Chapter 14

93) A 1.00 mol sample of CO₂ is heated to 1000. K with excess solid graphite in a container of volume 40.0 L. At 1000. K, K_c is 2.11x10⁻² for the reaction

 $C_{\text{graphite}} + CO_2(g) \iff 2 CO(g)$

a) What is the composition of the equilibrium mixture at 1000. K?

	CO_2	CO
Ι	1.00/40.0 L	0
С	-X	+2x
E	0.0250 - x	2x

$$K_{\rm c} = 2.11 \text{ x } 10^{-2} = \frac{[CO]^2}{[CO_2]} = \frac{(2x)^2}{0.0250 - x} = \frac{4x^2}{0.0250 - x}$$

 $0 = 4x^2 + 0.0211x - 0.0005275$ solve for x using quadratic equation

x = 0.009145

$$[CO] = 0.0183 \quad [CO_2] = 0.0159$$

b) If the volume of the flask is changed such that $[CO_2] = [CO]$, what is the volume of the new flask?

If $[CO_2] = [CO]$ then the following equality must hold true at equilibrium:

1.00 mol - x = 2x and x = 0.333

This would make it so there where $0.666 \text{ mol } \text{CO}_2$ and 0.666 mol CO.

$$K_c = 2.11x10^{-2} = \frac{\left(0.666M/xL\right)^2}{\left(0.666M/xL\right)} = \frac{0.666M}{xL}$$

x = 31.6 L

95 i and iii)

a) right, rightb) left, leftc) right, left

Chapter 16

7)

a) HNO₃(aq) + H₂O (l) ← H₃O⁺(aq) + NO₃⁻(aq) conjugate acid conjugate base
b) NH₄⁺(aq) + CN⁻(aq) ← NH₃(aq) + HCN(aq) conjugate base conjugate acid

9) Solution A has 100 times greater $[H_3O^+]$ than solution B

11)

a) HBr(aq) + H₂O (l)
$$\leftarrow \rightarrow$$
 H₃O⁺(aq) + Br⁻(aq)

- b) $CF_3COOH(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + CF_3COO^-(aq)$
- c) $HSO_4^{-}(aq) + H_2O(l) \leftrightarrow H_3O^{+}(aq) + SO_4^{-2}(aq)$
- d) HNO₂(aq) + H₂O (l) $\leftarrow \rightarrow$ H₃O⁺(aq) + NO₂⁻(aq)

15)

a)
$$H^{-}(aq) + H_2O(l) \leftrightarrow H_2(g) + OH^{-}(aq)$$

b)
$$HCO_3(aq) + H_2O(l) \leftrightarrow H_2O(l) + CO_2(g) + OH(aq)$$

c) NO₂(aq) + H₂O (l) $\leftarrow \rightarrow$ HNO₂(aq) + OH⁻(aq)

a)
$$H_2PO_4(aq) + HCO_3^-(aq) \leftrightarrow H_2O(1) + CO_2(aq) + HPO_4^-(aq)$$

acid base conjugate acid conjugate base
b) $NH_3(aq) + NH_2^-(aq) \leftrightarrow NH_2^-(aq) + NH_3(aq)$
acid base conjugate base conjugate acid
c) $HSO_4^-(aq) + CO_3^{-2}(aq) \leftrightarrow SO_4^{-2}(aq) + HCO_3^-(aq)$
acid base conjugate base conjugate acid

Note in this set of problems, HCO_3^- is serving as both a base (eq a) and a base (eq c). If you are perplexed about the fact that HCO_3^- decomposes when treated with acid to water and CO_2 , remember the Alka-Seltzer lab. The Alka-Seltzer is a source of HCO_3^- Vinegar (CH₃COOH) is an acid.

How could you look at the formula for H_2CO_3 and know that it would decompose into CO_2 and water? I don't think you could from first principles. However, watching the dramatic reaction will help you to remember this fact.

33)
$$pH = -log [H_3O^+]$$

 $[H_3O^+] = 5.0 \times 10^{-5} M$

47)

a) CH₃COOH(aq) + H₂O (l) $\leftarrow \rightarrow$ CH₃COO⁻(aq) + H₃O⁺(aq)

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

b) HCN(aq) + H₂O (l) $\leftarrow \rightarrow$ CN⁻(aq) + H₃O⁺(aq)

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

27)

c) $SO_3^{-2}(aq) + H_2O(l) \leftrightarrow OH^{-}(aq) + HSO_3^{-}(aq)$

$$K_{b} = \frac{[OH^{-}][HSO_{3}^{-}]}{[SO_{3}^{-}]}$$

d)
$$PO_4^{-3}(aq) + H_2O(l) \leftrightarrow OH^{-1}(aq) + HPO_4^{-2}(aq)$$

$$K_{b} = \frac{[OH^{-}][HPO4^{-2}]}{[PO_{4}^{-3}]}$$

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

$$K_{a} = \frac{[H_{3}O^{+}][NH_{3}]}{[NH_{4}^{+}]}$$

f) $H_2SO_4(aq) + H_2O(l) \leftrightarrow HSO_4(aq) + H_3O^+(aq)$

$$K_{a} = \frac{[H_{3}O^{+}][HSO_{4}^{-}]}{[H_{2}SO_{4}]}$$

49) For these problems, you need to look up the K_a value in Table 16.2. The large the value of Ka, the greater dissociation of the acid in water, the greater $[H_3O^+]$, and the more acidic the acid. In each example below, the more acidic acid is boxed.

- a) $H_2CO_3 = 4.2 \times 10^{-7}$ NH₄Cl = 5.6 x 10⁻¹⁰ b) HF = 7.2 x 10⁻⁴ KHSO₄ = 1.2 x 10⁻²
- c) NaHCO₃ = 4.8×10^{-11} Na₂HPO₄ = 3.6×10^{-13}
- d) $H_2S = 1 \times 10^{-7}$ HCN = 4.0 x 10^{-10}

53) 0.015 M cyanic acid as pH = 2.67. $2.67 = -\log[H_3O^+]$ $[H_3O^+] = 2.14 \times 10^{-3}$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(2.14x10^{-3})^2}{1.286x10^{-2}} = 3.58x10^{-4}$$

65) 0.650 g aspirin = 0.650g/180.16 g/mol = 0.00361 mols

0.00361 mol/0.200 L = 0.01804 M and
$$K_a = 3.27 \times 10^{-4}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{0.01804 - x} = 3.27x10^{-4}$$

solving quadratic equation x = 0.00227

$$pH = -log(0.00227) = 2.6$$

69)

a) $H_2O(1) + HNO_3(aq) \leftrightarrow H_3O^+(aq) + NO_3^-(aq) K_a=20$

For a 1 M solution the HNO₃ would be ~95% dissociated. The reaction favors products.

b)
$$H_3PO_4(aq) + H_2O(l) \leftrightarrow H_2PO4(aq) + H_3O^+(aq) = K_a = 7.5 \times 10^{-3}$$

For a 1 M solution the H_3PO_4 would be ~8% dissociated. The reaction favors reactants.

c) CN-(aq) + HCl(aq)
$$\leftarrow \rightarrow$$
 Cl-(aq) + HCN(aq)

HCl K _a =large	HCN K_{a} = 4.0 x 10 ⁻¹⁰
$CN^{-}K_{b}=2.5 \times 10^{-5}$	$Cl^{-}K_{b}$ = very small

The left side of this equation contains the stronger acid and the stronger base. This means the reaction will lie strongly to products.

d) $NH_4^+(aq) + F(aq) \leftrightarrow NH_3(aq) + HF(aq)$

$NH_4^+ K_a = 5.6 \times 10^{-10}$	HF $K_a = 7.2 \times 10^{-4}$
$F K_b = 1.4 \times 10^{-11}$	$NH_3 K_b = 1.8 \times 10^{-5}$

The right side of this equation contains the stronger acid and the stronger base. This means the reaction will lie strongly to reactants.