CEE 680 5 March 2015

FIRST EXAM (Solutions)

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 $10^{-3.5}$ moles of NaH_2PO_4. Graph paper is attached to this exam for this purpose.

PBE

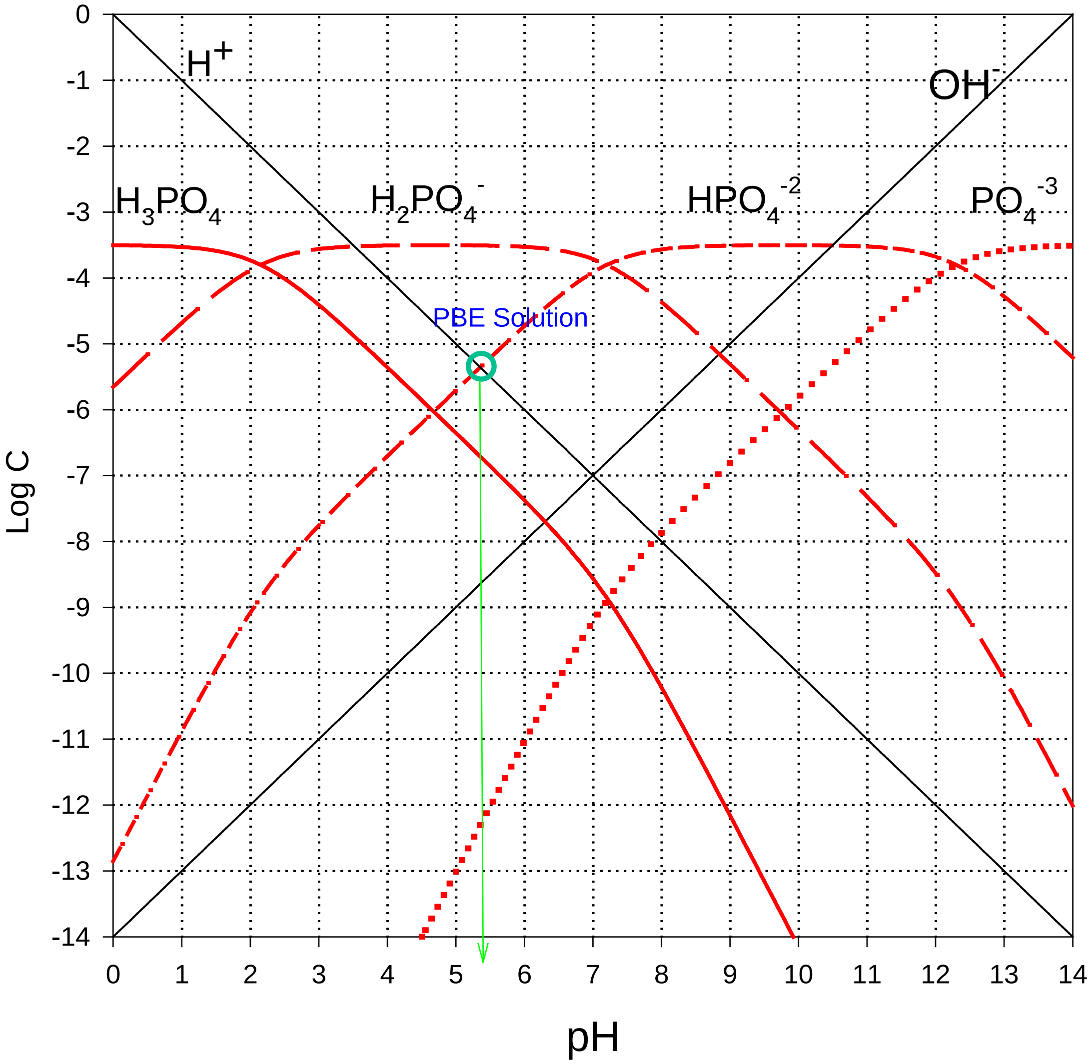
$$[H_3PO_4] + [H^+] = [OH^-] + [HPO_4^{-2}] + 2[PO_4^{-3}]$$

which reduces to:

$$[H^+] = [HPO_4^{-2}]$$

Equality (intersection) occurs at **pH ~ 5.35**

Species	pC	C (Molar)
H^+	5.35	4.5×10^{-6}
OH^-	8.65	2.2×10^{-9}
H_3PO_4	6.7	2.0×10^{-9}
$H_2PO_4^-$	3.5	3.1×10^{-4}
HPO_4^{-2}	5.35	4.5×10^{-6}
PO_4^{-3}	12.3	4.9×10^{-13}
Na^+	3.5	3.1×10^{-4}



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.

PBE

$$[HPO_4^{-2}] + 2[PO_4^{-3}] + [OH^-] = [H^+] + [H_3PO_4] + [HAc]$$

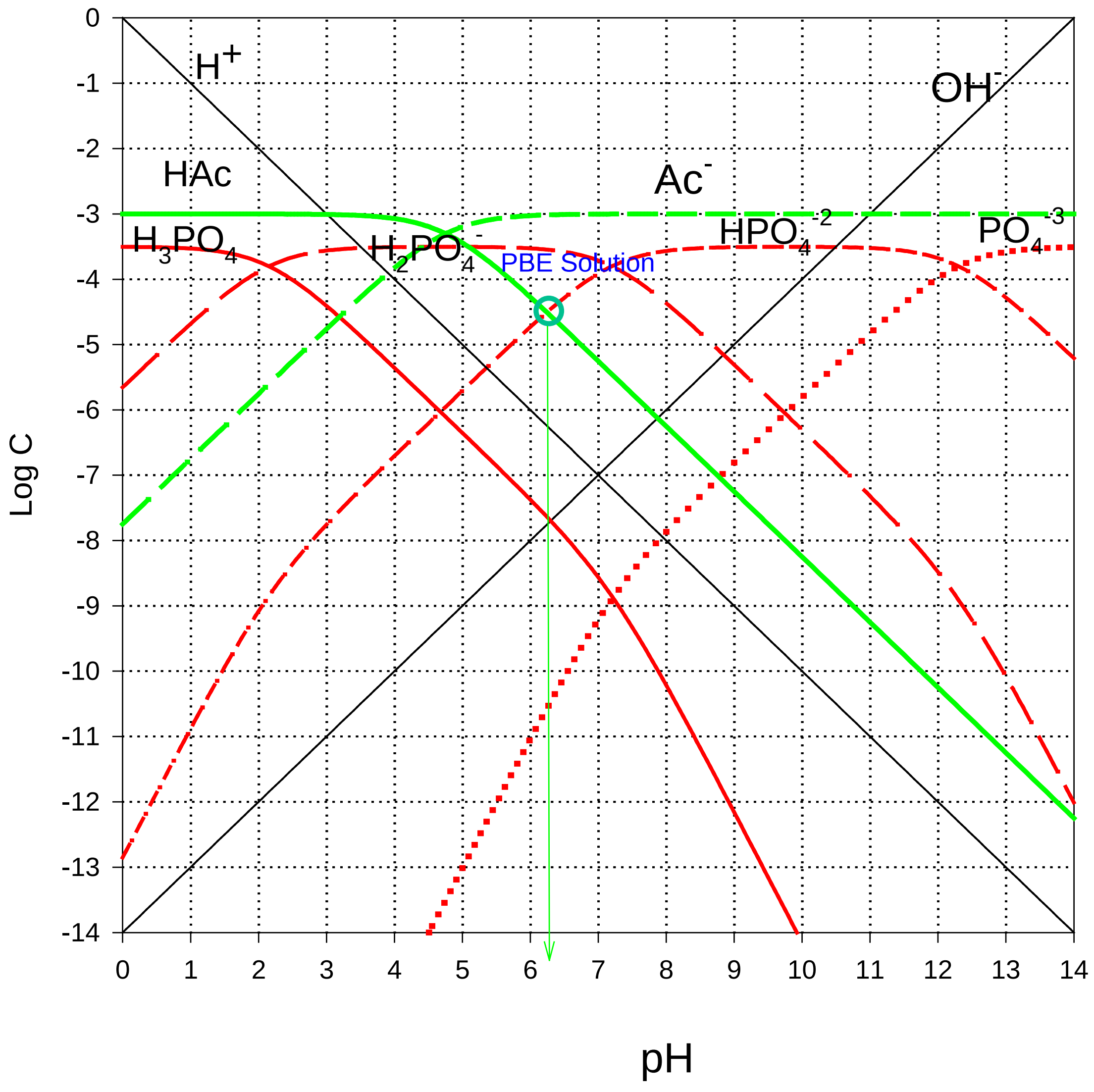
which reduces to:

$$[HPO_4^{-2}] = [HAc]$$

Equality (intersection) occurs at **pH ~ 6.2**

Species	pC	C (Molar)
H^+	6.2	6.3×10^{-7}
OH^-	7.8	1.6×10^{-8}
H_3PO_4	7.6	2.5×10^{-8}
$H_2PO_4^-$	3.6	2.5×10^{-4}
HPO_4^{-2}	4.5	3.2×10^{-5}
PO_4^{-3}	10.6	2.5×10^{-11}
HAc	4.5	3.2×10^{-5}
Ac^-	3.0	1.0×10^{-3}
Na^+	2.9	1.3×10^{-3}

Log C vs pH Diagram



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 only $10^{-4.5}$ moles of the conjugate base [i.e., Sodium Iodate ($NaIO_3$)] in 1 Liter of water. Remember to make simplifying assumptions.

A. Make acidic solution assumption, which leads to:

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

$[H^+]$ = 3.1616 x 10^{-5}
pH = 4.50001

but easier to make the combined acidic solution and strong acid assumption, which leads to:

$$[H^+] \approx C$$

$[H^+]$ = 3.1623 x 10^{-5}
pH = 4.50000

B. Make basic solution assumption, which leads to:

$$[OH^-] \approx \frac{-K_b + \sqrt{K_b^2 + 4K_bC}}{2}$$

$[OH^-]$ = 1.413 x 10^{-9}
$[H^+]$ = 7.079 x 10^{-6}
pH = 5.15

This is not a basic so the assumption is not good. Instead try the weak base assumption (i.e., $[IO_3^-] >> [HIO_3]$; since the strong acid assumption worked for the conjugate acid), which leads to:

$$[OH^-] \approx \sqrt{K_bC + K_w}$$

$[OH^-] = 1.0001 \times 10^{-7}$

$[H^+] = 9.999 \times 10^{-8}$

pH = 7.00004

now check the assumption that $[IO_3^-] >> [HIO_3]$ at this pH (7.00004).

$Ka = [H^+][IO_3^-]/[HIO_3]$

$10^{-0.8}=10^{-7}[IO_3^-]/[HIO_3]$

$[IO_3^-]/[HIO_3] = 10^{+6.2}$

Yes, the assumption is good

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

The pH shift pertains essentially to the second pK only. At I=0, pK_2=7.2. so, now calculate its value at I = 0.01.

$$K_2 = \frac{\{H^+\}\{HA^{-2}\}}{\{H_2A^-\}} = \frac{[H^+]\gamma_{H^+}[HA^{-2}]\gamma_{HA^{-2}}}{[H_2A^-]\gamma_{H_2A^-}} = \frac{\{H^+\}[HA^{-2}]\gamma_{HA^{-2}}}{[H_2A^-]\gamma_{H_2A^-}}$$

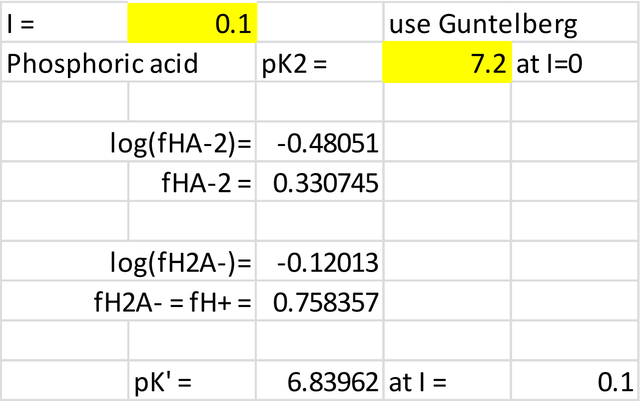
$$= \left(\frac{\{H^+\}[A^-]}{[HA]}\right)\left(\frac{\gamma_{HA^{-2}}}{\gamma_{H_2A^-}}\right)$$

and

$$K_2' \equiv \left(\frac{\{H^+\}[A^-]}{[HA]}\right) = \frac{K_2}{\left(\frac{\gamma_{HA^{-2}}}{\gamma_{H_2A^-}}\right)} = K_2\left(\frac{\gamma_{H_2A^-}}{\gamma_{HA^{-2}}}\right)$$

Use the Guntelberg approximation:

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



I =	0.1		use Guntelberg	
Phosphoric acid		pK2 =	7.2	at I=0
	log(fHA-2)=	-0.48051		
	fHA-2 =	0.330745		
	log(fH2A-)=	-0.12013		
	fH2A- = fH+ =	0.758357		
	pK' =	6.83962	at I =	0.1

Everything else just follows what was done in problem #1:

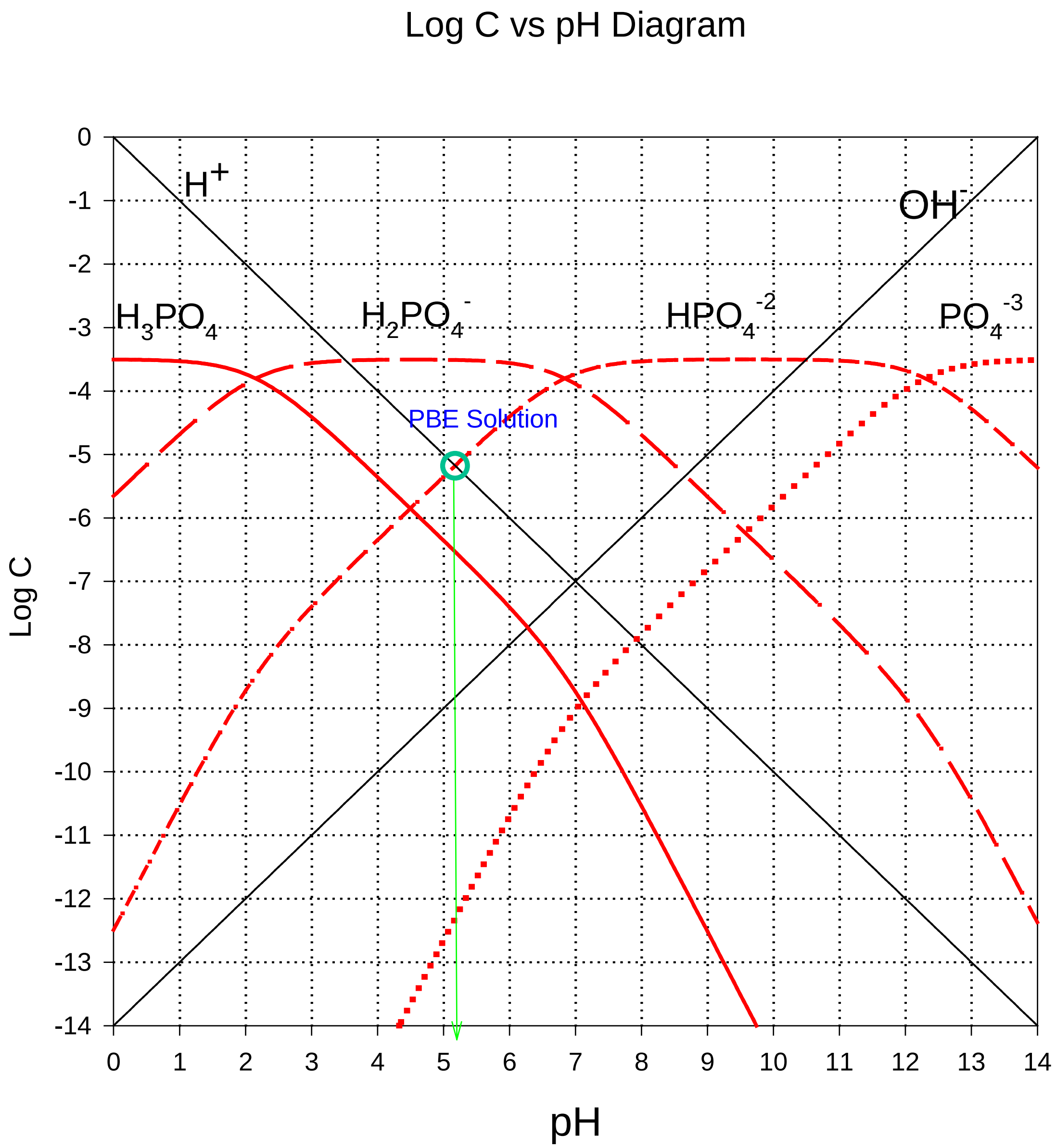
PBE

$$[H_3PO_4] + [H^+] = [OH^-] + [HPO_4^{-2}] + 2[PO_4^{-3}]$$

which reduces to:

$$[H^+] = [HPO_4^{-2}]$$

At this point you could recognize that the intersection will shift half a pH unit for each pH unit shift in the pK2. So for a 0.36 pH unit drop in the pK_2, the intersection should drop 0.18 pH units or from about 5.35 to 5.15. You could also re-draw the original figure and it would look like this:



Equality (intersection) occurs at **pH ~ 5.15**

You can them read off the concentrations as before.

Strictly speaking, to get the concentrations of the two extreme phosphate species (H_3PO_4 and PO_4^{-3}) you'd need to do a similar calculation for the pK_1 and the pK_3 and re-graph. Also, the exact PBE would require that you calculate a new H+ line as the ideal relationship between the molar $[H^+]$ and pH (which is related to activity, i.e., $pH=\{H^+\}$) is now affected by ionic strength too.

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

a. **T** The pH of pure water to which you add 10^{-2} M NaH_2PO_4 and 10^{-2} Na_2HPO_4 is about equal to the second pKa for the phosphate system (i.e., pH ~ 7.2)

b. **F** Conditional equilibrium constants are independent of ionic strength

c. **F** The sum of any pKa and the pKb of its conjugate base is always 1.

d. **T** pH = pKa at the mid-point of a titration

e. **F** Nitric acid always completely donates its proton to the solvent it is dissolve in, regardless of the nature of that solvent

f. **T** The principle of electroneutrality is always observed in aqueous solutions

g. **F** Non-carbonate hardness is equal to the magnesium concentration

h. **F** Increases in ionic strength have no effect on species with zero charge.

i. **F** Nitrate is a very strong base in water

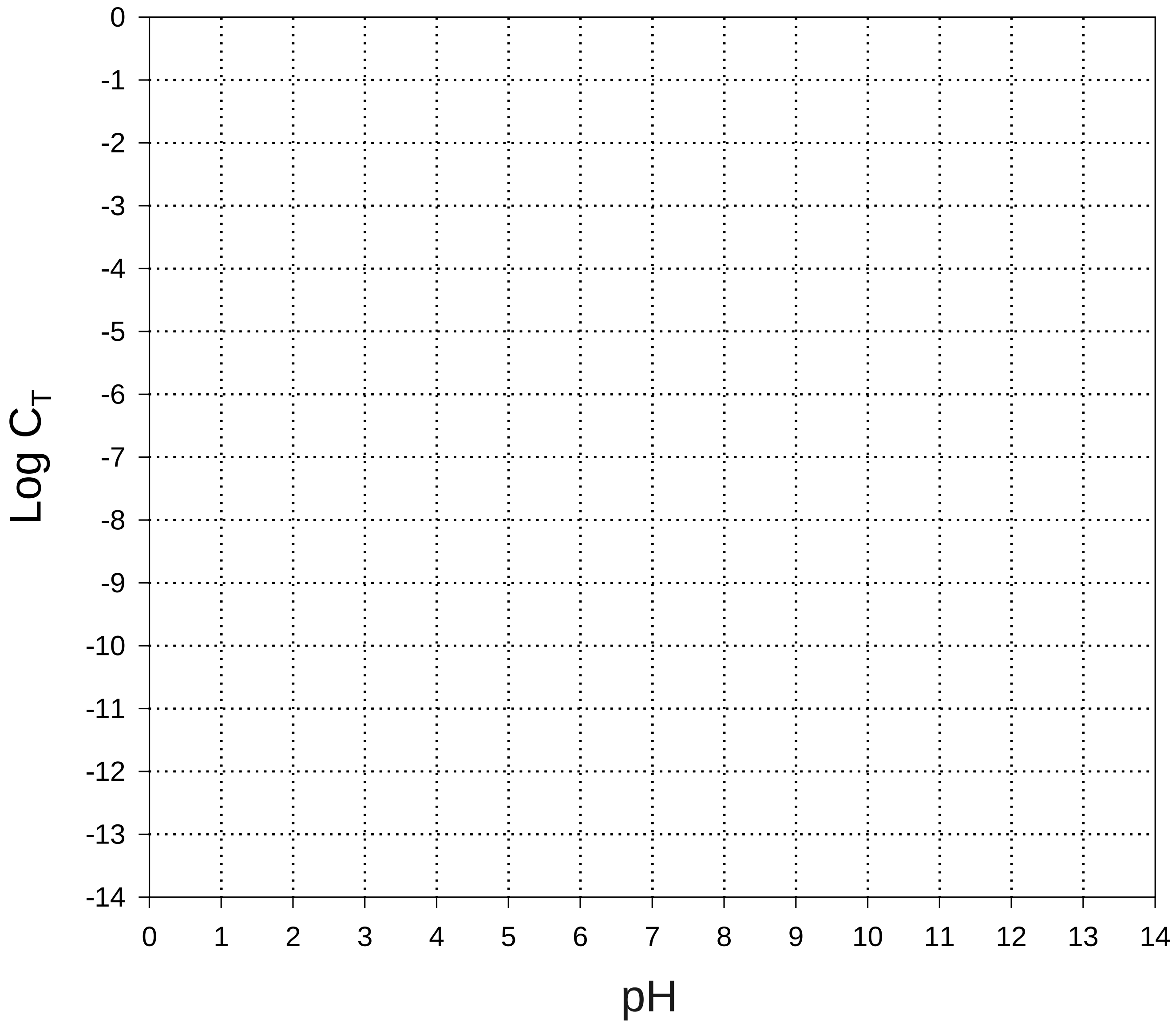
j. **F** The value of α_o plus α_1 must always equal 1 for any diprotic acid system.

Note the original had a typo in question a, so I accepted both T and F for this one.

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	$\Delta \overline{H}^o_f$ kcal/mole	$\Delta \overline{G}^o_f$ 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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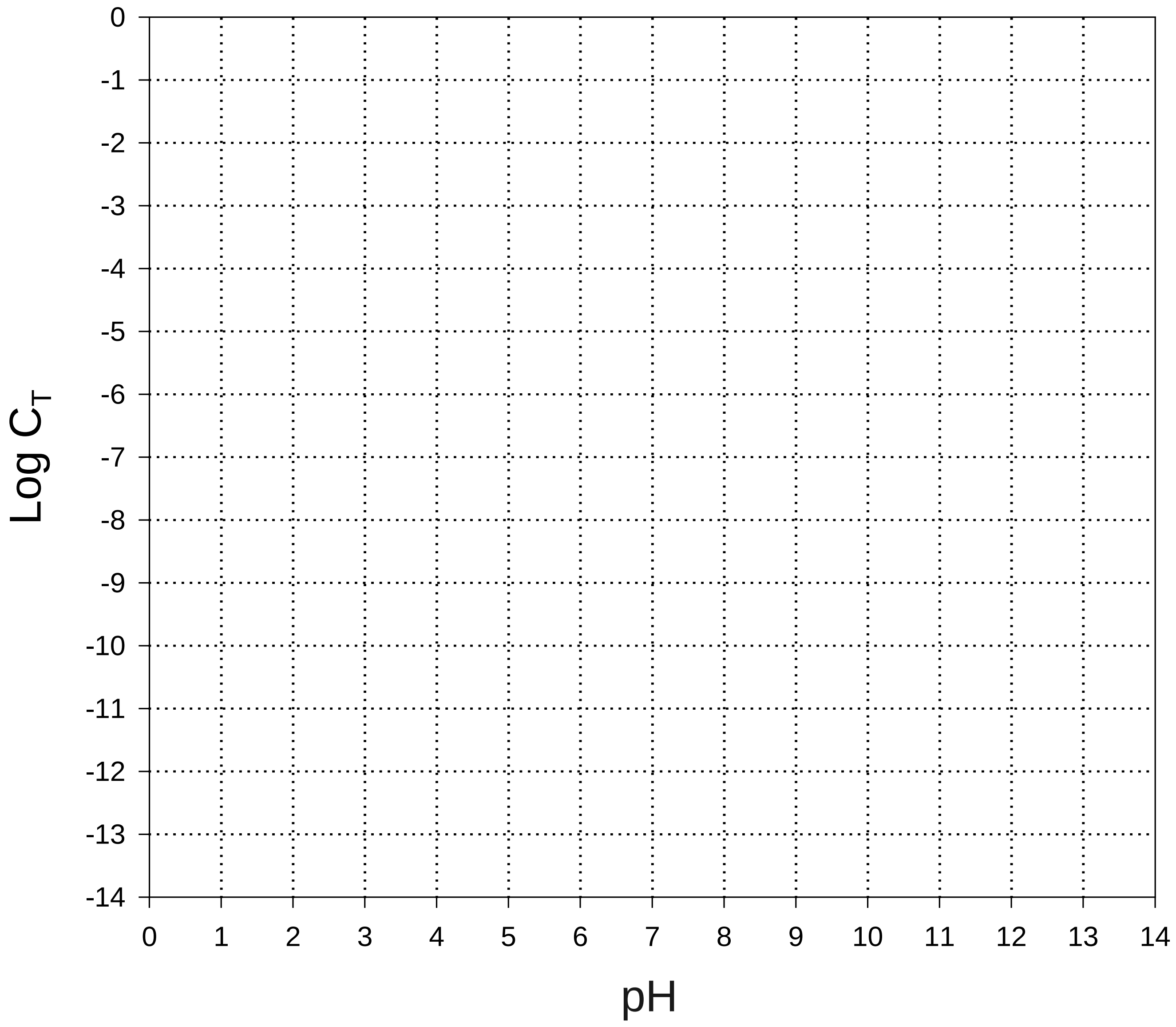
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