Answers to Study Questions and Problems

1. a. \( K = \frac{[\text{NO}_2]^4}{[\text{NH}_3]^4[\text{O}_2]^7} \)  
   \( \text{H}_2\text{O}(l) \) is a liquid and therefore not included.

b. \( K = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} \)  
   \( \text{H}_2\text{O}(l) \) is the solvent and is not included.

c. \( K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \)

d. \( K = [\text{CO}_2] \)  
   \( \text{CaCO}_3(s) \) and \( \text{CaO}(s) \) are not included.

e. \( K = \frac{[\text{O}_3]^2}{[\text{O}_2]^3} \)

f. \( K = [\text{H}_3\text{O}^+][\text{OH}^-] \)  
   \( \text{H}_2\text{O}(l) \) is the solvent and is not included.

g. \( K = \frac{[\text{Zn}^{2+}]^3}{[\text{Fe}^{3+}]^2} \)  
   \( \text{Zn}(s) \) and \( \text{Fe}(s) \) are not included.
2. 
   a. \[ 2\text{N}_2\text{O}(g) + 3\text{O}_2(g) \rightleftharpoons 4\text{NO}_2(g) \]
      \[ K_1 = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}]^2[\text{O}_2]^3} \]
   b. \[ \text{N}_2\text{O}(g) + \frac{3}{2} \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \]
      \[ K_2 = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}][\text{O}_2]^{3/2}} \]
   c. \[ 4\text{NO}_2(g) \rightleftharpoons 2\text{N}_2\text{O}(g) + 3\text{O}_2(g) \]
      \[ K_3 = \frac{[\text{N}_2\text{O}]^2[\text{O}_2]^{3/2}}{[\text{NO}_2]^4} \]
      \[ K_1 = (K_2)^2 \text{ and } K_1 = (K_3)^{-1} \text{ and } K_2 = (K_3)^{-1/2} \]

3. \[ K = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{(0.5 \times 3.0)}{(1.5 \times 2.5)} = 0.40 \]

4. \[ \text{Cl}_2(g) \rightleftharpoons 2\text{Cl}(g) \]
   \[ K_c = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} \text{ and } K_p = \frac{P_{\text{Cl}}^2}{P_{\text{Cl}_2}} \]
   \[ K_p = K_c(RT)^\Delta n = 0.55 \times 0.08206 \times 3273K = 1.48 \times 10^2 = \frac{P_{\text{Cl}}^2}{P_{\text{Cl}_2}} \]
   and therefore \[ P_{\text{Cl}} = 14.9 \text{ atm} \]

5. 
<table>
<thead>
<tr>
<th>I</th>
<th>H_2(g) + I_2(g) \rightleftharpoons 2\text{HI}(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Initial</td>
</tr>
<tr>
<td></td>
<td>0.25  0.25  0.375</td>
</tr>
<tr>
<td>E</td>
<td>Change</td>
</tr>
<tr>
<td></td>
<td>+x    +x   -2x</td>
</tr>
<tr>
<td>E</td>
<td>Equilibrium</td>
</tr>
<tr>
<td></td>
<td>0.25+x 0.25+x 0.375-2x</td>
</tr>
</tbody>
</table>

   \[ K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.375-2x)^2}{(0.25+x)(0.25+x)} = 2.0 \times 10^{-2} \]

   \[ (0.375-2x) = (0.25+x) \times 0.1414 \text{ so } x = 0.159 \]

   the equilibrium concentrations are:
   \[ [\text{H}_2] = 0.41 \text{ moles liter}^{-1} \]
   \[ [\text{I}_2] = 0.41 \text{ moles liter}^{-1} \]
   \[ [\text{HI}] = 0.058 \text{ moles liter}^{-1} \]

6. The equilibrium constant for the combination of two successive equilibria is the product of the equilibrium constants for the two steps.
   \[ K_c = K_{c1} \times K_{c2} \]

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An increase of one mole of gas

Remember always to use concentrations (or partial pressures). Convert amounts given in moles to concentrations by dividing by the volume.

Remember that the change is always in the stoichiometric ratio.

If you don't know which way the system will move, just choose a direction arbitrarily, then see if x turns out to be negative or positive.

Look out for the opportunity to take the square root of both sides—it avoids the quadratic.
Don't make problems like these more complicated than they have to be: there's no need for any algebra in this problem.

If 0.30 moles of \( \text{CCl}_4 \) are formed, then the changes in the other concentrations can be calculated directly from the stoichiometry.

Remember always to use concentrations (or partial pressures).
Convert amounts given in moles to concentrations by dividing by the volume.

Note that \( \text{C(s)} \) is not included in the equilibrium expression! However, it is sometimes useful to include the quantities in the table—just in case there's any likelihood of all the solid being used up.

Solving higher order equations like this for \( x \) using algebra is not especially easy. An iterative method using a good calculator or a spreadsheet is highly recommended. Using a spreadsheet for example, enter the expression for \( K \) in a cell, referencing another cell for \( x \). Then put values for \( x \) in that cell until the expression yields a value of 0.060. You should be able to narrow the value for \( x \) to a sufficient number of sig. fig. in 5 or 6 tries.

Must convert to moles and then to moles/liter.
11. \( \text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g) \)

The expression for \( K_p \) is:
\[
K_p = P_{\text{NH}_3} \times P_{\text{HCl}} = 0.640
\]

Since the partial pressures of ammonia and hydrogen chloride must be equal to one another, each must equal 0.80 atm.
The total pressure is the sum of the partial pressures, so the total pressure = 1.60 atm.

<table>
<thead>
<tr>
<th></th>
<th>( \text{Br}_2(g) )</th>
<th>( \text{Cl}_2(g) )</th>
<th>( \rightleftharpoons )</th>
<th>( 2\text{BrCl}(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.060</td>
<td>0.060</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(-x)</td>
<td></td>
<td>+2x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.060(-x)</td>
<td>0.060(-x)</td>
<td></td>
<td>+2x</td>
</tr>
</tbody>
</table>

\[
K = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]} = \frac{(2x)^2}{(0.060\(-x\))(0.060\(-x\))} = 36.0
\]

\( x = 0.045 \)

So the concentration of \( \text{BrCl} \) produced = \( 2x = 0.090 \) mol L\(^{-1}\).
Quantity produced = \( 0.090 \) mol L\(^{-1}\) \( \times \) 3 L = 0.27 mol = 31 grams.

Remember to change amounts to concentrations.

Take the square root of both sides.

Don’t assume \( x \) is the desired answer to the problem! In this case the required quantity is the concentration of \( \text{BrCl} \) (which is \( 2x \)) and the total amount of \( \text{BrCl} \) (which is the volume of 3 liters \( \times \) this concentration).

13. \( \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \)

<table>
<thead>
<tr>
<th></th>
<th>( \text{NH}_3 )</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \rightleftharpoons )</th>
<th>( \text{NH}_4^+ )</th>
<th>( \text{OH}^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.200</td>
<td>0.0</td>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td></td>
<td>(+x)</td>
<td>(+x)</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.200(-x)</td>
<td></td>
<td>(+x)</td>
<td>(+x)</td>
<td></td>
</tr>
</tbody>
</table>

\[
K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{(0.200\(-x\))} = 1.8 \times 10^{-5}
\]

\( x = 1.90 \times 10^{-3} \) M — this is the concentration of hydroxide ion.

14. \( \text{Ti}(s) + 2\text{Cl}_2(g) \rightleftharpoons \text{TiCl}_4(g) + \text{heat} \)

The yield of the product \( \text{TiCl}_4 \) is increased by moving the system to the right:
a. remove heat; cool the system down.
b. remove \( \text{TiCl}_4(g) \).
c. add chlorine gas \( \text{Cl}_2(g) \).
d. increase the pressure (or decrease the volume).

Note that:
adding more Ti(s) has no effect.
adding a catalyst has no effect.