Chem 338

Homework Set #8 solutions October 30, 2001

From Atkins: 8.1, 8.4, 8.8, 8.12, 8.17, 8.21, 8.24, 8.28, 8.29, 8.31 + 8.30

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

a) $H_2SO_4(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HSO_4^-(aq)$
Acid Base c.a. c.b

b) $HF(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + F^-(aq)$
Acid Base c.a. c.b

c) $C_6H_5NH_3^+(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + C_6H_5NH_2(aq)$
Acid Base c.a. c.b

d) $H_2PO_4^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HPO_4^{2-}(aq)$
Acid Base c.a. c.b

e) $HCOOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HCOO^-(aq)$
Acid Base c.a. c.b

f) $NH_2NH_3^+(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + NH_2NH_2(aq)$
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 equilbria of heavy atoms and bases. The K_w for heavy water at 25ºC is 1.35×10^{-15}. (a) Write the chemical equation for the autoprotolysis of D_2O. (b) Evaluate pK_w for D_2O at 25ºC. (c) Calculate the molar concentrations of D_3O^+ and OD^- in neutral heavy water at 25ºC. (d) Evalulate the pD and pOD of neutral heavy water at 25ºC. (e) Find the relation between pD, pOD, and $pK_w(D_2O)$.

a) $D_2O(l) + D_2O(l) \leftrightarrows D_3O^+(aq) + OD^-(aq)$

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

c) $K_w = [D_3O^+][OD^-]$

$[D_3O^+] = [OD^-] = \sqrt{1.35\times10^{-15}} = 3.67 \text{ x } 10^{-8}$ M

d) pD = –log$[D_3O^+]$ = –log(3.67 x 10^{-8}) = 7.44 (which = pOD)

e) $K_w = [D_3O^+][OD^-]$ and taking the –log of both sides:

$-\log K_w = -\log[D_3O^+] - \log[OD^-]$

pK_w = pD + pOD = 14.87

8.8) (a) A sample of potassium acetate, KCH_3CO_2, 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, NH_4Br, 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) $8.4 \text{ g of } KCH_3CO_2 \times \frac{1 \text{ mole}}{59.05 + 39.10} = 0.08558 \text{ moles}$

$[CH_3CO_2^-]$ = 0.08558 mol/0.25 L = 0.3423 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:

$CH_3CO_2^-(aq) + H_2O(l) \leftrightarrows CH_3COOH + OH^-(aq)$

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

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3CO_2^-]} = \frac{x^2}{0.3423 - x}$$

if $x << 0.34$, then $K_b = \frac{x^2}{0.3423}$ and x = 1.38 x 10^{-5} M = $[OH^-]$

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

So, pOH = –log$[OH^-]$ = 4.86

pH = 14.00 – pOH = 9.14

b) $3.75\ \text{g of } NH_4Br \times \dfrac{1\ \text{mole}}{18.04 + 79.91} = 0.03828\ \text{moles}$

$[NH_4^+] = 0.03828\ \text{mol}/0.10\ \text{L} = 0.3828\ \text{M}$

Since NH_4^+ is the conjugate acid of a weak base (NH_3) and Br^- is the conjugate base of a strong acid (HBr), the NH_4^+ ion will govern the pH of the solution through:

$NH_4^+(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + NH_3(aq)$

The K_a for this acid equilibrium can be found from Table 8.1 under NH_3 (or obtained from K_b as indicated in part a)

$$K_a = 5.6 \times 10^{-10} = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = \frac{x^2}{0.3828 - x}$$

if $x << 0.3828$, then $K_a = \dfrac{x^2}{0.3828}$ and $x = [H_3O^+] = 1.46 \times 10^{-5}$ M

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

$pH = -\log[H_3O^+] = 4.83$

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 $CH_3CH(OH)COOH(aq)$ (lactic acid), (b) 1.4×10^{-4} M $CH_3CH(OH)COOH(aq)$, (c) 0.10 M $C_6H_5SO_3H(aq)$ (benzenesulfonic acid).

a) 0..120 M HLac (Lactic acid)

$$K_a = \frac{[H_3O^+][Lac^-]}{[HLac]} = \frac{x^2}{0.120 - x} \qquad \text{where } K_a = 8.4 \times 10^{-4}$$

If $x << 0.12$, $[H_3O^+] = \sqrt{0.120 K_a}$ = 0.010 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[H_3O^+] = 2.00 (solving the quadratic yields a pH of 2.02)

pOH = 14.0 – pH = 12.0

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

b) 1.4 x 10^{-4} M HLac

as in part (a), if $x << 1.4 \times 10^{-4}$ then $[H_3O^+] = \sqrt{1.4 \times 10^{-4} K_a}$ = 3.4 x 10^{-4} M

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

$$[H_3O^+] = \frac{-K_a \pm \sqrt{K_a{}^2 - 4(-1.4 \times 10^{-4})(K_a)}}{2} = 1.22 \times 10^{-4} \text{ M}$$

pH = 3.91

pOH = 10.09

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

c) 0.10 M $C_6H_5SO_3H$ K_a = 0.20

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

So back to the quadratic eqn.:

$$[H_3O^+] = \frac{-K_a \pm \sqrt{K_a{}^2 - 4(-0.10)(K_a)}}{2} = 0.073 \text{ M}$$

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 pK_a=8.3 at 20ºC 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: $\text{Tris} + H_2O \leftrightarrows \text{TrisH}^+ + OH^-$

and $K_b = \dfrac{[OH^-][\text{TrisH}^+]}{[\text{Tris}]}$

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_3COOH(aq) and 0.10 M $NaCH_3CO_2$(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 [HAc]=0.10 M and [NaAc]=0.10 M,

a) $K_a = \dfrac{[H_3O^+][Ac^-]}{[HAc]}$ for $HAc + H_2O \leftrightarrows H_3O^+ + Ac^-$

or likewise, $pH = pK_a - \log\dfrac{[HAc]}{[Ac^-]}$ 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_4Cl(aq), (b) 0.15 M $NaCH_3CO_2$(aq), and (c) 0.150 M CH_3COOH(aq)

a) for a solution of 0.15 M NH_4Cl: $NH_4^+ + H_2O \leftrightarrows H_3O^+ + NH_3$

$$K_a = 5.6\times10^{-10} = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = \frac{x^2}{0.15 - x}$$

if $x << 0.15$, $[H_3O^+] = \sqrt{0.15K_a} = \sqrt{(0.15)(5.6\times10^{-10})} = 9.17\times10^{-6}$ M

(note approximation was valid)

pH = 5.04

b) for a solution of 0.15 M $NaCH_3CO_2$:

$$K_b = 5.6\times10^{-10} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{x^2}{0.15 - x}$$

if $x << 0.15$, $[OH^-] = \sqrt{0.15K_b} = \sqrt{(0.15)(5.6\times10^{-10})} = 9.17\times10^{-6}$ M

(note approximation was valid)

pH = 14.00 + log[OH^-] = 8.96

c) for a solution of 0.150 M CH_3COOH (HAc):

As in part (a), $[H_3O^+] = \sqrt{0.150 K_a} = \sqrt{(0.150)(1.8\times10^{-5})} = 0.0016$ M

pH = 2.78

8.28) Write the expression for the solubility constants of the following compounds: (a) AgI, (b) Hg_2S, (c) $Fe(OH)_3$, (d) Ag_2CrO_4.

a) $AgI \leftrightarrows Ag^+ + I^-$; $K_{sp} = [Ag^+][I^-]$

b) $Hg_2S \leftrightarrows Hg_2^{2+} + S^{2-}$; $K_{sp} = [Hg_2^{2+}][S^{2-}]$

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

d) $Ag_2CrO_4 \leftrightarrows 2Ag^+ + CrO_4^{2-}$; $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

8.29) Use the data in Table 8.4 to estimate the molar solubilities of (a) $BaSO_4$, (b) Ag_2CrO_4, (c) $Fe(OH)_3$, (d) Hg_2SO_4 in water.

a) For the molar solubility of $BaSO_4$:

$K_{sp} = 1.1 \text{ x } 10^{-10} = [Ba^{2+}][SO_4^{2-}]$

$S = \sqrt{1.1\times10^{-10}} = 1.0\times10^{-5}$ M

b) Ag_2CrO_4 $K_{sp} = 9 \text{ x } 10^{-12}$ (Handbook of Chemistry and Physics)

$9 \text{ x } 10^{-12} = [Ag^+]^2[CrO_4^{2-}] = (x)(2x)^2 = 4x^3$

$$x = S = \left(\frac{9\times10^{-12}}{4}\right)^{1/3} = 1.3\times10^{-4} \text{ M}$$

c) $Fe(OH)_3$

$K_{sp} = [Fe^{3+}][OH^-]^3 = 2.0 \text{ x } 10^{-39} = (x)(3x)^3 = 27x^4$

$$x = S = \left(\frac{2.0\times10^{-39}}{27}\right)^{1/4} = 9.3\times10^{-11} \text{ M}$$

d) Hg_2SO_4 K_{sp} unknown…..

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 25ºC from standard Gibbs energies of formation.

$HgCl_2(s) \leftrightarrows Hg^{2+}(aq) + 2Cl^-(aq)$

$$\Delta G_r^o = (164.40) + 2(-131.23) - (-178.6) = 80.54 \text{ kJ/mol}$$

$$\Delta G_r^o = -RT \ln K$$

$$K_{sp} = K = e^{\frac{-\Delta G_r^o}{RT}} = e^{\frac{-80.54\times10^3}{(8.31451)(298)}} = 7.64\times10^{-15}$$

$K_{sp} = [Hg^{2+}][Cl^-]^2 = (x)(2x)^2 = 4x^3$

$$x = S = \left(\frac{7.64\times10^{-15}}{4}\right)^{1/3} = 1.24\times10^{-5} \text{ M}$$

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 $1.4\text{x}10^{-3}$ M NaBr(aq), (b) magnesium carbonate in $1.1\text{x}10^{-5}$ M Na_2CO_3(aq), (c) lead(II) sulfate in 0.10 M $CaSO_4$(aq), (d) nickel(II) hydroxide in $2.7\text{x}10^{-5}$ M $NiSO_4$(aq).

a) AgBr in 1.4×10^{-3} M NaBr

$K_{sp} = 7.7 \times 10^{-13} = [Ag^+][Br^-]$

$= (x)(x + 1.4 \times 10^{-3})$

$\approx x\ (1.4 \times 10^{-3})$

$x = 7.7 \times 10^{-13}/1.4 \times 10^{-3} = 5.5 \times 10^{-10}$ M

b) $MgCO_3$ in 1.1×10^{-5} M Na_2CO_3

$K_{sp} = 1.0 \times 10^{-5} = [Mg^{2+}][CO_3^{2-}]$

$1.0 \times 10^{-5} = (x)\ (x + 1.1 \times 10^{-5})$

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

$x = 0.003$ M (which indeed is much larger than 1.1×10^{-5})

c) $PbSO_4$ in 0.10 M $CaSO_4$

$K_{sp} = 1.6 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}] \approx (x)(0.10)$ (assuming $x << 0.10$)

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

d) $Ni(OH)_2$ in 2.7×10^{-5} M $NiSO_4$

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

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

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