

Chapter 9 – Reaction Energetics

Introduction

We use the term *energetics* to combine two very important fields of study: thermodynamics and kinetics. Thermodynamics is the study of energy and its transformations. Kinetics is the study of the rates and mechanisms of reactions. A thermodynamic study of a reaction examines energy differences between the reactants and products. These studies allow us to predict how much product can be obtained. Thermodynamics is not concerned with how long the reaction takes or how it occurs. These latter concerns are the domain of kinetics. In this chapter, we examine the energetics of some reactions to better understand how reactions occur, to learn how to predict the feasibility of a reaction, and to determine the effect of temperature on both the amount of product and the rate of reaction.

9.1 First Law of Thermodynamics

Introduction

Thermodynamics is the study of energy and its transformations. In chemistry, thermodynamics studies consider the energy difference between the reactants and products. These studies allow us to predict the amount of product that we can expect. We start our study of thermodynamics with the first law of thermodynamics—energy cannot be created or destroyed.

Objectives

- Predict the sign of ΔE for common processes.
- Indicate the direction of energy flow from the sign of ΔE .
- Distinguish between system, surroundings, and universe.
- State the first law of thermodynamics.
- Define the terms q and w and explain what their signs indicate.
- Distinguish between *endothermic* and *exothermic*.
- Determine the energy change of a system given the amount of heat that it absorbs or gives off and the amount of work it does or has done on it.

9.1-1. Energy Change

The sign of ΔE indicates the direction of energy flow.

The energy change of a system is defined as the system's final energy minus its initial energy; that is, $\Delta E = E_{\text{final}} - E_{\text{initial}}$.

- $\Delta E > 0$ means that the energy of the final state of the system is greater than that of the initial state, so this **energy flows into the system**.
- $\Delta E < 0$ means that the energy of the final state of the system is less than that of the initial state, so this **energy flow out of the system**.
- $\Delta E = 0$ means that the energy of the final and initial states of the system are the same, so **there is no energy flow**.

9.1-2. Sign of ΔE Exercise

EXERCISE 9.1:

Indicate whether $\Delta E < 0$, $\Delta E > 0$, or $\Delta E = 0$ for each of the following. Assume that the system is the object mentioned in the problem.

heating water 25 °C to 50 °C

$$\Delta E < 0$$

$$\Delta E > 0$$

$$\Delta E = 0$$

moving positive charge closer to negative charge

$$\Delta E < 0$$

$$\Delta E > 0$$

$$\Delta E = 0$$

evaporating 1 g of water at 25 °C

$$\Delta E < 0$$

$$\Delta E > 0$$

$$\Delta E = 0$$

moving a ball from a table top to the floor

$$\Delta E < 0$$

$$\Delta E > 0$$

$$\Delta E = 0$$

heating a piece of zinc from 25 °C to 75 °C and then cooling it back to 25 °C

$$\Delta E < 0$$

$$\Delta E > 0$$

$$\Delta E = 0$$

9.1-3. First Law

Energy can be moved from one place to another, but it cannot be created or destroyed.

The **system** in a thermodynamic problem is simply that portion of the universe that is being studied. It exchanges energy with its **surroundings**. The system and its surroundings constitute the thermodynamic **universe**.

$$\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}}$$

Note that both the universe and surroundings quantities are subscripted, but the system quantity is not.

The *first law of thermodynamics*, states that energy is neither created nor destroyed.

$$\Delta E_{\text{univ}} = 0 \text{ for all processes} \quad \text{First Law of Thermodynamics} \quad (9.1)$$

$\Delta E_{\text{univ}} = 0$ implies the following.

$$\Delta E = -\Delta E_{\text{sur}} \quad \text{Energy Exchange} \quad (9.2)$$

We conclude that the first law of thermodynamics implies that **the energy of a system can be changed only by exchanging energy with its surroundings**.

9.1-4. Determining ΔE Exercise

EXERCISE 9.2:

75 J of energy is transferred when a hot rod is cooled in water. Determine the value of ΔE for the process when each of the following are considered to be the system.

rod _____ J

water _____ J

water and rod _____ J

A reaction releases 175 kJ of energy. Answer the following if the reaction is the system.

$$\Delta E = \text{_____ kJ}$$

$$\Delta E_{\text{sur}} = \text{_____ kJ}$$

$$\Delta E_{\text{univ}} = \text{_____ kJ}$$

9.1-5. Heat and Work

When q and w are positive, energy flows into the system.

Heat (q) and work (w) are the two most common ways to move energy between a system and its surroundings. The energy of a system increases when it absorbs heat or when work is done on it, and its energy decreases when it gives off heat or does work. Thus, the following is another expression for the first law of thermodynamics.

$$\Delta E = q + w \quad \text{Heat and Work in Energy Flow} \quad (9.3)$$

q is the heat absorbed by the system and w is the work done on the system.

$q > 0$	The system absorbs heat, which increases its energy. Processes in which heat enters the system are said to be endothermic .
$q < 0$	The system gives off heat, which lowers its energy. Processes in which heat leaves (exits) the system are said to be exothermic .
$w > 0$	Work is done on the system, so the energy of the system increases.
$w < 0$	Work is done by the system, so the energy of the system decreases.

Table 9.1: The Signs of Heat and Work and the Direction of Energy Flow

9.1-6. Heat and Work Exercise

EXERCISE 9.3:

A system absorbs 500 J of heat and does 300 J of work.

What is the value of q ?

$$q = \text{_____ J}$$

What is the value of w ?

$$w = \text{_____ J}$$

What is the energy change for the process?

$$\Delta E = \text{_____ J}$$

9.2 Enthalpy

Introduction

Typically, reactions are carried out at constant pressure and the initial and final temperatures are the same. Gases that are produced by a reaction that is open to the atmosphere can carry away some of the energy of the reaction (they do work when they escape), and that energy is lost. Thus, the thermodynamic property of a reaction that is carried out at constant pressure that is most important is the heat that is exchanged with the surroundings. In this section, we define that thermodynamic property.

Objectives

- Define the *enthalpy (heat) of reaction*.
- Determine the relative energies of the reactants and products given the enthalpy of reaction.
- Define the standard state.
- Explain the meaning of a superscript zero on a thermodynamic quantity.
- Explain what the *s*, *l*, or *g* after each substance in a thermochemical equation specifies.
- Determine the enthalpy change for the reaction of a given number of moles of a reactant given the thermochemical equation for the reaction.
- Determine the enthalpy change of a reaction given the enthalpy change for the reaction in which the coefficients have been multiplied by some number and/or the reaction is written in the reverse direction.

9.2-1. Enthalpy of Reaction

The enthalpy of reaction is the heat absorbed at constant T and P . It is positive for endothermic reactions and negative for exothermic reactions.

The *enthalpy of reaction*, ΔH , is the heat absorbed by a reaction when it is carried out at constant temperature and pressure. Its sign indicates the direction of heat flow. ΔH is defined as the heat absorbed, so it is positive if the reaction absorbs heat from the surroundings and negative if the reaction gives off heat to the surroundings. **The sign of the heat flow is often designated by indicating that the heat was absorbed (positive) or released (negative).** Thus, +10 J is read ‘ten joules are absorbed,’ while -10 J is read ‘ten joules are released.’

The reactants are at higher energy than the products in exothermic reactions.

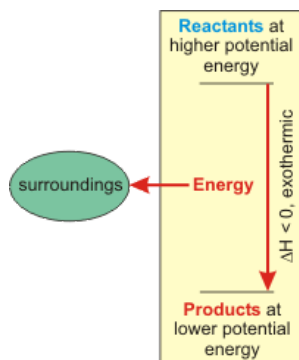


Figure 9.1a: Exothermic Processes

The reactants are higher in enthalpy than the products, so energy must be given off to the surroundings when the reactants are converted to products. Thus, $\Delta H < 0$ for the reaction. The reaction is exothermic because it gives off heat to the surroundings causing the surroundings to warm.

The reactants are at lower energy than the products in endothermic reactions.

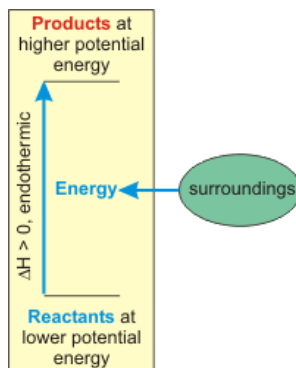


Figure 9.1b: Endothermic Processes

The reactants are lower in enthalpy than the products, so energy must be absorbed from the surroundings to convert the reactants to products. Thus, $\Delta H > 0$ for the reaction. The reaction is endothermic because it absorbs heat from the surroundings causing the surroundings to cool.

9.2-2. Standard States

Standard states are defined at 1 atm pressure, but there is no standard temperature.

Thermodynamic properties, such as ΔE and ΔH , depend upon the states of the substances. Consequently, tabulated values of thermodynamic properties are given for reactions in which the reactants and products are all in their *standard states*.

- The standard state of a pure substance at a given temperature is its most stable form at that temperature and 1 atm pressure. Unless indicated differently, assume that solids and liquids are pure.
- Gases are considered pure substances even when there is a mixture of gases because the molecules are far apart and do not interact. Thus, the standard state of a gas is a partial pressure of 1 atm.
- The standard state of a dissolved substance is a concentration of 1 mole of substance per liter of solution at a pressure of 1 atm.

The standard state of a substance also depends upon the temperature, but **there is no standard temperature**. Tabulated values of thermodynamic properties are most often given at a temperature of 298 K (25 °C), and 298 K should be assumed if no temperature is given.

EXERCISE 9.4:

Indicate the standard state of each of the following.

oxygen at $-20\text{ }^{\circ}\text{C}$

solid

liquid

1 atm gas

1 M concentration

water at $-20\text{ }^{\circ}\text{C}$

solid

liquid

1 atm gas

1 M concentration

water at $+20\text{ }^{\circ}\text{C}$

solid

liquid

1 atm gas

1 M concentration

table sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) at $20\text{ }^{\circ}\text{C}$

solid

liquid

1 atm gas

1 M concentration

table sugar dissolved in water at $20\text{ }^{\circ}\text{C}$

solid

liquid

1 atm gas

1 M concentration

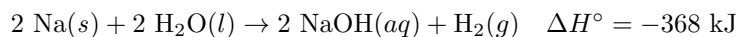
9.2-3. Standard Enthalpy of Reaction

The enthalpy change for a reaction in which all reactants and products are in their standard states is called the *standard enthalpy of reaction* and given the symbol ΔH° (the superscript '°' implies standard state conditions). Most enthalpies of reaction used in this course are standard enthalpies.

A *thermochemical equation* is a balanced chemical equation that includes a thermodynamic property such as ΔH° . Enthalpy changes depend upon the states of the substances, so the state is indicated by the following in parentheses.

- s = solid
- l = liquid
- g = gas
- aq = aqueous (water) solution

The amount of heat released during reaction depends upon the amount of material that is consumed or produced. The enthalpy given for a thermochemical equation is the amount of heat given off or absorbed when the specified number of moles of each substance reacts or is produced. As an example, consider the following thermochemical equation.

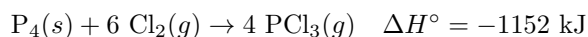


The above thermochemical equation tells us that 368 kJ of heat are liberated when

- two moles of solid sodium react,
- two moles of liquid water react,
- two moles of NaOH are produced in an aqueous solution, and
- one mole of H_2 gas is produced.

9.2-4. Stoichiometry and Thermodynamics

The thermochemical equation,



indicates that 1152 kJ of heat is liberated (negative sign) when one mole of solid phosphorus reacts with six moles of chlorine gas to produce four moles phosphorus trichloride gas. Consequently, the heat of reaction can also be expressed as any of the following.

$$\frac{-1152 \text{ kJ}}{1 \text{ mol P}_4} \quad \text{or} \quad \frac{-1152 \text{ kJ}}{6 \text{ mol Cl}_2} \quad \text{or} \quad \frac{-1152 \text{ kJ}}{4 \text{ mol PCl}_3}$$

Multiplication of any of the expressions above by the appropriate number of moles of product or reactant results in the ΔH° for the reaction in which that number of moles is formed or consumed. For example, the following determines the enthalpy change that would accompany the reaction of four moles of chlorine gas.

$$4 \text{ mol Cl}_2 \times \frac{-1152 \text{ kJ}}{6 \text{ mol Cl}_2} = -768 \text{ kJ}$$

9.2-5. Stoichiometry Exercise

EXERCISE 9.5:

Consider the thermochemical equation.



What would be the value of ΔH° under the following circumstances.

one mole of ammonia is formed _____ kJ

two moles of H_2 react _____ kJ

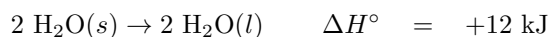
7.0 g of N_2 react _____ kJ

9.2-6. Properties of Enthalpy

We have seen that ΔH is proportional to the number of moles of substance that react. This means the following.

If the coefficients of a chemical equation are multiplied by some number, then the enthalpy of the resulting reaction equals the enthalpy of the original reaction multiplied by the same number.

For example consider the following two processes.

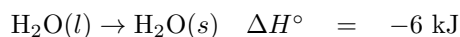
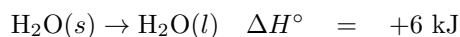


The second equation is obtained by multiplying the first by two, so the enthalpy change of the second reaction is twice the enthalpy change of the first.

A second important property of enthalpy is the following.

The sign of ΔH is changed when the direction of the reaction is reversed.

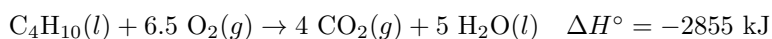
For example consider the following two processes.



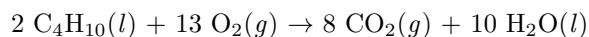
The first thermochemical equation indicates that 6 kJ are absorbed when 1 mole of ice melts. In the second equation, the direction of the process is reversed, so the sign of ΔH must be changed. We conclude that freezing 1 mole of liquid water releases 6 kJ of heat.

EXERCISE 9.6:

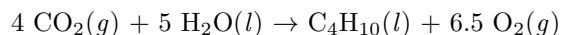
The following thermochemical equation for burning butane is given.



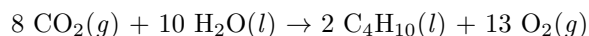
Determine the enthalpy of reaction for each of the following.



_____ kJ



_____ kJ



_____ kJ

9.3 Enthalpies of Combustion

Introduction

Most of the energy utilized by humans comes from combustion reactions (reactions with O_2). The internal combustion engine that runs our cars gets its energy from the combustion of gasoline. Many homes are heated by the combustion of coal, oil, or natural gas. Many power plants generate electricity by burning (combusting) coal, and humans obtain the energy needed to sustain life by the combustion of carbohydrates. The carbon in the fuel is converted to CO_2 and the hydrogen is converted to H_2O by the reaction with O_2 . In this section, we examine enthalpies (heats) of combustion.

Objectives

- Define enthalpy of combustion and write the chemical equation to which the enthalpy of combustion of a substance applies.

9.3-1. Enthalpies of Combustion

Combustion is the reaction of a substance with oxygen, and it is the major source of harnessed energy. Combustion reactions are always exothermic, and it is the energy released in combustion reactions that fuels our vehicles, heats our homes, and powers our bodies. The products of combustion are usually, but not always, the oxides of the elements comprising the molecule being combusted.

The standard molar *enthalpy of combustion* of a substance is the heat absorbed when one mole of the substance reacts with O_2 at standard conditions.

Consider the following thermochemical equations that deal with some common combustion reactions.

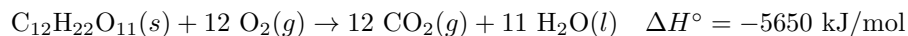
$C_6H_{12}O_6(s) + 6 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(l)$	$\Delta H^\circ = -2816 \text{ kJ}$	Our bodies derive energy from the combustion of glucose (a sugar).
$6 CO_2(g) + 6 H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6 O_2(g)$	$\Delta H^\circ = +2816 \text{ kJ}$	Plants make glucose in photosynthesis by reversing the glucose combustion reaction. The energy required to make this endothermic reaction proceed is supplied by the sun.
$4 Fe(s) + 3 O_2(g) \rightarrow 2 Fe_2O_3(s)$	$\Delta H^\circ = -1648 \text{ kJ}$	Rusting of iron is the basis of corrosion.

Table 9.2: Thermochemical Equations for Some Common Combustion Reactions

9.3-2. Combustion Exercise

EXERCISE 9.7:

The calorie content of carbohydrates, fats, and proteins are all derived from their heats of combustion because they are all burned in the body. In this example, we use the heat of combustion of sugar to determine the number of calories in a teaspoon of sugar. The thermochemical equation for the combustion of sucrose (table sugar) is the following.



How many calories are in a heaping teaspoon of sugar (4.8 g)?

What is the number of moles of sugar present ($M_m = 342 \text{ g/mol}$)?

_____ mol

What is the amount of heat liberated during the combustion?

_____ kJ

If there are 4.18 kJ in a dietary calorie, what is the number of dietary calories present in the sugar?

_____ Cal

9.4 Bond Energies

Introduction

Recall from Chapter 5 that bond formation involves a lowering of the energy of the system, i.e., bond formation is an exothermic process. Reversing the direction of the reaction, changes the sign of ΔH , so bond breaking is an endothermic process. The energy released or absorbed during a chemical reaction comes from or is stored in chemical bonds, and the enthalpy change of a reaction can be estimated from tabulated values of bond energies.

Prerequisites

- 5.1 The Covalent Bond

Objectives

- Define the bond or dissociation energy.
- Estimate the enthalpy of reaction from bond energies.

9.4-1. Bond Energies

The *bond energy* or *dissociation energy* (D) of a bond is the energy required to break one mole of bonds in the gas phase.

A table of bond energies can be found in the resource named Bond Energies.

Bond energies are always positive because bonds require energy to be broken.

$\text{H-H} \rightarrow 2\text{H}$	$\Delta H = D_{\text{H-H}} = +436 \text{ kJ}$	Breaking an H-H bond requires 436 kJ of energy.
$\text{F-F} \rightarrow 2\text{F}$	$\Delta H = D_{\text{F-F}} = +155 \text{ kJ}$	Breaking an F-F bond requires 155 kJ of energy.
$\text{H} + \text{F} \rightarrow \text{H-F}$	$\Delta H = -D_{\text{H-F}} = -(565) = -565 \text{ kJ}$	Forming an H-F bond releases 565 kJ of energy.

Table 9.3: Examples of Some Thermochemical Equations involving Bond Energies

9.4-2. Estimating Enthalpy

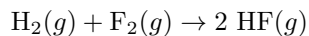
Reactions involve breaking and forming bonds, and the heat generated or absorbed during a reaction is the net result. If we knew the energies of all of the interactions involved, we could determine the enthalpy of reaction by determining how much energy must be supplied to break all of the interactions that had to be broken and subtracting the energy that is released when all of the new interactions form. Bond energies give us estimates of these energies, but tabulated bond energies are averages. For example, a C-Cl bond in CCl_4 is different from a C-Cl bond in COCl_2 , but only one C-Cl bond energy is tabulated. In addition, bond energies are defined only for gas phase molecules, so other interactions can be ignored, but many reactions occur in solution where solvation and other interactions complicate the problem. However, bond energies can be used to obtain approximate enthalpies from the following.

The enthalpy of a reaction can be *approximated* by the sum of the bond energies of the bonds that must be broken less the sum of the bond energies of those that must be formed.

$$\Delta H \sim \Sigma D_{\text{broken}} - \Sigma D_{\text{formed}} \quad \text{Enthalpy of Reaction from Bond Energies} \quad (9.4)$$

EXAMPLE:

For example, let us approximate the enthalpy of reaction for the following.



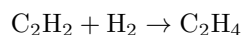
One H-H bond and one F-F bond must be broken and two H-F bonds must be formed. The needed bond energies are given in Table 9.3.

$$\begin{aligned} \Delta H &\sim \Sigma D_{\text{broken}} - \Sigma D_{\text{formed}} \\ &\sim D_{\text{H-H}} + D_{\text{F-F}} - 2D_{\text{H-F}} \\ &= 436 + 155 - 2(565) \\ &= -539 \text{ kJ} \end{aligned}$$

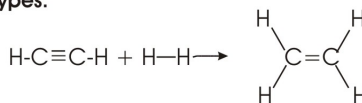
The above calculation works well for the HF example because there is only one kind of H-H, F-F, and H-F bonds and the reaction is a gas phase reaction.

EXAMPLE:

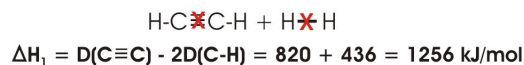
Use tabulated bond energies to estimate the enthalpy of the following reaction.



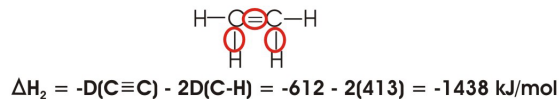
Step 1: Draw the Lewis structures to identify the bond types.



Step 2: Break all reactant bonds that are not present in the product.



Step 3: Form all product bonds that were not present in the reactants.



Step 4: Determine ΔH of reaction as the sum of Steps 2 & 3.

$$\Delta H = \Delta H_1 + \Delta H_2 = 1256 - 1438 = -182 \text{ kJ/mol}$$

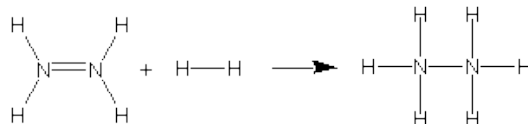
$$\Delta H = \sum D(\text{bonds broken}) - \sum D(\text{bonds formed})$$

$$\Delta H = [820 + 436] - [612 + 2(413)] = -182 \text{ kJ/mol}$$

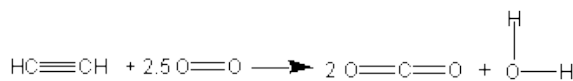
9.4-3. Bond Energy Exercise

EXERCISE 9.8:

Use the Bond Energies resource to estimate the enthalpy changes for the following reactions.



$$\Delta H = \text{_____} \text{ kJ/mol}$$

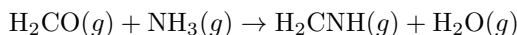


$$\Delta H = \text{_____} \text{ kJ/mol}$$

9.4-4. Bond Energy and Lewis Structure Exercise

EXERCISE 9.9:

Determine ΔH for the following reaction.



First determine the Lewis structures to get the bond orders of all bonds. Review Section 5.6 Determining Lewis Structures if you have forgotten how to determine Lewis structures.

Bond Orders: All bonds to hydrogen are single bonds, but the other bond orders need to be determined.

C-O bond order in H_2CO

C-N bond order in H_2CNH

Enthalpies: Use the Bond Energies resource to determine the following enthalpies. Break and form only those bonds that do not appear in both the reactant and product side.

energy required to break the reactant bonds

_____ kJ

energy released when product bonds are formed

_____ kJ

Finally, determine the enthalpy of reaction.

$\Delta H = \text{_____} \text{ kJ}$

9.5 Entropy

Introduction

A *spontaneous process* is one that takes place without intervention. A ball rolls down a hill spontaneously, but it does not roll uphill spontaneously. It can be made to roll uphill but only with intervention. We have used the concept that systems in nature strive to lower energy, so our first hypothesis might be that exothermic processes are spontaneous, while endothermic processes are not. However, there are spontaneous endothermic processes, such as evaporation. We saw in Chapter 8 that the energy of the molecules in the gas phase is much greater than those in the liquid phase, yet liquids do evaporate spontaneously, i.e., molecules go spontaneously from the lower energy

liquid state into the higher energy gas phase. Clearly, there is another factor, and, in this section, we consider that factor.

Objectives

- Distinguish between translational, rotational, and vibrational motion.
- Explain how the entropy of a system depends upon how freely its molecules move.
- Define entropy.
- Determine whether the entropy of reaction is positive, negative, or very small.
- State the relationship between the entropy of a system and the order of a system.
- Indicate the effects on the entropy of a system caused by adding heat and how the effect is dependent upon the temperature at which the heat is added .

9.5-1. Probability and Constraints

Unconstrained systems are statistically favored over constrained ones.

There are $10! = 3,628,800$ ways to arrange ten books on a shelf, but the books are alphabetized in only one. Thus, there are 3,628,799 ways to disburse the books in a random or disordered manner, but only one in which the books are **constrained** to be in alphabetical order. If the books were alphabetized originally but then removed and returned to the shelf without the intervention of a librarian, they would spontaneously move to a disordered state for strictly statistical reasons. If we assume that there are only two systems in our set of books, constrained or ordered and unconstrained or disordered, then the process constrained \rightarrow unconstrained is spontaneous because there are more ways in which the books can be disbursered in the unconstrained, disordered system. The process unconstrained \rightarrow constrained is not spontaneous and occurs only with intervention (a librarian in this example).

9.5-2. Types of Motion

The kinetic energy of a molecule is a combination of translational, rotational, and vibrational contributions.

We saw above that systems that can be disbursered in a less constrained manner are favored over those whose disbursement is highly constrained, and it is the disbursement of energy that drives chemical processes. We now show how molecular systems disburse their energy.

Recall from Section 7.1 Gases that thermal energy (RT) is a measure of the average kinetic energy of the molecules in a system. Kinetic energy is energy of motion, and the motion of a molecule is a combination of three types of motion called *degrees of freedom*.

- **translation:** straight line motion of the entire molecule through space
- **rotation:** circular motion of the atoms in a molecule about an axis fixed to the molecule
- **vibration:** atoms within a molecule moving relative to one another by causing small changes in bond lengths and bond angles

All atoms have three degrees of freedom because the motion of an atom can be described as a combination of its motion in the x -, y -, and z -directions. A molecule that contains n atoms has $3n$ degrees of freedom that are combinations of the three motions of its n atoms. The six degrees of freedom of a diatomic molecule are shown in Figure 9.2.

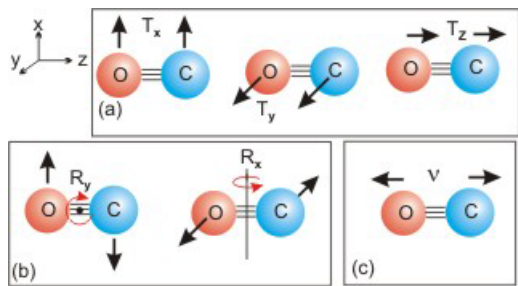


Figure 9.2: Degrees of Freedom of a Diatomic Molecule

Each atom of a diatomic molecule like CO has three degrees of freedom as they can each move in the x -, y -, or z -direction. Thus, the molecule has six degrees of freedom, which take the following forms.

- Motion of both atoms in the same direction translates the molecule in that direction.
- Motion in opposite directions along the x - or y -axis rotates the molecule about the y - or x -axis, respectively.
- Movement in opposite directions along a bonding axis results in a vibration as the bond elongates and contracts. A vibration is referred to with the greek symbol nu (ν).

9.5-3. Entropy

Entropy is a measure of the number of ways that a system can distribute its energy.

For purely statistical reasons, a system that has more ways in which it can distribute its energy is favored over one that has fewer ways. Indeed, the number of ways in which the energy of a system can be distributed is such an important property of the system that a thermodynamic property is used to measure it. The thermodynamic property is called the *entropy* (S) of the system, which has units of joules per kelvin (J/K).

- Systems with higher entropies can distribute energy in more different ways than those with lower entropies.

The entropy of a system increases as the freedom of motion of its molecules increases. Gas phase molecules have much more freedom of motion than do molecules in the liquid or solid states, so the entropy of a system of gas phase molecules is much greater than that of the same molecules in a condensed state. Molecules in the liquid state have slightly more freedom of motion than those in the solid, so the entropy of a system of molecules in the liquid state is slightly greater than in the solid state. We will use the following conclusion frequently.

$$S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$$

9.5-4. Systems Strive to Increase Their Entropy

The two driving forces behind a process are the tendencies for systems to minimize their potential energy ($\Delta H < 0$) and to maximize the number of ways in which they can distribute their energy ($\Delta S > 0$). However, unless the entropy change is large, the tendency to minimize enthalpy is the dominant driving force. We have seen how to estimate enthalpy changes from bond energies, and we now examine how to predict whether the entropy change is large and positive, large and negative, or negligible.

The entropy change of a reaction is given as $\Delta S = S_{\text{products}} - S_{\text{reactants}}$, so $\Delta S > 0$ when the entropy of the products is greater than that of the reactants. At this point, we need only predict whether ΔS is large, and, if so, what is its sign. To do this, we recall that $S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$. Indeed, we will assume that $S_{\text{liquid}} \sim S_{\text{solid}} \sim 0$ to conclude the following.

Entropy changes are large only in reactions in which the number of moles of gas changes.

Thus, the sign and magnitude of the entropy change during a reaction can be estimated from the following.

- $\Delta S > 0$ for reactions that produce gas.
- $\Delta S < 0$ for reactions that consume gas

- $\Delta S \sim 0$ (is usually negligibly small) for reactions that do not involve a change in the number of moles of gas.

ΔS can be calculated, but the procedure is beyond the scope of this course. It is covered in Chapter 4 of *Chemistry - A Quantitative Science*.

9.5-5. Constraints and Disorder as Predictors of Entropy

Constrained systems are more ordered and have lower entropies than systems that are less constrained.

We have seen that adding constraints to the motion of particles reduces their freedom of motion, which decreases their entropy. In other words, constrained systems have lower entropies than do unconstrained systems. In addition, putting constraints on a system usually results in some ordering of the system. For example, motion is unconstrained in the gas phase, so the entropy of a gas is high. However, when intermolecular forces constrain the molecules, they align to increase their interactions. The effect of such alignments is to produce the short range order found in the liquid state. Increasing the constraints on a liquid forces the molecules to align so as to maximize their interactions and produce the long range order found in the solid state. Thus, the degree to which a system is ordered is a good indicator of its freedom of motion and, therefore, of its entropy. We conclude the following.

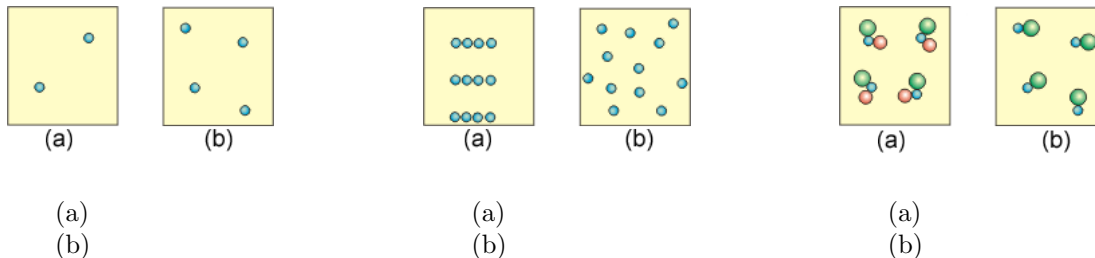
- The more disordered a system is, the greater is its entropy.

Indeed, entropy is commonly defined as a measure of the order in a system. However, entropy is a measure of the number of ways in which energy can be distributed in a system; the order of a system is simply a good predictive tool because ordered systems cannot distribute energy in as many ways as disordered ones.

9.5-6. Entropy Exercise

EXERCISE 9.10:

Predict which system in each pair has the greater entropy.



9.5-7. Effects of Heat and Temperature on Entropy

The number of ways a system can distribute its energy increases with the amount of energy it has to distribute, so the entropy of a system always increases with temperature. Similarly, adding heat to a system always increases the entropy of a system. However, 1 J of heat has much more impact when it is added to a system that has less energy (lower T) than it does when added to a system that has more energy (higher T). This relationship is expressed in the following equation, which defines entropy change.

$$\Delta S = \frac{\text{heat added reversibly}}{\text{temperature at which the heat is added}} = \frac{q_{\text{rev}}}{T} \text{ J/K} \quad (9.5)$$

q_{rev} is used to indicate that the heat must be added reversibly, which means that it must be added so slowly that the slightest change could reverse the direction of heat flow. Equation 9.5 can be rearranged to $T\Delta S = q_{\text{rev}}$, so $T\Delta S$ is an energy term.

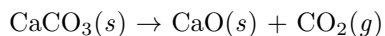
Using order as a predictor of entropy, we can understand the above with a simple analogy: the effect on the order of a room resulting when a book is casually dropped in it. The probability is very high that the book will NOT drop

into its allotted location, so the dropped book will increase the disorder (entropy) of the system. In a neat room (representing a more ordered, lower temperature system), the effect of the out-of-place book is dramatic. However, its effect on a messy room (representing a higher temperature, less ordered system) is negligible as the out-of-place book is hardly noticeable. Similarly, adding 1 J of heat to a solid at 5 K (very ordered, low entropy) has a much more dramatic effect on the entropy than adding 1 J to the vapor at 500 K (disordered, high entropy).

9.5-8. Predicting Entropy Change Example

EXERCISE 9.11:

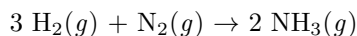
Predict the sign of ΔS° for each of the following reactions.



$$\Delta S < 0$$

$$\Delta S > 0$$

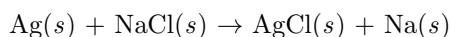
$$\Delta S \sim 0$$



$$\Delta S < 0$$

$$\Delta S > 0$$

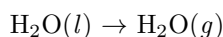
$$\Delta S \sim 0$$



$$\Delta S < 0$$

$$\Delta S > 0$$

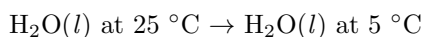
$$\Delta S \sim 0$$



$$\Delta S < 0$$

$$\Delta S > 0$$

$$\Delta S \sim 0$$



$$\Delta S < 0$$

$$\Delta S > 0$$

$$\Delta S \sim 0$$

9.5-9. Entropy Change Example

EXERCISE 9.12:

Indicate which process in each of the following pairs increases the entropy of the system more.

adding 10 J of heat to neon at 300 K

adding 50 J of heat to neon at 300 K

adding 10 J of heat to neon at 300 K

adding 10 J of heat to neon at 800 K

adding 50 J of heat to neon at 800 K

adding 10 J of heat to neon at 300 K

melting 1 g of neon at its melting point

evaporating 1 g of neon at its boiling point

9.6 Second Law of Thermodynamics

Introduction

The fact that systems seek to increase their entropy is the basis of the Second Law of Thermodynamics, the topic of this chapter.

Objectives

- State the Second Law of Thermodynamics.

9.6-1. The Second Law of Thermodynamics

Spontaneous processes must increase the entropy of the universe.

We have seen that systems with higher entropies are statistically favored over those with lower entropies, but processes impact the entropy of both the system and its surroundings. In order to determine the spontaneity of a process, we must consider the entropy change that it causes in the universe, not just the system. Indeed, the second law of thermodynamics defines spontaneity in terms of this change.

- **Second Law of Thermodynamics:** The entropy of the universe increases in all spontaneous processes; that is $\Delta S_{\text{univ}} > 0$ for all spontaneous processes.

In other words, *spontaneous processes are those that increase the entropy of the universe*. Processes that reduce the entropy of the system can be accomplished, but only if the entropy of the surroundings is increased more than the entropy of the system is decreased.

9.6-2. Entropy and Heat Flow

Heat flows spontaneously from hot to cold, never cold to hot. (It is forced to flow cold to hot in a heat pump, but energy is required, so it is not spontaneous.) We now show that this is a consequence of the second law. Consider to thermal reservoirs at T_1 and T_2 that are in thermal contact as shown below.

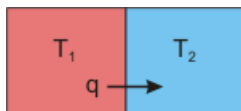


Figure 9.3

To determine the spontaneous direction of heat flow, we examine the entropy change associated with the flow of heat from T_1 to T_2 . Applying the second law to the problem, we can write the following.

$$\Delta S_{\text{univ}} = \Delta S_1 + \Delta S_2 > 0$$

ΔS_1 and ΔS_2 are the entropy changes that the heat flow causes in the two reservoirs, which can be obtained by using Equation 9.5.

$$\Delta S_1 = \frac{-q}{T_1} \quad \Delta S_2 = \frac{+q}{T_2}$$

The negative sign indicates that heat is leaving the reservoir at temperature T_1 , and the positive sign indicates that heat is entering the reservoir at temperature T_2 . Substitution of these ΔS values into the ΔS_{univ} expression yields the following.

$$\Delta S_{\text{univ}} = \frac{-q}{T_1} + \frac{+q}{T_2}$$

Thus, $\Delta S_{\text{univ}} > 0$ and the process is spontaneous only if $T_1 > T_2$. In other words, only if the heat flows from the hotter sources to a cooler one.

9.7 Free Energy

Introduction

We now show that ΔS_{univ} can be written as a sum of system quantities, and, in doing so, derive a new thermodynamic property that includes the effects of both ΔH and ΔS on the spontaneity of any process carried out at constant temperature and pressure. The new property is called the free energy because it is the energy that is free to do work.

Objectives

- Define *Gibbs free energy*, and explain why it is important.
- Describe the two driving forces behind the free energy change, and write the expression that shows how they are related to the free energy.

9.7-1. Free Energy

A spontaneous process at constant T and P is one in which $\Delta G < 0$.

Entropy changes in the universe can be broken down into the changes in the system and its surroundings.

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}}$$

During the process, heat can be exchanged between the system and the surroundings, which changes the entropy of the surroundings. For a reaction carried out at constant T and P , the amount of heat that is transferred from the system to the surroundings is $q_{\text{sur}} = -\Delta H$, so $\Delta S_{\text{sur}} = -\Delta H/T$. An exothermic reaction releases heat into the surroundings, which increases the entropy of the surroundings. The entropy change in the universe resulting from a reaction carried out at constant temperature and pressure is the following.

$$\Delta S_{\text{univ}} = \Delta S - \Delta H/T$$

Multiplying both sides by $-T$, we obtain the following.

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

The above expression for ΔS_{univ} is a function of system quantities only, so it too is a system quantity. This new thermodynamic function of the system is called the **Gibbs free energy**, ΔG or simply the **free energy**.

Thus, the driving forces behind a process carried out at constant T and P are combined into the Gibbs free energy expression.

$$\Delta G = \Delta H - T\Delta S \quad \text{Gibbs Free Energy} \quad (9.6)$$

- ΔG is the change in free energy. It is the energy that is free to do work, i.e., $-\Delta G = \text{maximum work that can be done by the process at constant } T \text{ and } P$. It dictates the spontaneous direction of the reaction. Reactions proceed spontaneously and do work in the direction in which $\Delta G < 0$.
- ΔH is the change in potential energy that results from breaking and forming interactions. Reactions that lower the potential energy of the system ($\Delta H < 0$) reduce the free energy, which is favorable.
- $T\Delta S$ is the change in free energy caused by changing the number of ways energy can be dispersed in the system. Processes that increase the entropy of a system ($\Delta S > 0$) are favored because they lower the free energy of the system by $T\Delta S$ joules.

9.7-2. Enthalpy and Free Energy

Equation 9.6 indicates that processes tend to minimize their potential energy ($\Delta H < 0$).

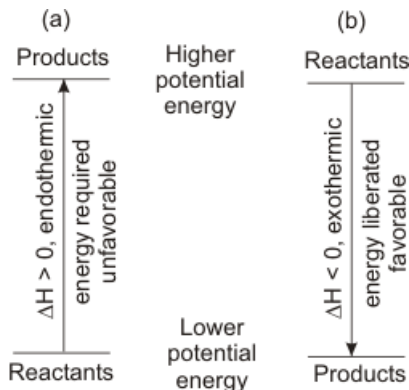


Figure 9.4: Enthalpy and Free Energy

- Endothermic reactions (Figure 9.4a) require energy, so they cannot occur spontaneously unless they can be driven by $T\Delta S$ energy. Thus, $T\Delta S > \Delta H$ for a spontaneous endothermic reaction.
- Exothermic reactions (Figure 9.4b) release energy, so they can occur spontaneously unless $T\Delta S$ is so negative that the released energy is not sufficient overcome the entropy term.

9.7-3. Entropy and Free Energy

Equation 9.6 indicates that processes tend maximize their entropy ($\Delta S > 0$).

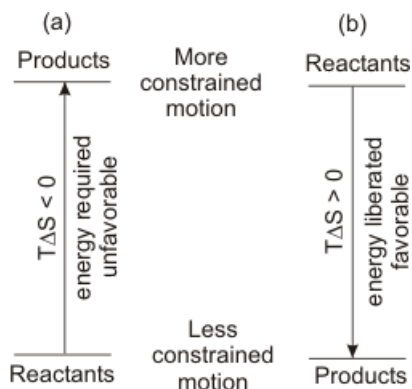


Figure 9.5: Entropy and Free Energy

- Processes for which $\Delta S > 0$ release energy that can be used to drive reactions uphill in enthalpy, but any $T\Delta S$ energy that is not used in this manner is free to do work.
- Processes for which $\Delta S < 0$ require energy, which must be supplied from ΔH if the process is to be spontaneous.

9.7-4. Free Energy and Reaction Spontaneity

There are driving forces in both the forward and reverse directions of most reactions, so double arrows are often used in chemical equations. $A \rightleftharpoons B$ shows that there are driving forces for both $A \rightarrow B$ and $A \leftarrow B$. ΔG is the difference between these forces. If $\Delta G < 0$, the forward driving force is greater, so there is a net force in the forward direction and the reaction consumes A to produce B. When $\Delta G > 0$, the reverse driving force is greater, so there is a net force in the reverse direction, and the reaction produces A by consuming B. If $\Delta G = 0$, the two forces are equal, and there is no net driving force. At this point there is no longer a change in concentrations as the reaction has reached equilibrium. Indeed, $\Delta G = 0$ is the thermodynamic definition of equilibrium at constant temperature and pressure. As summarized in the Table 9.5, the following is true.

The sign of ΔG indicates the spontaneous direction of reaction.

The value of ΔG varies with the concentrations of the reactants and products, so it changes as the process continues. Consider the evaporation of water: $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$. Initially, only liquid is present, so there is no driving force in the reverse direction (no condensation). Consequently, $\Delta G < 0$ and the liquid begins to evaporate. However, as the pressure of the vapor increases, so does the driving force in the reverse direction, so ΔG gets less negative. Eventually, the pressure of the vapor is such that the driving force in the reverse direction equals that in the forward direction, $\Delta G = 0$, and the process has reached equilibrium.

$\Delta G < 0$	Reaction spontaneous as written (\rightarrow).
$\Delta G = 0$	Reaction is at equilibrium (\rightleftharpoons).
$\Delta G > 0$	Spontaneous direction is the opposite of what is written (\leftarrow).

Table 9.4: The Sign of the Free Energy and the Direction of Reaction

9.8 Standard Free Energy and the Extent of Reaction

Introduction

The difference between the free energy of a reaction (ΔG) and the standard free energy of reaction (ΔG°) is an important one and one that is often confused by students. In this section, we examine the meaning of these two important thermodynamic properties.

Objectives

- Use the standard enthalpy and entropy of a reaction to predict the conditions of temperature at which the standard free energy is most likely negative.

9.8-1. Standard Free Energy

As is the case with enthalpies, entropies and free energies of reaction are usually given for the reaction carried out under standard conditions. The standard free energy is defined in terms of the standard enthalpy and entropy of reaction as the following.

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

Recall that the superscript zero means that all reactants and products are in their standard states at a specified temperature, so ΔG° is a constant for a reaction at that temperature.

EXERCISE 9.13:

Predict the signs of ΔH° and ΔS° . Then use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to predict the temperature conditions under which ΔG° is likely to be negative.



What is the sign of ΔH° ?

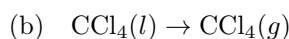
+
-

What is the sign of ΔS° ?

+
-
 ~ 0

ΔG° is most probably negative at which of the following?

all temperatures
no temperatures
low temperatures only
high temperatures only



What is the sign of ΔH° ?

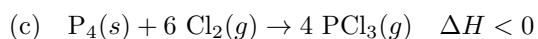
+
-

What is the sign of ΔS° ?

+
-
 ~ 0

ΔG° is most probably negative at which of the following?

all temperatures
no temperatures
low temperatures only
high temperatures only



What is the sign of ΔH° ?

+

-

What is the sign of ΔS° ?

+

-

~ 0

ΔG° is most probably negative at which of the following?

all temperatures

no temperatures

low temperatures only

high temperatures only

9.8-2. Extent of Reaction

ΔG° is the value of ΔG when all reactants and products are in their standard states. Consider the process: $\text{A}(g) \rightleftharpoons \text{B}(g)$. If $\Delta G^\circ < 0$, the reaction is spontaneous in the forward direction when both pressures are 1 atm, so equilibrium is attained by consuming A, which reduces P_A to less than 1 atm, and producing B, which increases P_B to more than 1 atm. If $P_B > P_A$ at equilibrium, the reaction is said to be extensive because the amount of product at equilibrium is much greater than the amount of reactant. If $\Delta G^\circ > 0$, the process is spontaneous in the reverse direction at standard conditions. Equilibrium in this case is attained when $P_A > P_B$, so there is more reactant than product at equilibrium and the reaction A equilibrium B is not extensive. We conclude the following.

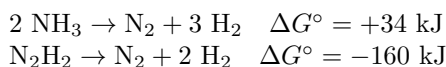
ΔG° indicates the extent of reaction.

9.8-3. Extent Exercise

EXERCISE 9.14:

One mole each of NH_3 and N_2H_2 are allowed to react in identical 1-L containers at 298 K. Which flask would contain the greater number of moles of H_2 when the reactions are complete?

You should read the replies to both answers to better understand the role of ΔG° .



9.8-4. Extent of Reaction Versus Temperature

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ can be re-arranged to give the common form of a straight line ($y = mx + b$) as follows.

y	=	m	x	+	b
ΔG°	=	$-\Delta S^\circ$	T	+	ΔH°

Thus, a plot of ΔG° versus T is a straight line with a slope of $-\Delta S^\circ$ and an intercept of ΔH° . The intercept is ΔH° , so $\Delta G^\circ = \Delta H^\circ$ at $T = 0$. Indeed, we will assume that the sign of ΔG° is the same as the sign of ΔH° at low temperatures. However, the slope of the line is $-\Delta S^\circ$, so ΔS° can dictate the sign of ΔG° at very high temperatures.

For example, consider the temperature dependence of ΔG° of reactions A - E as described in Table 9.5 and Figure 9.6.

Rxn	ΔH°	ΔS°	ΔG°
A	> 0	> 0	At low T , ΔH° dominates, so $\Delta G^\circ > 0$ and the reaction is not extensive. However, ΔS° is positive, so the slope is negative, which causes ΔG° to go negative at high T . Thus, the reaction is extensive at high T .
B	> 0	< 0	Both terms are unfavorable, so the reaction is not extensive at any temperature.
C	< 0	< 0	At low T , the favorable ΔH° dominates and the reaction is extensive. At high T , the unfavorable ΔS° dominates to make ΔG° positive and the reaction not extensive.
D	< 0	> 0	Both terms are favorable, so the reaction is extensive at all T .
E	< 0	~ 0	Reactions in which ΔS° is very small are dominated by ΔH° at all T .

Table 9.5: Standard Free Energy Versus Temperature

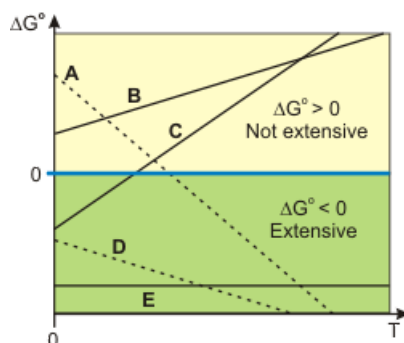


Figure 9.6: Standard Free Energy Versus Temperature

9.8-5. Summary

At very low temperatures, the $T\Delta S^\circ$ term is negligible, and ΔG° has the sign of ΔH° . At very high temperatures, the $T\Delta S^\circ$ term dominates (unless $\Delta S^\circ \sim 0$), and ΔG° has the sign of $-\Delta S^\circ$.

ΔH°	ΔS°	Extent
negative	positive	Exothermic reactions that increase entropy are always extensive because both terms are favorable.
negative	negative	Exothermic reactions that reduce entropy are more likely to be extensive at lower temperatures, where the unfavorable $T\Delta S$ term is negligible.
positive	positive	Endothermic reactions that increase entropy are more likely to be extensive at higher temperatures, where the favorable $T\Delta S$ term can dominate the unfavorable enthalpy change.
positive	negative	Both terms are unfavorable, so endothermic reactions that reduce entropy are never extensive.

Table 9.6: Predicting the Extent of Reaction

9.9 Activation Energy

Introduction

Thermodynamics compares the initial and final states only. It does not consider how the transition from one state to another is accomplished; that is the domain of kinetics. Energy considerations are also an important part of kinetics, and we use the one-step displacement of iodide by hydroxide to examine reaction energetics in this section.

Objectives

- Define *reaction coordinate*, *transition state*, and *activation energy*.
- Explain how the enthalpy of reaction is related to the activation energies of the forward and reverse reactions.

9.9-1. The Reaction

In this section we examine both the thermodynamics and kinetics of the following one-step reaction in which iodide is displaced by a hydroxide ion. Thermodynamics is concerned only with differences between the initial and final states of the reaction, while kinetics is concerned with how the reaction proceeds.

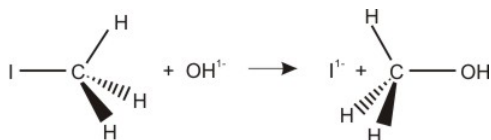
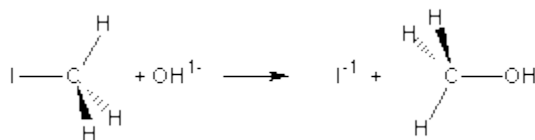


Figure 9.7

9.9-2. Thermodynamic View

Thermodynamics is concerned only with the difference between the initial and final states.

Consider the following reaction.



The properties of interest are ΔH° , ΔS° , and ΔG° . Although all of these properties can be determined from tables, our goal is to estimate their sign and whether they are large or small.

Enthalpy	<p>The reaction involves breaking one C-I bond and forming one C-O bond. Refer to the Bond Energies resource for the C-O bond energy (358 kJ/mol) and the C-I bond energy (234 kJ/mol).</p> $\Delta H^\circ \sim D_{\text{C-I}} - D_{\text{C-O}}$ $\Delta H^\circ \sim 234 - 358 \sim -120 \text{ kJ/mol}$ <p>This is only a very rough approximation because this reaction is carried out in solution not in the gas phase. However, the formed bond is clearly stronger than the broken bond, so we can conclude that the reaction is exothermic.</p>
Entropy	There are no gasses, so we assume that $\Delta S^\circ \sim 0$ (is small).
Free Energy	Since $\Delta S^\circ \sim 0$ and $\Delta H^\circ < 0$, we conclude that $\Delta G^\circ \sim \Delta H^\circ < 0$. The reaction should be extensive, i.e., it is a reaction that should produce a lot of product.
Summary	<p>$\Delta H^\circ < 0$, so the potential energy of the reactants is above that of the products because the C-O bond energy is stronger than the C-I bond.</p>

Table 9.7

9.9-3. Kinetic View

A video or simulation is available online.

Kinetics deals with the transition from reactants to products.

Kinetics is the study of the rates and mechanisms of reactions. In other words, kinetics looks at the transition from the initial to the final state. To do this, we define a reaction coordinate, which is normally a complicated combination of intermolecular distances and molecular structural changes. In order to form the C-O bond, the OH^{1-} ion must attack the carbon atom along the line through the center of the plane formed by the three H atoms. As the C-O distance decreases, the three H-C-H angles all increase from their original 109° as the H atoms separate, and the C-I bond elongates. Thus, the reaction coordinate involves changes in all of these parameters. As the C-O distance decreases, the H-C-H bond angles continue to increase, and the C-I bond continues to lengthen. The system reaches an energy maximum when the H-C-H bond angles are 120° and the CH_3 group is planar. The species that is formed at this point is called the transition state, which is the species that the reactants must pass through in their transition to the products. It is at the energy maximum, so it immediately changes into one of the species at lower energy. If the C-O bond shortens and the C-I bond breaks, the transition state leads to the products, but if the C-O bond breaks and the C-I bond shortens, the transition state leads to the reactants. Either action is possible.

Reactants must go through a transition state to reach the products, and the energy required to reach the transition state is called the activation energy.

The energy required to reach the transition state is called the activation energy (E_a). Once the products form, they can also collide to form the same transition state. The reaction between the substances on the right side of the chemical equation is called the *reverse reaction*, while reaction of the substances on the left side is called the *forward reaction*. Both reactions have activation energies. $E_a(f)$ is the activation energy for the forward reaction,

while $E_a(r)$ is the activation energy for the reverse reaction. Activation energies are always positive. Note that $\Delta H = E_a(f) - E_a(r)$, so $E_a(f) < E_a(r)$ for exothermic reactions, but $E_a(f) > E_a(r)$ for endothermic reactions.

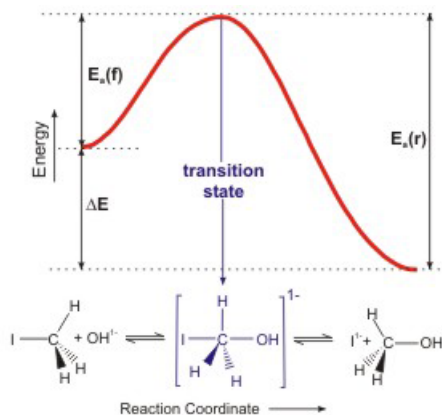


Figure 9.8: Reaction Diagram for $\text{CH}_3\text{I} + \text{OH}^- = \text{CH}_3\text{OH} + \text{I}^{1-}$

9.10 Rates of Reaction and The Rate Law

Introduction

In this section, we examine the factors that dictate the rate of a reaction, and then pull all of the factors together into a rate law for the reaction.

Prerequisites

- 7.1-11. Molarity (Determine the molarity of a substance in a mixture.)
- 7.1 Gases

Objectives

- Express the collision frequency between several particles in terms of their molar concentrations.
- State the two factors that dictate the fraction of collisions that lead to the transition state.
- Write the rate law that governs a reaction that occurs in one step given the balanced chemical equation for the reaction.
- Define the term *catalyst* and explain how a catalyst functions.

9.10-1. Collision Frequency

The frequency of collisions between two particles is proportional to the product of their concentrations.

We now turn our attention to the **rate of reaction**, i.e., how fast the concentrations change with time. In order for two molecules to react, they must collide. Thus, the rate of reaction is proportional to the frequency at which the *reactants* collide. The **collision frequency** is the number of collisions per unit volume per unit time, which normally has units of (moles of collisions) \cdot liter $^{-1}$ \cdot s $^{-1}$.

The frequency of collisions between particles is proportional to the product of the molar concentrations of the colliding particles. Recall that the molar concentration of particle A is the number of moles of A in a liter and given the symbol [A]. [A] = 1 M is read “the concentration of A is 1 molar or 1 mole per liter.”

In the following examples, C is a proportionality constant that differs for each reaction and increases with temperature.

Particles	Collision Frequency	Comments
A + B	$C[A][B]$	The collision frequency between two particles is proportional to the product of their molar concentrations. Increasing either concentration increases the frequency of collisions between the particles. If both concentrations are doubled, the collision frequency increases by a factor of four.
P + P = 2P	$C[P][P] = C[P]^2$	For collisions between two identical particles, the collision frequency is proportional to the square of the concentration of the particle. Note that the concentration is raised to an exponent equal to the number of times the particle appears in the collision.
X + Y + Z	$C[X][Y][Z]$	Simultaneous collisions between three particles are very rare, so C would be very small.

Table 9.8

9.10-2. Orientation Effects

Only a fraction of colliding particles are oriented properly for reaction.

Only a fraction of the collisions between reactants results in the transition state. In fact, the reaction rate can be very small or even zero when the collision frequency between reactants is high if the fraction of collisions, X , that lead to the transition state is very small. The fraction depends upon both the energy and the orientation of the colliding molecules. We consider orientation effects here and energy in the following section.

Consider the relative orientations of reactants shown in Figure 9.8. The orientations shown in (a) and (b) do not lead to the transition state, while orientation (c) does. There are many more ways in which the molecules can collide with an orientation that does not lead to the transitions, so the fraction that does lead to the transition state is fairly low in this reaction.

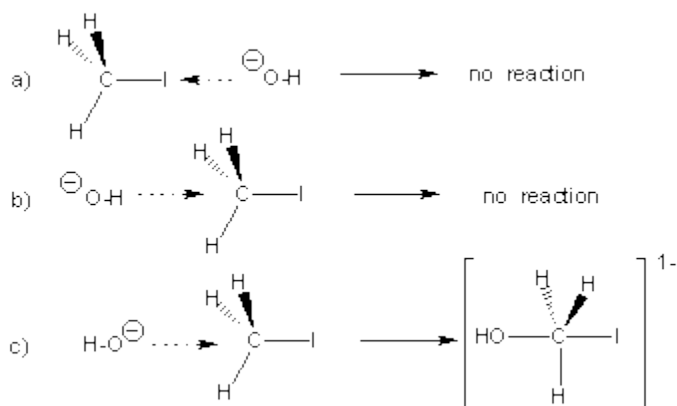


Figure 9.8: Orientation Effect (a) OH^{1-} ion attacks the iodine atom not the carbon, so transition state cannot form; (b) OH^{1-} ion attacks the correct position, but it is turned so that a C-O bond cannot form; (c) the only orientation that can lead to the transition state.

9.10-3. Energy Effect

Only a fraction of colliding particles have sufficient energy to react.

A collision must have enough energy to overcome the activation energy of the reaction. A collision between OH^{1-} and CH_3I must have enough energy to push the H atoms back and lengthen the C-I bond. The average energy of a collision depends upon the thermal energy ($\sim RT$). Consequently, the fraction of collisions leading to the transition state always increases with temperature.

9.10-4. Rate Law

Many reactions involve several steps to convert the reactants to the products. For example, the reaction between hydrogen and oxygen is a complicated reaction that involves many steps. However, some reactions, such as the displacement reaction between CH_3I and OH^{1-} , occur in a single collision (step).

Consider the rate of the reaction $\text{A} + \text{B} \rightarrow \text{products}$.

The rate of a reaction equals the fraction of collisions (X) that lead to the transition state times the collision frequency (F), so we may write the following.

$$\text{rate} = \text{XF}$$

The collision frequency is proportional to the concentrations of the reactants, or the following.

$$\text{F} = \text{C}[\text{A}][\text{B}]$$

Combining these two equations, we note that the rate of the reaction equals the product of two constants, which is also a constant $k = \text{XC}$, times the products of the reactant concentrations.

$$\text{rate} = \text{XC}[\text{A}][\text{B}] = k[\text{A}][\text{B}]$$

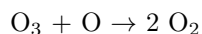
This expression is the **rate law** of the reaction, and k is the **rate constant** of the reaction. X and C are each temperature dependent, so k is also temperature dependent.

The **rate law** for a simple, one-step reaction is equal to the rate constant for the reaction times the product of the concentrations of the **reactants** each raised to an exponent equal to their coefficient in the balanced chemical equation.

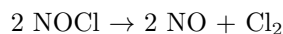
9.10-5. Rate Law Exercise

EXERCISE 9.15:

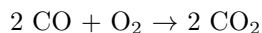
What are the rate laws for the following reactions, which all occur in a single step?



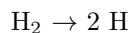
rate = _____



rate = _____



rate = _____



rate = _____

9.10-6. Catalysts

A catalyst increases the speed of a reaction by lowering its activation energy.

The rate law for the simple reaction $\text{A} + \text{B} \rightarrow \text{C}$ is $\text{rate} = k[\text{A}][\text{B}]$. Consequently, the rate of reaction can be changed by changing the concentrations: increasing the reactant concentrations increases the rate of reaction. Indeed, as a reaction proceeds, the rate of reaction slows because the reactants are consumed. The rate of reaction can also be changed by changing the rate constant. The rate constant can be increased in three ways.

- **Increasing the temperature.** Increasing the temperature increases the rate constant by increasing the thermal energy and the average energy of the collisions. Consequently, the fraction of collisions that reach the transition state increases.
- **Decreasing the activation energy.** Lowering the activation energy increases the rate constant by reducing the energy required to reach the transition state. Consequently, a larger fraction of collisions reaches the transition state.
- **Assuring the correct orientation of reactant.** Forcing the reactants to align correctly when they interact, increases the rate constant because a larger fraction of the interactions result in the transition state.

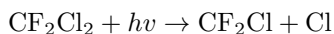
The last two methods of increasing the rate constant are accomplished with the use of catalysts. *Catalysts* speed reactions by assuring that the reacting molecules align correctly for reaction and/or by providing a pathway with a lower activation energy. *Enzymes* are proteins that bind to reacting molecules (substrates). The binding weakens the reactant bonds, which lowers the activation energy, and they can force close alignment of two reactants, which assures the correct orientation.

9.10-7. Ozone Depletion

As an example of catalytic behavior, we consider the problem of ozone depletion in the upper atmosphere. O_3 in the upper atmosphere protects us from ultraviolet radiation from the sun. It is removed by reaction by atomic oxygen.



Fortunately, the activation energy is so high that the reaction is very slow at the temperature of the upper atmosphere. However, chlorine atoms can catalyze the reaction. The chlorine atoms are produced when high energy light from the sun is absorbed by chlorofluorocarbons (CFC's), which were common in refrigeration and spray cans.



The chlorine atoms catalyze the depletion of ozone in two steps. Their chemical equations and activation energies follow.

- 1 $Cl + O_3 \rightarrow O_2 + ClO \quad E'_a = 2 \text{ kJ/mol}$
- 2 $ClO + O \rightarrow Cl + O_2 \quad E''_a = 0.4 \text{ kJ/mol}$

Summing the two steps yields the same ozone depletion reaction that occurs in the absence of chlorine atoms ($O + O_3 \rightarrow 2 O_2$). The chlorine atoms speed the reaction but are unchanged by it, so they are a catalyst for the reaction. They provide a different path with a lower activation energy (the activation energies for the two steps are 2 and 0.4 kJ/mol, respectively), so the reaction is much faster in the presence of chlorine.

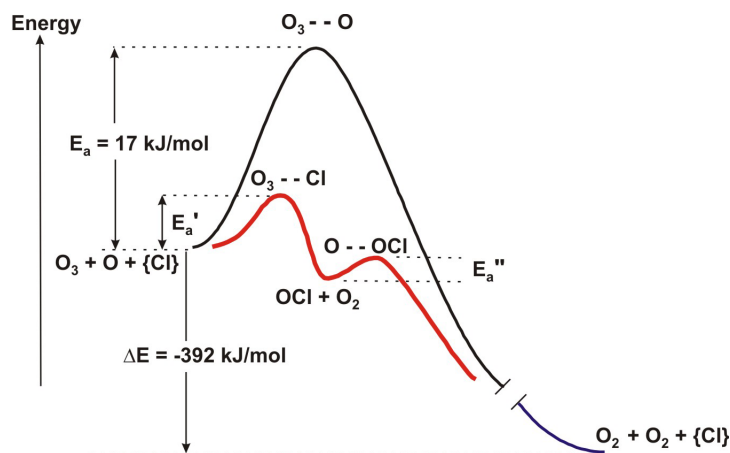


Figure 9.9: Reaction Diagram for Ozone Depletion Shown is the reaction diagram for the ozone depletion reaction in the absence (black curve) and presence (red curve) of chlorine atoms.

9.11 Equilibrium and the Equilibrium Constant

Introduction

Although it is common to say that a reaction has stopped, reactions don't really stop. Instead, they reach a dynamic equilibrium in which the molecules on the right side of the chemical equation continue to produce those on the left and vice versa. At equilibrium, however, the amounts of products and reactants are no longer changing because they are being consumed and produced at the same rate. In this section, we discuss the equilibrium process from the viewpoints of both kinetics and thermodynamics and introduce the equilibrium constant.

Objectives

- Explain what is meant by a 'dynamic equilibrium.'
- Write the equilibrium constant expression for a reaction from the balanced chemical equation.
- Determine the value of an equilibrium constant from the equilibrium concentrations (or pressures) of all reactants and products.
- Determine the equilibrium concentration (or pressure) of one substance from the equilibrium concentrations (or pressures) of all other substances in the equilibrium mixture and the value of the equilibrium constant.
- Explain what is meant by an *extensive reaction* and predict whether a reaction is extensive from the value of its equilibrium constant.
- Relate the equilibrium constant to the standard free energy of reaction.
- Use standard enthalpy and entropy changes to predict the extent of reaction.
- Predict the effect that a temperature change has on the equilibrium constant of a reaction.

9.11-1. Equilibrium and the Equilibrium Constant

A reaction reaches equilibrium when the rates of the forward and reverse reactions are equal.

As a reaction proceeds, the concentrations of the reactant molecules decrease while those of the product molecules increase. Consequently, the rate of the forward reaction decreases, while that of the reverse reaction increases. When the two rates are equal, reactants and products are formed at the same rate that they are consumed and the reaction reaches **equilibrium**. Chemical equilibria are *dynamic* because reaction continues, even though the concentrations of the reactants and products no longer change. Double or equilibrium arrows (\rightleftharpoons) are used in reactions at equilibrium to emphasize that the reaction takes place in both the forward and reverse directions. Consider the reaction: $\text{CH}_3\text{OH}^{1-} \rightleftharpoons \text{I}^{1-} + \text{CH}_3\text{OH}$.

	Reaction	Rate
Forward Reaction	$\text{CH}_3\text{I} + \text{OH}^{1-} \rightarrow \text{I}^{1-} + \text{CH}_3\text{OH}$	$R_f = k_f[\text{CH}_3\text{I}][\text{OH}^{1-}]$
Reverse Reaction	$\text{I}^{1-} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{I} + \text{OH}^{1-}$	$R_r = k_r[\text{CH}_3\text{OH}][\text{I}^{1-}]$

At equilibrium, $R_f = R_r$, so we can write the following.

$$k_f[\text{CH}_3\text{I}][\text{OH}^{1-}] = k_r[\text{CH}_3\text{OH}][\text{I}^{1-}]$$

Rearranging the above to get the rate constants on one side and the concentrations on the other, we obtain the following.

$$\frac{k_f}{k_r} = \frac{[\text{CH}_3\text{OH}][\text{I}^{1-}]}{[\text{CH}_3\text{I}][\text{OH}^{1-}]}$$

The ratio of concentrations equals the ratio of rate constants, which is a constant at a given temperature. Thus, the above expression is a constant, which is called the **equilibrium constant** for the reaction and given the symbol K .

$$K = \frac{[\text{CH}_3\text{OH}][\text{I}^{1-}]}{[\text{CH}_3\text{I}][\text{OH}^{1-}]}$$

The equilibrium constant expression equals the equilibrium concentrations of the substances on the right side of the chemical equation (the products) divided by the equilibrium concentrations of the substances on the left side of the chemical equation (the reactants). The concentration of each substance is raised to an exponent equal to the coefficient of the substance in the balanced chemical equation.

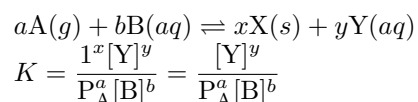
9.11-2. Some Examples of Equilibrium Constant Expressions

The concentration of a gas in an equilibrium constant expression equals its partial pressure in atmospheres, while the concentration of a solute is given by its molar concentration. Solids and liquids enter as unity (1).

The form of the ‘concentration’ of a substance in the equilibrium constant expression depends upon the state of the substance.

- Pure *solids* and *liquids* enter the equilibrium constant expression as one (1) because their concentrations do not change during a reaction.
- *Gases* enter K as their partial pressures in atmospheres. Thus, substance X would enter the expression as P_X if X was a gas.
- *Substances that are dissolved in solution* enter K as their molar concentrations. Substance X enters the expression as $[X]$ if X is dissolved in solution.

For example, consider the following equilibrium.



The ‘concentration’ of X appears as 1 because X is a solid; the ‘concentration’ of A is its partial pressure because A is a gas; and the ‘concentrations’ of B and Y are their molar concentrations because they are solutes in an aqueous solution.

The following examples should help.

Reaction	Expression	Comments
$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$	$K = \frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}}$	All substances are gases, so each should enter the K expression as its partial pressure. The exponent of the partial pressure of H_2 must be three and that of NH_3 must be two.
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	$K = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$	All substances are gases, so each should enter the K expression as its partial pressure. All coefficients are one, so no exponents are needed.
$2 HF(aq) + S^{2-}(aq) \rightleftharpoons H_2S(aq) + 2 F^{-}(aq)$	$K = \frac{[F^{-}]^2 [H_2S]}{[HF]^2 [S^{2-}]}$	All substances are in aqueous solution, so each should enter the K expression as its molar concentration. The coefficients of HF and F^{-} are each two so their concentrations must be squared.
$2 HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + OCl^{1-}(aq)$	$K = \frac{[H_3O^{1+}][OCl^{1-}]}{[HOCl]}$	$HOCl(aq)$, $H_3O^{1+}(aq)$, and $OCl^{1-}(aq)$ are all in aqueous solutions, so they each enter as their molar concentration. $H_2O(l)$ is a pure liquid, so it enters as unity (1). The ‘1’ is not included in the following expression because it has no effect on the value. HOCl is an acid, and the equilibrium constant is called the acid dissociation constant of HOCl.

Table 9.9: Some Examples of Equilibrium Constant Expressions

As shown in the following exercise, the equilibrium constant for a reaction can be determined from known equilibrium concentrations or it can be used with other known equilibrium concentrations to determine an unknown concentration.

9.11-3. K Calculation Exercise

EXERCISE 9.16:

Use the following chemical equation to answer the questions: $\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$.

Calculate the value of K at a temperature where the following equilibrium concentrations are found:

$P_{\text{NO}_2} = 0.12 \text{ atm}$ and $P_{\text{N}_2\text{O}_4} = 0.075 \text{ atm}$.

$K =$ _____

What is the equilibrium pressure of N_2O_4 if the equilibrium pressure of NO_2 is 0.36 atm and $K = 0.19$?

9.11-4. Extensive Reactions

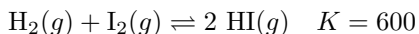
An extensive reaction is one in which $K \gg 1$; that is, one in which the equilibrium concentrations of the products exceed those of the reactants.

Determining how much reactant should be used in a reaction to produce a given amount of product is a common calculation in chemistry. In such calculations, it is often assumed that one of the reactants, called the limiting reactant, disappears completely, but this is the case only when K is very large. When the equilibrium constant is not very large, there will be a substantial amount of at least some reactants at equilibrium, so the amounts can be determined only if the value of the equilibrium constant is known.

A reaction with a very large equilibrium constant is said to be an *extensive reaction*. The value of K is large when at least one of the concentrations in the denominator is very small. Thus, almost no limiting reactant remains at equilibrium in an extensive reaction, and the approximation that it disappears completely is valid.

EXERCISE 9.17:

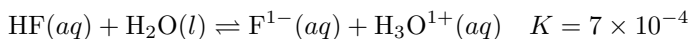
Indicate whether the products, reactants, or neither would dominate the equilibrium mixture formed by adding equal amounts of all reactants in each of the following reactions.



products

reactants

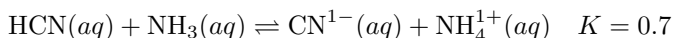
neither



products

reactants

neither



products

reactants

neither

9.11-5. Thermodynamic Definition of K

Thermodynamic Basis for Equilibrium

There is a driving force for the forward reaction that depends upon the concentrations of the substances on the left side of the chemical equation and one for the reverse direction that depends upon the concentrations of those on the right side. The difference between these two driving forces is ΔG . Thus, there are three possibilities.

- $\Delta G < 0$: the driving force in the forward direction is greater, so the reaction proceeds from left to right (\rightarrow).
- $\Delta G > 0$: the driving force in the reverse direction is greater, so the reaction proceeds from right to left (\leftarrow).
- $\Delta G = 0$: the driving forces are equal, so the reaction is at equilibrium (\rightleftharpoons).

Thus, $\Delta G = 0$ is the criterion for equilibrium, but it is the value of ΔG° that indicates where the equilibrium will be established. Indeed, the equilibrium constant for a reaction is related to the standard free energy of the following reaction.

$$\Delta G^\circ = -RT \ln K.$$

- $\Delta G \sim 0 \rightarrow K \sim 1$ ($\ln 1 = 0$). When $K \sim 1$, the numerator and denominator of the equilibrium constant expression are nearly the same, so the equilibrium mixture is composed of comparable concentrations of both the reactants and products.
- $\Delta G^\circ \ll 0 \rightarrow K \gg 1$. $K \gg 1$ when the numerator (product concentrations) is much larger than the denominator (reactant concentrations), so the equilibrium mixture is dominated by the products, i.e., the reaction is extensive.
- $\Delta G^\circ \gg 0 \rightarrow K \ll 1$. $K \ll 1$ when the numerator (product concentrations) is much smaller than the denominator (reactant concentrations), so the equilibrium mixture is dominated by the reactants, i.e., very little reaction takes place.

9.11-6. Predicting Extent of Reactions

The extent of reaction is determined by ΔG° , but ΔG° is related to the standard enthalpy and entropy changes by the following.

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

By analogy to the discussion in Section 9.7, we can draw the following conclusions about the extent of a reaction.

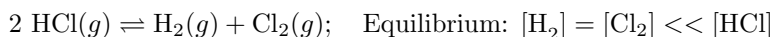
ΔH°	ΔS°	Extent
negative	positive	Exothermic reactions that create disorder are always extensive because both terms are favorable.
negative	negative	Exothermic reactions that create order are more likely to be extensive at lower temperatures, where the unfavorable $T\Delta S$ term is negligible.
positive	positive	Endothermic reactions that create disorder are more likely to be extensive at higher temperatures, where the favorable $T\Delta S$ term can dominate the unfavorable enthalpy change.
positive	negative	Both terms are unfavorable, so endothermic reactions that create order are never extensive.

Table 9.10

9.11-7. Predicting Extent of Reactions Exercise

EXERCISE 9.18:

Use the chemical equation and the equilibrium composition to determine the sign of ΔG° . Use the change in moles of gas to determine the sign of ΔS° . Determine the sign of ΔH° from the other two.



ΔG°	ΔS°	ΔH°
+	+	+
-	-	-
~ 0	~ 0	~ 0



ΔG°	ΔS°	ΔH°
+	+	+
-	-	-
~ 0	~ 0	~ 0



ΔG°	ΔS°	ΔH°
+	+	+
-	-	-
~ 0	~ 0	~ 0

9.11-8. Effect of T on K

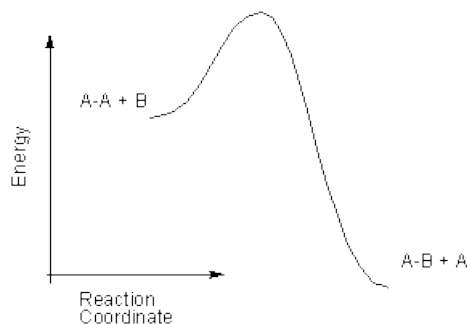
The value of an equilibrium constant varies with temperature. Changes in temperature change the thermal energy of the molecules, which changes the fraction of molecules at higher energy. *The fraction of molecules at higher energy increases when the temperature is increased.*

- **Exothermic reactions:** The reactants are on the higher energy side, so increasing the temperature increases the fraction of reactant molecules at equilibrium. Consequently, the equilibrium constants of exothermic reactions decrease when the temperature is increased.
- **Endothermic reactions:** The products are at higher energy, so increasing the temperature increases the fraction of product molecules at equilibrium. Consequently, the equilibrium constants of endothermic reactions increase when the temperature is increased.

9.11-9. Example

EXERCISE 9.19:

Assume that all reactants and products in the following are gases to answer the questions.



The equilibrium concentration of A-B is greater at which of the following?

- high T
- low T

Which is the stronger bond?

- A-A
- A-B

Is the reaction extensive?

- Yes
- No

Which reaction has the higher rate constant?

- forward
- reverse

9.12 Le Châtelier's Principle

Introduction

An open door that is not moving is at equilibrium. However, the equilibrium position of the door can be changed by applying pressure to either side. Reactions at equilibrium react in a similar fashion when they are exposed to a chemical stress.

Objectives

- Use Le Châtelier's Principle to determine the effect of changing the temperature or the concentration of one substance on the concentration of another substance in the equilibrium mixture.

9.12-1. Le Châtelier's Principle

Equilibrium mixtures respond to the addition or removal of material in a manner consistent with the following principle.

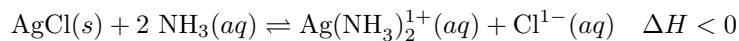
- Le Châtelier's Principle: a system at equilibrium will respond to a stress in such a way as to minimize the effect of the stress.**
- Increasing the concentration (or pressure) of one substance in an equilibrium mixture results in some reaction of that substance. The concentrations of the other substances on the same side of the equilibrium are reduced and the concentrations of those on the opposite side are increased by the reaction.
 - Decreasing the concentration (or pressure) of one substance in an equilibrium mixture results in some reaction of the other substances to replace some of what was removed. The concentrations of the other substances

on the same side of the equilibrium as the removed substance all increase, while those of the substances on the opposite side decrease as a result of this reaction.

Adding or removing a pure liquid or solid does not affect the equilibrium mixture because the concentration of the pure substance is unchanged. However, the concentrations of all solutes are changed when solvent is removed.

EXERCISE 9.20:

Consider the following equilibrium.



Indicate whether each of the following actions would increase, decrease, or not affect the equilibrium concentration of Cl^{1-}

adding $\text{Ag}(\text{NH}_3)_2^{1+}$	removing $\text{Ag}(\text{NH}_3)_2^{1+}$	adding solid AgCl
increase	increase	increase
decrease	decrease	decrease
not affect	not affect	not affect
adding NH_3	increasing temperature	
increase	increase	
decrease	decrease	
not affect	not affect	

9.13 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.