ) and the partially deprotonated bisulfide ( $\text{HS}^-$ ). 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).

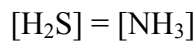
Thus, the PBE is:

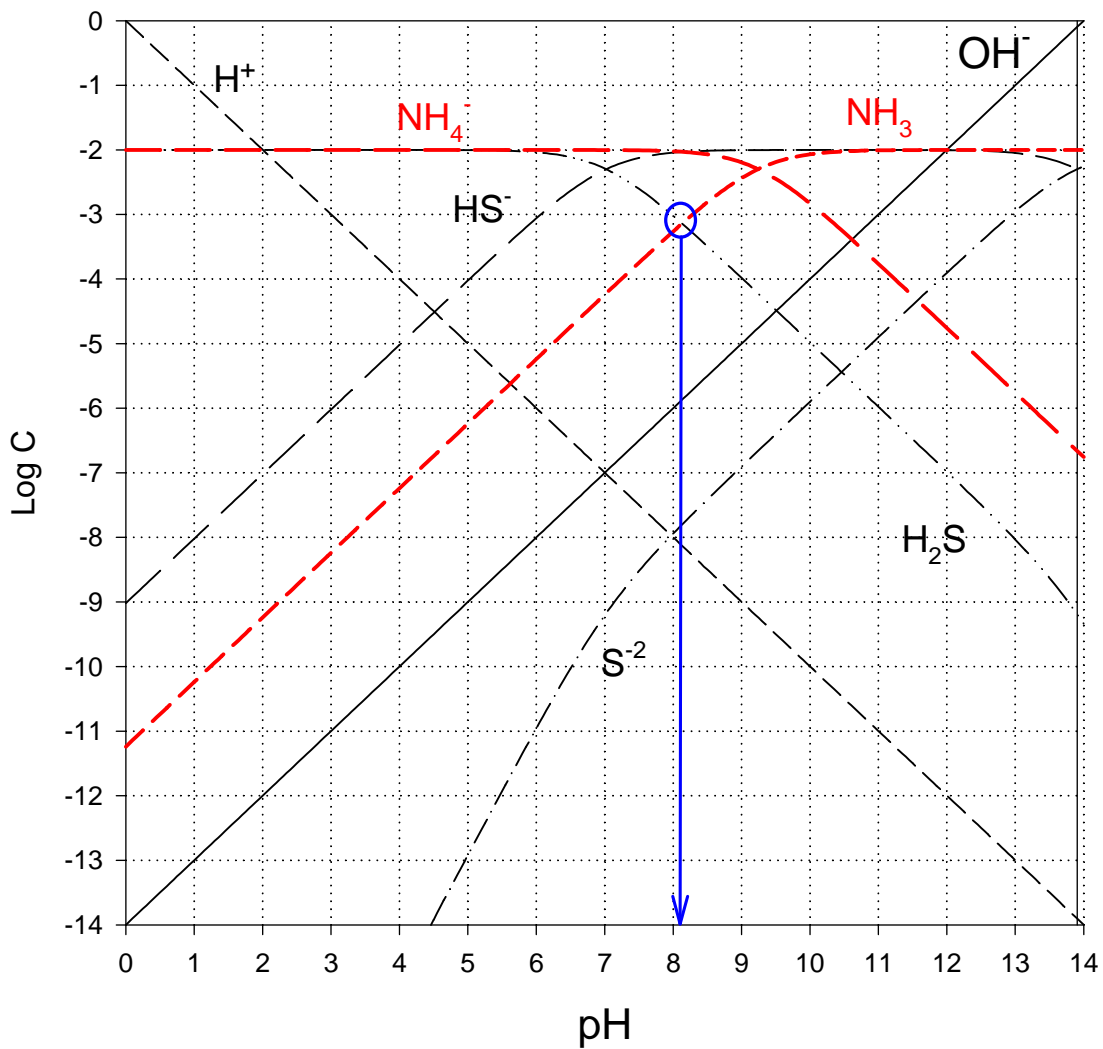


And if we presume that  $\text{H}^+$  and  $\text{OH}^-$  are insignificant, we get:



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





pH  $\approx$  8.15  
 log [H<sub>2</sub>S]  $\approx$  -3.15  
 log [HS<sup>-</sup>]  $\approx$  -2.0  
 log [S<sup>-2</sup>]  $\approx$  -7.8  
 log [NH<sub>4</sub><sup>+</sup>]  $\approx$  -2.0  
 log [NH<sub>3</sub>]  $\approx$  -3.1  
 log [OH<sup>-</sup>]  $\approx$  -5.85

[H<sup>+</sup>]  $\approx$  7.1 x 10<sup>-9</sup>  
 [H<sub>2</sub>S]  $\approx$  7.0 x 10<sup>-4</sup>  
 [HS<sup>-</sup>]  $\approx$  1 x 10<sup>-2</sup>  
 [S<sup>-2</sup>]  $\approx$  2 x 10<sup>-8</sup>  
 [NH<sub>4</sub><sup>+</sup>]  $\approx$  1 x 10<sup>-2</sup>  
 [NH<sub>3</sub>]  $\approx$  8 x 10<sup>-4</sup>  
 [OH<sup>-</sup>]  $\approx$  1.4 x 10<sup>-6</sup>

Check assumptions:

[H<sub>2</sub>S]  $\gg$  [H<sup>+</sup>]  
 10<sup>-3.15</sup>  $\gg$  10<sup>-8.15</sup>, YES

[NH<sub>3</sub>]  $\gg$  [OH<sup>-</sup>]  
 10<sup>-3.1</sup>  $\gg$  10<sup>-5.85</sup>, again 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, given its molecular weight.
- b.   **F**   The Bronsted-Lowry definition of an acid is a substance that turns red litmus blue.
- c.   **T**   Hardness is normally defined as the sum of all divalent cations
- d.   **F**   Organic forms of carbon are those in the  $-IV$  oxidation state.
- e.   **T**   Mass defects are directly proportional to nuclear binding energy
- f.   **F**   The alkalinity minus the acidity is equal to one-half the  $C_T$  (total carbonates)
- g.   **F**   The reactivity of neutral species is unaffected by changes in ionic strength.
- h.   **F**   Increases in ionic strength cause an increase in the  $pK_a$  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 a strong acid is that  $[A^-] \gg [HA]$ .
- j.   **T**   The value of  $\alpha_0$  plus  $\alpha_1$  must never equal unity for a diprotic acid.

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

NAME	FORMULA	pK <sub>a</sub>
Perchloric acid	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-7 STRONG
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3 (&2) ACIDS
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	-0
Hydronium ion	$\text{H}_3\text{O}^+ = \text{H}^+ + \text{H}_2\text{O}$	0
Trichloroacetic acid	$\text{CCl}_3\text{COOH} = \text{H}^+ + \text{CCl}_3\text{COO}^-$	0.70
Iodic acid	$\text{HIO}_3 = \text{H}^+ + \text{IO}_3^-$	0.8
Bisulfate ion	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.15 (&7.2,12.3)
o-Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2 = \text{H}^+ + \text{C}_6\text{H}_4(\text{COOH})\text{COO}^-$	2.89 (&5.51)
Citric acid	$\text{C}_3\text{H}_5\text{O}(\text{COOH})_3 = \text{H}^+ + \text{C}_3\text{H}_5\text{O}(\text{COOH})_2\text{COO}^-$	3.14 (&4.77,6.4)
Hydrofluoric acid	$\text{HF} = \text{H}^+ + \text{F}^-$	3.2
Aspartic acid	$\text{C}_2\text{H}_6\text{N}(\text{COOH})_2 = \text{H}^+ + \text{C}_2\text{H}_6\text{N}(\text{COOH})\text{COO}^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.06 (&9.92)
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.48 (&9.32)
Nitrous acid	$\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$	4.5
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75
Propionic acid	$\text{C}_2\text{H}_5\text{COOH} = \text{H}^+ + \text{C}_2\text{H}_5\text{COO}^-$	4.87
Carbonic acid	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	6.35 (&10.33)
Hydrogen sulfide	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	7.02 (&13.9)
Dihydrogen phosphate	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.2
Hypochlorous acid	$\text{HOCl} = \text{H}^+ + \text{OCl}^-$	7.5
Boric acid	$\text{B}(\text{OH})_3 + \text{H}_2\text{O} = \text{H}^+ + \text{B}(\text{OH})_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	9.24
Hydrocyanic acid	$\text{HCN} = \text{H}^+ + \text{CN}^-$	9.3
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COO}^- = \text{H}^+ + \text{C}_6\text{H}_4(\text{O})\text{COO}^{2-}$	9.32
Phenol	$\text{C}_6\text{H}_5\text{OH} = \text{H}^+ + \text{C}_6\text{H}_5\text{O}^-$	9.9
m-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COO}^- = \text{H}^+ + \text{C}_6\text{H}_4(\text{O})\text{COO}^{2-}$	9.92
Bicarbonate ion	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33
Monohydrogen phosphate	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.3
Bisulfide ion	$\text{HS}^- = \text{H}^+ + \text{S}^{2-}$	13.9
Water	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	14.00
Ammonia	$\text{NH}_3 = \text{H}^+ + \text{NH}_2^-$	23
Methane	$\text{CH}_4 = \text{H}^+ + \text{CH}_3^-$	34

Species	$\Delta \overline{H}_f^o$ kcal/mole	$\Delta \overline{G}_f^o$ kcal/mole
Ca <sup>+2</sup> (aq)	-129.77	-132.18
CaCO <sub>3</sub> (s), calcite	-288.45	-269.78
CaO (s)	-151.9	-144.4
C(s), graphite	0	0
CO <sub>2</sub> (g)	-94.05	-94.26
CO <sub>2</sub> (aq)	-98.69	-92.31
CH <sub>4</sub> (g)	-17.889	-12.140
H <sub>2</sub> CO <sub>3</sub> (aq)	-167.0	-149.00
HCO <sub>3</sub> <sup>-</sup> (aq)	-165.18	-140.31
CO <sub>3</sub> <sup>-2</sup> (aq)	-161.63	-126.22
CH <sub>3</sub> COOH	-116.79	-95.55
CH <sub>3</sub> COO <sup>-</sup> , acetate	-116.84	-89.0
H <sup>+</sup> (aq)	0	0
H <sub>2</sub> (g)	0	0
HF (aq)	-77.23	-71.63
F <sup>-</sup> (aq)	-80.15	-67.28
Fe <sup>+2</sup> (aq)	-21.0	-20.30
Fe <sup>+3</sup> (aq)	-11.4	-2.52
Fe(OH) <sub>3</sub> (s)	-197.0	-166.0
NO <sub>3</sub> <sup>-</sup> (aq)	-49.372	-26.43
NH <sub>3</sub> (g)	-11.04	-3.976
NH <sub>3</sub> (aq)	-19.32	-6.37
NH <sub>4</sub> <sup>+</sup> (aq)	-31.74	-19.00
HNO <sub>3</sub> (aq)	-49.372	-26.41
O <sub>2</sub> (aq)	-3.9	3.93
O <sub>2</sub> (g)	0	0
OH <sup>-</sup> (aq)	-54.957	-37.595
H <sub>2</sub> O (g)	-57.7979	-54.6357
H <sub>2</sub> O (l)	-68.3174	-56.690
PO <sub>4</sub> <sup>-3</sup> (aq)	-305.30	-243.50
HPO <sub>4</sub> <sup>-2</sup> (aq)	-308.81	-260.34
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> (aq)	-309.82	-270.17
H <sub>3</sub> PO <sub>4</sub> (aq)	-307.90	-273.08
SO <sub>4</sub> <sup>-2</sup>	-216.90	-177.34
HS <sup>-</sup> (aq)	-4.22	3.01
H <sub>2</sub> S(g)	-4.815	-7.892
H <sub>2</sub> S(aq)	-9.4	-6.54

