

FIRST EXAM

Closed book, one page of notes allowed.

Answer any 4 of the following 5 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:

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

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

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

$$10^\circ\text{F} = \text{the new } 30^\circ\text{F}$$

1. (25%) Use the graphical solution to determine the pH and complete solution composition for 1 liter of pure water to which you've added $10^{-3.5}$ moles of NaH_2PO_4 . Graph paper is attached to this exam for this purpose.
2. (25%) Determine the pH and solution composition of a mixture of $10^{-3.5}$ moles of NaH_2PO_4 plus 10^{-3} moles of Sodium Acetate in 1 liter of water. Please use a graphical solution for this one too.
3. (25%) Determine the complete solution composition of a solution of $10^{-4.5}$ moles of Iodic Acid (HIO_3) in 1 Liter of water, but for this one use an algebraic solution. Do this again, but this time assume you're adding $10^{-4.5}$ moles of the conjugate base [i.e., Sodium Iodate (NaIO_3)] in 1 Liter of water. Remember to make simplifying assumptions.
4. (25%) Repeat problem #1, but this time add 0.1 M of NaCl as well as the $10^{-3.5}$ moles of NaH_2PO_4 to your liter of water

5. (25%) True/False. Mark each one of the following statements with either a “T” or an “F”, whichever is most accurate

- a. _____ The pH of pure water to which you add 10^{-2} M NaHPO_4 and 10^{-2} Na_2HPO_4 is about equal to the second pKa for the phosphate system (i.e., pH ~ 7.2)
- b. _____ Conditional equilibrium constants are independent of ionic strength
- c. _____ The sum of any pKa and the pKb of its conjugate base is always 1.
- d. _____ pH = pKa at the mid-point of a titration
- e. _____ Nitric acid always completely donates its proton to the solvent it is dissolve in, regardless of the nature of that solvent
- f. _____ The principle of electroneutrality is always observed in aqueous solutions
- g. _____ Non-carbonate hardness is equal to the magnesium concentration
- h. _____ Increases in ionic strength have no effect on species with zero charge.
- i. _____ Nitrate is a very strong base in water
- j. _____ The value of α_0 plus α_1 must always equal 1 for any diprotic acid system.

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

NAME	FORMULA	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

Species	$\Delta \overline{H}_f^\circ$ kcal/mole	$\Delta \overline{G}_f^\circ$ 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

Guntelberg Approximation:

$$\log f = -0.5z^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$$



