## 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.

> <u>Miscellaneous Information</u>: 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<sub>2</sub>S. 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)
- 2. (60%) Determine the complete composition of a 1-liter volume of water to which you have added
  - a.  $10^{-3}$  M of Sodium Bicarbonate (NaHCO<sub>3</sub>), and  $10^{-2}$  M of Phenol (C<sub>6</sub>H<sub>5</sub>OH)
  - b.  $10^{-3}$  M of sodium hydroxide (NaOH), and  $10^{-3}$  M of sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>)

Approximate values ( $\pm$  0.2 log units) will suffice.

- 3. (10%) True/False. Mark each one of the following statements with either a "T" or an "F".
  - a. Water has an unusually high boiling point based on its molecular weight.
  - b. A nano gram is equivalent to one-thousanths of a milligram.
  - c. \_\_\_\_\_ The third most common gas in the atmosphere is carbon dioxide
  - Non-carbonate hardness only exists in waters with alkalinities less thanthan their total hardness.
  - e. \_\_\_\_\_ Mass defects are directly proportional to nuclear binding energy
  - f. \_\_\_\_\_ The Guntelberg Approximation says that activity coefficients are dependent on charge and ionic strenth, but not on ion size.
  - The reactivity of neutral species is unaffected by changes in ionic g. \_\_\_\_\_ strength.
  - h. \_\_\_\_\_ 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.
  - The standard assumption used for calculating the pH of buffer solutions i. \_\_\_\_\_ is that all positive ions are negligible.
  - j. The value of  $\alpha_0$  plus  $\alpha_1$  must always equal unity for a diprotic acid.

NAME	FORMULA	pK <sub>a</sub>
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	$H_{3}O^{+} = H^{+} + H_{2}O$	0
Trichloroacetic acid	$CCl_{3}COOH = H^{+} + CCl_{3}COO^{-}$	0.70
Iodic acid	$HIO_3 = H^+ + IO_3^-$	0.8
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid		2.15 (&7.2,12.3)
o-Phthalic acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.89 (&5.51)
Citric acid	$C_{6}H_{4}(COOH)_{2} = H^{+} + C_{6}H_{4}(COOH)COO^{-}$	3.14 (&4.77,6.4)
Hydrofluoric acid	$C_{3}H_{5}O(COOH)_{3}=H^{+}+C_{3}H_{5}O(COOH)_{2}COO^{-}$	3.14 (&4.77,0.4)
Aspartic acid	$HF = H^+ + F^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$C_2H_6N(COOH)_2 = H^+ + C_2H_6N(COOH)COO^-$	4.06 (&9.92)
	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.00 (&9.92)
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	. ,
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	$\mathrm{NH_4^+} = \mathrm{H^+} + \mathrm{NH_3}$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
p-Hydroxybenzoic acid	$C_{6}H_{4}(OH)COO^{-} = H^{+} + C_{6}H_{4}(O)COO^{-2}$	9.32
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
m-Hydroxybenzoic acid	$C_{6}H_{4}(OH)COO^{-} = H^{+} + C_{6}H_{4}(O)COO^{-2}$	9.92
Bicarbonate ion	$HCO_{3}^{-} = H^{+} + CO_{3}^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
		13.9
Bisulfide ion	$HS^{-} = H^{+} + S^{-2}$	15.9
Bisulfide ion Water	$HS^{-} = H^{+} + S^{-2}$ $H_2O = H^{+} + OH^{-}$	14.00

Selected Acidity Constants (Aqueous Solution,  $25^{\circ}$ C, I = 0)

Species	${}^{\Delta}\overline{H}{}^{o}_{f}$	${}^{\scriptscriptstyle \Delta}\overline{G}^o_f$
Species	kcal/mole	kcal/mole
Ca <sup>+2</sup> (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 <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
$H_2CO_3$ (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
$\mathrm{H}^{+}(\mathrm{aq})$	0	0
$H_{2}(g)$	0	0
$\mathrm{Fe}^{+2}$ (aq)	-21.0	-20.30
$\mathrm{Fe}^{+3}$ (aq)	-11.4	-2.52
Fe(OH) <sub>3</sub> (s)	-197.0	-166.0
NO <sub>3</sub> (aq)	-49.372	-26.43
NH <sub>3</sub> (g)	-11.04	-3.976
NH <sub>3</sub> (aq)	-19.32	-6.37
$\mathrm{NH_4^+}(\mathrm{aq})$	-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
$PO_4^{-3}$ (aq)	-305.30	-243.50
$HPO_4^{-2}$ (aq)	-308.81	-260.34
$H_2PO_4^-(aq)$	-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

