14.8 Write equilibrium constant expressions, for $K_C$ and for $K_p$, for the following processes:

(d) $\text{H}_2\text{O} (g) + \text{C} (s) \rightleftharpoons \text{CO} (g) + \text{H}_2 (g)$  

Given

$K_C = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$; $K_P = \frac{P_{\text{CO}}P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$

14.15 Given $K_C = 4.17 \times 10^{-34}$ for the reaction $2\text{HCl} (g) \rightleftharpoons \text{H}_2 (g) + \text{Cl}_2 (g)$, what is the equilibrium constant for the reaction, $\text{H}_2 (g) + \text{Cl}_2 (g) \rightleftharpoons 2\text{HCl} (g)$?

The second reaction is merely the reverse of the first, so:

$K_C' = K_C^{-1} = (4.17 \times 10^{-34})^{-1} = 2.40 \times 10^{33}$

14.20 A reaction vessel contains $\text{NH}_3$, $\text{N}_2$, and $\text{H}_2$ at equilibrium at a certain temperature. The equilibrium concentrations are $[\text{NH}_3] = 0.25 \text{ M}$, $[\text{N}_2] = 0.11 \text{ M}$, and $[\text{H}_2] = 1.91 \text{ M}$. Calculate the equilibrium constant $K_C$ for the synthesis of ammonia when the reaction is represented by each of the following chemical equations:

(a) $\text{N}_2 (g) + 3\text{H}_2 (g) \rightleftharpoons 2\text{NH}_3 (g)$;  

(b) $\frac{1}{2} \text{N}_2 (g) + \frac{3}{2} \text{H}_2 (g) \rightleftharpoons \text{NH}_3 (g)$;

- $K_C' = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.25)^2}{(0.11)(1.91)^3} = 0.082$
- $K_C' = \frac{[\text{NH}_3]}{[\text{N}_2]^\frac{1}{2}[\text{H}_2]^\frac{3}{2}} = \frac{(0.25)}{(0.11)^\frac{1}{2}(1.91)^\frac{3}{2}} = 0.29$

Note: Notice that $K_C'_{for\ b} = (K_C'_{for\ a})^\frac{1}{3}$

14.22 At equilibrium, the pressure of the reacting mixture, $\text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g)$ is 0.105 atm at 350°C. Calculate $K_P$ and $K_C$ for this reaction.

*Hint: Convert Pressure to Molarity (using $PV=nRT$) to get $K_C$.*

$K_P = P_{\text{CO}_2} = 0.105$  

(Remember, solids are not included in expression.)

For $K_C$, need $[\text{CO}_2] = \frac{n}{V} = \frac{P}{RT} = \frac{0.105 \text{ atm}}{0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 623 \text{ K}} = 2.05 \times 10^{-3} \text{ M}$

$K_C = [\text{CO}_2] = 2.05 \times 10^{-3}$

14.24 Given $\text{NH}_4\text{CO}_2\text{NH}_2 (s) \rightleftharpoons 2 \text{NH}_3 (g) + \text{CO}_2 (g)$; at 40°C the solid decomposes to give $P_{\text{total}} = 0.363 \text{ atm}$. Calculate $K_P$ for the reaction.

The total pressure in the flask (0.363 atm) is a sum of the partial pressures of $\text{NH}_3$ and $\text{CO}_2$.

$P_T = P_{\text{NH}_3} + P_{\text{CO}_2} = 0.363 \text{ atm}$

If $P_{\text{CO}_2} = x$, $P_{\text{NH}_3} = 2P_{\text{CO}_2} = 2x$, setting the partial pressures equal to the total pressure,

$P_T = P_{\text{NH}_3} + P_{\text{CO}_2}$

$P_T = 2x + x = 3x = 0.363 \text{ atm}$

$x = P_{\text{CO}_2} = 0.121 \text{ atm}$ and $P_{\text{NH}_3} = 2x = 0.242 \text{ atm}$

$K_P = P_{\text{NH}_3}^2P_{\text{CO}_2} = (0.242)(0.121) = 7.09 \times 10^{-3}$
14.30 Given the following equilibrium constants for oxalic acid at 25°C:

\[
\text{C}_2\text{H}_2\text{O}_4 \text{(aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{C}_2\text{HO}_4^- \text{(aq)} \quad K_{c,1} = \frac{[\text{H}^+][\text{C}_2\text{HO}_4^-]}{[\text{C}_2\text{H}_2\text{O}_4]} = 6.5 \times 10^{-2}
\]

\[
\text{C}_2\text{HO}_4^- \text{(aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{C}_2\text{O}_4^{2-} \text{(aq)} \quad K_{c,2} = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{C}_2\text{HO}_4^-]} = 6.1 \times 10^{-5}
\]

Calculate the equilibrium constant for the following reaction at the same temperature:

\[
\text{C}_2\text{H}_2\text{O}_4 \text{(aq)} \rightleftharpoons 2 \text{H}^+ \text{(aq)} + \text{C}_2\text{O}_4^{2-} \text{(aq)}
\]

\[
K_c = \frac{[\text{H}^+]^2[\text{C}_2\text{O}_4^{2-}]}{[\text{C}_2\text{H}_2\text{O}_4]} = K_{c,1} \times K_{c,2}
\]

\[
K_c = (6.5 \times 10^{-2})(6.1 \times 10^{-5}) = 4.0 \times 10^{-6}
\]

14.32 At a certain temperature, the following reactions have the constants shown:

\[
\text{S(s) + O}_2\text{(g)} \rightleftharpoons \text{SO}_2\text{(g)} \quad K'_c = 4.2 \times 10^{52}
\]

\[
2\text{S(s)} + 3\text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)} \quad K''_c = 9.8 \times 10^{128}
\]

Calculate \(K_c\) for the following reaction at that same temperature:

\[
2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}
\]

To have \(2\text{SO}_2\) as a reactant in the final equation, reverse the first equation and multiply by two. For the equilibrium, \(2\text{SO}_2\text{(g)} \rightleftharpoons 2\text{S(s)} + 2\text{O}_2\text{(g)}\), then \(K''_c\) is the reciprocal of the square \(K'_c\):

\[
K''_c = (K'_c)^{-2} = (4.2 \times 10^{52})^{-2} = 5.7 \times 10^{-106}
\]

Now we can add the above equation to the second equation to obtain the final equation. Since we add the two equations, the equilibrium constant is the product of the equilibrium constants for the two reactions.

\[
2\text{SO}_2\text{(g)} \rightleftharpoons 2\text{S(s)} + 2\text{O}_2\text{(g)} \quad K''_c = 5.7 \times 10^{-106}
\]

\[
2\text{S(s)} + 3\text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)} \quad K''_c = 9.8 \times 10^{128}
\]

\[
2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)} \quad K_c = K''_c \times K''_c = 5.6 \times 10^{31}
\]

14.36 Consider the following reaction, which takes place in a single elementary step:

\[
2\text{A} + \text{B} \xrightleftharpoons[k_f]{k_r} \text{A}_2\text{B}
\]

If \(K_c = 12.6\) at a certain temperature and \(k_r = 5.1 \times 10^{-2} \text{ s}^{-1}\), calculate the value of \(k_f\).

\[
K_c = \frac{k_f}{k_r} = \frac{k_f}{5.1 \times 10^{-2}} = 12.6
\]

\[
k_f = (12.6)(5.1 \times 10^{-2}) = 0.64
\]

The forward reaction is third order overall, so the units of \(k_f\) must be:

\[
\text{rate} = k_f[\text{A}]^2[\text{B}]; \quad k_f = \frac{\text{rate}}{\text{(concentration)}^3} = \frac{\text{M/s}}{\text{M}^3} = 1/ \text{M}^2 \cdot \text{s}; \quad k_f = 0.64 \text{ M}^2 \cdot \text{s}^{-1}
\]