Chapter 15: Equilibrium part 3

Read: BLB 15.6–7
HW: BLB 15:51,53,70
Supplemental 15:11–13

Know:
• LeChatelier’s principle
• catalysis
• math refresher in BLB Appendix A

Final Exam: ________________ Know your section’s Exam Location. Know your section number. Bring your ID!

Points to Ponder

❖ The equilibrium ratio of products and reactants (size of $K_c$) says nothing about the rate of the reaction.

\[
N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K \sim 10^{-30}
\]

So,

\[
2NO(g) \rightleftharpoons N_2(g) + O_2(g) \quad K \sim 10^{30}
\]

BUT NO(g) is stable at 298 K!

❖ CATALYSTS affect the RATE of a reaction, but not the size of $K_{eq}$.

❖ What changes DO affect equilibrium?
  1. change in concentration
  2. change in volume or pressure (only if gases are involved)
  3. change in temperature (this changes the value of $K_c$)
Le Chatelier’s Principle

If a system at equilibrium is disturbed, the concentrations of reactants and products will shift to minimize the effect of the disturbance.

Predicts the effect on a system at equilibrium when it is disturbed by changing the following parameters:

- concentration of soluble species
- partial pressure (gases in \( K_{eq} \))
- volume (gases in \( K_{eq} \))
- pressure (gases in \( K_{eq} \))
- temperature

To illustrate this principle use the following chemical system in a closed 1L container:

\[
4 \text{HBr}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(g) + 2 \text{Br}_2(g)
\]

\( \Delta H_{\text{rxn}} = -466 \text{kJ/mol} \)

Initial conditions:

\[
\begin{align*}
T &= 500 \text{K} \\
[\text{HBr}] &= 4.0 \text{M} \\
[\text{O}_2] &= 1.0 \text{M} \\
[\text{H}_2\text{O}] &= 0.0 \text{M} \\
[\text{Br}_2] &= 0.0 \text{M}
\end{align*}
\]

At equilibrium:

\[
\begin{align*}
[\text{HBr}] &= 1.0 \text{M} \\
[\text{O}_2] &= 0.25 \text{M} \\
[\text{H}_2\text{O}] &= 1.5 \text{M} \\
[\text{Br}_2] &= 1.5 \text{M}
\end{align*}
\]

What is \( K_c \)?
What will happen to $[\text{Br}_2]$ if 4.0 moles of HBr are added to the system at equilibrium?

*System is no longer at equilibrium. Which direction will it go to get to equilibrium?*

Using LeChatelier’s principle:
Reactant or product added to a mixture at equilibrium will cause reaction to shift in the direction that consumes part of the added material.

$4\text{HBr}(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + 2\text{Br}_2(g)$

Calculate $Q =$

Which direction will the reaction proceed if the *volume is decreased* to 0.5L?

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium</th>
<th>After volume change</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{HBr}]$</td>
<td>1.0 M</td>
<td></td>
</tr>
<tr>
<td>$[\text{O}_2]$</td>
<td>0.25 M</td>
<td></td>
</tr>
<tr>
<td>$[\text{H}_2\text{O}]$</td>
<td>1.5 M</td>
<td></td>
</tr>
<tr>
<td>$[\text{Br}_2]$</td>
<td>1.5 M</td>
<td></td>
</tr>
</tbody>
</table>

As $V \downarrow$, concentration ______

$P = n/V(RT) = (\text{concentration})(RT)$

So, as $V \downarrow$, $P$ ______

*Use LeChatelier’s principle: Since pressure is increased by disturbance, reaction will shift in direction that will reduce pressure.*

Remember: less *pressure* is caused by fewer collisions, which requires less *moles* of molecules.

$4\text{HBr}(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + 2\text{Br}_2(g)$

5 moles gas $\rightleftharpoons$ 4 moles gas

Calculate $Q =$
4HBr(g) + O_2(g) ⇌ 2H_2O(g) + 2Br_2(g)

What happens when 5.0 moles of an inert gas are added?

**Inert gas:**

How does the presence of an inert gas affect the concentrations of reactants and products?

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium</th>
<th>After inert gas added</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HBr]</td>
<td>1.0 M</td>
<td></td>
</tr>
<tr>
<td>[O_2]</td>
<td>0.25 M</td>
<td></td>
</tr>
<tr>
<td>[H_2O]</td>
<td>1.5 M</td>
<td></td>
</tr>
<tr>
<td>[Br_2]</td>
<td>1.5 M</td>
<td></td>
</tr>
</tbody>
</table>

Examples:

- Change concentration
  
  Fe^{3+}(aq) + SCN^- (aq) ⇌ FeSCN^{2+}(aq)
  
  yellow  colorless  red

- Change pressure
  
  2NO_2(g) ⇌ N_2O_2(g)
  
  brown  colorless
Summary so Far:

• changing concentration (or V so that \([\text{ }]\) changes) puts a stress on the system.

• Stresses *do not change* \(K_{eq}\)!

• \(Q\) changes; system shifts to re-establish equilibrium
  \[Q \rightarrow K\]

What happens when the temperature is increased to 1000K?

\[
4\text{HBr} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Br}_2
\]

\[\Delta H_{rxn} = -466\text{kJ/mol}\]

Treat heat like a product (exothermic) or reactant (endothermic).

**Le Chatelier’s Principle:**

• When heat is added to a system, the reaction will shift in the direction that *absorbs* heat

• Reaction is *exothermic* (heat is a product) so adding heat will cause reaction to shift to left.

**Example:** endothermic reaction

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

*pink* \(\rightarrow\) *blue*
Which of the following actions would increase production of CO$_2$(g) in the following *endothermic* reaction?

$$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

1) Increase amount of CaCO$_3$
2) Remove CO$_2$ gas as it is formed
3) Increase temperature
4) Remove CaO(s)
5) Add Ar to the system, increasing total pressure
6) Add H$_2$O(l) to the system
7) Increase the volume of the system

---

**Haber process**

Industrial process used to produce ammonia

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

To produce氨气，

**Do we want high or low temperature?**

**Do we want high or low pressure?**

Liquefy ammonia as process proceeds. **WHY?**

**Problem:** rate of reaction increases as T increases.

**Solution:**
Put it all together - Example:

At temperatures near 800°C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H₂ (water gas):

\[ C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \]

1) At 800°C \( K_p = 14.1 \). What are the equilibrium partial pressures of the gases in the mixture if we start with solid C and 0.100 moles of H₂O in a 1.00 L flask?

\[
P_{H_2O} = \frac{n_{H_2O}RT}{V} = \left( \frac{(0.0821 Latm/molK)(K)}{L} \right)
\]

\[
P_{H_2O} = \text{initial change equilibrium}
\]
Solve for $K_p$:

$$K_p = \frac{P_{CO}P_{H2}}{P_{H2O}} = \left( \frac{ }{ } \right) = 14.1$$

Solving for $x$ gives a quadratic equation in $x$:

Use the quadratic formula (Appendix A3):

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

One of the answers will not make chemical sense.

$x = $  

$P_{CO} = x =$  

$P_{H2} = x =$  

$P_{H2O} = 8.81 - x =$

2) What is the minimum amount of carbon required to achieve equilibrium?

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

How much $H_2O$ REACTED to get to equilibrium? This will tell us how much carbon is needed to react with this amount.

$$n_{H2O} = \frac{PV}{RT} = \frac{( ) (1.00L)}{(0.0821L \cdot atm/mole \cdot K)(1073K)}$$

$$n_{H2O} = \quad n_C = \quad (use \ FW) \rightarrow 0.836 \text{ g}$$
3) At 25°C the value of $K_p$ for this reaction is $1.7 \times 10^{-21}$. Is the reaction exothermic or endothermic?

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

$K_p$ at 800°C = 14.1  
$K_p$ at 25°C = $1.7 \times 10^{-21}$

4) To produce the maximum amount of CO and H$_2$ at equilibrium should the pressure of the system be increased or decreased?

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$