Chapter 19
Chemical Thermodynamics

Chemical
Thermodynamics

Enthalpy

- A thermodynamic quantity that equal to the internal energy of a system plus the product of its volume and pressure exerted on it by its surroundings;

  "Enthalpy is the amount of energy in a system capable of doing mechanical work"

  Using the symbol **H** for the enthalpy:
  $$H = E + p\,V$$

Chemical Thermodynamics

- in **endothermic** chemical reactions, the change in enthalpy is the amount of energy absorbed by the reaction;
- in **exothermic** reactions, it is the amount given off
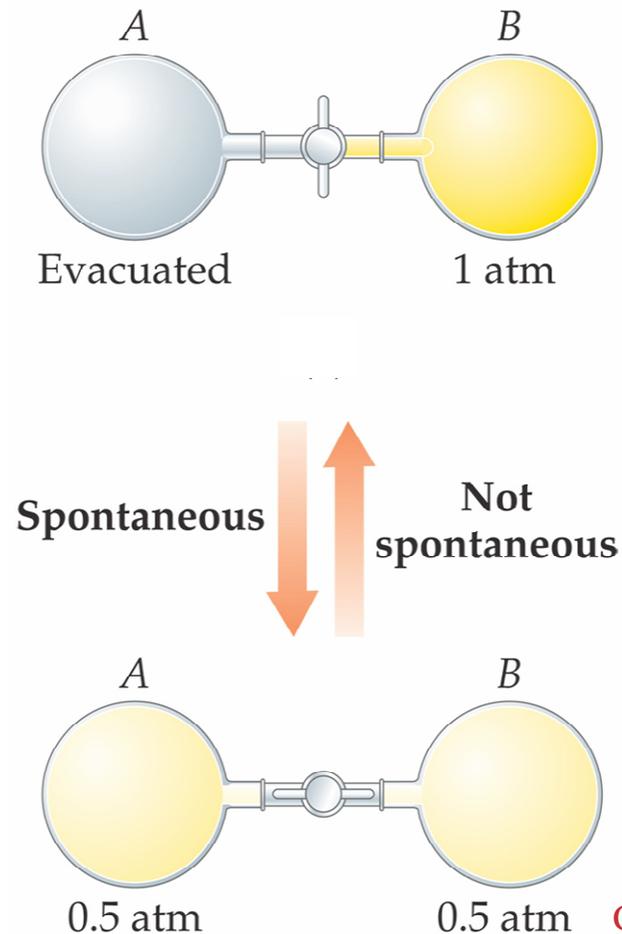
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First Law of Thermodynamics

- You will recall from Chapter 5 that energy cannot be created nor destroyed.

- Therefore, the total energy of the universe is a constant.

- Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.

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Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.

- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* spontaneously

  separate back

A   B

Evacuated   1 atm

Spontaneous   Not spontaneous

A   B

0.5 atm   0.5 atm

- Why do physical or chemical changes favor one reaction over the other
- Thermodynamics helps us to understand the directionalities of these reactions.

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Spontaneous Processes
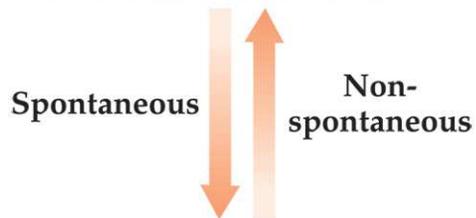
A spontaneous process is one that proceeds on its own without any outside assistance.

Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

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Spontaneous Processes

- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.
- At 0° the reactions are in equilibrium

Spontaneous for $T > 0°C$

Spontaneous for $T < 0°C$

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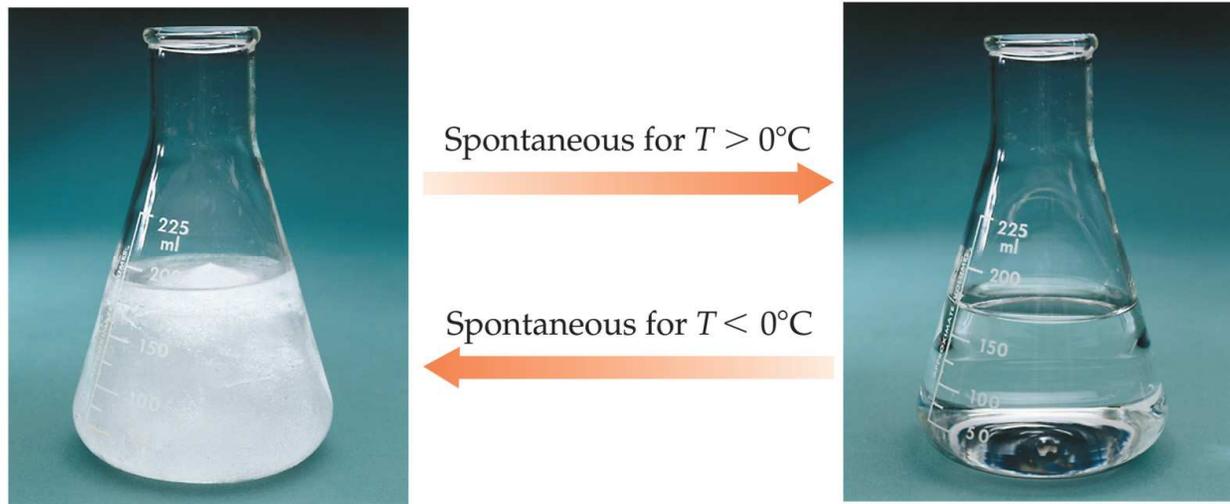
- A spontaneous reaction can be slow like rusting of the nail or fast as an acid base reaction.

- Thermodynamics can tell us the direction and extent of the reaction but not the speed.

Chemical Thermodynamics

What makes a process spontaneous?

- Is it true that all spontaneous processes would be exothermic.

What makes a process spontaneous?

Is it true that all spontaneous processes would be exothermic?

- Melting, an endothermic process is spontaneous.
- Spontaneous solution processes are endothermic.

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The direction of a spontaneous change

- Apparent driving force of a spontaneous change is the tendency of the energy and matter to become disordered.

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- These examples tell us that though most spontaneous processes are exothermic, there are many endothermic processes that are spontaneous.

- So there are other factors that are at work that make a process spontaneous.

Chemical Thermodynamics
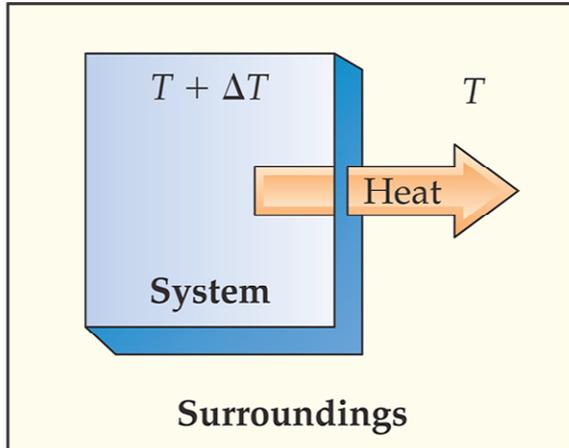
Reversible and Irreversible processes.

- 1824 Sadi Carnot publishes the analysis on the factors that determine the efficiency of the steam engines.

- He stated that it is impossible to convert the energy content of the fuel completely to work because a significant amount of heat is always lost to the surroundings.

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- Rudolph Clausius extended the observation and concluded that a special relationship can be derived between the ratio of the heat delivered to an ideal engine and the and the temperature at which it is delivered
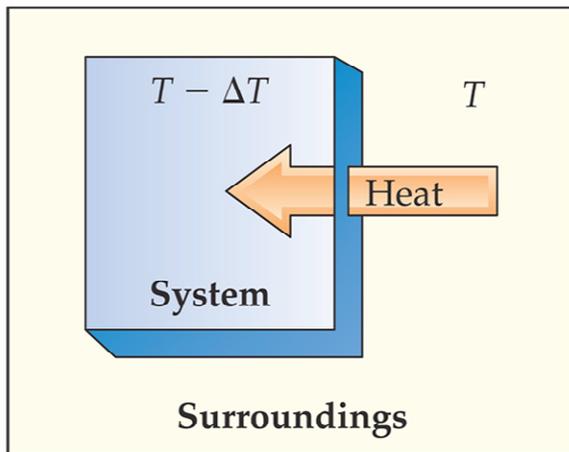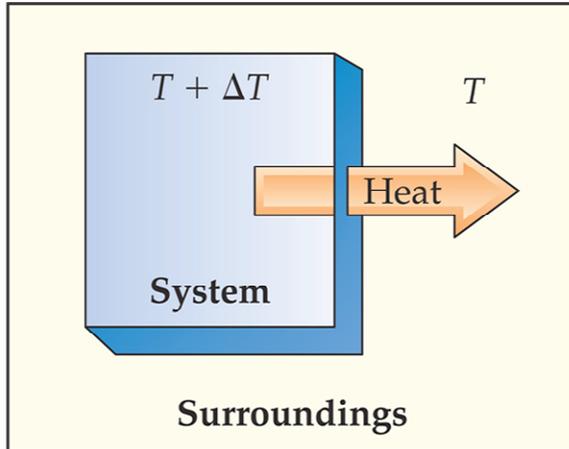
$$q/T$$

He names this ratio as entropy.

Reversible Processes
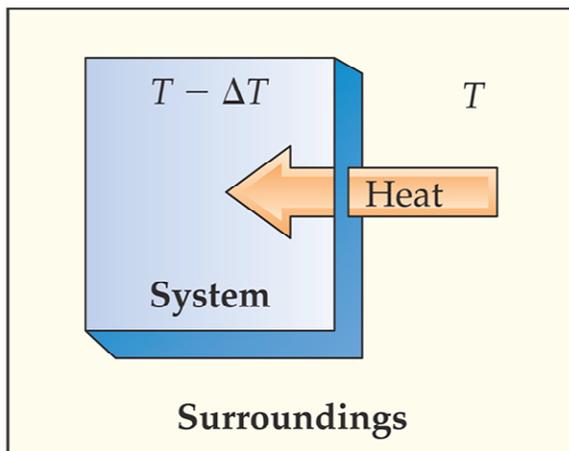
In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

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Reversible Processes

Reversible processes are those that reverse direction whenever an infinitesimal change is made in some property of the system

Irreversible Processes
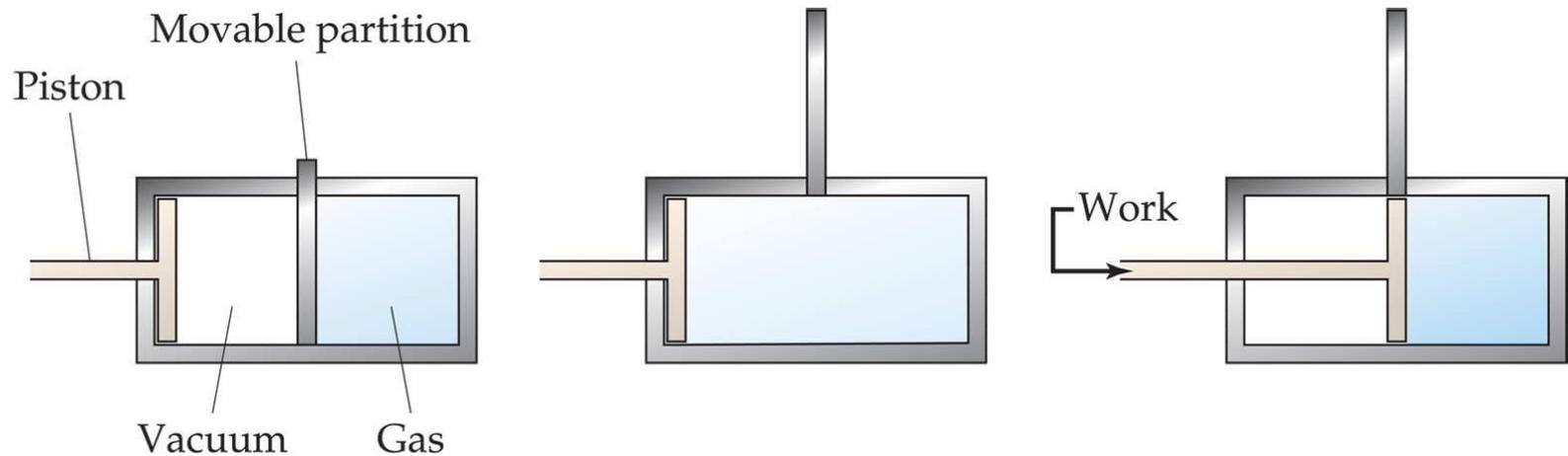
- Irreversible processes cannot be undone by exactly reversing the change to the system.
- Spontaneous processes are irreversible.

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Spontaneous processes are irreversible. Even if the system is returned to the original condition the surrounding would have changed.

Entropy

- Entropy can be thought of as a measure of the randomness of a system.

- It is related to the various modes of motion in molecules.

Vibrations ——————————————— Rotation

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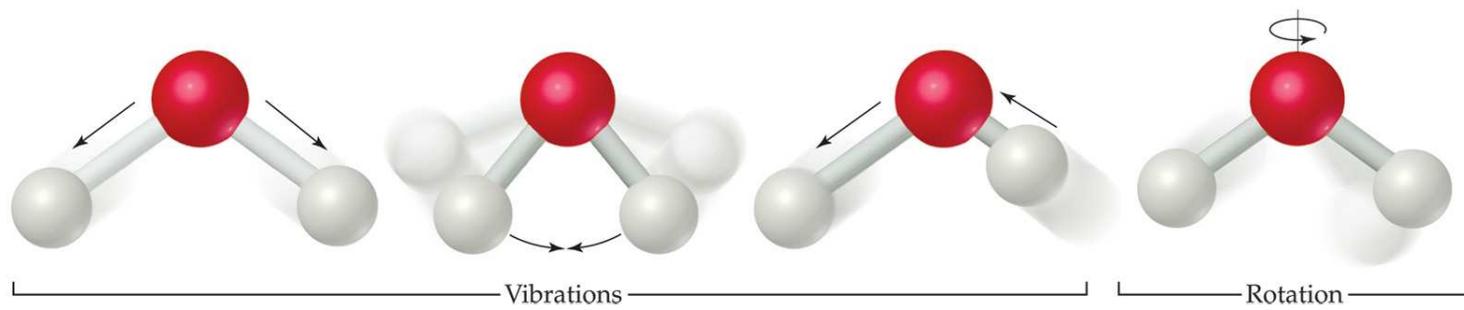
- Let us see how we can relate the entropy changes to heat transfer and temperature.

Chemical Thermodynamics

Entropy

- Like total energy, *E*, and enthalpy, *H*, entropy, S is a state function.
- Therefore,

$$\Delta S = S_{final} - S_{initial}$$

Entropy

- For a process occurring at constant temperature (an isothermal process), the change in entropy is equal to the heat that would be transferred if the process were reversible divided by the temperature:

$$\Delta S = \frac{q_{rev}}{T}$$

at constant temperature

(Rudolph Clausius)

- Since S is a state function, we can use this equation to calculate the ΔS for any process.

ΔS For Phase Change

Consider the melting of ice

- At 1 atm and 0°C ice and water are in equilibrium with each other.
- If we melt one mole of ice at 0°C/1 atm to form 1 mole of water still at 0°C
- We need to give the water heat that would be equal to ΔH_{fusion}.
- If the process is done extremely slowly the process can be reversible if we remove that amount of heat.

$$\Delta S_{fusion} = \frac{q_{rev}}{T} = \frac{\Delta H}{T} = \frac{(1mol)(6.01x10^3 J / mol)}{273K}$$

$$= 22.0 J / K$$

Dictionary Meaning for Entropy

A measure of the unavailable energy in a closed thermodynamic system

that is also usually considered to be a measure of the system's disorder,

that is a property of the system's state, and

that varies directly with any reversible change in heat in the system and inversely with the temperature of the system;

broadly : the degree of disorder or uncertainty in a system

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Calculating change in entropy

- Transferring 100kJ of heat to a large mass of water at 0°C results in a change in entropy of

$$\Delta S = \frac{q_{rev}}{T} = \frac{100 \times 10^3 \text{ J}}{273 \text{ K}} = +366 JK^{-1}$$

- Same transfer at 100°C results in

$$\Delta S = \frac{100 \times 10^3 \text{ J}}{373 \text{ K}} = +268 JK^{-1}$$

- Increase in entropy is greater at lower temperature

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Example 9.2

The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is –38.9°C, and its molar enthalpy of fusion is ΔH_{fusion} = 2.29 kJ/mol.
What is the entropy change of the system when 50.0 g of Hg(l) freezes at the normal freezing point?

1. Convert the g of Hg to moles
2. From the enthalpy of fusion calculate the heat that would be exchanges for this amount in joules. Remember that freezing is an exothermic process so the energy is going to leave the system so it will have a negative value

$-\Delta H_{fusion}$ = -2.29 kJ/mol

3. Convert the temperature to K
4. Now plug this in the formula

$$\Delta S = \frac{q_{rev}}{T}$$

5. This would be a negative value because heat flows from the system.

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Thermodynamics

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$-\Delta H_{fusion}$ = -2.29 kJ/mol

$$q = (50.0 \text{ g Hg})\left(\frac{1 \text{ mol Hg}}{200.59 \text{ g Hg}}\right)\left(\frac{-2.29 \text{ kJ}}{1 \text{ mol Hg}}\right)\left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) = -571 \text{ J}$$

3. Convert the temperature to K
4. Now plug this in the formula

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{-571 \text{ J}}{234.3 \text{ K}} = -2.44 \text{ J/K}$$

5. This would be a negative value because heat flows from the system.

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The normal boiling point of ethanol, C_2H_5OH, is 78.3°C, and its molar enthalpy of vaporization is 38.56 kJ/mol. What is the change in entropy in the system when 68.3 g of $C_2H_5OH(g)$ at 1 atm condenses to liquid at the normal boiling point?

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Answer: -163 J / K

- There are many versions of the second law, but they all have the same effect, which is to explain the phenomenon of irreversibility in nature

Chemical Thermodynamics

Second Law of Thermodynamics

The entropy of an isolated system tends to increase.

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Second Law of Thermodynamics

- Entropy increases in any spontaneous (irreversible) process where as a non spontaneous (reversible) process results in no overall change in entropy.

- The sum of the entropy change of the system and surroundings for any spontaneous process is always greater than zero

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- What happens when a mole of ice melts in our hand ….

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Example of melting ice in the hand.

- The entropy change we calculated earlier for melting of ice:

$$\Delta S_{fusion} = \frac{q_{rev}}{T} = \frac{\Delta H}{T} = \frac{(1mol)(6.01x10^3 J/mol)}{273K} = 22.0 J/K$$

- The surrounding here is the hand and the body temperature is

  37°C= 310K

$$\Delta S_{fusion} = \frac{q_{rev}}{T} = \frac{\Delta H}{T} = \frac{(1mol)(6.01x10^3 J/mol)}{310K}$$

$$= -19.4 J/K$$

- Thus the total entropy change is positive

$$\Delta S = S_{final} - S_{initial}$$

$$= (22.0 J/K) - (-19.4 \ J/K)$$

$$= 2.6 \ J/K$$

- If the temperature of the surrounding (in this case the hand,) was infinitesimally close to 273K the entropy change would have been zero and

  then the reaction would have been reversible

Second Law of Thermodynamics

In other words:

For reversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For irreversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

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Second Law of Thermodynamics

The second law of thermodynamics states that the entropy of the universe increases for spontaneous processes, and the entropy of the universe does not change for reversible processes.

Chemical Thermodynamics

Second Law of Thermodynamics

These last truths mean that as a result of all spontaneous processes the entropy of the universe increases.

Chemical Thermodynamics

Entropy on the Molecular Scale

- Ludwig Boltzmann described the concept of entropy on the molecular level.

- Temperature is a measure of the average kinetic energy of the molecules in a sample.

Vibrations ——————————— Rotation

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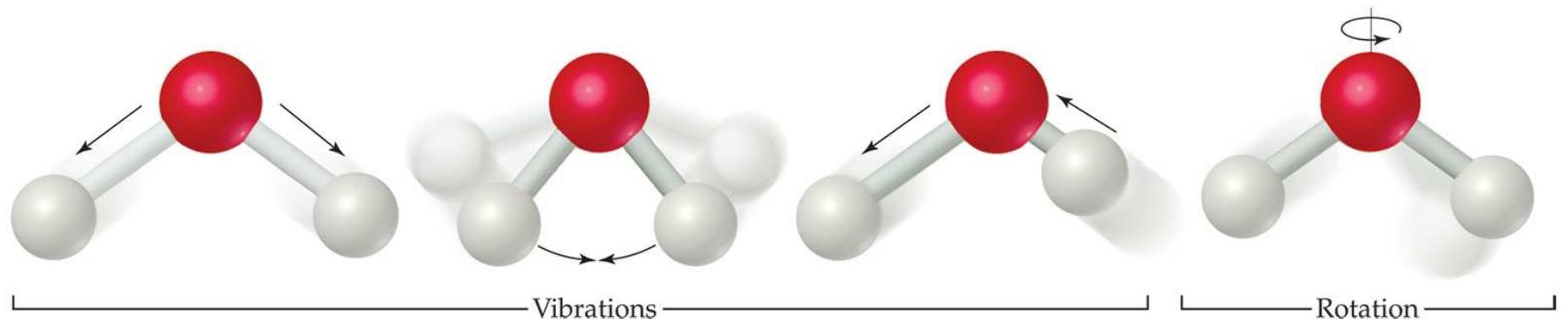
Entropy on the Molecular Scale

- Molecules exhibit several types of motion:
  - ➢ Translational: Movement of the entire molecule from one place to another.
  - ➢ Vibrational: Periodic motion of atoms within a molecule.
  - ➢ Rotational: Rotation of the molecule on about an axis or rotation about σ bonds.

Vibrations ——————— Rotation

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Thermodynamics
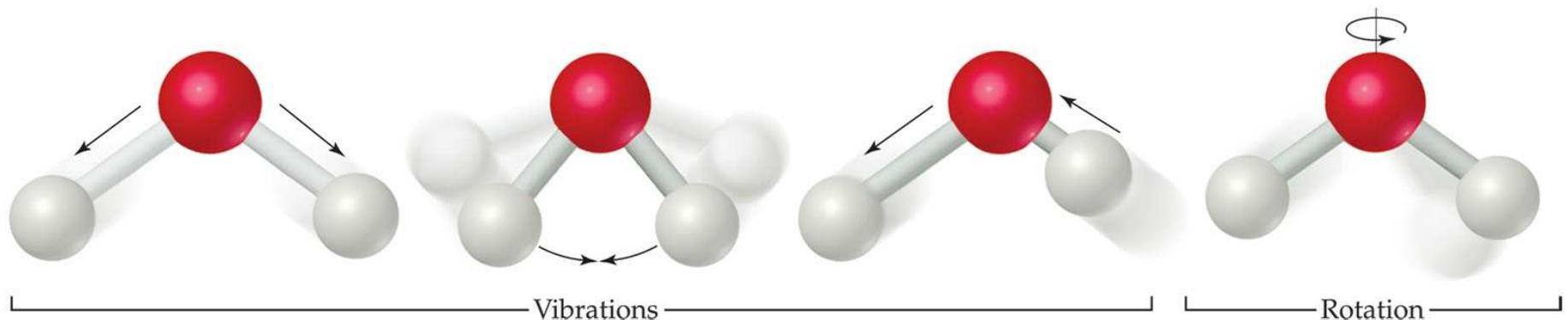
Entropy on the Molecular Scale

- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
  - This would be similar to taking a snapshot of all the molecules.

- He referred to this sampling as a microstate of the thermodynamic system.

Vibrations ———— Rotation

Chemical
Thermodynamics
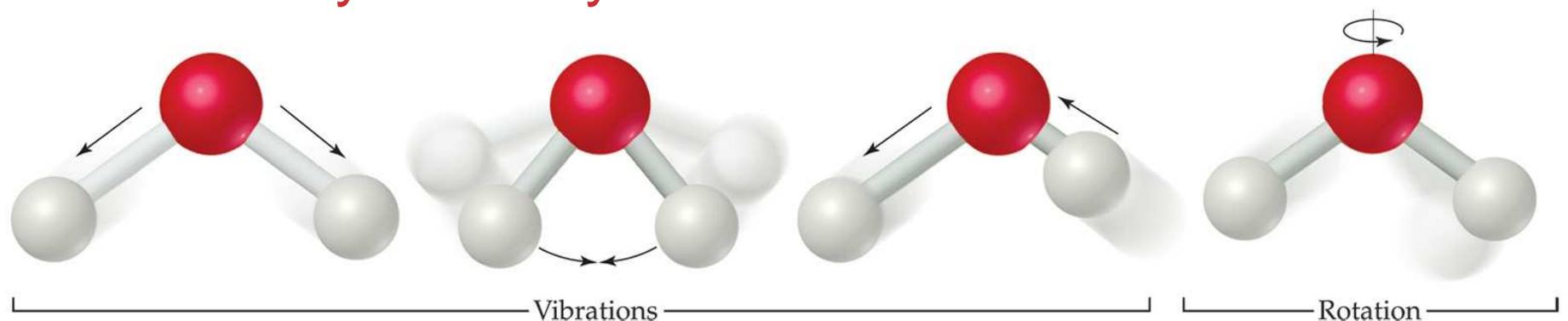
Entropy on the Molecular Scale

- Each thermodynamic state has a specific number of microstates, *W*, associated with it.
- Entropy is

$$S = k \ln W$$

where *k* is the Boltzmann constant, 1.38×10^{-23} J/K.

Vibrations — Rotation
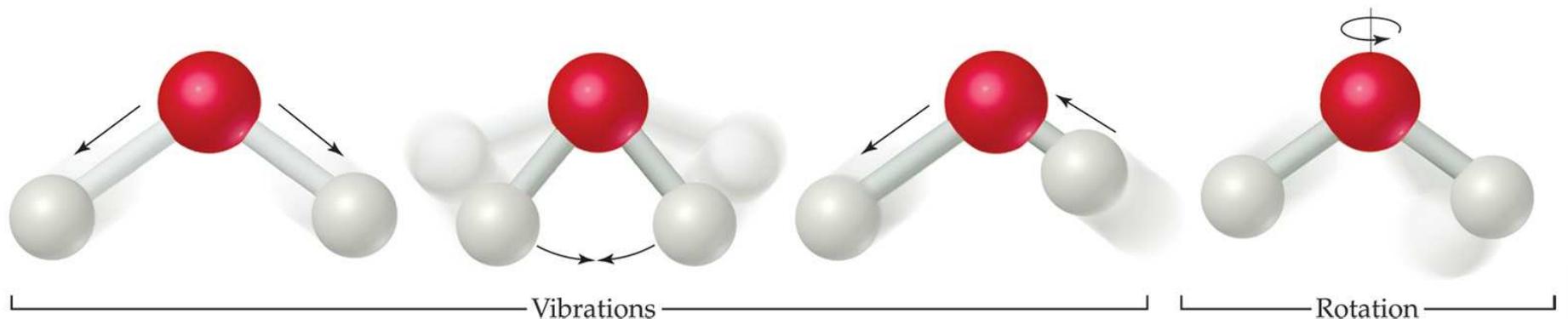
Entropy on the Molecular Scale

- The change in entropy for a process, then, is

$$\Delta S = k \ln W_{final} - k \ln W_{initial}$$

$$= k \ln \frac{W_{final}}{W_{initial}}$$

- Entropy increases with the number of microstates in the system.

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Entropy on the Molecular Scale

- The number of microstates and, therefore, the entropy tends to increase with increases in
  - Temperature.
  - Volume.
  - The number of independently moving molecules.

Chemical Thermodynamics

- I want you to read the page 815 and come, in the next class I will ask you a question that will be a crazy interpretation of the page, and you will have to answer it………..if you forget to read it you will not be able to answer.

Chemical Thermodynamics

A crazy homework

- You are the system,

  Interpret entropy as increase in your relaxed state and comparing the factors that affect entropy with things in real life that will increase your entropy.

  No more than half a page.

  Answers will be collected in the first five minutes of the next class.

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Entropy and Physical States

- Entropy increases with the freedom of motion of molecules.
- Therefore,

  $S(g) > S(l) > S(s)$

O
H

Hydrogen bond
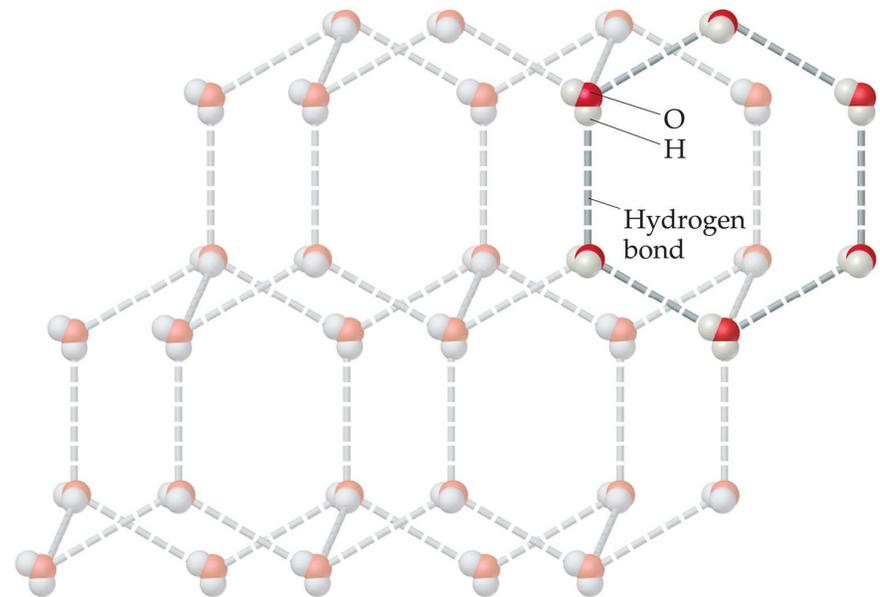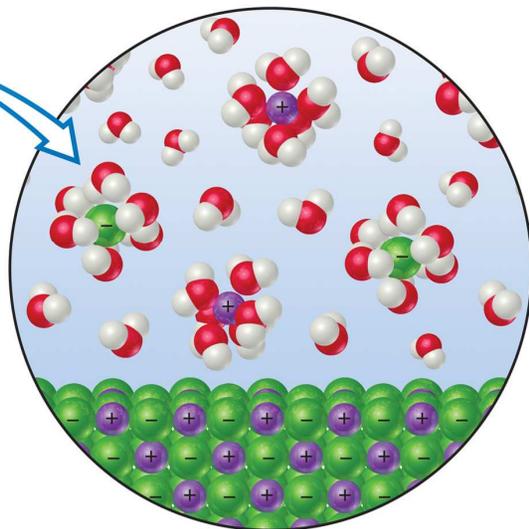
Solutions

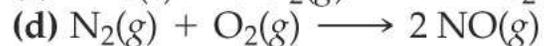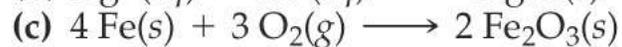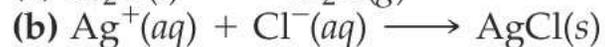Generally, when a solid is dissolved in a solvent, entropy increases.

Entropy Changes

- In general, entropy increases when
  - ➢ Gases are formed from liquids and solids.
  - ➢ Liquids or solutions are formed from solids.
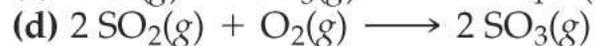 - ➢ The number of gas molecules increases.
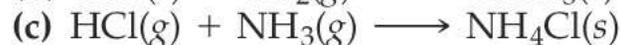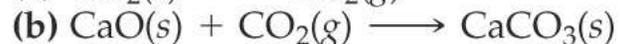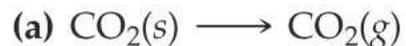 - ➢ The number of moles increases.
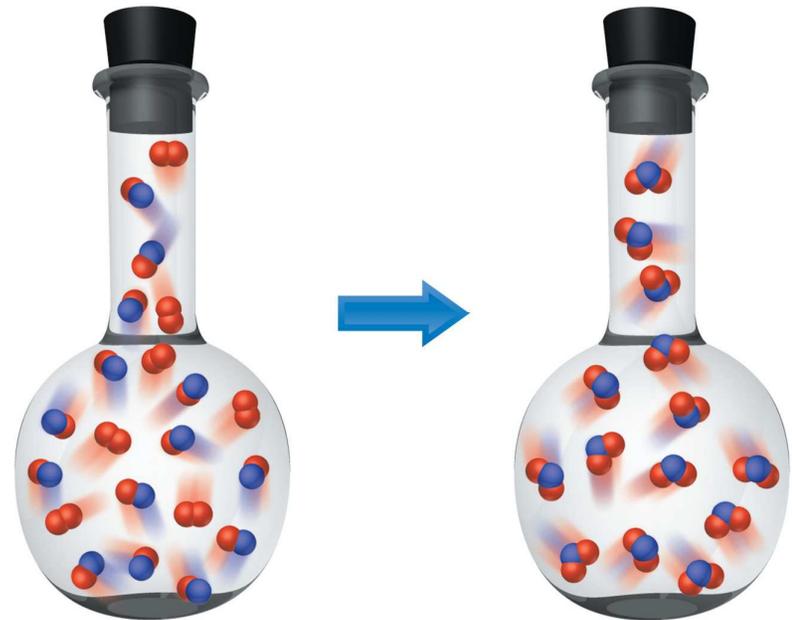
Chemical
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Problems

Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:

(a) $H_2O(l) \longrightarrow H_2O(g)$
(b) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(c) $4\,Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)$
(d) $N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$

(a) $CO_2(s) \longrightarrow CO_2(g)$
(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
(c) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
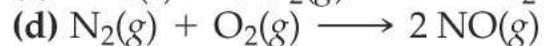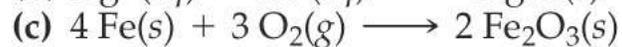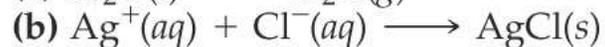**(d)** $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

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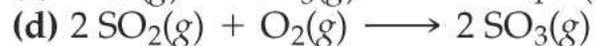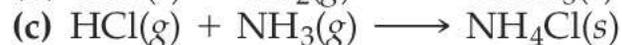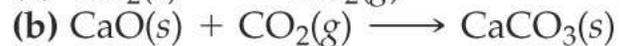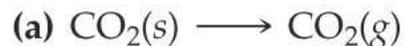
Answers   a. Positive

Problems

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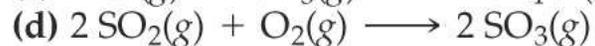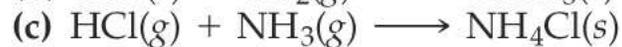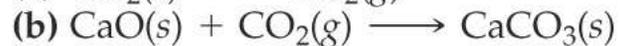
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Answers   a. Positive

                 b. negative

Chemical
Thermodynamics

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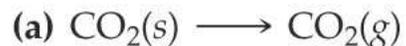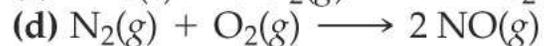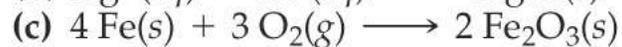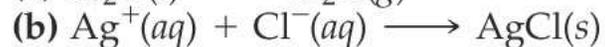
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Answers 　　　　　　　　a. Positive

　　　　　　　　　　　　　b. negative

　　　　　　　　　　　　　c. negative

Chemical
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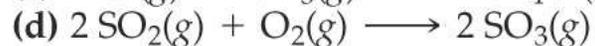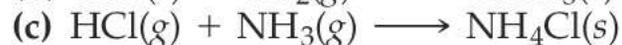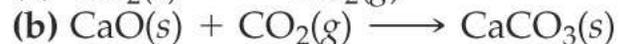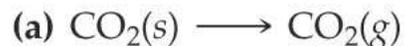
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(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
(c) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
(d) $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

Answers

a. Positive

b. negative

c. negative

d. close to zero

Chemical
Thermodynamics
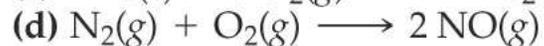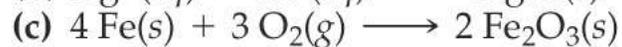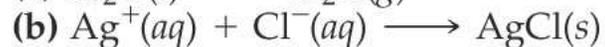
Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:

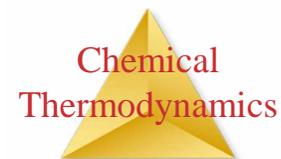(a) $H_2O(l) \longrightarrow H_2O(g)$
(b) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(c) $4\ Fe(s) + 3\ O_2(g) \longrightarrow 2\ Fe_2O_3(s)$
(d) $N_2(g) + O_2(g) \longrightarrow 2\ NO(g)$

(a) $CO_2(s) \longrightarrow CO_2(g)$
(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
(c) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
(d) $2\ SO_2(g) + O_2(g) \longrightarrow 2\ SO_3(g)$

Answers

a. Positive

b. negative

c. negative

d. close to zero

a. positive

Chemical
Thermodynamics

Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:

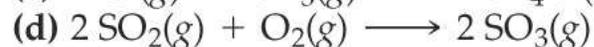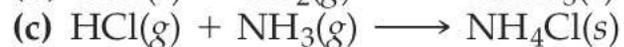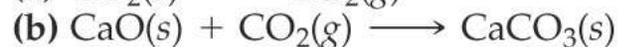(a) $H_2O(l) \longrightarrow H_2O(g)$
(b) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(c) $4 Fe(s) + 3 O_2(g) \longrightarrow 2 Fe_2O_3(s)$
(d) $N_2(g) + O_2(g) \longrightarrow 2 NO(g)$

(a) $CO_2(s) \longrightarrow CO_2(g)$
(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
(c) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
(d) $2 SO_2(g) + O_2(g) \longrightarrow 2 SO_3(g)$

Answers

a. Positive

b. negative

c. negative

d. close to zero

a. positive

b. negative

Chemical
Thermodynamics

Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:
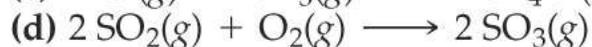
(a) $H_2O(l) \longrightarrow H_2O(g)$
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(d) $N_2(g) + O_2(g) \longrightarrow 2 NO(g)$

(a) $CO_2(s) \longrightarrow CO_2(g)$
(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
(c) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
(d) $2 SO_2(g) + O_2(g) \longrightarrow 2 SO_3(g)$

Answers   a. Positive

                 b. negative

                 c. negative

                 d. close to zero

                 a. positive

                 b. negative

                 c. negative

Chemical
Thermodynamics

Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:
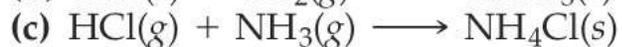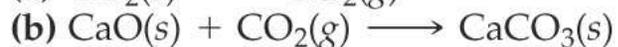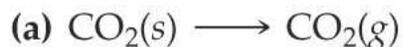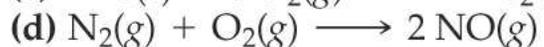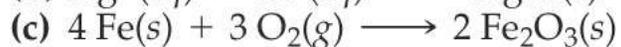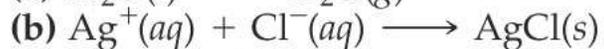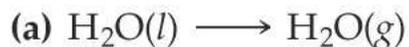
(a) $H_2O(l) \longrightarrow H_2O(g)$
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(c) $4\ Fe(s) + 3\ O_2(g) \longrightarrow 2\ Fe_2O_3(s)$
(d) $N_2(g) + O_2(g) \longrightarrow 2\ NO(g)$

(a) $CO_2(s) \longrightarrow CO_2(g)$
(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
(c) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
(d) $2\ SO_2(g) + O_2(g) \longrightarrow 2\ SO_3(g)$

Answers   a. Positive

                 b. negative

                 c. negative

                 d. close to zero

                 a. positive

                 b. negative

                 c. negative

                 d. negative

Choose the sample of matter that has greater entropy in each pair, and explain your choice: **(a)** 1 mol of NaCl(s) or 1 mol of HCl(g) at 25°C, **(b)** 2 mol of HCl(g) or 1 mol of HCl(g) at 25°C, **(c)** 1 mol of HCl(g) or 1 mol of Ar(g) at 298 K.

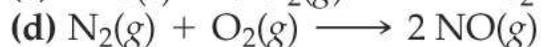**(c)** The HCl sample has the higher entropy because the HCl molecule is capable of storing energy in more ways than is Ar. HCl molecules can rotate and vibrate; Ar atoms cannot.

Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero(0 K) is 0.

Increasing temperature

0 K
$S = 0$

$> 0 K$
$S > 0$

Chemical
Thermodynamics
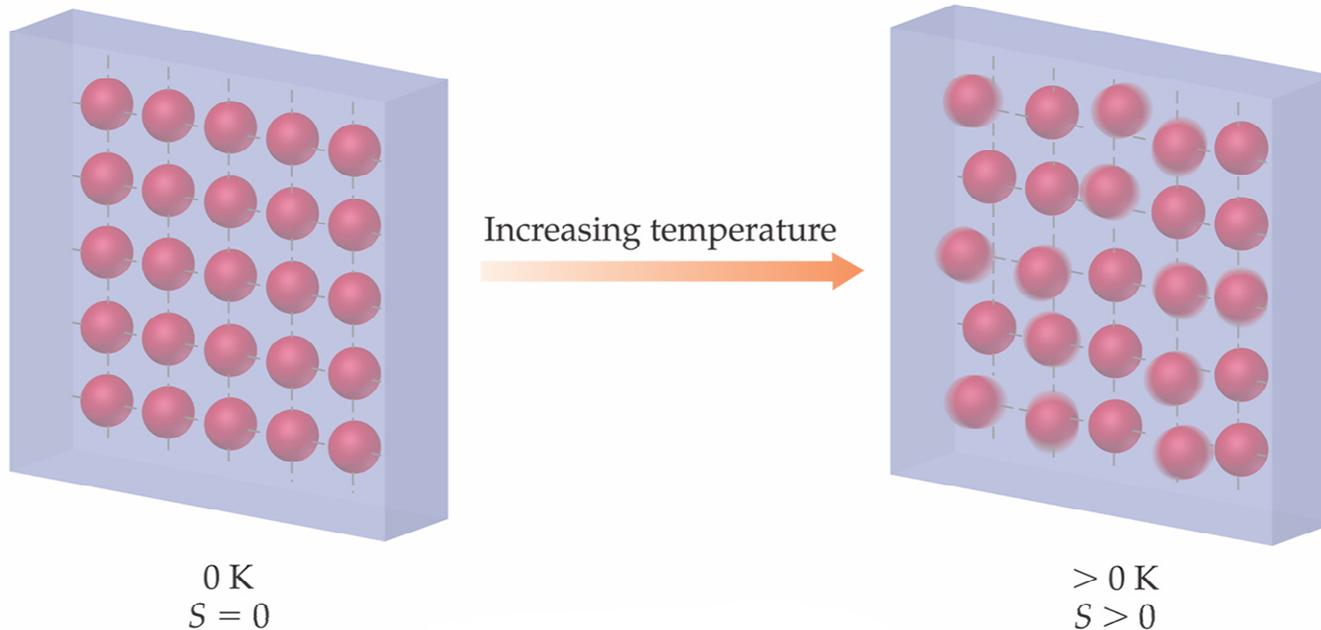
$$S = k \ln W$$

At 0 K there is no thermal motion and so there is only one microstate

Therefore

$S = k \ln 1$

$S = k \times 0$

$S = 0$

- When we see this now the Kelvin scale makes more sense an absolute zero seems like the more scientific place to start.

Chemical
Thermodynamics

- As the temperature increases the atoms and molecules in the crystal gain energy in the form of vibrational motion about their lattice positions.

- Then the microstates and hence the entropy of the system increases.

Chemical Thermodynamics

- The entropy of phases of given substance follows the order

$$S_{solid} < S_{liquid} < S_{gas}$$

Chemical
Thermodynamics

At phase Changes

Copyright © 2006 Pearson Prentice Hall, Inc.
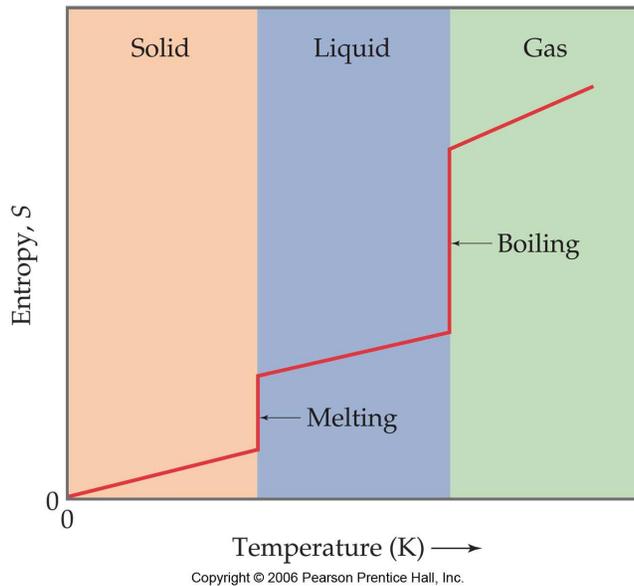
- At the melting points there is a sharp increase in the entropy as the phase of the matter changes and the molecules have more freedom to move about in the entire volume of the substance.

- At the boiling point an abrupt change in entropy occurs as the molecules get a lot of space to move about.

Chemical
Thermodynamics

Standard Entropies

These are molar entropy values of substances in their standard states.

Why 298 K?

298.15 is the conventional temperature for reporting data.

Standard state of any substance is defined as the pure substance at 1 atm pressure

The substance will be solid liquid or gas depending on its nature.

Standard entropies are denoted as S^o.

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K	
Substance	S°, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Chemical Thermodynamics

Standard molar entropies of gases is higher than solids.

Standard entropies tend to increase with increasing molar mass between elements.

Standard molar entropies increases with the increase in the number of atoms in a molecule

TABLE 19.2   Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
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$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Chemical Thermodynamics

About Graphite and Diamond

Standard molar entropies

Graphite 5.7 J / K mol

Diamond 2.4 J / K mol

The C atoms in Diamond are more rigid than Graphite.
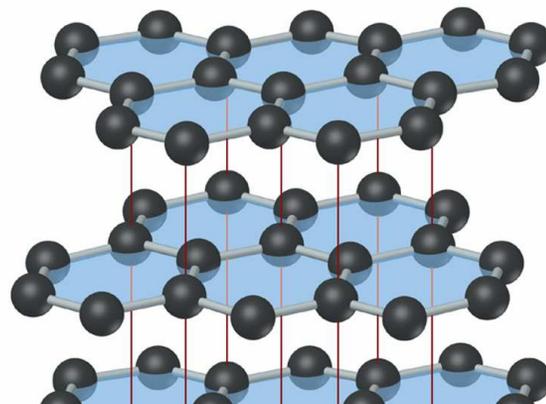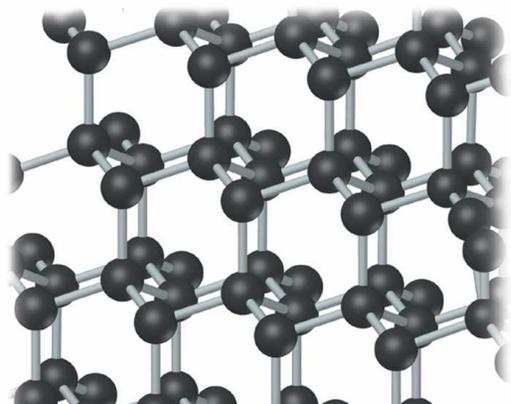
Standard Entropies

Larger and more complex molecules have greater entropies.
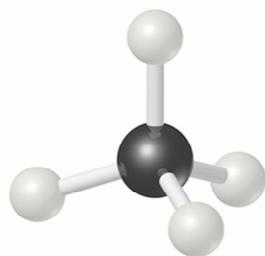
Methane, CH$_4$
$S° = 186.3$ J mol^{-1} K^{-1}
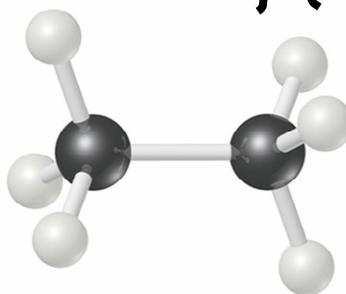
Ethane, C$_2$H$_6$
$S° = 229.6$ J mol^{-1} K^{-1}
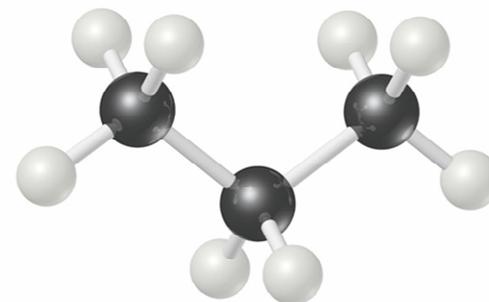
Propane, C$_3$H$_8$
$S° = 270.3$ J mol^{-1} K^{-1}

Chemical
Thermodynamics
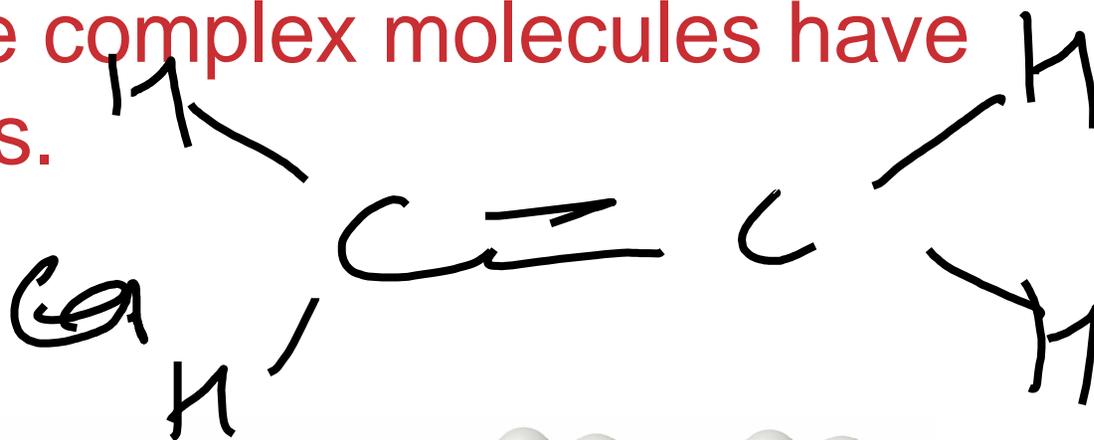
Entropy Changes in Chemical Reactions

Entropy changes for a reaction can be estimated in a manner analogous to that by which ΔH is estimated:

$$\Delta S° = \Sigma n \Delta S°(\text{products}) - \Sigma m \Delta S°(\text{reactants})$$

where n and m are the coefficients in the balanced chemical equation.

- **SAMPLE EXERCISE 19.5**

Calculate $\Delta S°$ for the synthesis of ammonia from $N_2(g)$ and $H_2(g)$ at 298 K:
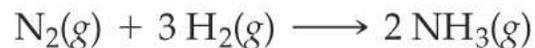
$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

Using Equation 19.8, we have

$$\Delta S° = 2S°(NH_3) - [S°(N_2) + 3S°(H_2)]$$

Substituting the appropriate $S°$ values from Table 19.2 yields

$$\Delta S° = (2\text{ mol})(192.5\text{ J/mol-K}) - [(1\text{ mol})(191.5\text{ J/mol-K}) + (3\text{ mol})(130.6\text{ J/mol-K})]$$

$$= -198.3\text{ J/K}$$

Chemical
Thermodynamics

The value for $\Delta S°$ is negative, in agreement with our qualitative prediction based on the decrease in the number of molecules of gas during the reaction.

PRACTICE EXERCISE

Using the standard entropies in Appendix C, calculate the standard entropy change, $\Delta S°$, for the following reaction at 298 K:

$$Al_2O_3(s) + 3\,H_2(g) \longrightarrow 2\,Al(s) + 3\,H_2O(g)$$

$Al_2O_3(s)$ 51.00

$H_2(g)$ 130.58

$Al(s)$ 28.32

$H_2O(g)$ 188.83

Chemical Thermodynamics

PRACTICE EXERCISE

Using the standard entropies in Appendix C, calculate the standard entropy change, $\Delta S°$, for the following reaction at 298 K:

$$Al_2O_3(s) + 3\,H_2(g) \longrightarrow 2\,Al(s) + 3\,H_2O(g)$$

Answer: 180.39 J/K

Entropy Changes in Surroundings

- Heat that flows into or out of the system changes the entropy of the surroundings.

- For an isothermal process:

$$\Delta S_{sur} = \frac{-q_{sys}}{T}$$

- At constant pressure, q_{sys} is simply $\Delta H°$ for the system.

Chemical
Thermodynamics

Gibbs Free Energy

- Though we have learnt in this chapter that the spontaneous process is one in which there is an increase in the entropy of a system we do come across some spontaneous processes that result in a decrease in the entropy of the system!

Chemical Thermodynamics

- An example is the highly exothermic process of reaction of sodium metal with chlorine gas to form sodium chloride.

FORMATION OF SODIUM CHLORIDE

When metals and nonmetals react, electrons are transferred from the metal atoms to the nonmetal atoms, forming ions. The principal reason that ionic compounds are stable is the attraction between ions of unlike charge, which draws them together, releasing energy and causing the ions to form a solid array or lattice.

Cl_2

Na

A container of chlorine gas and a container of sodium metal.

Formation of NaCl begins as sodium is added to the chlorine.

The reaction a few minutes later, strongly exothermic, giving off both heat and light.

Chemical Thermodynamics

- Spontaneous processes that result in a decrease in entropy are always exothermic.
- So this suggests that enthalpy also has something to do with spontaneity.

Gibbs Free Energy

- Willard Gibbs proposed a new state function *now* named Gibbs Free Energy (G):

$$G \quad = \quad H \quad - \quad TS$$

Enthalpy term   Entropy term

Where T is the absolute temperature.

Change in free energy of the system

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

Entropy Change in the Universe

- The universe is composed of the system and the surroundings.
- Therefore,

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

Since

$$\Delta S_{surr} = \frac{-q_{sys}}{T}$$

Chemical
Thermodynamics

- This becomes:

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H_{system}}{T}$$

Multiplying both sides by $-T$,

$$\Delta S_{universe} \times -T = \Delta S_{system} \times -T + \frac{-\Delta H_{system}}{T} \times -T$$

$$\Delta S_{universe} \times -T = \Delta S_{system} \times -T + \frac{-\Delta H_{system}}{\cancel{T}} \times -\cancel{T}$$

$$-T\Delta S_{universe} = -T\Delta S_{system} + \Delta H_{system}$$

$$-T\Delta S_{universe} = \Delta H_{system} - T\Delta S_{system}$$

We know from before

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

So $\quad \Delta G = -T\Delta S_{universe}$

Chemical
Thermodynamics

- $-T\Delta S_{universe}$ is defined as the Gibbs free energy, ΔG.

- It is more convenient to use ΔG as the criterion for spontaneity than $\Delta S_{universe}$ because ΔG relates to the system and avoids the complication of having to study the surroundings

When $\Delta S_{universe}$ is positive, ΔG is negative.

Therefore, when ΔG is negative, a process is spontaneous.

Gibbs Free Energy

1. If ΔG is negative, the forward reaction is spontaneous.

2. If ΔG is 0, the system is at equilibrium.

3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

Chemical Thermodynamics

In any spontaneous process at constant pressure and temperature the free energy of the system always decreases

- Let us remember Reaction Quotient Q

If $Q = K$,

the system is at equilibrium.

Reaction forms products

Equilib-rium

Reaction forms reactants

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Spontaneous

Spontaneous

Free energy →

$Q < K$

$Q > K$

Pure
$N_2 + H_2$

Equilibrium
mixture
$(Q = K, \Delta G = 0)$

Pure
NH_3

Chemical
Thermodynamics
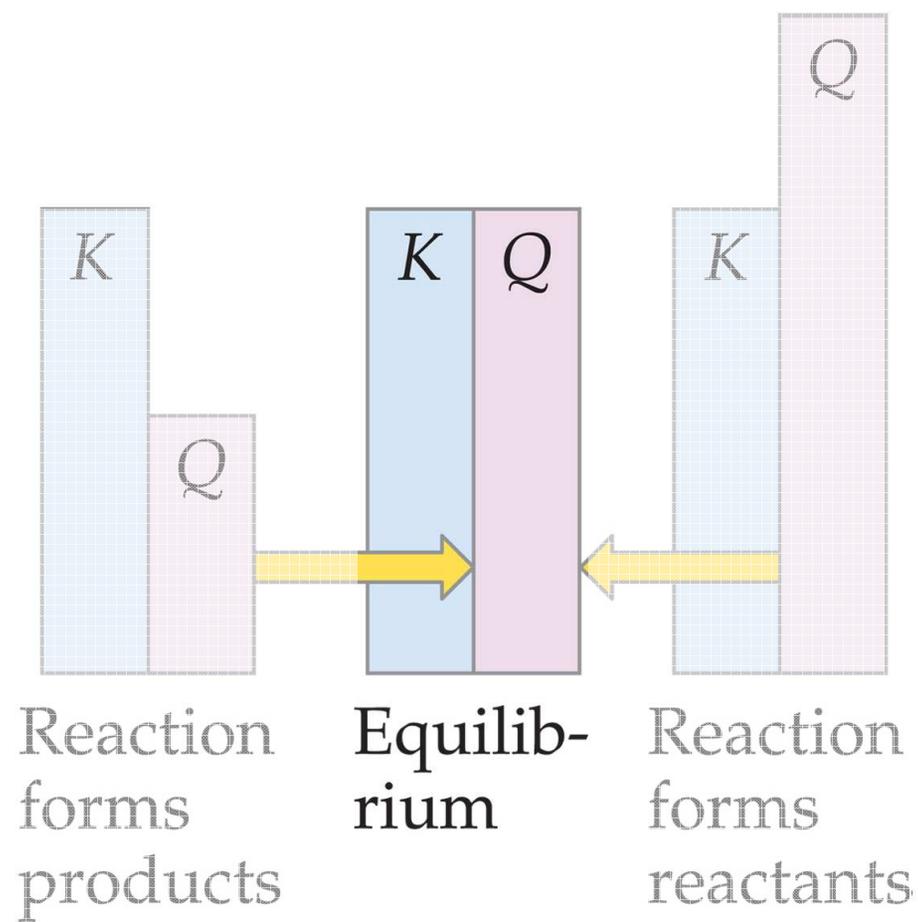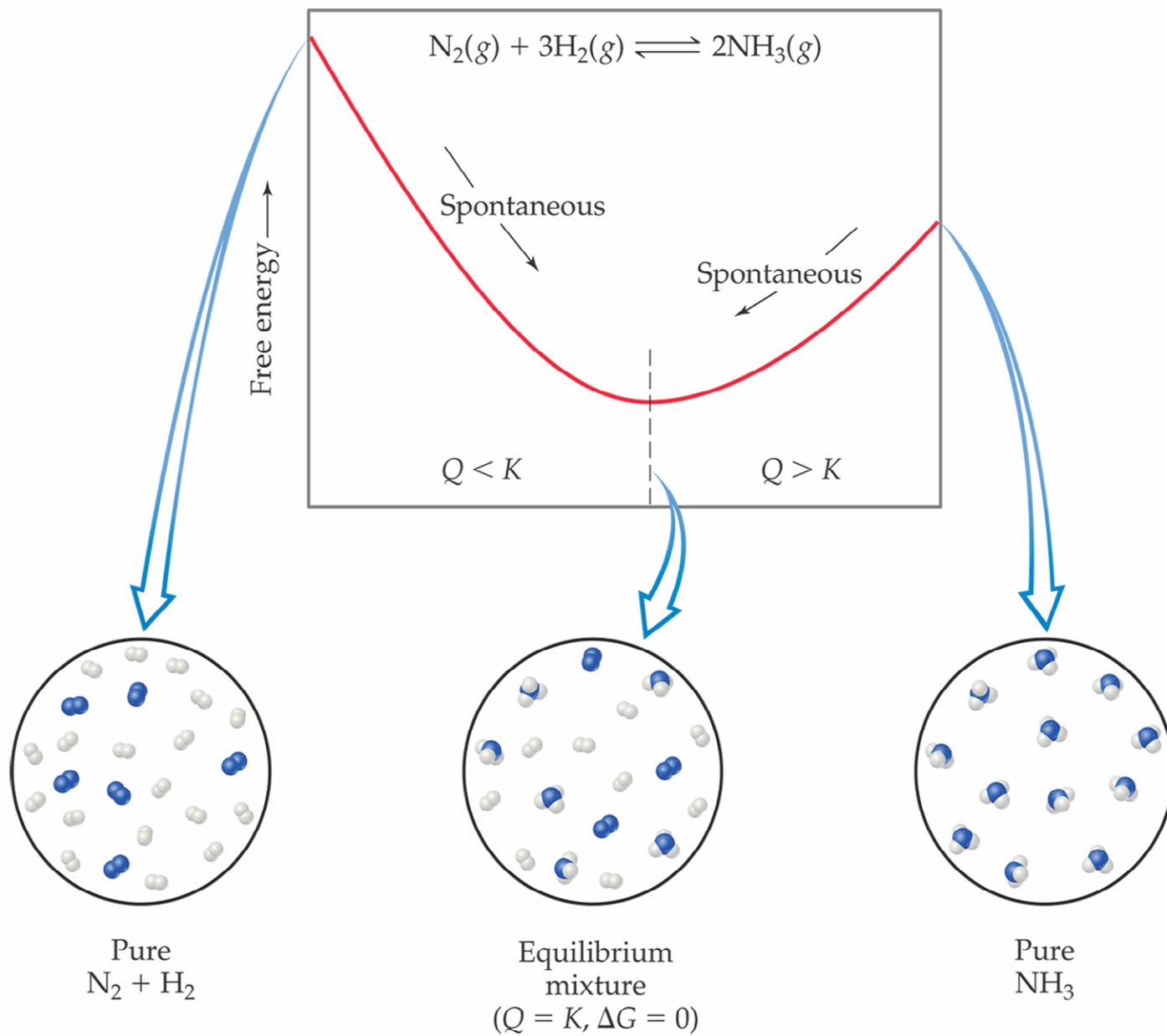
Standard Free Energy Changes

Analogous to standard enthalpies of formation ΔH°, are standard free energies of formation, ΔG_f°.

$$\Delta G^\circ = \Sigma n \Delta G_f^\circ(\text{products}) - \Sigma m \Delta G_f^\circ(\text{reactants})$$

where *n* and *m* are the stoichiometric coefficients.

SAMPLE EXERCISE 19.6

(a) By using data from Appendix C, calculate the standard free-energy change for the following reaction at 298 K:

$$P_4(g) + 6\,Cl_2(g) \longrightarrow 4\,PCl_3(g)$$
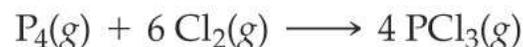
Solve: (a) $Cl_2(g)$ is in its standard state, so ΔG_f° is zero for this reactant. $P_4(g)$, however, is not in its standard state, so ΔG_f° is not zero for this reactant. From the balanced equation and using Appendix C, we have:

$$\Delta G_{rxn}^\circ = 4\Delta G_f^\circ[PCl_3(g)] - \Delta G_f^\circ[P_4(g)] - 6\Delta G_f^\circ[Cl_2(g)]$$

$$= 4\,mol(-269.6\ kJ/mol) - (24.4\ kJ/mol) - 0$$

$$= -1102.8\ kJ$$

The fact that G° is negative tells us that the reaction would proceed spontaneously in the forwa

direction to form more PCl3 .

(b) What is ΔG° for the reverse of the above reaction?

(b) Remember that $\Delta G = G$ (products) $- G$ (reactants). If we reverse the reaction, we reverse the roles of the reactants and products. Thus, reversing the reaction changes the sign of ΔG, just as reversing the reaction changes the sign of ΔH. • (Section 5.4) Hence, using the result from part (a):

$$4\,PCl_3(g) \longrightarrow P_4(g) + 6\,Cl_2(g) \qquad \Delta G^\circ = +1102.8\ kJ$$

Chemical
Thermodynamics

PRACTICE EXERCISE

By using data from Appendix C, calculate $\Delta G°$ at 298 K for the combustion of methane:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g).$$

- $CH_4(g)$ -50.8   kJ/mol
- $CO_2(g)$ -394.4
- $H_2O(g)$ -228.57

PRACTICE EXERCISE

By using data from Appendix C, calculate $\Delta G°$ at 298 K for the combustion of methane:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g).$$

- $CH_4(g)$ -50.8   kJ/mol
- $CO_2(g)$ -394.4
- $H_2O(g)$ -228.57

Answer: –800.7 kJ

SAMPLE EXERCISE 19.7

In Section 5.7 we used Hess's law to calculate $\Delta H°$ for the combustion of propane gas at 298 K:

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H° = -2220 \text{ kJ}$$
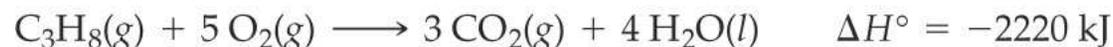
(a)   *Without using data from Appendix C, predict whether Δ G° for this reaction is more negative or less negative than Δ H°.*

$$\Delta G° = \Delta H° - (T\,\Delta S°)$$

(a)   We see that the reactants consist of six molecules of gas, and the products consist of three molecules of gas and four molecules of liquid.

Thus, the number of molecules of gas has decreased significantly during the reaction.

we would expect a number of gas molecules to lead to a decrease in the entropy of the system—the products have fewer accessible microstates than the reactants.

We therefore expect Δ S° and (T Δ S°) to be negative numbers.

Because we are subtracting T Δ S°, which is a negative number, we would predict that Δ G° is *less negative* than Δ H°.

Chemical
Thermodynamics

(b) Use data from Appendix C to calculate the standard free-energy change for the reaction at 298 K. Is your prediction from part (a) correct?

(b) Using Equation 19.13 and values from Appendix C, we can calculate the value of $\Delta G°$:

$$\Delta G° = 3\Delta G_f°[CO_2(g)] + 4\Delta G_f°[H_2O(l)] - \Delta G_f°[C_3H_8(g)] - 5\Delta G_f°[O_2(g)]$$

$$= 3 \text{ mol}(-394.4 \text{ kJ/mol}) + 4 \text{ mol}(-237.13 \text{ kJ/mol}) -$$

$$1 \text{ mol}(-23.47 \text{ kJ/mol}) - 5 \text{ mol }(0 \text{ kJ/mol}) = -2108 \text{ kJ}$$

Chemical
Thermodynamics

PRACTICE EXERCISE

Consider the combustion of propane to form $CO_2(g)$ and $H_2O(g)$ at 298 K:

$C_3H_8(g) + 5 O_2(g) \longrightarrow 3 CO_2(g) + 4 H_2O(g)$. Would you expect $\Delta G°$ to be higher or lower

$$\Delta G° = \Delta H° - (T \Delta S°)$$

Consider the combustion of propane to form $CO_2(g)$ and $H_2O(g)$ at 298 K:

$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$. Would you expect $\Delta G°$ to be more negative or less negative than $\Delta H°$?

Answer: lower

Free Energy Changes

At temperatures other than 25°C,

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

How does $\Delta G°$ change with temperature?

Chemical
Thermodynamics

Free Energy and Temperature

- There are two parts to the free energy equation:
  - $\Delta H°$— the enthalpy term
  - $T\Delta S°$ — the entropy term
- The temperature dependence of free energy, then comes from the entropy term.

Free Energy and Temperature

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

TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2\,O_3(g) \longrightarrow 3\,O_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	+	+ or −	Spontaneous at low T; nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	+ or −	Spontaneous at high T; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

Chemical
Thermodynamics

- Generally ΔH and ΔS do not change much with temperature, but the magnitude of TΔS changes directly with temperature.

Under standard conditions:

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

The values of ΔH^o and ΔS^o can be obtained from any source and they change very little with temperature, the value of ΔG^o can be calculated.

Chemical
Thermodynamics

The Haber process for the production of ammonia involves the equilibrium

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
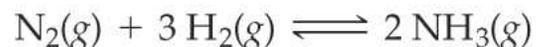
Assume that $\Delta H°$ and $\Delta S°$ for this reaction do not change with temperature.

(a) Predict the direction in which $\Delta G°$ for this reaction changes with increasing temperature.

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

We expect this reaction to have a negative S as the number of molecules is decreasing

So $-T\Delta S°$ will be positive and will increase with the increase in temperature.

So G keeps becoming larger with increase in temperature and the reaction becomes less inclined to go forward.

The Haber process for the production of ammonia involves the equilibrium

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

(b) Calculate the values of Δ $G°$ for the reaction at 25°C and 500°C.

Now:

ΔH will be calculated as we learnt in chapter 15 and ΔS in this chapter

Then plug the values in the above equation

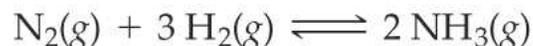Recall that the standard enthalpy change for a reaction is given by the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient in the balanced chemical equation, less the same quantities for the reactants. At 25°C, ΔH_f° for $NH_3(g)$ is $-46.19\ \text{kJ/mol}$. The ΔH_f° values for $H_2(g)$ and $N_2(g)$ are zero by definition because the enthalpies of formation of the elements in their normal states at 25°C are defined as zero (Section 5.7). Because 2 mol of NH_3 is formed, the total enthalpy change is

$$(2\ \text{mol})(-46.19\ \text{kJ/mol}) - 0 = -92.38\ \text{kJ}$$

Using Equation 19.8, we have

$$\Delta S° = 2S°(NH_3) - [S°(N_2) + 3S°(H_2)]$$

Substituting the appropriate $S°$ values from Table 19.2 yields

$$\Delta S° = (2\ \text{mol})(192.5\ \text{J/mol-K}) - [(1\ \text{mol})(191.5\ \text{J/mol-K}) + (3\ \text{mol})(130.6\ \text{J/mol-K})]$$

$$= -198.3\ \text{J/K}$$

Chemical
Thermodynamics

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

$$\Delta G° = -92.38 \text{ kJ} - (298 \text{ K})(-198.4 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= -92.38 \text{ kJ} + 59.1 \text{ kJ} = -33.3 \text{ kJ}$$

At $T = 500 + 273 = 773$ K we have

$$\Delta G° = -92.38 \text{ kJ} - (773 \text{ K})\left(-198.4\frac{\text{J}}{\text{K}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= -92.38 \text{ kJ} + 153 \text{ kJ} = 61 \text{ kJ}$$

Chemical
Thermodynamics

Homework Question

Practice Exercise on page 829.

I want to see all the work done **<u>fully</u>**. I want to see the formula written, plugged and then the answer.

NO SHORTCUTS

Again I will collect it **either in the first five or the last five minutes of class.**

Chemical
Thermodynamics

- S far we learnt to calculate the value of ΔG under standard conditions.

- Now we will learn to calculate the ΔG under non standard conditions.

  And

- We will learn to relate the value of ΔG^o with the equilibrium constant K.

Chemical
Thermodynamics

Free Energy and Equilibrium

The relationship between the standard free energy change and the nonstandard free energy change is

$$\Delta G = \Delta G° + RT \ln Q$$

\

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Under standard conditions, all concentrations are 1 M, so $Q = 1$ and the $\ln Q = 0$ the last term drops out.

$$\Delta G = \Delta G^\circ$$

Chemical
Thermodynamics

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

- We know that phase change, say boiling point, is an equilibrium condition and at equilibrium $\Delta G = 0$
- So $\Delta G°$ becomes 0

$$0 = \Delta H° - T_b \Delta S°$$

$$\Delta H° = T_b \Delta S°$$

$$\frac{\Delta H°}{\Delta S°} = T_b$$

Chemical
Thermodynamics

Free Energy and Equilibrium

- At equilibrium, $Q = K$, and $\Delta G = 0$.
- The equation becomes

$$0 = \Delta G^{\circ} + RT \ln K$$

- Rearranging, this becomes

$$\Delta G^{\circ} = -RT \ln K$$

or,

$$K = e^{-\Delta G^{\circ}/RT}$$

Chemical
Thermodynamics

SAMPLE EXERCISE 19.9 Relating ΔG to a Phase Change at Equilibrium

As we saw in Section 11.5, the *normal boiling point* is the temperature at which a pure liquid is in equilibrium with its vapor at a pressure of 1 atm. **(a)** Write the chemical equation that defines the normal boiling point of liquid carbon tetrachloride, CCl4(*l*). **(b)** What is the value of $G°$ for the equilibrium in part (a)? **(c)** Use thermodynamic data in Appendix C and Equation 19.20 to estimate the normal boiling point of CCl4.

(a) The normal boiling point of CCl_4 is the temperature at which pure liquid CCl_4 is in equilibrium with its vapor at a pressure of 1 atm:

$$CCl_4(l) \rightleftharpoons CCl_4 \, (g, \, 1 \text{ atm})$$

(b) Δ $G°$ = 0 for the equilibrium involved in the normal boiling point of any liquid

(c) Combining Equation 19.20 with the result from part (b), we see that the equality at the normal boiling point, *Tb*, of $CCl_4(l)$ or any other pure liquid is

$$\Delta G° = \Delta H° - T_b \Delta S° = 0$$

Solving the equation for *Tb*, we obtain

$$T_b = \Delta H° / \Delta S°$$

Chemical
Thermodynamics

$$CCl_4(l) \rightleftharpoons CCl_4\ (g,\ 1\ atm)$$

Strictly speaking, we would need the values of $\Delta H°$ and $\Delta S°$ for the equilibrium between $CCl_4(l)$ and $CCl_4(g)$ at the normal boiling point to do this calculation. However, we can *estimate* the boiling point by using the values of $\Delta H°$ and $\Delta S°$ for CCl_4 at 298 K, which we can obtain from the data in Appendix C and Equations 5.31 and 19.8:

$$\Delta H° = (1\ \text{mol})(-106.7\ \text{kJ/mol}) - (1\ \text{mol})(-139.3\ \text{kJ/mol}) = +32.6\ \text{kJ}$$
$$\Delta S° = (1\ \text{mol})(309.4\ \text{J/mol-K}) - (1\ \text{mol})(214.4\ \text{J/mol-K}) = +95.0\ \text{J/K}$$

Notice that, as expected, the process is endothermic ($\Delta H > 0$) and produces a gas in which energy can be more spread out ($\Delta S > 0$). We can now use these values to estimate *Tb* for $CCl_4(l)$:

$$T_b = \frac{\Delta H°}{\Delta S°} = \left(\frac{32.6\ \text{kJ}}{95.0\ \text{J/K}}\right)\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right) = 343\ \text{K} = 70°\text{C}$$

Chemical
Thermodynamics

We will continue to explore the Haber process for the synthesis of ammonia:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
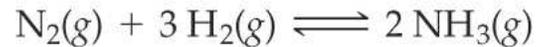
Calculate ΔG at 298 K for a reaction mixture that consists of 1.0 atm N_2, 3.0 atm H_2, and 0.50 atm NH_3.
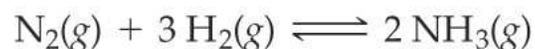
- The formula we need to use is :

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$= (-33.3\ \text{kJ/mol}) + (8.314\ \text{J/mol-K})(298\ \text{K})(1\ \text{kJ/1000 J})\ln(9.3 \times 10^{-3})$$
$$= (-33.3\ \text{kJ/mol}) + (-11.6\ \text{kJ/mol}) = -44.9\ \text{kJ/mol}$$

- We need Q for this so

$$Q = \frac{P_{NH_3}{}^2}{P_{N_2} P_{H_2}{}^3} = \frac{(0.50)^2}{(1.0)(3.0)^3} = 9.3 \times 10^{-3}$$

Use standard free energies of formation to calculate the equilibrium constant, K, at 25°C for the reaction involved in the Haber process:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

The standard free-energy change for this reaction was calculated in Sample Exercise 19.8: $\Delta G° = -33.3$ kJ/mol = $-33,300$ J/mol.

$$K = e^{-\Delta G°/RT}$$

Solving Equation for the exponent $-\Delta G°/RT$, we have

$$\frac{-\Delta G°}{RT} = \frac{-(-33,300\ \text{J/mol})}{(8.314\ \text{J/mol-K})(298\ \text{K})} = 13.4$$

$$K = e^{-\Delta G°/RT} = e^{13.4} = 7 \times 10^5$$

Chemical
Thermodynamics

Homework Question

- Chapter 17

  Question # 30

I will check for correctness.

Look at all the fun you have been missing!!!!

Chemical
Thermodynamics

- QUESTION#19.73

The reaction is $2NO_2(g) \rightarrow N_2O_4(g)$

$$\Delta G = \Delta G^\circ + RT \ln K$$

$$K = \frac{P_{N_2O_4}}{P_{NO_2}^2}$$

- $$\Delta G = \Delta G^\circ + RT \ln \frac{P_{N_2O_4}}{P_{NO_2}^2}$$

Chemical
Thermodynamics

Question #17.29

- You have to prepare a pH 3.5 solution and you have 0.1 M $HCHO_2$ and 0.1 N $NaCHO_2$. How many ml of each solution would you use.

K_a= 1.8 x 10 $^{-4}$

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$3.50 = p(1.8x10-4) + \log\frac{[base]}{[acid]}$$

$$3.50 = -\log(1.8x10-4) + \log\frac{[base]}{[acid]}$$

$$3.50 = 3.74 + \log\frac{[base]}{[acid]}$$

$$3.50 - 3.74 = \log\frac{[base]}{[acid]}$$

$$-0.2447 = \log\frac{[base]}{[acid]}$$

$$\frac{[base]}{[acid]} = 10^{-.0.2447} = 0.5692$$

Chemical Thermodynamics

$$\frac{[base]}{[acid]} = 0.5692 = \frac{\text{final M of the base(not the M of the stock solution)}}{\text{final M of acid (not the M of the stock solution)}}$$

$$= \frac{\text{moles of base added from stock / L}}{\text{moles of acid added from the stock/ L}}$$

$$\left(we \text{know that M} = \frac{\text{moles}}{L} \text{ and moles=ML} \right)$$

$$= \frac{\left[\text{M of stock x (y) ml of base stock} \right]/L}{\left[\text{M of stock x (1-y) ml of base stock} \right]/L}$$

$$0.5692 = \frac{0.1M \text{ x y/L}}{0.1Mx(1\text{-}y)/L} = \frac{y}{1-y}$$

$$y = 0.5692(1 - y) = 0.5692 - 0.5692y$$

$$y + 0.5692y = 0.5692$$

$$1 + .5692)y = 0.5692$$

$$y = \frac{0.5692}{1.5692} = 0.3627 \text{L of the 0.1 M base solution}$$

and 1L-0.36l =0.64 l of .1 M acid solution

- Homework question
- 17.29
- Show all work to get credit.

Chemical
Thermodynamics