8.1) Write the proton transfer equilibria for the following acids in aqueous solution and identify the conjugate acid-base pairs in each one:

a) \( \text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) \)
   Acid     Base       c.a.        c.b

b) \( \text{HF}(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq}) \)
   Acid     Base       c.a.        c.b

c) \( \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_6\text{H}_5\text{NH}_2(\text{aq}) \)
   Acid     Base       c.a.        c.b

d) \( \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}) \)
   Acid     Base       c.a.        c.b

e) \( \text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq}) \)
   Acid     Base       c.a.        c.b

f) \( \text{NH}_2\text{NH}_3^+(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_2\text{NH}_2(\text{aq}) \)
   Acid     Base       c.a.        c.b

8.4) Suppose that something had gone wrong in the Big Bang, and instead of ordinary hydrogen there was an abundance of deuterium in the universe. There would be many subtle changes in equilibria, particularly the deuteron transfer equilibria of heavy atoms and bases. The \( K_w \) for heavy water at 25ºC is 1.35x10⁻¹⁵. (a) Write the chemical equation for the autoprotolysis of \( \text{D}_2\text{O} \). (b) Evaluate \( pK_w \) for \( \text{D}_2\text{O} \) at 25ºC. (c) Calculate the molar concentrations of \( \text{D}_3\text{O}^+ \) and \( \text{OD}^- \) in neutral heavy water at 25ºC. (d) Evaluate the pD and pOD of neutral heavy water at 25ºC. (e) Find the relation between pD, pOD, and \( pK_w(\text{D}_2\text{O}) \).

a) \( \text{D}_2\text{O}(l) + \text{D}_2\text{O}(l) \rightleftharpoons \text{D}_3\text{O}^+(\text{aq}) + \text{OD}^-\text{(aq)} \)

b) given that \( K_w = 1.35 \times 10^{-15} \), \( pK_w = -\log(1.35 \times 10^{-15}) = 14.87 \)

c) \( K_w = [\text{D}_3\text{O}^+][\text{OD}^-] \)
[D₃O⁺] = [OD⁻] = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8} \text{ M}

d) \quad pD = -\log[D₃O⁺] = -\log(3.67 \times 10^{-8}) = 7.44 \quad (\text{which} = pOD)

e) \quad K_w = [D₃O⁺][OD⁻] \quad \text{and taking the -log of both sides:}

-\log K_w = -\log[D₃O⁺] - \log[OD⁻] = pD + pOD = 14.87

8.8) (a) A sample of potassium acetate, KCH₃CO₂, of mass 8.4 g is used to prepare 250 mL of solution. What is the pH of the solution? (b) What is the pH of a solution when 3.75 g of ammonium bromide, NH₄Br, is used to make 100 mL of solution? (c) An aqueous solution of volume 1.0 L contains 10.0 g of potassium bromide. What is the percentage of Br⁻ ions that are protonated?

a) \quad 8.4 \text{ g of KCH₃CO₂} \times \frac{1 \text{ mole}}{59.05 + 39.10} = 0.08558 \text{ moles}

[CH₃CO₂⁻] = 0.08558 \text{ mol/0.25 L} = 0.3423 \text{ M}

Acetate ion is the conjugate base of a weak acid (acetic) and K⁺ is essentially neutral (conjugate acid of KOH), so the acetate ion will govern the pH of the solution through:

CH₃CO₂⁻(aq) + H₂O(l) ⇌ CH₃COOH + OH⁻(aq)

\( K_b \) for this equilibrium is found from Table 8.1 under acetic acid to be 5.6 \times 10^{-10}
(or we could get \( K_b \) from \( K_a \) using the fact that \( K_aK_b = K_w \))

\[
K_b = \frac{[\text{CH₃COOH}][\text{OH}^-]}{[\text{CH₃CO₂⁻}]} = \frac{x^2}{0.3423 - x}
\]

if \( x \ll 0.34 \), then \( K_b = \frac{x^2}{0.3423} \) and \( x = 1.38 \times 10^{-5} \text{ M} = [\text{OH}^-] \)

NOTE: 1.38 \times 10^{-5} really is much less than 0.34 – approximation was valid

So, \( pOH = -\log[\text{OH}^-] = 4.86 \)

pH = 14.00 – pOH = 9.14

b) 3.75 g of NH₄Br × \( \frac{1 \text{ mole}}{18.04 + 79.91} \) = 0.03828 moles

\[ [\text{NH}_4^+] = 0.03828 \text{ mol/0.10 L} = 0.3828 \text{ M} \]

Since NH₄⁺ is the conjugate acid of a weak base (NH₃) and Br⁻ is the conjugate base of a strong acid (HBr), the NH₄⁺ ion will govern the pH of the solution through:

\[ \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \]

The \( K_a \) for this acid equilibrium can be found from Table 8.1 under NH₃ (or obtained from \( K_b \) as indicated in part a)

\[ K_a = 5.6 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x^2}{0.3828 - x} \]

If \( x \ll 0.3828 \), then \( K_a = \frac{x^2}{0.3828} \) and \( x = [\text{H}_3\text{O}^+] = 1.46 \times 10^{-5} \text{ M} \)

NOTE: 1.46 \times 10^{-5} really is much less than 0.38

\( \text{pH} = –\log[\text{H}_3\text{O}^+] = 4.83 \)

c) 10.0 g of KBr

Br⁻ is the conjugate base of a strong acid (HBr) and hence \( K_b \sim 0 \) and the fraction that is protonated = 0

8.12) Calculate the pH, pOH, and fraction of solute protonated or deprotonated in the following aqueous solutions: (a) 0.120 M CH₃CH(OH)COOH(aq) (lactic acid), (b) 1.4 \times 10^{-4} \text{ M CH}_3\text{CH(OH)COOH(aq)}, (c) 0.10 \text{ M C}_6\text{H}_5\text{SO}_3\text{H(aq)} (benzenesulfonic acid).

a) 0.120 M HLac (Lactic acid)

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{Lac}^-]}{[\text{HLac}]} = \frac{x^2}{0.120 - x} \text{ where } K_a = 8.4 \times 10^{-4} \]
If $x << 0.12$, 

$$[\text{H}_3\text{O}^+] = \sqrt{0.120 K_a} = 0.010 \text{ M}$$

NOTE: this is only about 8% smaller than 0.12, hence the approximation is borderline (5% is the accepted cutoff point). But we’ll go with it.

pH = $-\log[\text{H}_3\text{O}^+] = 2.00$ (solving the quadratic yields a pH of 2.02)

pOH = 14.0 – pH = 12.0

fraction ionized = \frac{0.010}{0.120} = 0.083

\textbf{b)} 1.4 \times 10^{-4} \text{ M HLac}

as in part (a), if $x << 1.4 \times 10^{-4}$ then 

$$[\text{H}_3\text{O}^+] = \sqrt{1.4 \times 10^{-4} K_a} = 3.4 \times 10^{-4} \text{ M}$$

NOTE: the approximation is definitely not valid in this case. We have to solve the quadratic equation.

$$[\text{H}_3\text{O}^+] = \frac{-K_a \pm \sqrt{K_a^2 - 4(-1.4 \times 10^{-4})(K_a)}}{2} = 1.22 \times 10^{-4} \text{ M}$$

pH = 3.91

pOH = 10.09

fraction ionized = \frac{1.22 \times 10^{-4}}{1.4 \times 10^{-4}} = 0.87

\textbf{c)} 0.10 \text{ M C}_6\text{H}_5\text{SO}_3\text{H}

$K_a = 0.20$

Can we use our approximation? \( \sqrt{\frac{K_a}{[HA]_{initial}}} = 1.4 \), which is >> than 0.05

So back to the quadratic eqn.:

$$[\text{H}_3\text{O}^+] = \frac{-K_a \pm \sqrt{K_a^2 - 4(-0.10)(K_a)}}{2} = 0.073 \text{ M}$$

pH = 1.14

pOH = 12.86

fraction ionized = \frac{0.073}{0.10} = 0.73
8.17) The weak base colloquially known as Tris, and more precisely as tris(hydroxymethyl)aminomethane, has \( \text{pK}_a = 8.3 \) at 20\(^\circ\)C and is commonly used to produce a buffer for biochemical applications. At what pH would you expect Tris to act as a buffer in a solution that has equal molar concentrations of Tris and its conjugate acid?

The equilibrium is: \( \text{Tris} + \text{H}_2\text{O} \rightleftharpoons \text{TrisH}^+ + \text{OH}^- \)

and \( K_b = \frac{[\text{OH}^-][\text{TrisH}^+]}{[\text{Tris}]} \)

or taking \(-\log\) of both sides and rearranging:

\[
pOH = pK_b + \log \frac{[\text{TrisH}^+]}{[\text{Tris}]} 
\]

\[
pK_b = pK_w - pK_a = 14.00 - 8.3 = 5.7
\]

For the case when \([\text{Tris}] = [\text{TrisH}^+]\), \( pOH = pK_b = 5.7 \)

Thus, \( pH = 14 - pOH = 8.3 \)

8.21) A buffer solution of volume 100 mL consists of 0.10 M CH\(_3\)COOH(aq) and 0.10 M NaCH\(_3\)CO\(_2\)(aq). (a) What is its pH? (b) What is the pH after the addition of 3.3 mmol NaOH to the buffer solution? (c) What is the pH after the addition of 6.0 mmol HNO\(_3\) to the initial buffer solution?

For a 100 mL buffer solution that has \([\text{HAc}] = 0.10 \text{ M} \) and \([\text{NaAc}] = 0.10 \text{ M} \),

a) \( K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} \) for \( \text{HAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Ac}^- \)

or likewise, \( pH = pK_a - \log \frac{[\text{HAc}]}{[\text{Ac}^-]} \) where the \( pK_a \) of acetic acid = 4.75

\[
pH = 4.75 - \log \frac{0.10}{0.10} = 4.75
\]
b) add 0.033 moles of NaOH

initial moles of HAc : 0.10 M x 0.100 L = 0.01 moles HAc
initial moles of Ac\(^-\) : 0.10 M x 0.100 L = 0.01 moles of Ac\(^-\)

Addition of strong base will shift the equilibrium to the right:

\[
pH = 4.75 - \log \frac{0.01 - 0.0033}{0.01 + 0.0033} = 5.05
\]

(note that in the log term the volumes cancel out in the molar concentrations so that we can just use moles)

c) add 0.0060 moles of HNO\(_3\)

addition of strong acid will shift the equilibrium to the left:

\[
pH = 4.75 - \log \frac{0.01 + 0.0060}{0.01 - 0.0060} = 4.15
\]

8.24) Calculate the pH of (a) 0.15 M NH\(_4\)Cl(aq), (b) 0.15 M NaCH\(_3\)CO\(_2\)(aq), and (c) 0.150 M CH\(_3\)COOH(aq)

a) for a solution of 0.15 M NH\(_4\)Cl: \(\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3\)

\[
K_a = 5.6 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x^2}{0.15 - x}
\]

if \(x \ll 0.15\), \([\text{H}_3\text{O}^+] = \sqrt{0.15 K_a} = \sqrt{(0.15)(5.6 \times 10^{-10})} = 9.17 \times 10^{-6} \text{ M}
\]

(note approximation was valid)

\(\text{pH} = 5.04\)

b) for a solution of 0.15 M NaCH\(_3\)CO\(_2\):

\[
K_b = 5.6 \times 10^{-10} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.15 - x}
\]

if \(x \ll 0.15\), \([\text{OH}^-] = \sqrt{0.15 K_b} = \sqrt{(0.15)(5.6 \times 10^{-10})} = 9.17 \times 10^{-6} \text{ M}
\]

(note approximation was valid)

\(\text{pH} = 14.00 + \log[\text{OH}^-] = 8.96\)
c) for a solution of 0.150 M CH₃COOH (HAc):

As in part (a), \[ [\text{H}_3\text{O}^+] = \sqrt{0.150 K_a} = \sqrt{(0.150)(1.8 \times 10^{-5})} = 0.0016 \text{ M} \]
\[ \text{pH} = 2.78 \]

8.28) Write the expression for the solubility constants of the following compounds:

(a) AgI, (b) Hg₂S, (c) Fe(OH)₃, (d) Ag₂CrO₄.

a) \( \text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^- \); \( K_{sp} = [\text{Ag}^+][\text{I}^-] \)

b) \( \text{Hg}_2\text{S} \rightleftharpoons \text{Hg}_2^{2+} + \text{S}^{2-} \); \( K_{sp} = [\text{Hg}_2^{2+}][\text{S}^{2-}] \)

c) \( \text{Fe(OH)}_3 \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^- \); \( K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 \)

d) \( \text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-} \); \( K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \)

8.29) Use the data in Table 8.4 to estimate the molar solubilities of (a) BaSO₄, (b) Ag₂CrO₄, (c) Fe(OH)₃, (d) Hg₂SO₄ in water.

a) For the molar solubility of BaSO₄:
\( K_{sp} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \)
\[ S = \sqrt{1.1 \times 10^{-10}} = 1.0 \times 10^{-5} \text{ M} \]

b) \( \text{Ag}_2\text{CrO}_4 \quad K_{sp} = 9 \times 10^{-12} \) (Handbook of Chemistry and Physics)
\[ 9 \times 10^{-12} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (x)(2x)^2 = 4x^3 \]
\[ x = S = \left( \frac{9 \times 10^{-12}}{4} \right)^{1/3} = 1.3 \times 10^{-4} \text{ M} \]

c) \( \text{Fe(OH)}_3 \)
\[ K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 2.0 \times 10^{-39} = (x)(3x)^3 = 27x^4 \]
\[ x = S = \left( \frac{2.0 \times 10^{-39}}{27} \right)^{1/4} = 9.3 \times 10^{-11} \text{ M} \]

d) \( \text{Hg}_2\text{SO}_4 \quad K_{sp} \text{ unknown} \ldots. \)
8.31) Thermodynamic data can be used to predict the solubilities of compounds that would be very difficult to measure directly. Calculate the solubility of mercury(II) chloride in water at 25°C from standard Gibbs energies of formation.

\[ \text{HgCl}_2(s) \rightleftharpoons \text{Hg}^{2+}(aq) + 2\text{Cl}^-(aq) \]
\[ \Delta G^\circ_r = (164.40) + 2(-131.23) - (-178.6) = 80.54 \text{ kJ/mol} \]

\[ \Delta G^\circ_r = -RT \ln K \]
\[ K_{sp} = \frac{-\Delta G^\circ_r}{RT} = e^{\frac{80.54 \times 10^3}{(8.31451)(298)}} = 7.64 \times 10^{-15} \]

\[ K_{sp} = [\text{Hg}^{2+}][\text{Cl}^-]^2 = (x)(2x)^2 = 4x^3 \]
\[ x = S = \left( \frac{7.64 \times 10^{-15}}{4} \right)^{\frac{1}{3}} = 1.24 \times 10^{-5} \text{ M} \]

8.30) Use the data in Table 8.4 to estimate the solubility of each sparingly soluble substance in its respective solution: (a) silver bromide in 1.4x10^-3 M NaBr(aq), (b) magnesium carbonate in 1.1x10^-5 M Na_2CO_3(aq), (c) lead(II) sulfate in 0.10 M CaSO_4(aq), (d) nickel(II) hydroxide in 2.7x10^-5 M NiSO_4(aq).

a) AgBr in 1.4 x 10^-3 M NaBr
\[ K_{sp} = 7.7 \times 10^{-13} = [\text{Ag}^+][\text{Br}^-] \]
\[ = (x)(x + 1.4 \times 10^{-3}) \approx x (1.4 \times 10^{-3}) \]
\[ x = 7.7 \times 10^{-13}/1.4 \times 10^{-3} = 5.5 \times 10^{-10} \text{ M} \]

b) MgCO_3 in 1.1 x 10^-5 M Na_2CO_3
\[ K_{sp} = 1.0 \times 10^{-5} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] \]
1.0 \times 10^{-5} = (x) (x + 1.1 \times 10^{-5})

If \ x \gg 1.1 \times 10^{-5}, 1.0 \times 10^{-5} = x^2

x = 0.003 \text{ M} \quad \text{(which indeed is much larger than 1.1 \times 10^{-5})}

c) \ \text{PbSO}_4 \ \text{in 0.10 M CaSO}_4

K_{sp} = 1.6 \times 10^{-8} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] \approx (x)(0.10) \quad \text{(assuming} \ x \ll 0.10)

x = 1.6 \times 10^{-7} \text{ M}

d) \ \text{Ni(OH)}_2 \ \text{in 2.7 \times 10^{-5} M NiSO}_4

K_{sp} = 6.5 \times 10^{-18} = [\text{Ni}^{2+}][\text{OH}^-]^2 = (x + 2.7 \times 10^{-5})(2x)^2

\text{if} \ x \ll 2.7 \times 10^{-5}, \ 6.5 \times 10^{-18} = (2.7 \times 10^{-5})4x^2

x = 2.5 \times 10^{-7} \text{ M} \quad \text{(which is sufficiently less than 2.7 \times 10^{-5})}