Thermodynamics

Why reactions occur.

Topics of this Lecture

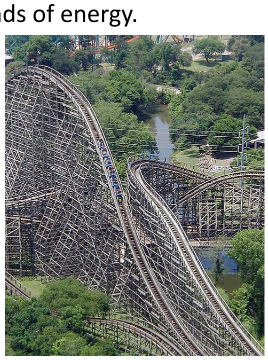
- Potential Energy/Kinetic Energy
- Energy and Chemical Bonds
- Heat of Reaction/Enthalpy (ΔH)
- Free Energy (ΔG)
- Entropy (ΔS)
- Spontaneous Reactions
- Forward and Backward Reactions
- Rate of Reaction and Catalysts

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.

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

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

Going uphill

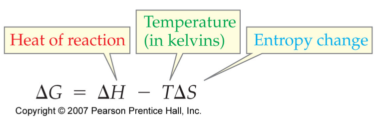
If we only consider potential and kinetic energy then the reaction between baking soda and vinegar would be like rollercoaster cars moving up the track from a stopped position.

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 change

Free energy is measured in kcal and joules.



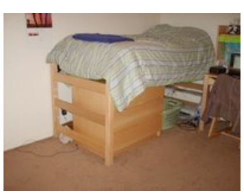
Temperature is in Kelvins
Degree K = degrees Celsius + 273

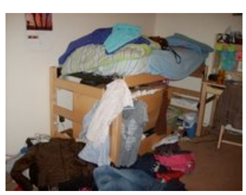
Free Energy, Enthalpy and Entropy

- $\Delta G = \Delta H - T\Delta S$
- **ΔG** is the **free energy change** that is associated with a reaction. When,
  - $\Delta G < 0$ the reaction is spontaneous
  - $\Delta G > 0$ 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.

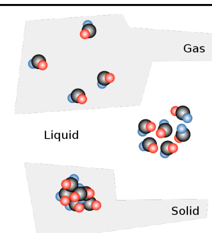




Ordered – The room is only orderly when things are in their places.

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

Entropy Increases



$\Delta S > 0$, when disorder ↑.

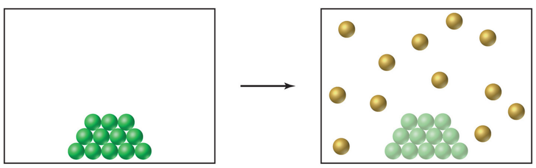
For example:

- 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

Solid ⟶ Liquid ⟶ Gas

Fewer moles of reactants ⟶ More moles of products

Lower entropy … Higher entropy

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.

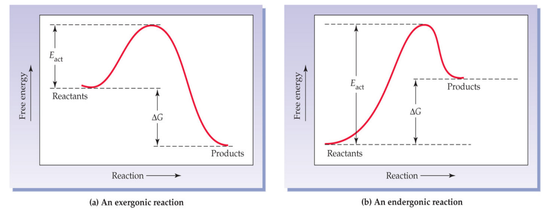
What Determines Spontaneity

- 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 Free Energy Diagrams



A reaction begins on the left and proceeds to the right. The difference between reactant and product energy levels is the free energy change, ΔG. (a) is spontaneous, (b) is nonspontaneous

One Way Reactions-Free Energy Diagrams

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

Double Arrow Reactions

- $NH_3+H_2O \leftrightarrow NH^{4+} + OH^-$
- $CH_3COOH \leftrightarrow CH_3COO + H^+$

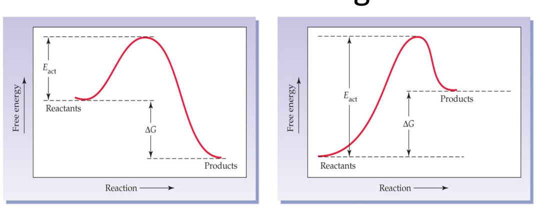
How far toward completion?

- The more negative ΔG the farther the reaction goes toward completion.
- ΔG can be changed by changing the temperature or the environment
- But the amount of product produced relative to the amount of reactant is determined by ΔG.

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.

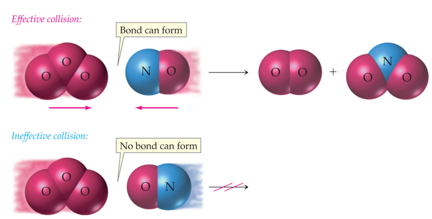
Activation Energies



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

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

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.

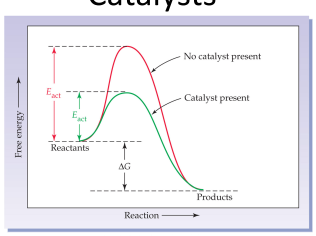
Exercises

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

Catalysts

- It is not possible to shift the ratio of reactants and products, but reactions can be speeded up.
- This is what a catalyst does.

Catalysts



A reaction energy diagram in the presence (green curve) and absence (red curve) of a catalyst. The free energy change for the reaction (delta *G* value) is unaffected by the presence of the catalyst.

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- Heat of Reaction/Enthalpy (ΔH) Defined-kinetic energy
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- Entropy (ΔS)
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