Chemical Equilibrium
Chapter 13
LeChatelier’s Principle
LeChatelier’s Principle & Concentration

If a component (reactant or product) is added to a reaction system at equilibrium (at constant T and P or constant T and V) the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs.

*DOES NOT CHANGE K.*

\[
\text{As}_4\text{O}_6\text{(s)} + 6\text{C(s)} \rightleftharpoons \text{As}_4\text{(g)} + 6\text{CO(g)}
\]

What happens if you...
Add CO to the system?
Add \(\text{As}_4\text{O}_6\) to the system?
Remove \(\text{As}_4\)?
Increasing a the pressure favors the side with the fewest particles
Decreasing the pressure favors the side with the most particles

*DOES NOT CHANGE K.*

Three way to change pressure
1. Add or remove a gaseous reactant or product.
2. Add an inert gas (one not involved in the reaction).
3. Change the volume of the container.

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

\[
P_4 (s) + 6Cl_2 (g) \leftrightarrow 4PCl_3 (l)
\]

\[
PCl_3 (g) + Cl_2 (g) \leftrightarrow PCl_5 (g)
\]

\[
PCl_3 (g) + 3NH_3 (g) \leftrightarrow P(NH_2)_3 (g) + 3HCl (g)
\]
LeChatelier’s Principle & Temperature

Increasing the energy favors the endothermic reaction.
Decreasing the energy favors the exothermic reaction.
The value of K changes with temperature.

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{s}) \leftrightarrow \text{NH}_3(\text{g}) + 92\text{kJ} \quad \text{What will happen to } K \text{ if temp. is increased?} \]

\[ 92\text{kJ} + \text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{s}) \quad \text{What will happen to } K \text{ if temp. is increased?} \]
LeChatelier’s Principle & Temperature

Predict how the value of $K$ changes as the temperature increases.

$$N_2(g) + O_2(g) \leftrightarrow 2NO(g) \quad \Delta H^\circ = 181 \text{ kJ}$$

$$2SO_2(g) + O_2(g) \leftrightarrow SO_3(g) \quad \Delta H^\circ = -198 \text{ kJ}$$
Add water to the system until a change is noted. What has happened?

Add NaCl to the system until a change is noted. What has happened?

What is happen to this reaction if it is heated?

Where is the energy? Which reaction is exothermic?
The Copper Complex Equilibrium System

\[
[\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O} \rightleftharpoons [\text{Co(H}_2\text{O})_6]^{2+} + 4\text{Cl}^-
\]

Blue \hspace{1cm} Pink

Add a pea size piece of CoCl$_2$•6H$_2$O to the beaker then add 6M HCl to the beaker.

What is favored at this equilibrium?

Add water to the beaker until you notice a change.

How did the equilibrium system shift?

What happened to the concentration of [CoCl$_4$]$^{2-}$?

Heat the beaker in a hot water bath.

How did the equilibrium system shift?

Where is energy in this system?

Which reaction is the endothermic reaction?

What do you think will happen if the beaker is cooled?
Suppose the reaction system below has already reached equilibrium. Predict the effect that each of the following changes will have on the equilibrium position. Tell whether the equilibrium will shift to the right or left or will not be affected.

\[ \text{UO}_2(\text{s}) + 4\text{HF}(g) \leftrightarrow \text{UF}_4(g) + 2\text{H}_2\text{O}(g) \]

a. Additional \text{UO}_2(\text{s}) is added to the system.
b. The reaction is performed in a glass reaction vessel; \text{HF}(g) attacks and reacts with glass.
c. Water vapor is removed.

a. Right  b. left  c. right
An important reaction in the commercial production of hydrogen is below. How will this system at equilibrium shift in each of the following cases?

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

a. Gaseous carbon dioxide is removed.
b. Water vapor is added.
c. The pressure is increased by adding helium gas.
d. The temperature is increased (the reaction is exothermic).
e. The pressure is increased by decreasing the volume of the container.

Problem #59

a. Right    b. right    c. no shift    d. left   e. left
Old fashioned “smelling salts” consist of ammonium carbonate. The reaction for the decomposition of ammonium carbonate is exothermic. Would the smell of ammonia increase or decrease as the temperature is increased?

\[
\text{(NH}_4\text{)}_2\text{CO}_3 (s) \leftrightarrow 2\text{NH}_3 (g) + \text{CO}_2 (g) + \text{H}_2\text{O} (g)
\]

If the salts were in equilibrium then increasing the temperature would favor the reverse reaction. This would produce less \(\text{NH}_3\) and more “salts”.
Ammonia is produced by the Haber process, in which nitrogen and hydrogen are reacted directly using an iron mesh impregnated with oxides as a catalyst. For the reaction below the equilibrium constants ($K_p$ values) as a function of temperature are

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°C</td>
<td>$4.34 \times 10^{-3}$</td>
</tr>
<tr>
<td>500°C</td>
<td>$1.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>600°C</td>
<td>$2.25 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Is the reaction exothermic or endothermic?

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$$

exothermic