Problems - Chapter 15 (with solutions)

1) What is the significance of the equilibrium constant? What does a large equilibrium constant tell us about a reaction? A small one?

   The equilibrium constant tells you the relationship between product and reactant concentrations that exists, at equilibrium, in a system at some temperature T. A large equilibrium constant tells you that at equilibrium the concentrations of products will be much larger than the concentrations of reactants. A small equilibrium constant means the opposite, that the concentrations of reactants at equilibrium will be large in comparison to the concentrations of products.

2) (15.18 a-d) Write equilibrium constants for $K_C$, and, if applicable, for $K_p$, for the following processes:

   a) $2 \text{CO}_2(\text{g}) \leftrightarrow 2 \text{CO}(\text{g}) + \text{O}_2(\text{g})$
   
   $K_C = \frac{[\text{CO}]^2 [\text{O}_2]}{[\text{CO}_2]^2}$
   
   $K_p = \frac{(p_{\text{CO}})^2 (p_{\text{O}_2})}{(p_{\text{CO}_2})^2}$

   b) $3 \text{O}_2(\text{g}) \leftrightarrow 2 \text{O}_3(\text{g})$
   
   $K_C = \frac{[\text{O}_3]^2}{[\text{O}_2]^3}$
   
   $K_p = \frac{(p_{\text{O}_3})^2}{(p_{\text{O}_2})^3}$

   c) $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \leftrightarrow \text{COCl}_2(\text{g})$
   
   $K_C = \frac{[\text{COCl}_2]}{[\text{CO}] [\text{Cl}_2]}$
   
   $K_p = \frac{(p_{\text{COCl}_2})}{(p_{\text{CO}})(p_{\text{Cl}_2})}$

   d) $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
   
   $K_C = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]^2}$
   
   $K_p = \frac{(p_{\text{CO}})(p_{\text{H}_2})}{(p_{\text{H}_2\text{O}})^2}$

   e) $\text{HCOOH}(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$
   
   $K_C = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$
   
   $K_p = \text{no expression}$

   f) $2 \text{HgO}(\text{s}) \leftrightarrow 2 \text{Hg}(\text{l}) + \text{O}_2(\text{g})$

   $K_C = [\text{O}_2]$
   
   $K_p = (p_{\text{O}_2})$

In doing these problems recall that solids, pure liquids, and solvents do not appear in the expression for the equilibrium constant. The easiest way to decide if a value of $K_p$ can be written is to look at the expression for $K_C$. If everything in $K_C$ is a gas, then $K_p$ can be written by substituting gas pressure for concentration in each term. Otherwise, an expression for $K_p$ cannot be written (as in e, above).
3) The reaction below has an equilibrium constant $K_p = 2.2 \times 10^6$ at 298 K

$$2 \text{COF}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CF}_4(\text{g})$$

Calculate $K_p$ for each of the reactions below (at the same temperature) and predict whether reactants or products will be favored at equilibrium

a) $\text{COF}_2(\text{g}) \rightleftharpoons \frac{1}{2} \text{CO}_2(\text{g}) + \frac{1}{2} \text{CF}_4(\text{g})$

b) $6 \text{COF}_2(\text{g}) \rightleftharpoons 3 \text{CO}_2(\text{g}) + 3 \text{CF}_4(\text{g})$

c) $2 \text{CO}_2(\text{g}) + 2 \text{CF}_4(\text{g}) \rightleftharpoons 4 \text{COF}_2(\text{g})$

For the reaction as written, $K_p = \left(\frac{p_{\text{CO}_2} \cdot p_{\text{CF}_4}}{p_{\text{COF}_2}^2}\right) = 2.2 \times 10^6$. Therefore

$$a)\, K_p = \left(\frac{p_{\text{CO}_2}^{1/2} \cdot p_{\text{CF}_4}^{1/2}}{p_{\text{COF}_2}}\right)^{1/2} = \frac{1}{2} \left(\frac{p_{\text{CO}_2} \cdot p_{\text{CF}_4}}{p_{\text{COF}_2}^2}\right)^{1/2} = \left(2.2 \times 10^6\right)^{1/2} = 1.5 \times 10^3 \text{ (products favored)}$$

$$b)\, K_p = \left(\frac{p_{\text{CO}_2}^3 \cdot p_{\text{CF}_4}^3}{p_{\text{COF}_2}^6}\right)^3 = \left(\frac{p_{\text{CO}_2} \cdot p_{\text{CF}_4}}{p_{\text{COF}_2}^2}\right)^3 = \left(2.2 \times 10^6\right)^3 = 1.1 \times 10^{19} \text{ (products favored)}$$

$$c)\, K_p = \left(\frac{p_{\text{COF}_2}^4}{p_{\text{CO}_2}^2 \cdot p_{\text{CF}_4}^2}\right)^2 = \left(\frac{p_{\text{CO}_2} \cdot p_{\text{CF}_4}}{p_{\text{COF}_2}^2}\right)^{-2} = \left(2.2 \times 10^6\right)^{-2} = 2.1 \times 10^{-13} \text{ (reactants favored)}$$

4) (15.12) The equilibrium constant for the reaction

$$2 \text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$$

is $K_C = 1.6 \times 10^{-2}$ at a certain temperature. It is found that there are $1.17 \times 10^{-2}$ moles of $\text{H}_2$ and $3.46 \times 10^{-7}$ moles of $\text{CH}_3\text{OH}$ in a 5.60 L system at equilibrium at this temperature. What is the concentration of CO in the system?

$$K_C = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2 \cdot [\text{CO}]}$$

so

$$[\text{CO}] = \frac{[\text{CH}_3\text{OH}]}{K_C \cdot [\text{H}_2]^2} \quad [\text{H}_2] = \frac{1.17 \times 10^{-2} \text{ mol}}{5.6 \text{ L}} = 2.09 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{OH}] = \frac{3.46 \times 10^{-7} \text{ mol}}{5.6 \text{ L}} = 6.18 \times 10^{-8} \text{ M}$$

$$[\text{CO}] = \frac{(6.18 \times 10^{-8})}{(1.6 \times 10^{-2}) (2.09 \times 10^{-3})^2} = 0.884 \text{ M}$$
5) (15.22) What is the numerical value for $K_p$ at $T = 1273 \, ^\circ C$ for the reaction

$$2 \text{ CO}(g) + \text{ O}_2(g) \leftrightarrow 2 \text{ CO}_2(g)$$

At this temperature $K_C = 2.24 \times 10^{22}$.

The general relationship to use is $K_p = K_c \left(\frac{RT}{\Delta n}\right)$, where $\Delta n =$ change in the number of moles of gas per mole of reaction.

$$\Delta n = 2 - 3 = -1 \quad T = 1273 + 273 = 1546. \, K$$

$$K_p = (2.24 \times 10^{22}) \left[ \left(0.0826\right) (1546) \right]^{-1} = 1.77 \times 10^{20}$$

Notice that we use the value $R = 0.08206 \, \text{L atm/mol K}$ in the conversion and convert temperature to K, but we do not include units for R or T, since $K_p$ and $K_C$ have no units.

6) Consider the following reaction

$$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{ HI}(g)$$

Complete the table below. You may assume that all concentrations are equilibrium concentrations in units of mol/L.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>[H$_2$]</th>
<th>[I$_2$]</th>
<th>[HI]</th>
<th>$K_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>0.0355</td>
<td>0.0388</td>
<td>0.922</td>
<td>----</td>
</tr>
<tr>
<td>340.0</td>
<td>----</td>
<td>0.0455</td>
<td>0.387</td>
<td>9.6</td>
</tr>
<tr>
<td>445.0</td>
<td>0.0485</td>
<td>0.0468</td>
<td>----</td>
<td>50.2</td>
</tr>
</tbody>
</table>

For this reaction $K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

At 25 °C, missing $K_C$, so $K_C = \frac{(0.922)^2}{(0.0355)(0.0388)} = 617$.

At 340. °C, missing $[H_2]$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad \text{so} \quad [\text{H}_2] = \frac{[\text{HI}]^2}{K_C[\text{I}_2]} = \frac{(0.387)^2}{(9.6)(0.0455)} = 0.343 \, \text{M}$$

At 445. °C, missing [HI]

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad \text{so} \quad [\text{HI}] = \{K_C[\text{H}_2][\text{I}_2]\}^{1/2} = \{(50.2)(0.0485)(0.0468)\}^{1/2} = 0.338 \, \text{M}$$
7) (15.34) The following equilibrium constants have been determined for hydrosulfuric acid at T = 25.0 °C

\[ \text{H}_2\text{S}(aq) \rightleftharpoons \text{H}^+(aq) + \text{HS}^{-}(aq) \quad \text{K}_c' = 9.5 \times 10^{-8} \]

\[ \text{HS}^{-}(aq) \rightleftharpoons \text{H}^+(aq) + \text{S}^2^{-}(aq) \quad \text{K}_c'' = 1.0 \times 10^{-19} \]

Find the equilibrium constant for the following reaction at the same temperature

\[ \text{H}_2\text{S}(aq) \rightleftharpoons 2 \text{H}^+(aq) + \text{S}^2^{-}(aq) \quad \text{K}_c = ? \]

The expressions for \( \text{K}_c' \) and \( \text{K}_c'' \) are

\[ \text{K}_c' = \frac{[\text{H}^+][\text{HS}^{-}]}{[\text{H}_2\text{S}]} \]

\[ \text{K}_c'' = \frac{[\text{H}^+][\text{S}^2^{-}]}{[\text{HS}^{-}]} \]

\[ \text{K}_c = \frac{[\text{H}^+]^2[\text{S}^2^{-}]}{[\text{H}_2\text{S}][\text{HS}^{-}]} = \frac{[\text{H}^+][\text{HS}^{-}]}{[\text{H}_2\text{S}]} \frac{[\text{H}^+][\text{S}^2^{-}]}{[\text{HS}^{-}]} = \text{K}_c' \text{K}_c'' \]

\[ = (9.5 \times 10^{-8})(1.0 \times 10^{-19}) = 9.5 \times 10^{-27} \]

8) For the reaction below, \( \text{K}_c = 255. \) at T = 1000. K

\[ \text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \]

A reaction mixture (kept at T = 1000. K) initially contains no \( \text{COCl}_2 \). The initial concentrations of CO and \( \text{Cl}_2 \) are [CO] = 0.1500 M, and [Cl\(_2\)] = 0.1750 mol/L. What are the equilibrium concentrations of CO, \( \text{Cl}_2 \), and \( \text{COCl}_2 \)?

\[ \text{K}_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = 255. \]

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.1500</td>
<td>- x</td>
<td>0.1500 - x</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>0.1750</td>
<td>- x</td>
<td>0.1750 - x</td>
</tr>
<tr>
<td>COCl(_2)</td>
<td>0.000</td>
<td>+ x</td>
<td>x</td>
</tr>
</tbody>
</table>

(Note we have defined x as the concentration of \( \text{COCl}_2 \) that forms).

\[ \frac{(x)}{(0.1500 - x)(0.1750 - x)} = 255. \]

Since it does not look like x is small compared to 0.1500, we will have to solve the above by the quadratic formula.
\[ x = (0.1500 \ - \ x) \ (0.1750 \ - \ x) \ (255.) = 6.6938 - 82.875 \ x + 255 \ x^2 \]

\[ 255 \ x^2 - 83.875 \ x + 6.6938 = 0 \]

\[ x = \frac{83.875 \pm \sqrt{(83.875)^2 - 4 \ (255) \ (6.6938)}}{2 \ (255)} = 0.1927, \ 0.1362 \]

The underlined root is correct. The other root (0.1927) would lead to a negative value for the concentration of both CO and Cl\(_2\).

So at equilibrium

\[ [\text{CO}] = 0.1500 - x = 0.0138 \ \text{M} \]
\[ [\text{Cl}_2] = 0.1750 - x = 0.0388 \ \text{M} \]
\[ [\text{COCl}_2] = x = 0.1362 \ \text{M} \]

As a check, if we substitute into our expression for \(K_C\), we get

\[ K_C = \frac{(0.1362)}{(0.0138 \ (0.0388)} = 254. \approx 255. \]

9) Consider the reaction

\[ \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \quad K_C = 2.99 \times 10^{-7} \text{ at } T = 227. \ ^\circ C \]

If the reaction (kept at \(T = 227. \ ^\circ C\)) initially contains 0.175 mol/L SO\(_2\)Cl\(_2\) (and no SO\(_2\) or Cl\(_2\)), what is the equilibrium concentration of Cl\(_2\)?

\[ K_C = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = 2.99 \times 10^{-7} \]

\[
\begin{array}{c|c|c|c}
 & \text{Initial} & \text{Change} & \text{Equilibrium} \\
\hline
\text{SO}_2 & 0.000 & + x & x \\
\text{Cl}_2 & 0.000 & + x & x \\
\text{SO}_2\text{Cl}_2 & 0.1750 & - x & 0.1750 - x \\
\end{array}
\]

(Note we have defined \(x\) as the concentration of SO\(_2\) that forms).

\[ \frac{(x)^2}{(0.1750 - x)} = 2.99 \times 10^{-7} \]

Since \(K_C \ll 1\), it looks like it is worth assuming that \(x \ll 0.1750\) If we make that assumption, then
\[
\frac{(x)^2}{0.1750 - x} \approx \frac{x^2}{0.1750} = 2.99 \times 10^{-7}
\]

So \( x^2 = (2.99 \times 10^{-7}) \times (0.1750) = 5.23 \times 10^{-8} \)

\( x = (5.23 \times 10^{-8})^{1/2} = 2.29 \times 10^{-4} \)

Now we go back and check our assumption. Is \( 2.29 \times 10^{-4} \ll 0.1750 \)? YES, so our assumption was good.

So at equilibrium \( [\text{SO}_2] = [\text{Cl}_2] = x = 2.29 \times 10^{-4} \text{ M} \)
\( [\text{SO}_2\text{Cl}_2] = 0.175 - x = 0.1748 \text{ M} \)

10) In which direction will a reaction proceed for each of the following conditions:
   a) \( Q < K \)
   b) \( Q > K \)
   c) \( Q = K \)

   a) If \( Q < K \) the reaction will shift from left to right (from reactants to products) as equilibrium is approached.
   b) If \( Q > K \) the reaction will shift from right to left (from products to reactants) as equilibrium is approached.
   c) If \( Q = K \) then the system is at equilibrium, and so no shifting will occur.

11) Consider the reaction

\( 2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g) \quad K_p = 2.4 \times 10^{-4} \text{ at } T = 1073. \text{ K} \)

A reaction mixture contains 0.112 atm of \( \text{H}_2 \), 0.055 atm of \( \text{S}_2 \), and 0.445 atm of \( \text{H}_2\text{S} \). Is the reaction mixture at equilibrium? If not, in what direction will the reaction proceed?

\[
Q_p = \frac{(p_{\text{H}_2})^2 (p_{\text{S}_2})}{(p_{\text{H}_2\text{S}})^2} = \frac{(0.112)^2 (0.055)}{(0.445)^2} = 3.5 \times 10^{-3}.
\]

As stated in the problem, \( K_p = 2.4 \times 10^{-4} \). Since \( Q_p > K_p \) we need to reduce its value. Therefore the reaction will shift from right to left (more \( \text{H}_2\text{S} \) will form).

12) Consider this reaction at equilibrium

\( 2 \text{BrNO}(g) \rightleftharpoons 2 \text{NO}(g) + \text{Br}_2(g) \)

Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.
   a) \( \text{NO} \) is added to the reaction mixture.
   b) \( \text{BrNO} \) is added to the reaction mixture.
   c) \( \text{Br}_2 \) is removed from the reaction mixture.
We use Le Chatlier's principle here (we could also use the reaction quotient, but that takes longer and will give the same result).

a) System will shift from right to left (to get rid of some of the added NO).

b) System will shift from left to right (to get rid of some of the added BrNO).

c) System will shift from left to right (to replace some of the Br\textsubscript{2} that was removed).

13) Each of the following reactions is allowed to come to equilibrium, and the volume is then changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

a) CO(g) + H\textsubscript{2}O(g) \rightleftharpoons CO\textsubscript{2}(g) + H\textsubscript{2}(g) \hspace{1cm} \text{volume is decreased}

b) PCl\textsubscript{3}(g) + Cl\textsubscript{2}(g) \rightleftharpoons PCl\textsubscript{5}(g) \hspace{1cm} \text{volume is increased}

c) CaCO\textsubscript{3}(s) \rightleftharpoons CaO(s) + CO\textsubscript{2}(g) \hspace{1cm} \text{volume is increased}

a) Since volume is decreased all of the concentrations will increase. The system will respond by trying to reduce the total concentration. However, since there are the same number of moles of reactants and products, there will be no shift in the reaction.

b) Since volume is increased all of the concentrations will decrease. The system will respond by trying to increase the total concentration. Since there are more moles of reactants than products, the system will shift from right to left.

c) Since volume is increased the concentration of CO\textsubscript{2} will decrease. Note we don't have to consider the "concentration" of solids, since they don't enter into the expression for the equilibrium constant.

So the system will respond by increasing the concentration of CO\textsubscript{2}. Therefore the reaction will shift from left to right.

14) (15.70) Consider the following reaction

\[ A(g) \leftrightarrow 2 B(g) \]

Data for this reaction for systems at equilibrium are given below.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>[A] (M)</th>
<th>[B] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200.0</td>
<td>0.0125</td>
<td>0.843</td>
</tr>
<tr>
<td>300.0</td>
<td>0.171</td>
<td>0.764</td>
</tr>
<tr>
<td>400.0</td>
<td>0.250</td>
<td>0.724</td>
</tr>
</tbody>
</table>

a) Find the value for \(K_C\) and \(K_p\) at each of the above temperatures.
b) Is the above reaction exothermic or endothermic? Justify your answer.
a) \[ K_C = \frac{[B]^2}{[A]} \]

\[ K_p = K_C (RT)^\Delta n \quad \Delta n = 2 - 1 = 1 \]

At \( T = 200. \, ^\circ C = 473. \, K \)

\[ K_C = (0.843)^2 = 56.9 \]

\[ K_p = (56.9) \times [(0.08206) (473.)] = 2210. \]

At \( T = 300. \, ^\circ C = 573. \, K \)

\[ K_C = (0.764)^2 = 3.41 \]

\[ K_p = (3.41) \times [(0.08206) (573.)] = 161. \]

At \( T = 400. \, ^\circ C = 673. \, K \)

\[ K_C = (0.724)^2 = 2.09 \]

\[ K_p = (2.09) \times [(0.08206) (673.)] = 116. \]

b) \( K \) (either \( K_C \) or \( K_p \)) gets smaller as temperature increases. By Le Chatlier's principle we would expect that to occur if heat were a product of the reaction, since at higher temperatures there is more heat, so the reaction will shift from right to left to reduce the heat in the system. Therefore the reaction is \textit{exothermic}. 