CEE 680 9 October 2013

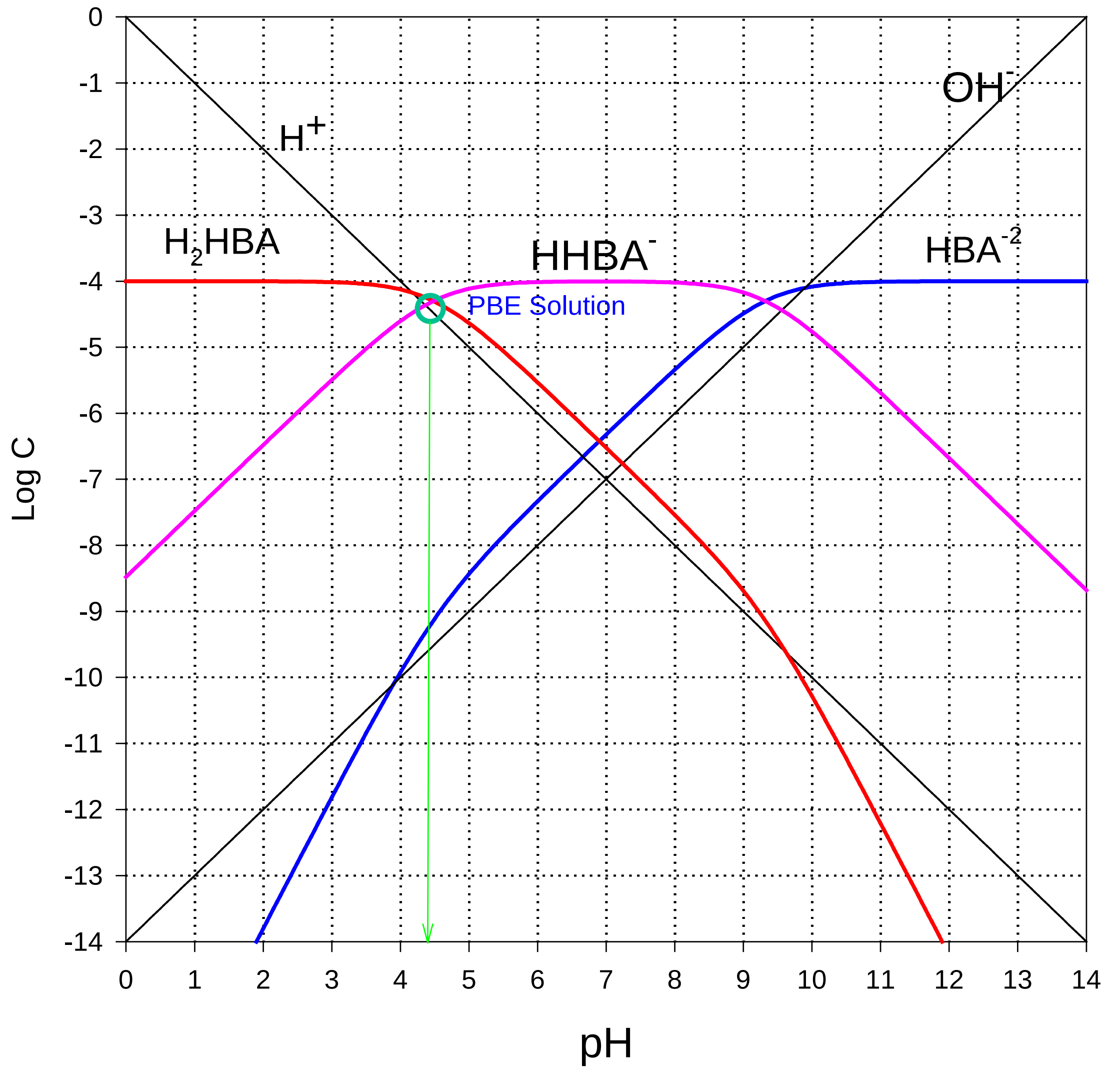
FIRST EXAM

Closed book, one page of notes allowed.

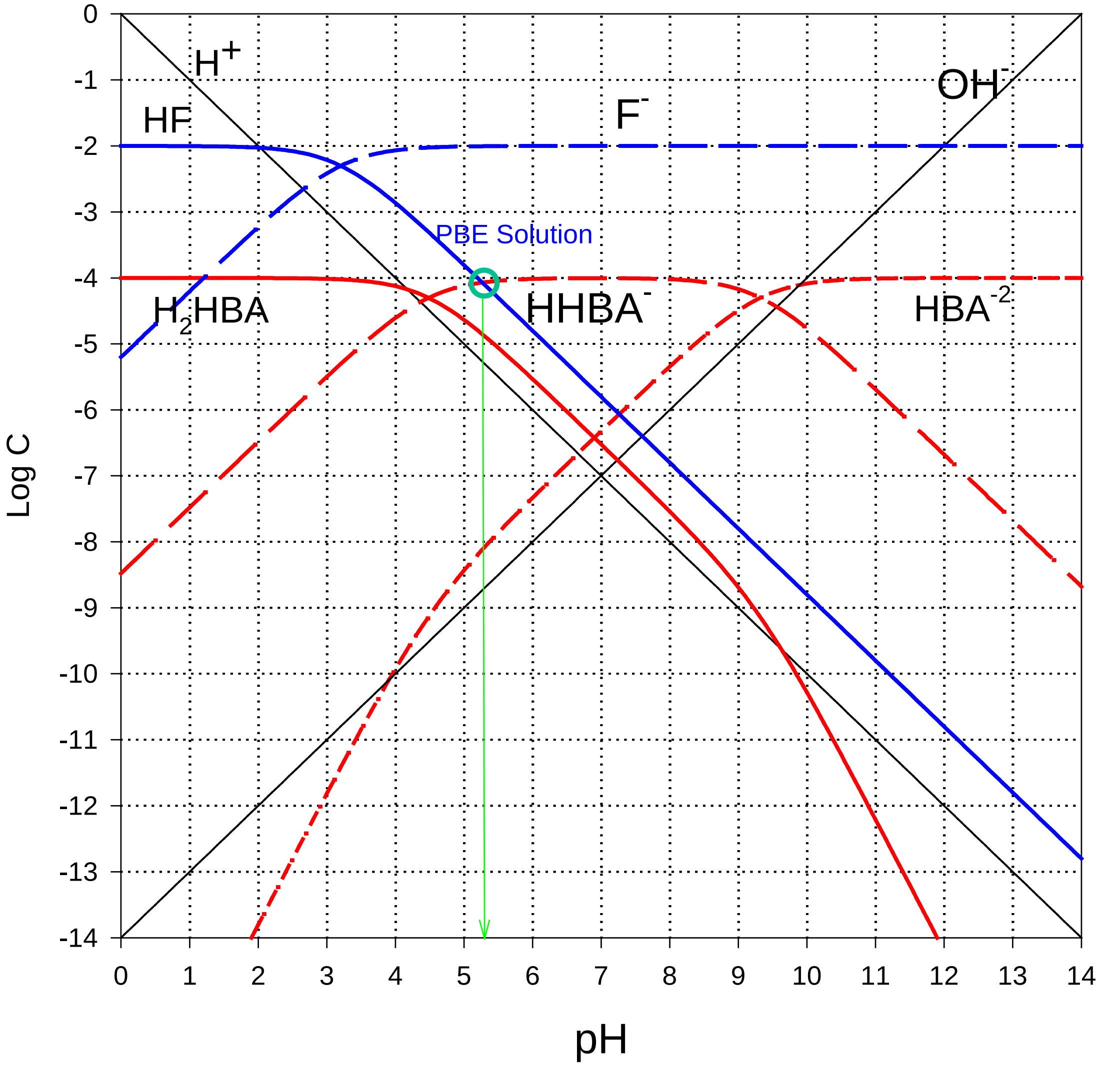
Answer any 4 of the following 5 questions. Please state any additional assumptions you made, and show all work. You are welcome to use a graphical method of solution if it is appropriate.

Miscellaneous Information:
R = 1.987 cal/mole°K = 8.314 J/mole°K
Absolute zero = -273.15°C
1 joule = 0.239 calories
-20°C = wicked cold

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^{-4} moles of p-hydroxybenzoic acid. Graph paper is attached to this exam for this purpose.



2. (25%) Determine the pH and solution composition of a mixture of 10^{-4} moles of p-hydroxybenzoic acid plus 10^{-2} moles of Sodium Fluoride in 1 liter of water. You invited to use a graphical solution for this one too.



3. (25%) Determine the complete solution composition of a solution of 10^{-4} moles of Nitrous Acid (HNO_2) in 1 Liter of water, but for this one use an algebraic solution. Remember to make simplifying assumptions.

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

$[H^+]$ = 4.26 x 10^{-5}

pH = 4.37

4. (25%) Repeat problem #3, but this time add 0.1 M of NaCl as well as the 10^{-4} moles of Nitrous Acid (HNO_2) to your liter of water

$$K = \frac{\{H^+\}\{A^-\}}{\{HA\}} = \frac{[H^+]\gamma_{H^+}[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}}$$

$$= \left(\frac{[H^+][A^-]}{[HA]}\right)\left(\frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}}\right)$$

Use the Guntelberg approximation:

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

log(fH+) = log(fA-) =		-0.12013
	fH+ = fA- =	0.758357
	pK =	4.259747

5. (25%) True/False. Mark each one of the following statements with either a "T" or an "F"

a. ___**T**___ pH electrodes measure hydrogen ion activity rather than concentration

b. ___**T**___ The Bronsted-Lowry definition of an acid is a substance that can donate a proton

c. ___**F**___ Hardness is normally defined as the sum of all monovalent cations

d. ___**T**___ Total dissolved solids is the sum (in weight) of all solutes in water that are not lost by filtration or drying.

e. ___**T**___ Mass defects are directly proportional to nuclear binding energy

f. ___**F**___ The Henderson Hasselbalch equation describes the impacts of ionic strength on chemical equilibria

g. ___**T**___ Water forms cage-like structures that are due to hydrogen bonding between adjacent molecules

h. ___**F**___ Increases in ionic strength have relatively minor effects on species with high charge.

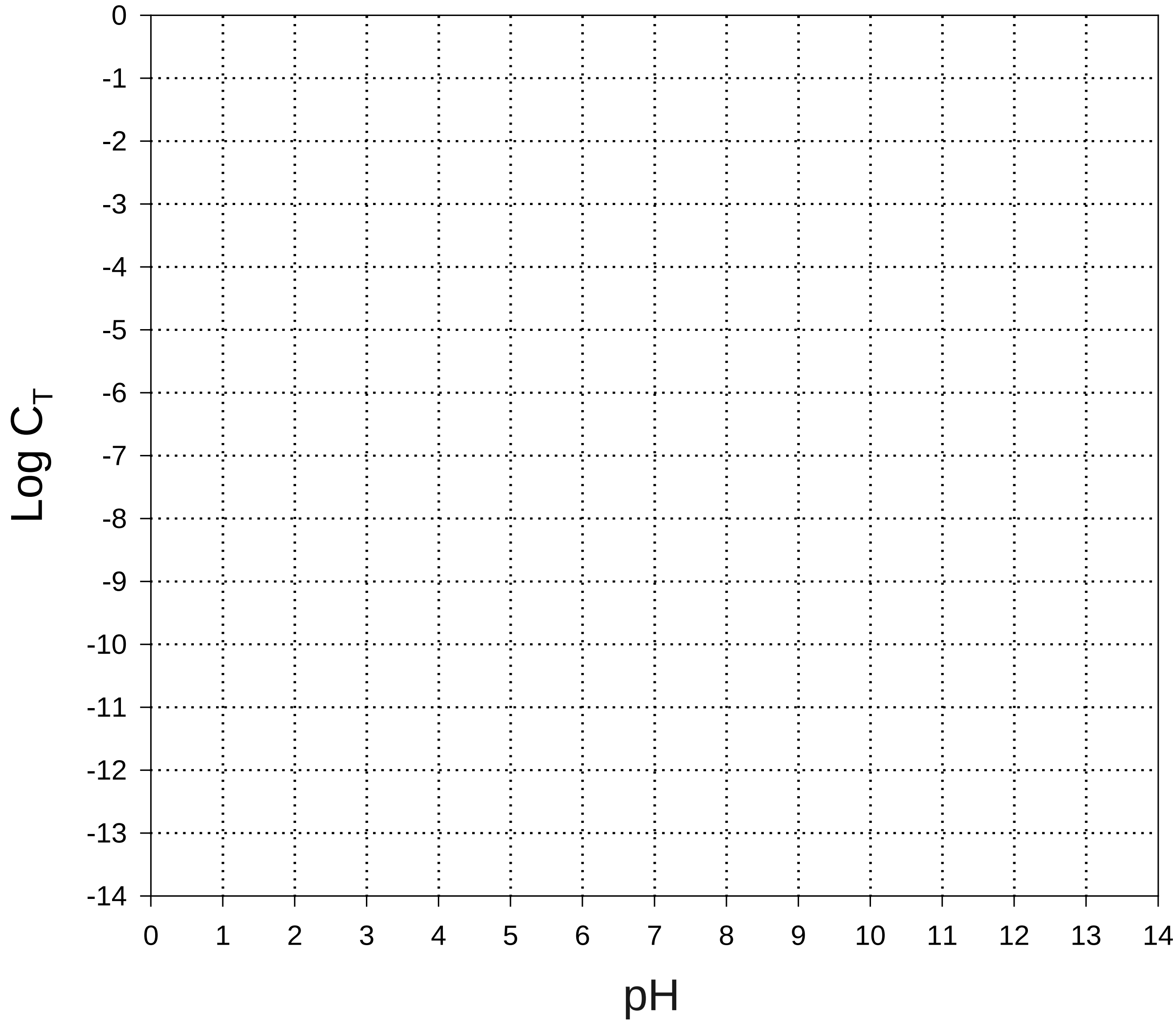
i. ___**T**___ The standard assumption used for calculating the pH of a strong acid is that [A-] >> [HA].

j. ___**T**___ The value of α_o plus α_1 must never exceed unity for any monoprotic acid system.

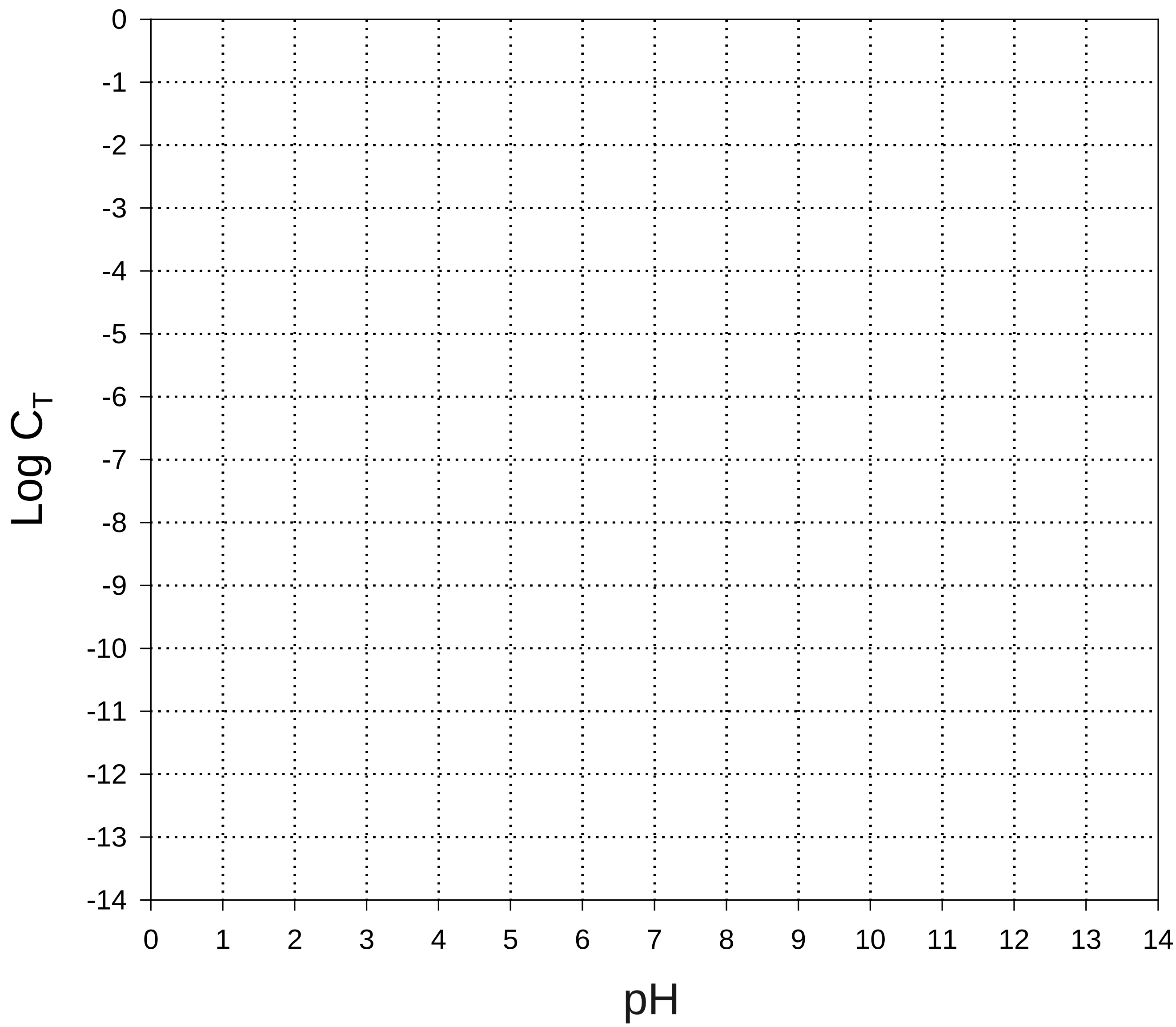
Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

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
$CaCO_3$(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_2CO_3 (aq)	-167.0	-149.00
HCO_3^- (aq)	-165.18	-140.31
CO_3^{-2} (aq)	-161.63	-126.22
CH_3COOH	-116.79	-95.5
CH_3COO^-, 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_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



Log C_T
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14


0
-1
-2
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-10
-11
-12
-13
-14
Log C_T
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pH