CHEM 311
Chapter 9

9-1

$HA + H_2O \leftrightarrow A^- + H_3O^+$ Ka $= 1.0*10^{-4}$

$HA + H_2O \leftrightarrow H_2A^+ + OH^-$ Kb $= 1.0*10^{-8}$

But OH^- and H_3O^+ readily react to form water
$OH^- + H_3O^+ \rightarrow 2H_2O$ K $= 1.0*10^{14}$
This last reaction drives both reactions forward until equilibrium is reached, at which point the concentrations of A^- and H_2A^+ are nearly equal.

9-4

a) 0.100 M solution of H_2M

$H_2M + H_2O \leftrightarrow HM^- + H_3O^+$ Ka_1 $= 1.0*10^{-4}$

$HM^- + H_2O \leftrightarrow M^- + H_3O^+$ Ka_2 $= 1.0*10^{-8}$

$Ka_1 >>> Ka_2$, so we can ignore the effects of the Ka_2 reaction when we calculate $[H_2M]$ and $[HM^-]$.

$Ka_1 = 1.00*10^{-4} = [H_3O^+][HM^-] / [H_2M]$
Assume $[H_3O^+] = [HM^-]$, and let $[HM^-] = x$
Assume $F_{H2M} \cong [H_2M]$, then

$1.00*10^{-4} = x^2/(0.100-x)$
$x = [HM^-] = 3.16*10^{-3}$ M
(or $3.11*10^{-3}$ M w/o assumption)

$[H_3O^+] = 3.16*10^{-3}$ M
pH = 2.507

$[H_2M] = F_{H2M} – x = 9.69*10^{-2}$ M

$Ka_2 = 1.00*10^{-8} = [H_3O^+][M^{-2}] / [HM^-]$
$= x[M^{-2}]/x$

So, $[M^{-2}] = 1.00*10^{-8}$ M

b)
$F_{HM-} = 0.100$ M
Here we are starting with the intermediate species that when dissolved in water acts as both an acid and a base.

$HM^- + H_2O \leftrightarrow M^{-2} + H_3O^+$ Ka_2 $= 1.0*10^{-8}$

$HM^- + H_2O \leftrightarrow H_2M + OH^-$ Kb_2 $= 1.0*10^{-10}$

Both dissociations are important and we use the following equation derived in your book and in class to calculate the H^+ of such a solution.

$[H^+] = \{(Ka_1Ka_2F + Ka_1Kw)/(Ka_1+F)\}^{1/2}$

$Ka_1 = 1.0*10^{-4}$
$Ka_2 = 1.0*10^{-8}$
F = 0.100 M
$Kw = 1.00*10^{-14}$

$[H^+] = \{[(10^{-4})(10^{-8})(0.1) + (10^{-4})(10^{-14})]/(10^{-4}+0.1)\}^{1/2}$
$= 1.00*10^{-6}$ M
pH = 6.000

$Ka_1 = 1.00*10^{-4} = [H_3O^+][HM^-] / [H_2M]$
$[H_3O^+] = 10^{-6}$ M
Assume $[HM^-] \approx 0.100$ M (weak acid and base)

$1.00*10^{-4} = (10^{-6})(0.100)/x$
$x = [H_2M] = 10^{-3}$ M (assumption justified)

$Ka_2 = 1.00*10^{-8} = [H_3O^+][M^{-2}] / [HM^-]$

$[H_3O^+] = 10^{-6}$ M

Assume $[HM^-] \approx 0.100$ M (weak acid and base)

$1.00*10^{-8} = (10^{-6})(x)/(0.100)$

$x = [M^{-2}] = 10^{-3}$ M (assumption justified)

notice $[M^{-2}] = [H_2M]$ even though $Ka_2 > Kb_2$

c) Now we are starting with the most basic species, M^{2-}

$M^{2-} + H_2O \leftrightarrow HM^- + OH^-$

$Kb_1 = Kw/Ka_2 = 1.00*10^{-6} = [HM^-][OH^-]/ (F_{M-2} - [HM^-])$

$HM^- + H_2O \leftrightarrow H_2M + OH^-$

$Kb_2 = Kw/Ka_1 = 1.00*10^{-10} = [H_2M][OH^-]/ ([HM^-])$

$Kb_1 >>> Kb_2$, so we can ignore the effects of the Kb_2 reaction when we calculate $[M^{-2}]$ and $[HM^-]$.

$Kb_1 = 1.00*10^{-6} = [HM^-][OH^-]/ (F_{M-2} - [HM^-])$ Assume $[OH^-] = [HM^-]$, and let $[HM^-] = x$

Assume $F_{M-2} \cong [M^{-2}]$, then

$1.00*10^{-6} = x^2/(0.100)$

$x = [HM^-] = 3.16*10^{-4}$ M

$[OH^-] = 3.16*10^{-4}$ M

$pH = -\log(Kw/[OH^-]) = 10.500$

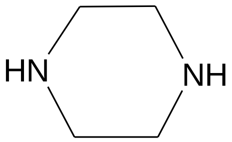
$[M^{-2}] = F_{M-2} - x = 9.97*10^{-2}$ M

$Kb_2 = 1.00*10^{-10} = [H_2M][OH^-]/ ([HM^-]) =$
$x[H_2M]/x$

So, $[H_2M] = 1.00*10^{-10}$ M

9.6

peperazine



Let P = peperazine

Now we are starting with the most basic species, P

$P + H_2O \leftrightarrow HP^+ + OH^-$

$Kb_1 = Kw/Ka_1 = 5.38*10^{-5} = [HP^+][OH^-]/ (F_P - [HP^+])$

$HP^+ + H_2O \leftrightarrow H_2P^+2 + OH^-$

$Kb_2 = Kw/Ka_2 = 2.15*10^{-9} = [H_2P^{2+}][OH^-]/ ([HP^+])$

$Kb_1 >>> Kb_2$, so we can ignore the effects of the Kb_2 reaction when we calculate [P] and $[HP^+]$.

$Kb_1 = 1.00*10^{-6} = [HP^+][OH^-]/ (F_P - [HP^+])$

Assume $[OH^-] = [HP^+]$, and let $[HP^+] = x$

Assume $F_P \cong [P]$, then

$5.38*10^{-5} = x^2/(0.300)$

$[HP^+] = [OH^-] = 4.02*10^{-3}$ M

$[H_3O^+] = 2.489*10^{-12}$ M

pH = 11.604

$[P] = 0.300 - 4.02*10^{-3} = 0.296$ M

$[H_2P^{+2}] = Kb_2 = 2.15*10^{-9}$ M
$Kb_2 = 2.15*10^{-9} = [H_2P^{+2}][OH^-]/([HP^+])$
$= x[H_2P^{+2}]/x$
So, $[H_2P^{+2}] = 2.15*10^{-9}$ M

9.11

$[H_2CO_{2(aq)}] = P_{CO2(g)}$ K

$P_{CO2(g)} = (10^{-3.4}$ atm)(1.01325 bar/atm) = 4.034E-4 bar
$[CO_{2(aq)}] = P_{CO2(g)}$ K = 1.276E-5 M
$[CO_{2(aq)}] + H_2O \Rightarrow H_2CO_3$
$[H_2CO_3]$ = 1.276E-5 M
Ka = 4.46E-7 M = $[H^+][HCO_3^-]/[H_2CO_3]$ = x2/(1.276E-5)
$[H^+]$ = x = 2.39E-6 M
pH = 5.6
IMPORTANT CONCEPTUAL POINT:
The actual concentration $[H_2CO_3]$ at equilibrium is 1.276E-5 M, not 1.276E-5 – x, because it is controlled by P_{CO2}, as some H_2CO_2 dissociates it is replenished by the $CO_{2(g)}$ equilibrium.

9-13

pH = pKa + log[mol CO_3^{-2}/mol HCO_3^-]

pKa = 10.329
pH = 10.00

-0.329 = log[mol CO_3^{-2}/mol HCO_3^-]
0.4688 = (mol CO_3^{-2})/(mol HCO_3^-)11.14

(5.00 g $NaHCO_3$/1)*(1 mol HCO_3^-/84.005 g $NaHCO_3$) =
$5.95*10^{-2}$ mol HCO_3^-

mol CO_3^{2-} need = $0.4688*(5.95*10^{-2}) = 2.79*10^{-2}$ mol CO_3^{2-}

($2.79*10^{-2}$ mol CO_3^{2-}/1)*(105.987 g Na_2CO_3/1 mol) =
2.96 g Na_2CO_3

10-12 in 7th Ed.

pKa1 = 2.972

$H_2S + OH^- \rightarrow HS^-$

Initial
mmol H_2S = (25.0 mL)*(0.0233 M)

Let x be number of mmol OH- added

Final
mmol H_2S = (25.0 mL)*(0.0233 M) – x
mmol HS^- = x

3.50 = 2.971 + log { x/((25.0 mL)*(0.0233 M) – x)}
X = 0.4539 mmol OH-

Volume OH- required = (0.4539)/(0.202 M) = 2.25 mL

9-17

The pKa of the $H_2PO_4^-/HPO_4^{2-}$ system is 7.2. At pH = 8.5, this system does not provide a high buffer capacity and therefore would not be very effective.

9.19

$F_{H2PO4-} = 0.050$ M
Here we are starting with the intermediate species that when
dissolved in water acts as both an acid and a base.

$H_2PO_4^- + H_2O \leftrightarrow HPO_4^{-2} + H_3O^+$ Ka_2 $= 6.32*10^{-8}$

$H_2PO_4^- + H_2O \leftrightarrow H_3PO_4 + OH^-$ Kb_3 $= 1.41*10^{-8}$

Both dissociations are important and we use the following equation derived in your book and in class to calculate the pH of such a solution.

$[H^+] = \{(Ka_1Ka_2F + Ka_1Kw)/(Ka_1+F)\}^{1/2}$

$Ka_1 = 7.11*10^{-3}$
$Ka_2 = 6.32*10^{-8}$
$F = 0.0500$ M
$Kw = 1.00*10^{-14}$

$[H^+] = \{[(7.11*10^{-3})(6.32*10^{-8})(0.05) + (7.11*10^{-3})(10^{-14})]/(7.11*10^{-3} + 0.05)\}^{1/2}$
$= 1.98*10^{-5}$ M

$H_3PO_4 + H_2O \leftrightarrow H_2PO_4^- + H_3O^+$
$Ka_1 = 7.11*10^{-3} = [H_2PO_4^-][H_3O^+]/[H_3PO_4]$
$[H_3PO_4]/[H_2PO_4^-] = [H_3O^+]/Ka_1 = 1.98*10^{-5}/7.11*10^{-3}$
$= 2.79*10^{-3}$

b)
$F_{HPO4-} = 0.050$ M
Here we are also starting with the intermediate species that when dissolved in water acts as both an acid and a base.

$HPO_4^{-2} + H_2O \leftrightarrow PO_4^{-3} + H_3O^+$ Ka_3 $= 7.1*10^{-13}$

$HPO_4^{-2} + H_2O \leftrightarrow H_2PO_4^- + OH^-$ Kb_2 $= 1.58*10^{-7}$

Both dissociations are important and we use the following equation derived in your book and in class to calculate the pH of such a solution.

$[H^+] = \{(Ka_1Ka_2F + Ka_1Kw)/(Ka_1+F)\}^{1/2}$

$Ka_1 = 6.32*10^{-8}$
$Ka_2 = 7.1*10^{-13}$
$F = 0.0500$ M
$Kw = 1.00*10^{-14}$

$[H^+] = \{[(6.32*10^{-8})(7.1*10^{-13})(0.05) + (6.32*10^{-8})(10^{-14})]/(6.32*10^{-8} + 0.05)\}^{1/2}$
$= 2.398*10^{-10}$

$H_3PO_4 + H_2O \leftrightarrow H_2PO_4^- + H_3O^+$
$Ka_1 = 7.11*10^{-3} = [H_2PO_4^-][H_3O^+]/[H_3PO_4]$

$[H_3PO_4]/[H_2PO_4^-] = [H_3O^+]/Ka_1 = 2.40*10^{-10}/7.11*10^{-3}$
$= 3.37*10^{-8}$

9.20

a)
$H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$ pKa = 7.2

Therefore, I would use NaH_2PO_4 and Na_2HPO_4

b)

0.0500 M buffer at pH 7.2 (the pKa of the system) in 1 L of solution is needed. I need to add 0.0250 moles of each to a 1 liter flask.

$(2.50*10^{-2}$ mol $Na_2HPO_4/1)*(141.96$ g $Na_2HPO_4/1$ mol$) =$

3.55 g Na_2HPO_4

$(2.50*10^{-2}$ mol $NaH_2PO_4/1)*(119.98$ g $NaH_2PO_4/1$ mol$) =$
3.00 g NaH_2PO_4
c) Add 6.00 M NaOH dropwise until you reach the desired pH.
$7.45 = 7.2 + \log[(25+x)/(25-x)]$, $x = 7$ mmol required.
It should take about1.2 mL.

9-24
a) HA
b) A-
c) at pH 7, quotient = 1.00; at pH 6, quotient = 0.100; at pH = 8, quotient = 10.0

9-25
a) $pH = pKa_1 = 4.00$
b) $pH = pKa_2 = 8.00$
c) H_2A
d) HA^-
e) A^{-2}

9-26
a) $pKa = 14.00 - pKb = 9.00$
b) $pH = pKa = 9.00$
c) BH^+
d) $Ka = [B][H^+]/[BH^+]$, so
$[B]/[BH+] = Ka/[H+] = 10^{-9}/10^{-12} = 10^{-3}$

9-28

$\alpha_{HA} = [H^+]/([H^+]+Ka) = 10^{-5}/(10^{-4}+10^{-5}) = 0.0909$

$\alpha_{A-} = [Ka]/([H^+]+Ka) = 10^{-4}/(10^{-4}+10^{-5}) = 0.909$

$\alpha_{HA}/\alpha_{A-} = 0.100 = [HA]/[A^-]$
$Ka = [H_3O^+][A^-] / [HA]$
A little algebra and

$[HA]\ [A^-] = [H_3O^+]/ Ka = 10^{-5}/10^{-4} = 0.100$
The answers do match!!!!!

9.31

Using the fractional composition equation for a diprotic system derived on pg 255 of your book in conjunction with a spread sheet analysis this problem can be done in about 5 minutes using excel.

The answers in units of mol/L are

	1.00	1.19	6.00	6.33	10.00
α_{H2A}	0.89	0.500	$5.5*10^{-5}$	$1.9*10^{-5}$	$1.74*10^{-12}$
α_{HA}^-	0.110	0.500	0.682	0.500	2.14*10-4
α_A^{-2}	$5.10*10^{-7}$	$1.89*10^{-5}$	0.318	0.500	0.9998

9.32

$H_3A \leftrightarrow H_2A^- + H^+$ (K_1)
$H_2A^- \leftrightarrow HA^{2-} + H^+$ (K_2)
$HA^{2-} \leftrightarrow A^{3-} + H^+$ (K_2)

$K_1 = [H^+][H_2A^-]/[H_3A]$ → $[H_2A^-] =[H_3A]\{K_1/[H^+]\}$ (1)
$K_2 = [H^+][HA^{2-}]/[H_2A^-]$ → $[HA^{2-}] =[H_2A^-]\{K_2/[H^+]\}$ (2)
$K_3 = [H^+][A^{3-}]/[HA^{2-}]$ → $[A^{3-}] = [HA^{2-}]\{K_3/[H^+]\}$ (3)

Mass balance equation
$F = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}]$

First solve for the α_{H3A}. To do these we need to write expression that put the three other species in terms of H_3A.

We already have eq 1 $[H_2A^-] = [H_3A]\{K_1/[H^+]\}$

Now substitute this into eq 2 to get

$[HA^{2-}] = [H_3A]\{K_1K_2/[H^+]^2\}$

Substitute this into eq 3 to get

$[A^{3-}] = [H_3A]\{K_1K_2K_3/[H^+]^3\}$

Substitute these three new equations into the mass balance equation

$F = [H_3A] + [H_3A]\{K_1/[H^+]\} + [H_3A]\{K_1K_2/[H^+]^2\} + [H_3A]\{K_1K_2K_3/[H^+]^3\}$

$F = [H_3A]\ (1+ K_1/[H^+] + K_1K_2/[H^+]^2 + K_1K_2K_3/[H^+]^3)$

$F/[H_3A] = 1+ K_1/[H^+] + K_1K_2/[H^+]^2 + K_1K_2K_3/[H^+]^3$

Get a common denominator

$F/[H_3A] = ([H^+]^3+ [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3) / [H^+]^3$

Flip the numerator and denominator on both sides

$\alpha_{H3A} = [H_3A]/F = [H^+]^3/([H^+]^3+ [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3)$

Next I will solve for α_{H2A-}.. To do these we need to write expression that put the three other species in terms of H_2A-.

rearranging eq 1we get $[H_3A] = [H_2A^-]\{[H^+]/K_1\}$

eq 2 gives us the expression for HA^{2-}

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

Substitute this into eq 3 to get

$[A^{3-}] = [H_2A^-]\{K_2K_3/[H^+]^2\}$

Substitute these three new equations into the mass balance equation

$F = [H_2A^-]\{[H^+]/K_1\} + [H_2A^-] + [H_2A^-]\{K_2/[H^+]\} + [H_2A^-]\{K_2K_3/[H^+]^2\}$

$F = [H_2A^-]\ ([H^+]/K_1 + 1 + K_2/[H^+] + K_2K_3/[H^+]^2)$

$F/[H_2A^-] = [H^+]/K_1 + 1 + K_2/[H^+] + K_2K_3/[H^+]^2$

Get a common denominator

$F/[H_2A^-] = ([H^+]^3+ [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3) / K_1[H^+]^2$

Flip the numerator and denominator on both sides

$\alpha_{H2A-} = [H_2A^-]/F = (K_1[H^+]^2) / ([H^+]^3+ [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3)$

Next I will solve for α_{HA2-}.. To do these we need to write expression that put the three other species in terms of HA^{2-}.

Eq 3 gives us an expression for A^{-3} $[A^{3-}] = [HA^{2-}]\{K_3/[H^+]\}$

Rearrange eq 2 to get $[H_2A^-] = [HA^{2-}]\{[H^+]/K_2\}$

Rearrange eq 1 and substitute $[H_3A] = [HA^2]\{[H^+]^2/K_1K_2\}$

$F = [HA^2]\{[H^+]^2/K_1K_2\} + [HA^{2-}]\{[H^+]/K_2\} + [HA^{-2}] + [HA^{2-}]\{K_3/[H^+]\}$

$F = [HA^{-2}]\ ([H^+]^2/K_1K_2 + [H^+]/K_2 + 1 + K_3/[H^+])$

$F/[H_2A^-] = [H^+]^2/K_1K_2 + [H^+]/K_2 + 1 + K_3/[H^+]$

Get a common denominator

$F/[H_2A^-] = ([H^+]^3+ [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3) / K_1K_2[H^+]$

Flip the numerator and denominator on both sides

$\alpha_{HA2-} = [HA^{2-}]/F = (K_1K_2[H^+]) / ([H^+]^3+ [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3)$

Finally I will solve for α_{A3-}.. To do these we need to write expression that put the three other species in terms of HA^{2-}.

rearrange eq 3 to get $[HA^{2-}] = [A^{3-}]\{[H^+]/K_3\}$

Rearrange eq 2 and substitute $[H_2A^-] = [A^{3-}]\{[H^+]^2/K_2K_3\}$

Rearrange eq 1 and substitute $[H_3A] = [A^{3-}]\{[H^+]^3/K_1K_2K_3\}$

$F = [A^{3-}]\{[H^+]^3/K_1K_2K_3\} + [A^{3-}]\{[H^+]^2/K_2K_3\} + [A^{3-}]\{[H^+]/K_3\} + [A^{3-}]$

$F = [A^{-3}]\ ([H^+]^3/K_1K_2K_3 + [H^+]^2/K_2K_3 + [H^+]/K_3 + [A^{3-}])$

$F/[A^{3-}] = [H^+]^3/K_1K_2K_3 + [H^+]^2/K_2K_3 + [H^+]/K_3 + [A^{3-}]$
Get a common denominator

$F/[A^{3-}] = ([H^+]^3 + [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3) / K_1K_2K_3$

Flip the numerator and denominator on both sides

$\boldsymbol{\alpha_{A3-} = [A^{3-}]/F = (K_1K_2K_3) / ([H^+]^3 + [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3)}$

9.33

It does not matter what else is in solution, the alpha fraction is dictated by the $[H^+]$ and the Ka for the ammonia/ammonium monoprotic system.

$Ka(NH_4^+) = 5.69 \cdot 10^{-10}$
$[H^+] = 1.000 \cdot 10^{-9}$ M

$\alpha_{NH3} = (5.69 \cdot 10^{-10})/(5.69 \cdot 10^{-10} + 1.000 \cdot 10^{-9}) = 0.363$

9.40

Isoionic point is given by

$[H^+] = [(K_1K_2F+K_wK_1)/(K_1+F)]^{1/2} =$

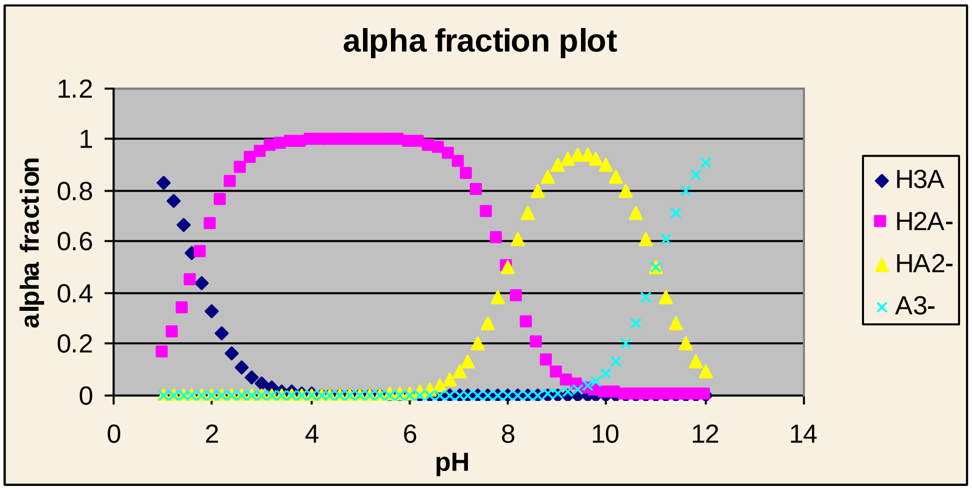
For a 0.010 M solution of threonine, $K_1 = 8.17 \cdot 10^{-3}$, $K_2 = 7.94 \cdot 10^{-10}$, and F = 0.010 M

$[H^+] = [(K_1K_2F+K_wK_1)/(K_1+F)]^{1/2} = 2.449 \cdot 10^{-6}$ M, pH = 5.61

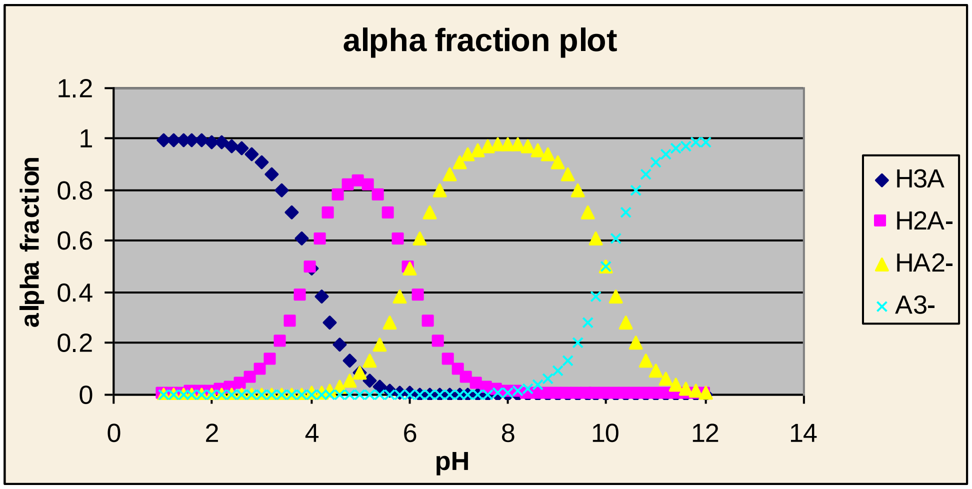
Isoelectric point = (Pka1+pKa2)/2 = 5.59

Alpha fraction plots for a triprotic system are shown below. Notice how (plot 1 and 3), when two dissociation constant are within 2 orders of magnitude, the alpha fraction for the corresponding intermediate species will never approach very close to 1. Also notice (plot 2) the strong weak acids (K>.001) and strong weak bases (Kb<.001), the alpha fraction of the principle species never reach 1. This is because dissociation is not negligible.

$K1 = 10^{-4}$
$K2 = 10^{-8}$
$K3 = 10^{-10}$



$K1 = 10^{-2}$
$K2 = 10^{-8}$
$K3 = 10^{-11}$



$K1 = 10^{-4}$
$K2 = 10^{-6}$
$K3 = 10^{-10}$