Chapter 6
Chemical Reactions 2

Suggested problems: 19, 26, 37, 41, 49, 56

Objectives

1. Understand the factors that affect reaction rates.
2. Describe how a catalyst works in a chemical reaction.
3. Understand reversible reactions and reactions at equilibrium.
4. Understand the factors that affect equilibrium in reversible reactions.
5. Understand the opposing effects of temperature on endothermic and exothermic reactions.
6. Give the possible characteristics of oxidation and reduction reactions.
7. Identify elements or compounds that have been reduced or oxidized by looking at a chemical equation.

Rate of Reaction

- The speed of a reaction is dependent upon the size of the hill.
- To which energy does the hill correspond?

- Speed does not depend upon whether the reaction is endothermic or exothermic.
Rate of Reaction

- Starting the reaction requires getting the molecules moving (What’s their motivation?) and bumping into one another.
- Several ways to get them to bump into one another:
  - Heat them up – increase kinetic energy of the reactants
  - Increase amounts of reactants – the more reactants, the more likely they will bump into each other
  - Catalyst – make an alternative route to get over the hill
    - Not a reactant, not used up in reaction

Examples of catalysts

- Catalytic converter
  - Speeds up reactions in cars to reduce emissions
- Enzymes
  - Biological catalysts - metabolism

Chemical Equilibrium

- In many reactions, products can react to form reactants
- A reversible reaction occurs in both directions.

\[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \]

- When forward and reverse reactions occur at the same rate, the system is at equilibrium.
- Equilibrium is the lowest energy situation for the reversible system.
- The amounts of products and reactants will not change anymore
- The ratio of product to reactant will remain constant.
Chemical Equilibrium

- Equilibrium does not mean that the amount of product and reactant are equal.
- Some reactions prefer to make a lot of product and leave little reactant.
- Others make little product and use not much reactant.
- By changing the rate of the forward or reverse reactions we affect the equilibrium.

Equilibrium

- In the reaction of sulfur dioxide and oxygen, equilibrium favors product formation.
  - At equilibrium there is more SO₃ than oxygen or SO₂.
  - What happens if we add more SO₂ and O₂?
  - What happens if we add more SO₃?
  - What if we remove SO₃?
  - The equilibrium will always end up with mostly SO₃ because products are favored.

LeChatlier’s Principle

- Increasing species on either side of the arrow will push things away in the direction of the arrow.
- Decreasing species on either side will pull things toward that side in the direction of the arrow.
- In response to changes the system will push and pull until equilibrium is restored.
Equilibrium: Reactants favored

- The decomposition of COCl₂ into CO and Cl₂ favors COCl₂.

\[
\text{COCl}_2 \quad \rightleftharpoons \quad \text{CO} \quad + \quad \text{Cl}_2 
\]

- At equilibrium which species is most abundant?
- At equilibrium which reaction occurs at the faster rate?
- What will happen if we add more COCl₂?
- What if we collect the chlorine gas formed and remove it?

Temperature Effects on Equilibrium

- The formation of sulfur trioxide is exothermic.

\[
2\text{SO}_3 \quad + \quad \text{O}_2 \quad \rightleftharpoons \quad 2\text{SO}_3 \quad + \quad \text{heat} 
\]

- What will occur if we remove heat from the system?
- What will occur if we put heat into the system?
- Temperature changes the ratio of products to reactants.
  - As far as we are concerned, the results are the same as changing concentrations of reacting species.

Temperature Effects

- An exothermic reaction gives off heat, so adding heat pushes the equilibrium back to products. –
  - Result: increases reactants just as if we had added product

- An endothermic reaction requires heat, so adding heat pushes the equilibrium to products.
  - Result: increases products just as if had added reactants.
Chemical Equilibrium: Example

- The reaction of nitrogen and oxygen to form nitrogen monoxide is endothermic.

\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) + \text{heat} \rightleftharpoons 2\text{NO}(\text{g}) \]

- How can we push the reaction to produce more NO?
- How can we prevent the reaction from producing NO?

Summary of Equilibrium Effects.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Change</th>
<th>Reaction direction</th>
<th>Favored species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>Add reactant</td>
<td>forward</td>
<td>product</td>
</tr>
<tr>
<td></td>
<td>Remove reactant</td>
<td></td>
<td>reactant</td>
</tr>
<tr>
<td></td>
<td>Add product</td>
<td>Reverse</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Remove product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Raise T of endo</td>
<td>Forward</td>
<td>Products</td>
</tr>
<tr>
<td></td>
<td>Lower T of endo</td>
<td></td>
<td>Reactants</td>
</tr>
<tr>
<td></td>
<td>Raise T of exo</td>
<td>Reverse</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower T of exo</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The smog problem

- Nitrogen dioxide is formed in automobile exhaust.

\[ 2\text{NO}_2(\text{g} \text{red/brown}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g} \text{colorless}) \]

- The reaction to form dinitrogen tetraoxide is exothermic.
  - What will be favored if we add heat?
Equilibrium between oxygen and hemoglobin

- The process of hemoglobin picking up oxygen in our blood is reversible.
  \[
  \text{Hb} + \text{O}_2 \rightleftharpoons \text{HbO}_2
  \]

- If available Hb decreases, what will happen?
  - Less Hb will give less HbO₂ to circulate in our body.
  - CO can bind to Hb better than O₂, what will happen to HbO₂ levels when CO is present?
  - How can we increase the amount of HbO₂?
  - Hyperbaric chamber.

Another look at rate and endo/exo

- The rate of a reaction is dependent upon the activation energy.
- Endothermic and exothermic are not related to activation energy.
- We said adding heat will speed up a reaction.
- What about an exothermic reaction?

Exothermic Reaction, heat and rate

- What is the effect of adding heat (raising T) to an exothermic reaction?

  - Initially, the heat will help the reactants go to product faster, but the reaction will not last long because of the heat present.
  - The reaction will make product fast because of the heat increasing the rate, but we will not get as much product in the end.
If you want more product in an exothermic reaction, you may just have to let it react slowly at lower temperatures to favor the forward reaction.

- Cooling the reaction will favor the formation of product over time to release heat.
- Cooling will also make the reactants move more slowly, so the reaction slows down.

**Example**

Consider the effects of each change on each quantity in the reaction given:

\[ H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) + \text{heat} \]

<table>
<thead>
<tr>
<th>change</th>
<th>( H_2 )</th>
<th>( Br_2 )</th>
<th>HBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing hydrogen gas pressure</td>
<td>NA</td>
<td></td>
<td>increases</td>
</tr>
<tr>
<td>Increasing pressure of HBr</td>
<td></td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Increasing temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Another classification of reactions**

- Oxidation-Reduction reactions involve a loss and gain of electrons among reactants.
  - Oxidation –
    - loss of electrons – LEO
    - Charge becomes more positive
  - Reduction –
    - gain of electrons – GER
    - Charge becomes more negative
## Oxidation-Reduction

- What kind of reaction is shown?
- What kind of compound is calcium sulfide?
- Formation of ions can be shown in half reactions:
  - Ca → Ca²⁺ + 2e⁻
  - S + 2e⁻ → S²⁻
- We say that calcium was oxidized.
- Sulfur was reduced.

## Oxidation-Reduction

- Oxidation and reduction occur simultaneously; it is a paired reaction.
- The number of electrons lost by one species must be equal to the number gained by the other.
- Many of the basic types of reactions we discussed may also be classified as oxidation-reduction.

## Oxidation-Reduction

- You don’t have to write out the half reactions.
- You can write out the ions that occur on each side of the reaction and see how they change:
  - Remember, when an element is by itself (monatomic or diatomic), it has a 0 charge.
  - Zn + CuSO₄ → ZnSO₄ + Cu
  - Zinc changes from 0 to 2⁺ charge, did it lose or gain electrons?
  - What about copper?
  - Did sulfate change?

  How else can you classify this reaction?
Oxidation-Reduction

- The following decomposition reaction occurs in photographic film in the presence of light:
  \[ \text{AgBr} \rightarrow 2\text{Ag} + \text{Br}_2 \]

Determine what is oxidized and what is reduced:

Metals and oxidation

- When a metal changes from its elemental form (as a solid metal) to its ionic form (in an ionic compound) it always donates electrons, so it is always oxidized in the process.

- Before it is oxidized, the metal is often identified as being in its reduced form.
  - Reduced iron: elemental iron

Another view of Oxidation-reduction

- An early definition of oxidation involved the addition of oxygen to an element or compound.
  - It still involves loss of electrons.
  - It is paired with gain of electrons.
  - \[ 4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \]

What is oxidized?
What is reduced?

If addition of oxygen is oxidation, what would loss of oxygen be considered?
**Biological Oxidation-reduction**

- Metabolism involves oxidation-reduction: ethanol is oxidized to acetaldehyde:

\[
\text{CH}_3\text{OH} \\ \text{H}_2\text{C} = \text{O} + \text{2H}
\]

- Ethanol was oxidized:
  - count the number of electrons in ethanol vs. acetaldehyde
  - also, you added a bond to O

- You can also tell ethanol was oxidized because it lost two H atoms.
  - note these are neutral H atoms, not H+ cations
  - How many electrons does each H atom carry?

**Biological Oxidation-reduction**

- If ethanol was oxidized, something had to be reduced:

  It was not shown in the reaction, but our bodies have molecules that accept or donate H atoms in oxidation reduction reactions.

  The molecule that accepted the hydrogens from ethanol was reduced in order for ethanol to be oxidized.

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Always</strong></td>
<td><strong>Always</strong></td>
</tr>
<tr>
<td>Loss of electrons</td>
<td>Gain of electrons</td>
</tr>
<tr>
<td>Addition/gain of oxygen</td>
<td>Loss of hydrogen</td>
</tr>
<tr>
<td>Loss of oxygen</td>
<td>Gain of hydrogen</td>
</tr>
<tr>
<td><strong>Sometimes</strong></td>
<td><strong>Sometimes</strong></td>
</tr>
<tr>
<td>Loss of hydrogen</td>
<td>Gain of hydrogen</td>
</tr>
</tbody>
</table>
In the combustion of propane, is propane oxidized or reduced?

\[ C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + \text{energy} \]

An interesting example:

- A half reaction for the formation of partially hydrogenated oil is shown below.
- An unsaturated fat is changed to a saturated fat.

\[ C_{18}H_{32}O_2 + 2H_2 \rightarrow C_{18}H_{36}O_2 \]

Is the fat oxidized or reduced in the process?

Identifying Oxidation-Reduction

- Determine whether each reaction is an oxidation-reduction reaction:

  \[ \text{Zn} + \text{Cl}_2 \rightarrow \text{ZnCl}_2 \]

  \[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \]

  \[ \text{BaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{BaCO}_3 + 2\text{NaCl} \]
Some practice

Identify what is oxidized and what is reduced in each reaction:

\[ \text{Cl}_2 + 2\text{NaBr} \rightarrow 2\text{NaCl} + \text{Br}_2 \]

\[ 2\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Sn}^{4+} \]

\[ 2\text{PbO} \rightarrow 2\text{Pb} + \text{O}_2 \]

\[ 2\text{Li} + \text{F}_2 \rightarrow 2\text{LiF} \]

\[ \text{C}_4\text{H}_8 + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10} \]