## Chapter 14

93) A 1.00 mol sample of $\mathrm{CO}_{2}$ is heated to 1000 . K with excess solid graphite in a container of volume 40.0 L . At $1000 \mathrm{~K}, K_{\mathrm{c}}$ is $2.11 \times 10^{-2}$ for the reaction

$$
\mathrm{C}_{\text {graphite }}+\mathrm{CO}_{2} \cdot(\mathrm{~g}) \leftarrow \rightarrow 2 \mathrm{CO}(\mathrm{~g})
$$

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

|  | $\mathrm{CO}_{2}$ | CO |
| :---: | :---: | :---: |
| I | $1.00 / 40.0 \mathrm{~L}$ | 0 |
| C | -x | +2 x |
| E | $0.0250-\mathrm{x}$ | 2 x |

$K_{\mathrm{c}}=2.11 \times 10^{-2}=\frac{[\mathrm{CO}]^{2}}{\left[\mathrm{CO}_{2}\right]}=\frac{(2 x)^{2}}{0.0250-x}=\frac{4 x^{2}}{0.0250-x}$
$0=4 x^{2}+0.0211 x-0.0005275$ solve for $x$ using quadratic equation
$x=0.009145$
$[\mathrm{CO}]=0.0183 \quad\left[\mathrm{CO}_{2}\right]=0.0159$
b) If the volume of the flask is changed such that $\left[\mathrm{CO}_{2}\right]=[\mathrm{CO}]$, what is the volume of the new flask?

If $\left[\mathrm{CO}_{2}\right]=[\mathrm{CO}]$ then the following equality must hold true at equilibrium:
$1.00 \mathrm{~mol}-\mathrm{x}=2 \mathrm{x}$ and $\mathrm{x}=0.333$
This would make it so there where $0.666 \mathrm{~mol} \mathrm{CO}_{2}$ and 0.666 mol CO .
$K_{c}=2.11 \times 10^{-2}=\frac{(0.666 M / x L)^{2}}{(0.666 M / x L)}=\frac{0.666 M}{x L}$
$x=31.6 \mathrm{~L}$

95 i and iii)
a) right, right
b) left, left
c) right, left

## Chapter 16

## 7)

a) $\mathrm{HNO}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NO}_{3}{ }^{-}(\mathrm{aq})$ acid base conjugate acid conjugate base
b) $\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{CN}^{-}(\mathrm{aq}) \quad \longleftrightarrow \mathrm{NH}_{3}(\mathrm{aq})+\operatorname{HCN}(\mathrm{aq})$ acid base conjugate base conjugate acid
9) Solution A has 100 times greater $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$than solution B
11)
a) $\operatorname{HBr}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq})$
b) $\mathrm{CF}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftarrow \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CF}_{3} \mathrm{COO}^{-}(\mathrm{aq})$
c) $\mathrm{HSO}_{4}{ }^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{SO}_{4}^{-2}(\mathrm{aq})$
d) $\mathrm{HNO}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NO}_{2}{ }^{-}(\mathrm{aq})$
15)
a) $\mathrm{H}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightarrow \mathrm{H}_{2}(\mathrm{~g})+\mathrm{OH}^{-}(\mathrm{aq})$
b) $\mathrm{HCO}_{3}{ }^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightarrow \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{OH}^{-}(\mathrm{aq})$
c) $\mathrm{NO}_{2}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \rightarrow \mathrm{HNO}_{2}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
27)
a) $\mathrm{H}_{2} \mathrm{PO}_{4}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq}) \quad \leftarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{CO}_{2}(\mathrm{aq})+\mathrm{HPO}_{4}^{-}(\mathrm{aq})$ acid base conjugate acid conjugate base
b) $\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{NH}_{2}^{-}(\mathrm{aq}) \quad \longleftrightarrow \mathrm{NH}_{2}{ }^{-}(\mathrm{aq})+\mathrm{NH}_{3}(\mathrm{aq})$
acid base conjugate base conjugate acid
c) $\mathrm{HSO}_{4}^{-}(\mathrm{aq})+\mathrm{CO}_{3}^{-2}(\mathrm{aq}) \longleftrightarrow \mathrm{SO}_{4}^{-2}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})$
acid base conjugate base conjugate acid

Note in this set of problems, $\mathrm{HCO}_{3}{ }^{-}$is serving as both a base (eq a) and a base (eq c). If you are perplexed about the fact that $\mathrm{HCO}_{3}{ }^{-}$decomposes when treated with acid to water and $\mathrm{CO}_{2}$, remember the Alka-Seltzer lab. The Alka-Seltzer is a source of $\mathrm{HCO}_{3}{ }^{-}$ Vinegar $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ is an acid.
How could you look at the formula for $\mathrm{H}_{2} \mathrm{CO}_{3}$ and know that it would decompose into $\mathrm{CO}_{2}$ and water? I don't think you could from first principles. However, watching the dramatic reaction will help you to remember this fact.
33) $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.0 \times 10^{-5} \mathrm{M}
$$

47) 

a) $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftarrow \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

b) $\mathrm{HCN}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \mathrm{CN}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CN}^{-}\right]}{[\mathrm{HCN}]}$
c) $\mathrm{SO}_{3}^{-2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightarrow \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{HSO}_{3}^{-}(\mathrm{aq})$
$K_{b}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HSO}_{3}{ }^{-}\right]}{\left[\mathrm{SO}_{3}^{-}\right]}$
d) $\mathrm{PO}_{4}^{-3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{HPO}_{4}^{-2}(\mathrm{aq})$
$K_{b}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HPO}^{-2}\right]}{\left[\mathrm{PO}_{4}^{-3}\right]}$
e) $\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{NH}_{4}{ }^{+}\right]}$
f) $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftrightarrow \mathrm{HSO}_{4}{ }^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HSO}_{4}{ }^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]}$
49) For these problems, you need to look up the $K_{\mathrm{a}}$ value in Table 16.2. The large the value of Ka, the greater dissociation of the acid in water, the greater $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, and the more acidic the acid. In each example below, the more acidic acid is boxed.
a) $\mathrm{H}_{2} \mathrm{CO}_{3}=4.2 \times 10^{-7} \quad \mathrm{NH}_{4} \mathrm{Cl}=5.6 \times 10^{-10}$
b) $\mathrm{HF}=7.2 \times 10^{-4}$
$\mathrm{KHSO}_{4}=1.2 \times 10^{-2}$
c) $\mathrm{NaHCO}_{3}=4.8 \times 10^{-11}$
$\mathrm{Na}_{2} \mathrm{HPO}_{4}=3.6 \times 10^{-13}$
d) $\mathrm{H}_{2} \mathrm{~S}=1 \times 10^{-7}$
$\mathrm{HCN}=4.0 \times 10^{-10}$
53) 0.015 M cyanic acid as $\mathrm{pH}=2.67 . \quad 2.67=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=2.14 \times 10^{-3}$
$K_{a}=\frac{\left[H_{3} O^{+}\right]\left[A^{-}\right]}{[H A]}=\frac{\left(2.14 \times 10^{-3}\right)^{2}}{1.286 \times 10^{-2}}=3.58 \times 10^{-4}$
65) 0.650 g aspirin $=0.650 \mathrm{~g} / 180.16 \mathrm{~g} / \mathrm{mol}=0.00361 \mathrm{mols}$

$$
0.00361 \mathrm{~mol} / 0.200 \mathrm{~L}=0.01804 \mathrm{M} \text { and } K_{\mathrm{a}}=3.27 \times 10^{-4}
$$

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[H A]}=\frac{x^{2}}{0.01804-x}=3.27 \times 10^{-4}
$$

solving quadratic equation $x=0.00227$

$$
\mathrm{pH}=-\log (0.00227)=2.6
$$

69) 

a) $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{HNO}_{3}(\mathrm{aq}) \longleftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NO}_{3}{ }^{-}(\mathrm{aq}) \quad K_{\mathrm{a}}=20$

For a 1 M solution the $\mathrm{HNO}_{3}$ would be $\sim 95 \%$ dissociated. The reaction favors products.
b) $\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longleftrightarrow \mathrm{H}_{2} \mathrm{PO} 4-(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \quad K_{\mathrm{a}}=7.5 \times 10^{-3}$

For a 1 M solution the $\mathrm{H}_{3} \mathrm{PO}_{4}$ would be $\sim 8 \%$ dissociated. The reaction favors reactants.
c) $\mathrm{CN}-(\mathrm{aq})+\mathrm{HCl}(\mathrm{aq}) \longleftrightarrow \mathrm{Cl}-(\mathrm{aq})+\mathrm{HCN}(\mathrm{aq})$
$\mathrm{HCl} K_{\mathrm{a}}=$ =large
HCN $K_{\mathrm{a}}=4.0 \times 10^{-10}$
$\mathrm{CN}^{-} K_{\mathrm{b}}=2.5 \times 10^{-5}$
$\mathrm{Cl}^{-} K_{\mathrm{b}}=$ 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) $\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{F}^{-}(\mathrm{aq}) \longleftrightarrow \rightarrow \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{HF}(\mathrm{aq})$
$\mathrm{NH}_{4}{ }^{+} K_{\mathrm{a}}=5.6 \times 10^{-10}$
HF $K_{\mathrm{a}}=7.2 \times 10^{-4}$
$\mathrm{F}^{-} K_{b}=1.4 \times 10^{-11}$
$\mathrm{NH}_{3} K_{b}=1.8 \times 10^{-5}$

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

