Thermodynamics

Why reactions occur.

Topics of this Lecture

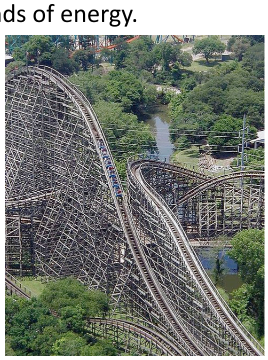
- Potential Energy/Kinetic Energy
- Energy and Chemical Bonds
- Heat of Reaction/Enthalpy (ΔH)
- Free Energy (ΔG)
- Entropy (ΔS)
- Spontaneous Reactions
- Forward and Backward Reactions
- Rate of Reaction and Catalysts

Kinetic and Potential Energy

The two fundamental kinds of energy.

Potential energy is stored energy. The car poised at the top of the roller coaster has potential energy waiting to be released. As the cars move down the track their potential energy decreases.

Kinetic energy is the energy of motion. When the car rolls downhill the potential energy is converted to kinetic energy.



Potential Energy in Chemicals

- Potential energy is stored in chemical bonds.
- When chemical bonds break, potential energy is changed into kinetic energy.*
- When this happens heat is released to the environment around the bonds.
- This heat is measured in calories or joules.
- Calories and joules are both units of energy.

*This is like the roller coaster car traveling down the track. The potential energy decreases as the car moves down the track but the car's velocity, and so its kinetic energy, increases.

Energy from Chemical Reactions

Burning natural gas can be described by the following chemical reaction.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

- In this reaction the potential energy stored in the C-H and O=O bonds is greater than the potential energy of the C=O and H-O bonds.
- In this reaction the potential energy drops by 213 kcal for each mole of CH_4 that reacts.
- Just as in the case of the rollercoaster, a drop in the potential energy of the system means there is an increase in kinetic energy.

Exothermic Reactions

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

- When the potential energy drops by 213kcal/mole the kinetic energy increases by this amount.*
- This increase in kinetic energy means there is an increase in temperature, so this reaction gives off heat.
- When a chemical reaction warms things up it is called an **exothermic** reaction.

* Why is this written are 213kcal**/mole?**

Energy for Chemical Reactions

Oxygen and nitrogen react to form nitric oxide.

$N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$

- In this reaction the potential energy stored in the N≡N and O=O bonds is less than the potential energy of the N=O bonds.
- When this reaction takes place the potential energy of the system increases by 43 kcal for each mole of $N_{2(g)}$ that reacts.
- Just as in the case of the rollercoaster, an increase in the potential energy of the system means there is a drop in kinetic energy.
- When a car travels up the hill, its velocity slows as its potential energy increases.*

*This is not the case when the car is pulled up a hill, by a motor.

Endothermic Reaction

$N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$

- When the potential energy of the system increases by 43 kcal/mole the kinetic energy of the system must decrease this amount.
- This is because the sum of the potential and kinetic energy mush stay the same. (Energy is conserved.)
- A decrease in the kinetic energy of the particles means that there is a decrease in the temperature of the particles.
- When a chemical reaction is cooling it is called an **endothermic** reaction.

Enthalpy

- The energy that is absorbed in a reaction, or released in a reaction, is called the enthalpy change of the reaction. The enthalpy change is given the symbol ΔH.
- When:
- **ΔH<0** heat is given off during the reaction and the reaction is called **exothermic**.
- **ΔH>0** the reaction is cooling and the reaction is called **endothermic**.

Spontaneous Reactions

Methane burns readily once the process is started. It is a spontaneous process

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

A **spontaneous reaction** is one that proceeds without any external influence, once started.

The reaction between nitrogen and oxygen, does not occur spontaneously under usual circumstances.*

$$N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$$

It is **nonspontaneous.**

*Nitrogen and Oxygen in the air around us are not reacting.

Spontaneous Reactions and Enthalpy Changes

- Many chemical reactions that are spontaneous have a negative enthalpy change (**ΔH<0**). But not all.
- The reaction between vinegar and baking soda is cooling.

$$HCO_3^- + CH_3COOH \rightarrow CH_3COO^- + H_2O + CO_{2(g)}$$

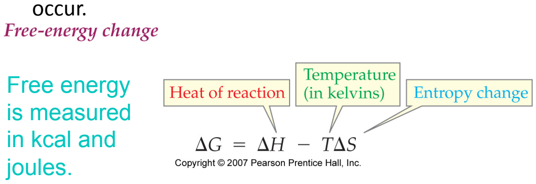
- When did you see this reaction in lab?
- Other cooling reactions?

Going uphill

If we only consider potential and kinetic energy then the reaction between baking soda and vinegar would be like rollercoaster cars moving up the track from a stopped position.

Spontaneity and Free Energy

- Changes in potential energy determine whether or not a reaction will be exothermic or endothermic, but it is **free energy** that determines if a reaction will occur.



Free energy is measured in kcal and joules.

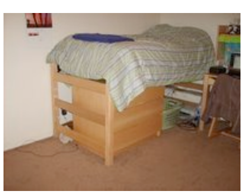
Temperature is in Kelvins
Degree K = degrees Celsius + 273

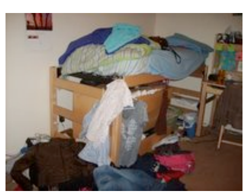
Free Energy, Enthalpy and Entropy

- $\Delta G = \Delta H - T\Delta S$
- **ΔG** is the **free energy change** that is associated with a reaction. When,
  - ΔG < 0 the reaction is spontaneous
  - ΔG > 0 the reaction is not spontaneous
- Whether or not a reaction is spontaneous depends on the balance of **ΔH**, *enthalpy*, and **ΔS**, *entropy*.

Entropy

Entropy is a measure of the disorder in a system.

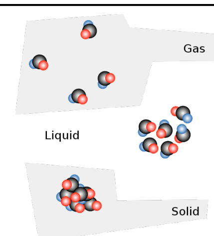




Ordered – The room is only orderly when things are in their places.

Disordered – When a room is disordered there are many places something might be.

Entropy Increases



ΔS >0, when disorder ↑.

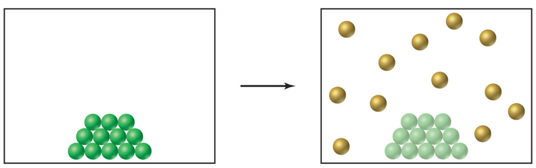
For example:

- solid→liquid
- liquid→gas

- A solid is like a room with things where they should be and the drawers closed properly.
- A liquid is like a room where things are almost where they should.
- The room is like a gas when things belong where ever they happen to be.

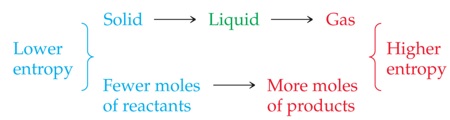
Entropy Increases

In some reactions disorder increases. This happens when there are more arrangements atoms in the products than there are in the reactants. (Decomposition)



ΔS is positive when…

- solids become liquids and when liquids become gases.
- the disorder in the products is greater than the disorder in the reactants



Entropy and Free Energy

$$\Delta G = \Delta H - T\Delta S$$

- Temperature, in units Kelvin, is always positive, so the larger the value of ΔS the smaller ΔG.
- ΔS has units joules/K or kcal/K
- A reaction that increases the disorder of the system is a reaction that is favored by entropy.

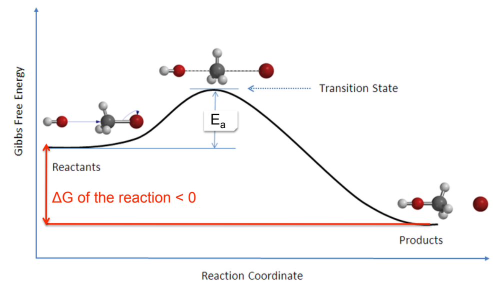
What Determines Spontaneity

- If a reaction is exothermic ($\Delta H<0$) and involves an increase in disorder ($\Delta S>0$)the reaction will happen.
- If a reaction is endothermic ($\Delta H>0$) and involves a decrease in disorder ($\Delta S<0$)the reaction will not happen.
- Otherwise you can't tell, unless you know more about ΔH, ΔS and T.

$\Delta G = \Delta H - T\Delta S$

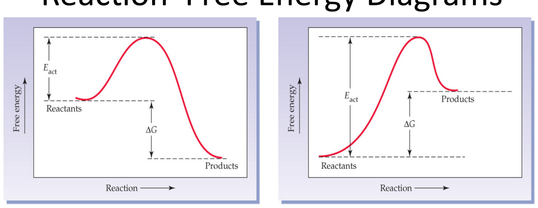
ΔH	ΔS	ΔG
(-) favorable	(+) favorable	(-) spontaneous always
(+) unfavorable	(-) unfavorable	(+) nonspontaneous always
(-) favorable	(-) unfavorable	(-) spontaneous @ Low T (+) nonspontaneous @ High T
(+) unfavorable	(+) favorable	(+) nonspontaneous @ Low T (-) spontaneous @ High T

Reaction Coordinates--ΔG



Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^\ddagger \rightarrow CH_3OH + Br^-$

Reaction Free Energy Diagrams



(a) An exergonic reaction (b) An endergonic reaction

The difference between reactant and product energy levels is the free energy change, *ΔG*. (a) is spontaneous, (b) is nonspontaneous. A reaction that is favored has *ΔG*<0. The reaction in (a) will occur without support once it is started.

One Way Reactions-Large ΔG

- $2Na(s) + Cl_2(g) \rightarrow 2NaCl$
- $N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$

Double Arrow Reactions-Small ΔG

- NH_3+H_2O<-->NH^{4+} + OH^-
- CH_3COOH <-->CH_3COO + H^+

How far toward completion?

- The more negative ΔG the farther the reaction goes toward completion.
- The amount of product produced relative to the amount of reactant is determined by ΔG.

Reaction Barriers

Not all spontaneous reactions happen as soon as the reactants are near each other, and not all reactions take place quickly. Often even though are reaction will turn all of the reactants into products it still takes a long time.

What keeps a reaction from just happening?

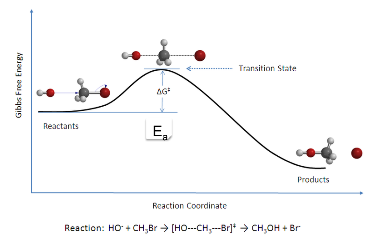
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

- Natural gas and oxygen do not immediately react. A spark is needed.
- There is an energy barrier to reactions even when they are spontaneous.
- A spark heats up the gas and the oxygen near it and this gets some of the reactants over the energy barrier.

7.5 How Do Chemical Reactions Occur? Reaction Rates

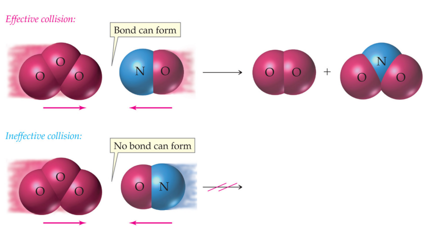
- For a chemical reaction to occur, reactant particles must collide, some chemical bonds have to break, and new bonds have to form. Not all collisions lead to products, however.
- In order for a reaction to take place molecules or atoms must collide with sufficient speed and in the correct orientation.

Activation Energies



In order for the reaction to take place the energy available must be greater than the activation energy, E_a.

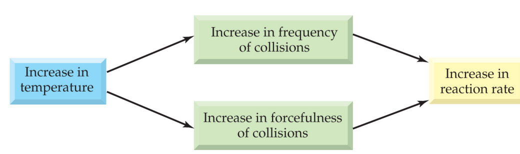
Activation Barrier



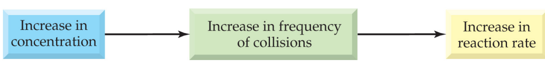
- For a collision between NO and O_3 molecules to give O_2 and NO_2, the molecules must collide so that the right atoms come into contact. No bond can form if the molecules collide with the wrong orientation.

7.6 Effects of Temperature, Concentration, and Catalysts on Reaction Rates

Reaction rates increase with temperature. With more energy the reactants move faster. The frequency of collisions and the force with which collisions occur both increase. As a rule of thumb, a 10°C rise in temperature causes a reaction rate to double.

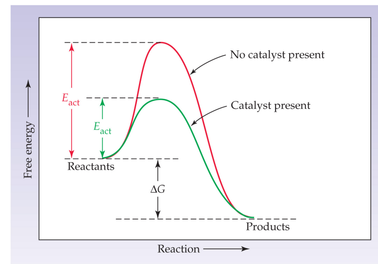


- A second way to speed up a reaction is to increase the concentrations of the reactants.
- With reactants crowded together, collisions become more frequent and reactions more likely. Flammable materials burn more rapidly in pure oxygen than in air because the concentration of molecules is higher (air is approximately 21% oxygen).
- Hospitals must therefore take extraordinary precautions to ensure that no flames are used near patients receiving oxygen.



- A third way to speed up a reaction is to add a **catalyst**—a substance that accelerates a chemical reaction but is itself unchanged in the process.

- A catalyst speeds a chemical reaction by lowerering the activation energy.



The table below summarizes ways that reactions can be speeded up, or made to occur.
In biological systems all of these methods for speeding reactions are important, but enzymes, which are the catalysts commonly found in organisms, are the most commonly noted example.

TABLE 7.2 Effects of Changes in Reaction Conditions on Reaction Rate

CHANGE	EFFECT
Concentration	Increase in reactant concentration increases rate.
	Decrease in reactant concentration decreases rate.
Temperature	Increase in temperature increases rate.
	Decrease in temperature decreases rate.
Catalyst added	Increases reaction rate.

Enzymes

- The thousands of biochemical reactions continually taking place in our bodies are catalyzed by large protein molecules called enzymes. Enzymes promote reactions by controlling the orientation of the reacting molecules. Since almost every reaction is catalyzed by its own specific enzyme, the study of enzyme structure, activity, and control is a central part of biochemistry.

Exercises

- Draw an energy diagram for a reaction that is very fast but has only a small negative free energy change.

Exercises

- Draw an energy diagram for a reaction that is very slow but has only a small negative free energy change.

Topics of this Lecture

- Potential Energy/Kinetic Energy-roller coaster
- Energy and Chemical Bonds-Potential Energy in Bonds
- Heat of Reaction/Enthalpy (ΔH) Defined-kinetic energy
- Free Energy (ΔG)-Spontaneous Reactions
- Entropy (ΔS)
- Forward and Backward Reactions
- Rate of Reaction and Catalysts