

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°C , $I = 0$
 - b. 100°C , $I = 0$

2. (40%) What is the complete composition of a 1-liter volume of water containing 10^{-2} M of ammonium chloride (NH_4Cl) and 10^{-2} M of sodium bisulfide (NaHS)? Approximate values (± 0.2 log units) will suffice.

Each one of the following statements with either a

- a. _____ Water has an unusually high boiling point, given its molecular weight.
- b. _____ The Bronsted-Lowry definition of an acid is a substance that turns red litmus blue.
- c. _____ Hardness is normally defined as the sum of all divalent cations
- d. _____ Organic forms of carbon are those in the +IV oxidation state.
- e. _____ Mass defects are directly proportional to nuclear binding energy
- f. _____ The alkalinity minus the acidity is equal to one-half the C_T (total carbonates)
- g. _____ The reactivity of neutral species is unaffected by changes in ionic strength.
- h. _____ 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. _____ The standard assumption used for calculating the pH of a strong acid is that $[A^-] \gg [HA]$.
- j. _____ The value of α_0 plus α_1 must never equal unity for a diprotic acid.

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

	DLA	pK _a
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

	$\Delta \bar{G}_f^\circ$	
	kcal/mole	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 ₂ CO ₃ (aq)	-167.0	-149.00
HCO ₃ ⁻ (aq)	-165.18	-140.31
CO ₃ ⁻² (aq)	-161.63	-126.22
CH ₃ COOH	-116.79	-95.5
CH ₃ COO ⁻ , 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 ₂ O (g)	-57.7979	-54.6357
H ₂ O (l)	-68.3174	-56.690
PO ₄ ⁻³ (aq)	-305.30	-243.50
HPO ₄ ⁻² (aq)	-308.81	-260.34
H ₂ PO ₄ ⁻ (aq)	-309.82	-270.17
H ₃ PO ₄ (aq)	-307.90	-273.08
SO ₄ ⁻²	-216.90	-177.34
HS ⁻ (aq)	-4.22	3.01
H ₂ S(g)	-4.815	-7.892
H ₂ S(aq)	-9.4	-6.54

