Chemistry 1310 I
Lecture Notes

F, October 1, 2004

Evaluating equilibrium constants

OFB, p. 336, #10

\[ \text{Keq} = \frac{\text{products}}{\text{reactants}} \]

The reversible reaction

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

was studied at 425 °C. Hydrogen gas, at a partial pressure of 2.75 atm was mixed with iodine vapor, at a partial pressure of 1.50 atm. The system reached equilibrium and the partial pressure of hydrogen iodide gas was found to be 2.79 atm. Find the value of \( K \) for the reaction.

<table>
<thead>
<tr>
<th>Initial</th>
<th>( P_{\text{H}_2} )</th>
<th>( P_{\text{I}_2} )</th>
<th>( P_{\text{HI}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(atm)</td>
<td>2.75</td>
<td>1.50</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ \text{Change} \]

\[ -x \quad -x \quad +2x \]

\[ \text{Equilibrium} \]

\[ 2.75-x \quad 1.50-x \quad 2.79 \]

\[ 2x = 2.79 \]

\[ x = 1.395 \text{ atm.} \]

\[ \text{Keq.} = \frac{(P_{\text{H}_2})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} \]

\[ = \frac{(2.75)^2}{(2.75)(1.50)} \]

\[ = 54.7 \]

\[ P_{\text{H}_2} = (2.75 - 1.395) \text{ atm} = 1.355 \text{ atm} \]

\[ P_{\text{I}_2} = (1.50 - 1.395) \text{ atm} = 0.105 \text{ atm} \]
Question: How did you know that the system was at equilibrium?
Answer: Some visible factor might have stopped changing. Iodine vapor is purple while hydrogen and hydrogen iodide gases are colorless. The intensity of the purple color would decrease from its initial value and would remain constant once equilibrium was achieved.

If you are working with a system for which the value of the equilibrium constant is known, you can do calculations to see if the system is at equilibrium.

We define the reaction quotient \((Q)\) as a fraction that has the same form as \(K\). The only difference is that we plug experimental values into \(Q\) while only equilibrium values are used in \(K\).
Suppose the reaction

\[
\text{SbF}_5 (g) + 4 \text{Cl}_2 (g) \rightleftharpoons \text{SbCl}_3 (g) + 5 \text{ClF} (g)
\]

has an equilibrium constant of 0.0200 at 300 °C. Is a mixture that has the partial pressures specified below at equilibrium? If it isn’t, what must it do to reach equilibrium?

\[
K_{eq} = 0.0200
\]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbF₅</td>
<td>0.945 atm</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.330 atm</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>0.455 atm</td>
</tr>
<tr>
<td>ClF</td>
<td>0.225 atm</td>
</tr>
</tbody>
</table>

\[
Q = \frac{(P_{\text{ClF}})^5 (P_{\text{SbCl}_3})}{(P_{\text{Cl}_2})^4 (P_{\text{SbF}_5})} = \frac{(0.225)^5 (0.455)}{(0.330)^4 (0.945)} = 0.0234
\]

\[
\underline{Q > K}
\]

more products
Sometimes, we need to find equilibrium pressures, rather than just saying which way the mixture must move to attain equilibrium.

**OFB, p. 338, #32**

Fluorine oxidizes oxygen to form oxygen difluoride. The reaction is:

$$F_2 (g) + \frac{1}{2} O_2 (g) \Leftrightarrow OF_2 (g)$$

and has an equilibrium constant of 40.1 at 298 K. Some OF$_2$ was introduced into a reaction vessel and decomposed until equilibrium was established. At that time, the partial pressure of OF$_2$ was 1.10 atm. What were the equilibrium partial pressures of fluorine and oxygen in the vessel?

<table>
<thead>
<tr>
<th>Initial (P$_{F_2}$)</th>
<th>P$_{O_2}$</th>
<th>P$_{OF_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>y</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>+2x</td>
</tr>
<tr>
<td>Equilibrium (P$_{F_2}$)</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td></td>
<td>?</td>
<td>1.10</td>
</tr>
</tbody>
</table>

$$OF_2 \rightarrow F_2 + \frac{1}{2} O_2$$

$$K_{eq} = \frac{1}{40.1}$$

$$\frac{1}{40.1} = \frac{(x)(\frac{1}{2}x)^{\frac{1}{2}}}{y}$$

$$\frac{1}{40.1} = \frac{x}{1.10}$$

$$\frac{x(0.5x)^{\frac{1}{2}}}{(0.0275)^2} = 0.057626$$

$$0.5x^3 = 0.057626$$

$$x = 0.115 \text{ atm}$$

P$_{F_2}$ = 0.115 atm

P$_{O_2}$ = 0.057626 atm.
Sometimes, an equilibrium position is not favorable. For instance, the direct synthesis of ammonia from nitrogen and hydrogen proceeds very slowly at room temperature although, if equilibrium were achieved, the equilibrium mixture would be rich in ammonia. When the reaction is heated up (most reactions go faster at high temperature), ammonia is made more rapidly but the ammonia produced decomposes quickly and the equilibrium mixture contains very little ammonia.

The question is, "Which changes will increase the production of ammonia?".

LeChatelier's Principle: When a system at equilibrium is subject to a stress, it will attempt to achieve a new equilibrium position in a manner that minimizes the stress.

What are possible stresses?
- Raising or lowering the temperature
- Adding or removing reactants
- Adding or removing products
- Changing the volume of the reaction mixture
- Etc.
The reaction shown is endothermic. Explain the effect of each of the listed stresses on the equilibrium position.

\[ \text{SO}_3 (g) \rightleftharpoons \text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \]

a. Add sulfur trioxide without changing temperature or volume.

b. Expand the reaction mixture at constant temperature. \( \text{all partial pressures decrease} \)

c. Heat the equilibrium mixture.

d. Add an inert gas while keeping the total gas pressure and the temperature constant. \( \text{same as b. (expansion)} \)

e. Add an inert gas while keeping the temperature and volume constant. \( \text{No effect} \)

[Diagram: Fixed Temp]