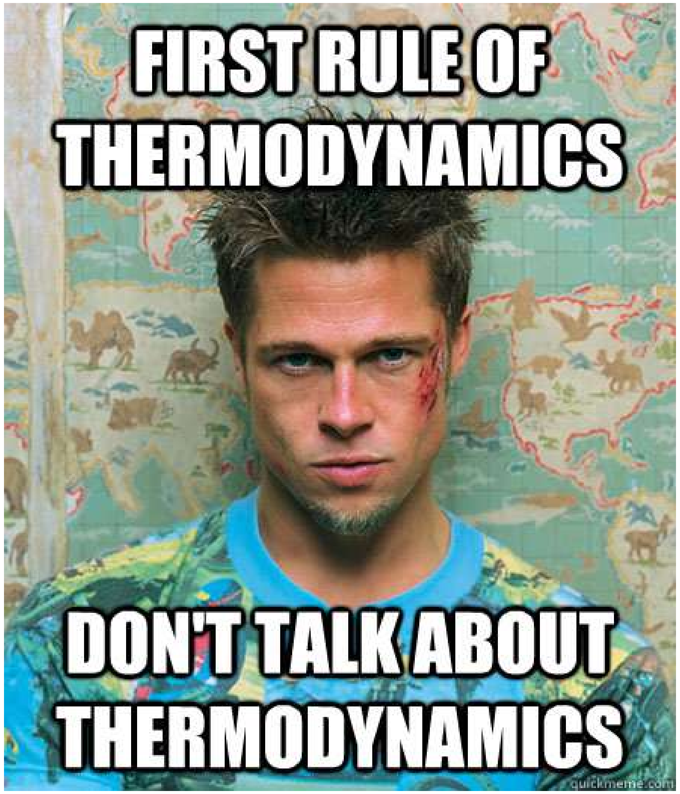
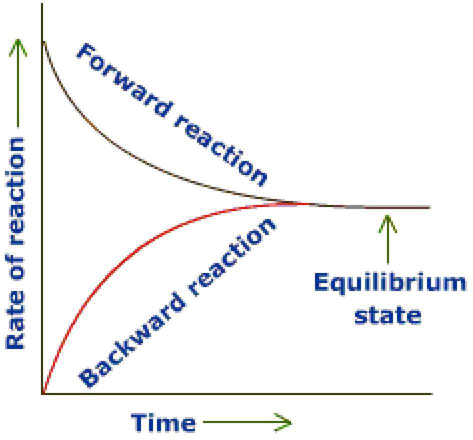
Chapter 19 – Chemical Thermodynamics



Jennie L. Borders

Section 19.1 – Spontaneous Processes

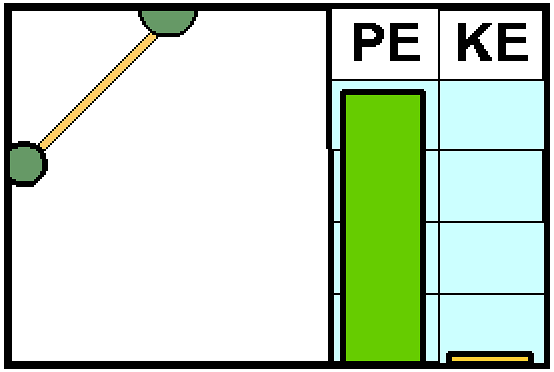
- The rates of chemical reactions are controlled by the activation energy.
- Equilibrium is when opposite processes occur at the same rate, so equilibrium is also controlled by energy.



Attainment of equilibrium in a reversible reaction

First Law of Thermodynamics

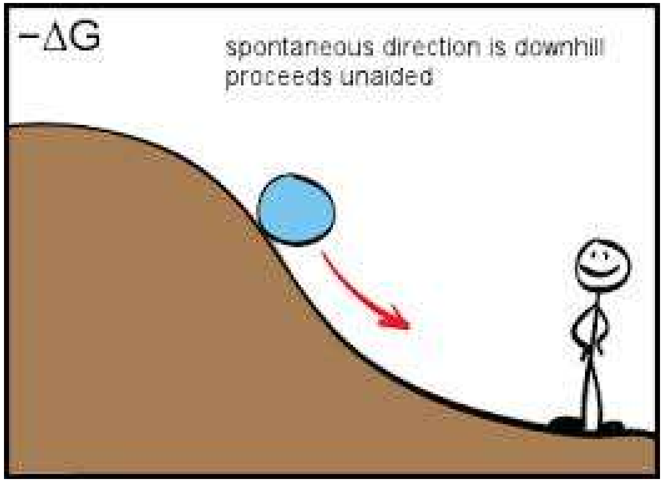
- The first law of thermodynamics states that energy is conserved.
- Energy can be transferred or change forms, but the total energy of the universe remains constant.

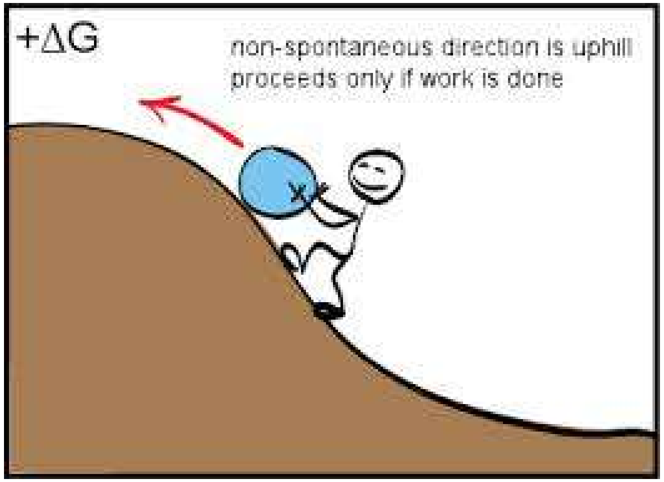


$\Delta E = q + w$

Spontaneous Processes

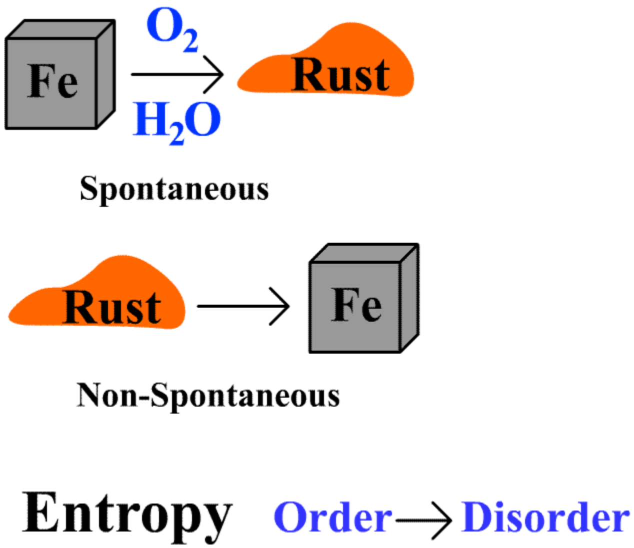
- A spontaneous process is one that proceeds on its own without any outside assistance.
- The AP exam will sometimes refer to spontaneous as “thermodynamically favored.”





Spontaneous Processes

- Processes that are spontaneous in one direction are nonspontaneous in the opposite direction.
- Even though a process is spontaneous, that does not mean that it happens quickly.



Sample Exercise 19.1

- Predict whether the following processes are spontaneous as described, spontaneous in the reverse direction, or in equilibrium:

a. When a piece of metal is heated to 150^{o}C is added to water at 40^{o}C, the water gets hotter.

Sample Exercise 19.1 con’t

b. Water at room temperature decomposes into $H_{2(g)}$ and $O_{2(g)}$

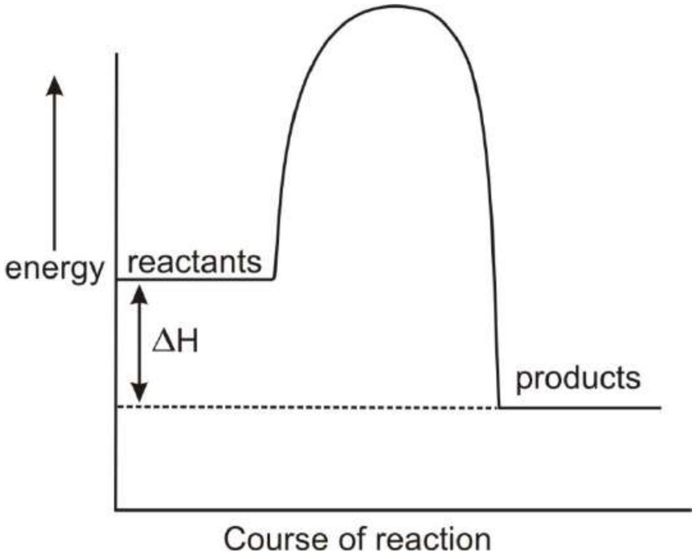
c. Benzene, $C_6H_{6(g)}$, at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene, $80.1^{o}C$.

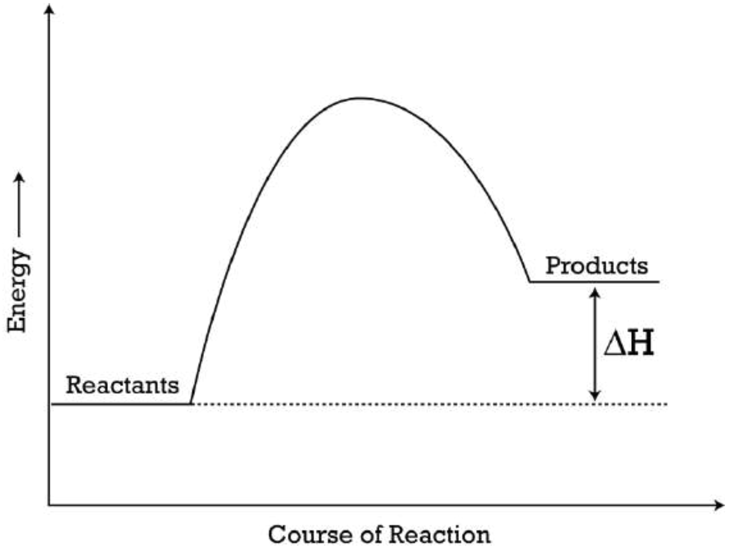
Practice Exercise

- Under 1 atm pressure $CO_{2(s)}$ sulimes at -78^oC. Is the transformation of $CO_{2(s)}$ to $CO_{2(g)}$ a spontaneous process at -100^oC and 1 atm pressure?

Spontaneity

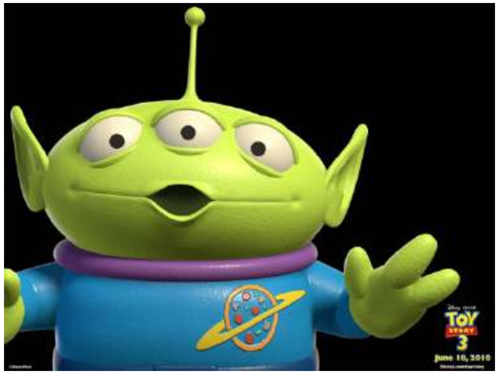
- The loss of energy is a common feature of spontaneous change.
- Exothermic reactions tend to be spontaneous; however, endothermic reactions can be spontaneous too.





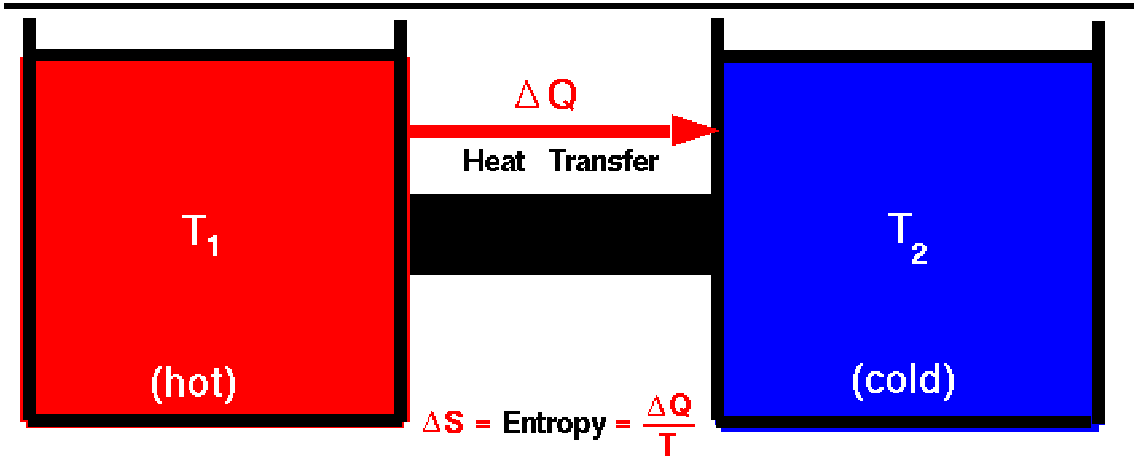
Reversible vs. Irreversible

- A reversible process is when a system is changed in such a way that the system and surroundings can be restored to their original state by exactly reversing the change.
- This is an ideal situation which does not exist.



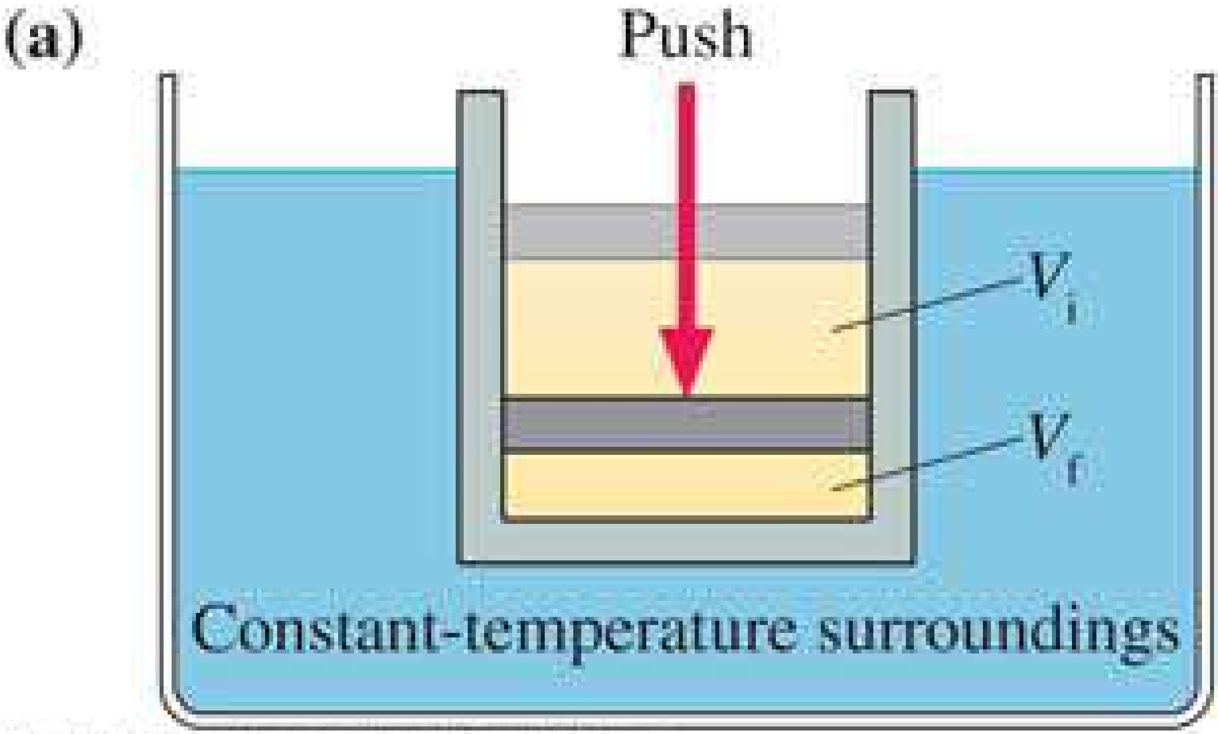
Reversible vs. Irreversible

- An irreversible process is one that cannot simply be reversed to restore the system and its surroundings to their original states.
- All processes that we see are irreversible.



Isothermal

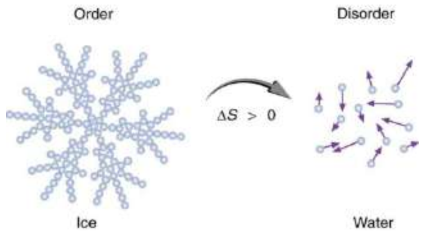
- A process that occurs at a constant temperature is called isothermal.



Section 19.2 – Entropy and the Second Law of Thermodynamics

- Entropy (S) is the degree of randomness of distribution of energy of the molecules of a system.
- For an isothermal process,

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



- The units for entropy are usually J/K.

Sample Exercise 19.2

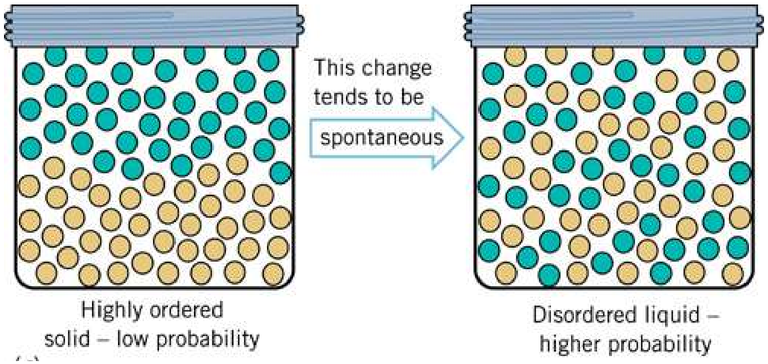
- The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is -38.9^{o}C, and its molar enthalpy of fusion is ΔH_{fusion} = 2.29 kJ/mol. What is the entropy change of the system when 50.0g of $Hg_{(l)}$ freezes at the normal freezing point?

Practice Exercise

- The normal boiling point of ethanol, C_2H_5OH, is 78.3^{o}C, and its molar enthalpy of vaporization is 38.56 kJ/mol. What is the change in entropy in the system when 68.3g of $C_2H_5OH_{(g)}$ at 1 atm condenses to liquid at the normal boiling point?

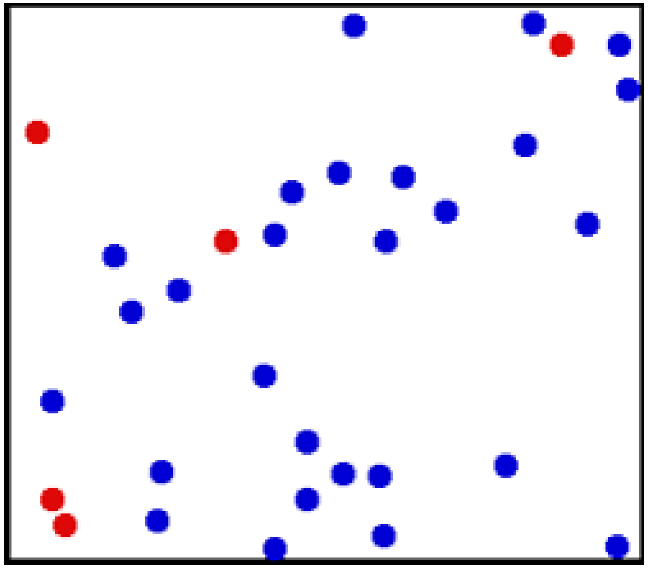
Second Law of Thermodynamics

- The change in entropy for a spontaneous process is always positive.
- The second law of thermodynamics states that any spontaneous irreversible process results in an overall increase in entropy.



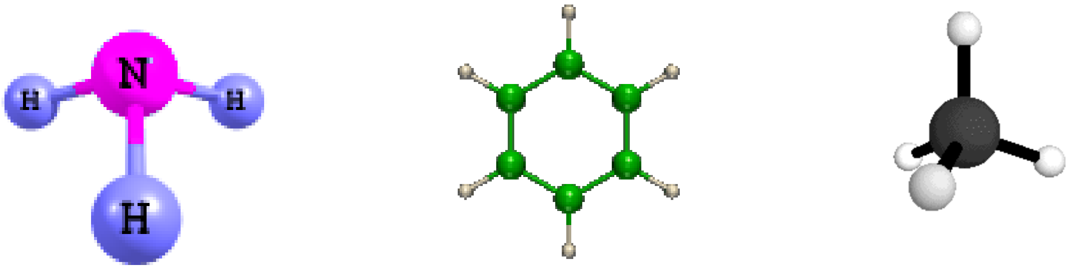
Section 19.3 – The Molecular Interpretation of Entropy

- Molecules can possess different types of motion.
- Translational motion is the movement of an entire particle from one place to another.

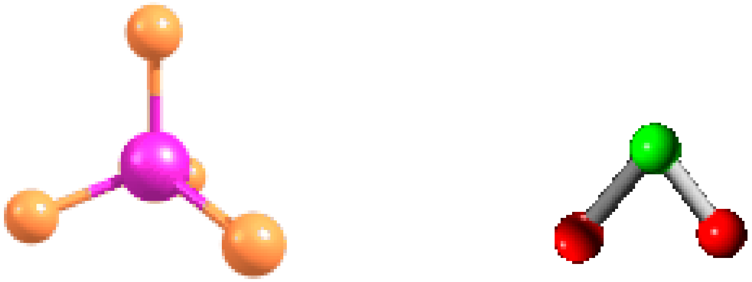


Motion of Particles

- Vibrational motion is when the atoms in a molecule stretch or shift the bonds.

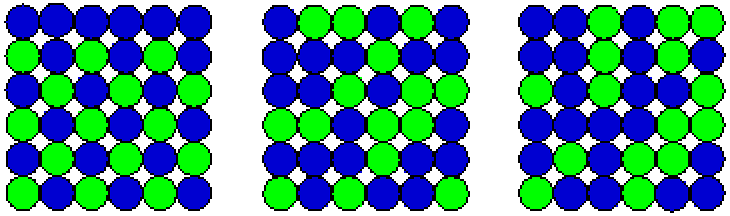


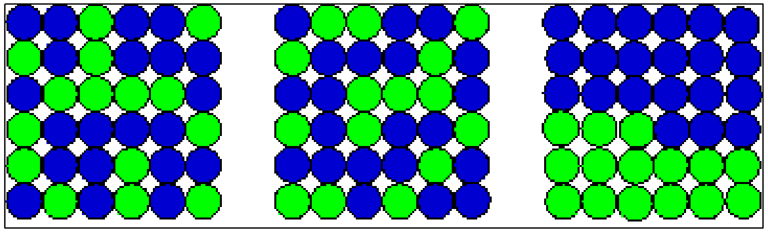
- Rotational motion is when the entire molecule spins.



Microstates

- A microstate is a single possible arrangement of the positions and kinetic energies of the gas molecules when the gas is in a specific thermodynamic state.
- Entropy increases as the number of microstates increases.

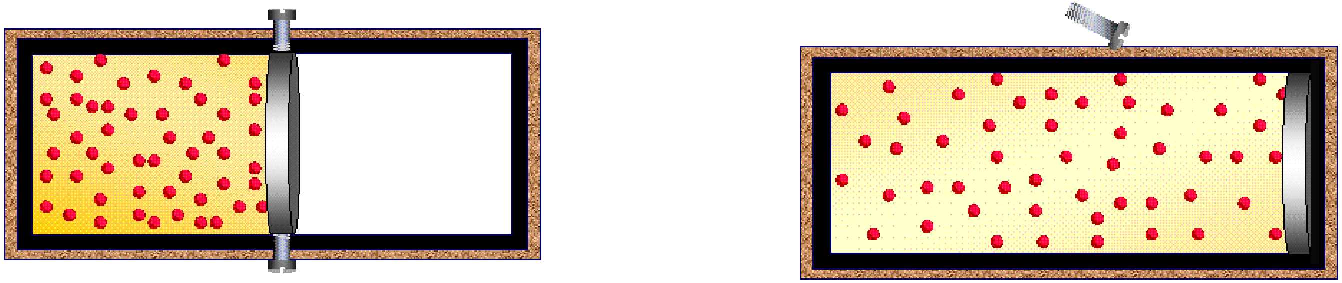




Entropy

- In most cases, and increase in entropy and the number of microstates can be caused by the following:

1. An increase in temperature
2. An increase in volume
3. An increase in the number of independently moving particles



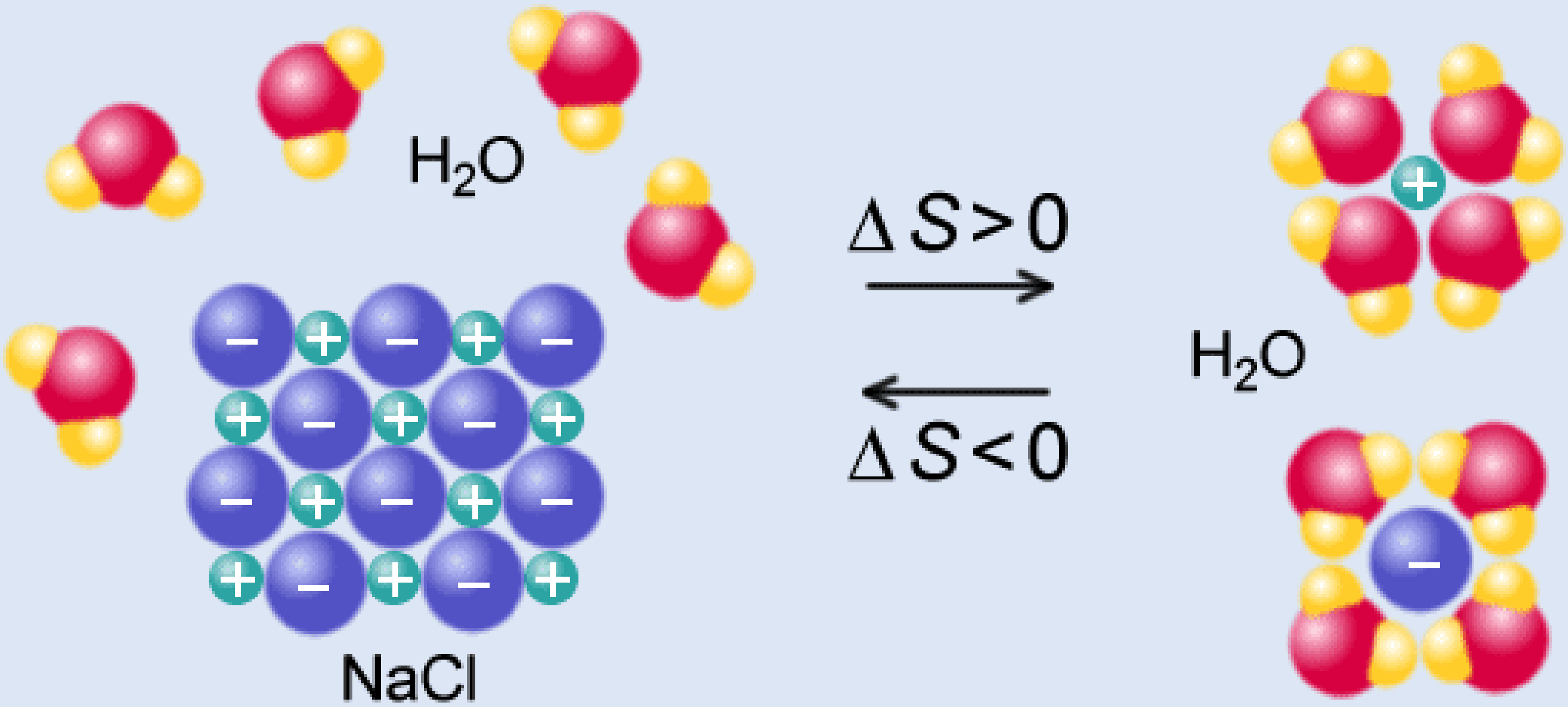
Solutions

- When a solution is formed by dissolving a solid into water, the solute particles gain entropy by separating form one another.
- The water molecules have a decrease in entropy due to the attractions for the solute particles.

Dissolution of NaCl increases entropy

Less randomness
(less entropy)

More randomness
(more entropy)



$\Delta S > 0$

$\Delta S < 0$

NaCl(*s*) + H_2O(*l*)

Na^+(*aq*) + Cl^-(*aq*)

Solutions

- The attractions of the water molecules to the solute particles increases as the charge of the ions increases.
- The solution process normally has a net increase in entropy.

Entropy

- We expect an increase in entropy for the following:

1. Gases are formed from liquids or solids.
2. Liquids or solutions are formed from solids.
3. The number of gas molecules increases during a chemical reaction.

Sample Exercise 19.3

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

a. $H_2O_{(l)} \rightarrow H_2O_{(g)}$

b. $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$

c. $4Fe_{(s)}\ 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$

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

Practice Exercise

- Indicate whether each of the following processes produces an increase or decrease in the entropy of the system:

a. $CO_{2(s)} \rightarrow CO_{2(g)}$

b. $CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$

c. $HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)}$

d. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

Sample Exercise 19.4

- Choose the sample of matter that has greater entropy in each pair, and explain your choice:

a. 1 mol $NaCl_{(s)}$ or 1 mol $HCl_{(g)}$ at 25°C.

b. 2 mol $HCl_{(g)}$ or 1 mol $HCl_{(g)}$ at 25°C.

c. 1 mol $HCl_{(g)}$ or 1mol $Ar_{(g)}$ at 298K.

Practice Exercise

- Choose the substance with the greater entropy in each case:

a. 1 mol $H_{2(g)}$ at STP or 1 mol $H_{2(g)}$ at 100°C and 0.5 atm.

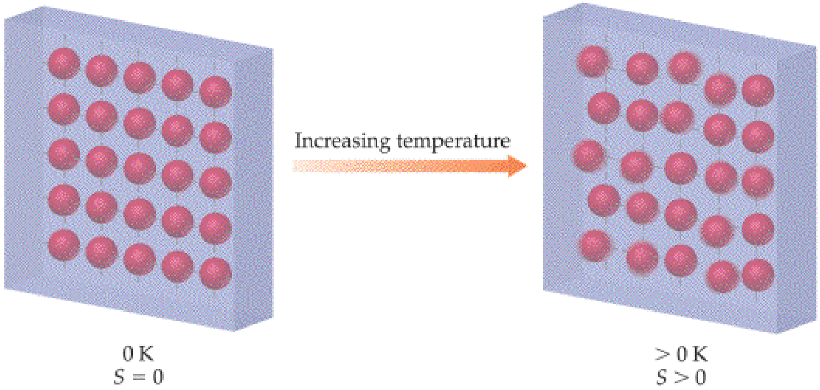
b. 1 mol $H_2O_{(s)}$ at 0°C or 1 mol $H_2O_{(l)}$ at 25°C.

c. 1 mol $H_{2(g)}$ at STP or 1 mol $SO_{2(g)}$ at STP

d. 1 mol $N_2O_{4(g)}$ at STP or 2 mol $NO_{2(g)}$ at STP.

Third Law of Thermodynamics

- The third law of thermodynamics states that the entropy of a pure crystalline substance at absolute zero is zero.
- Entropy increases as a substance is heated, so $\Delta S_{solid} < \Delta S_{liquid} < \Delta S_{gas}$.



Section 19.4 – Entropy Changes in Chemical Reactions

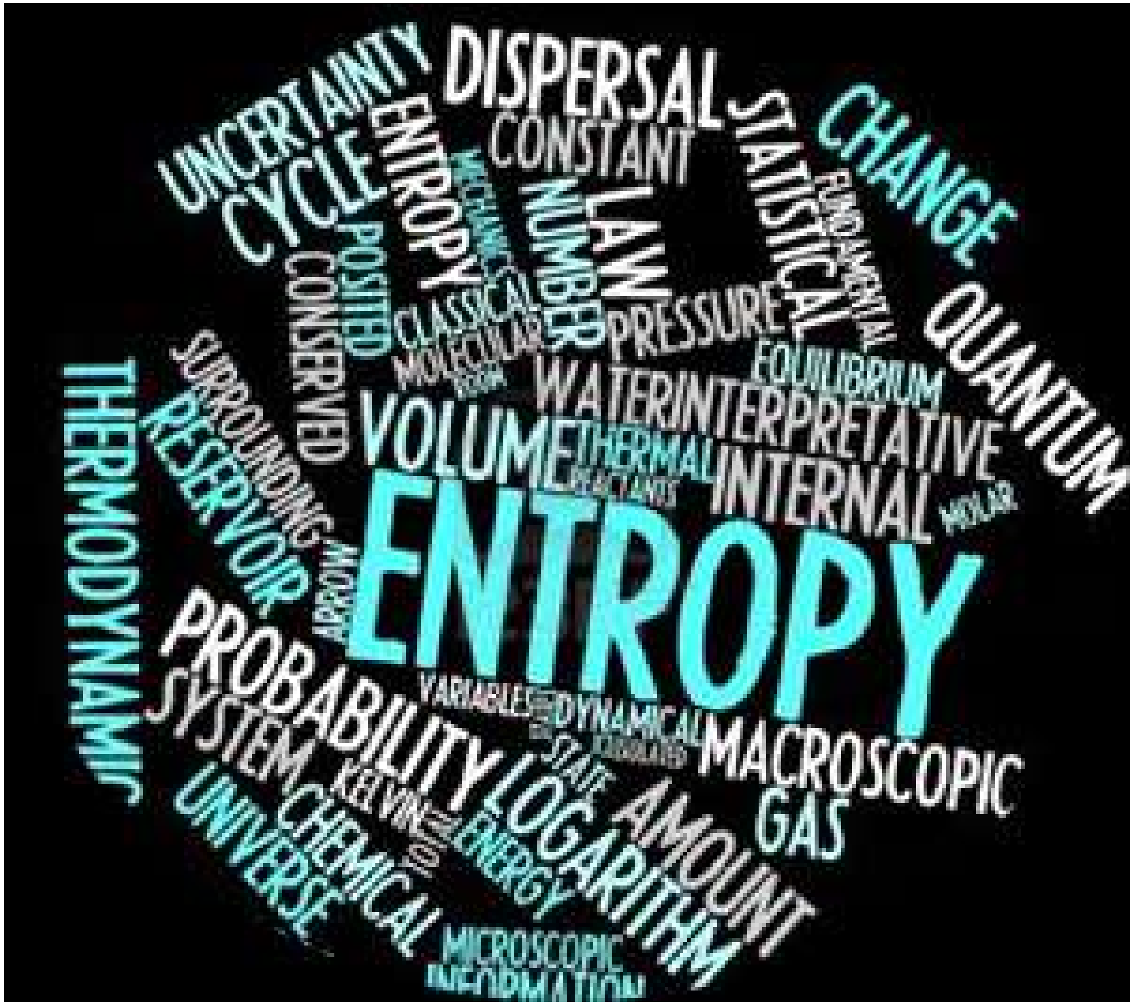
- The molar entropy values of substances in their standard states are known as standard molar entropies and are denoted S^o. The standard state for any substance is defined as the pure substance at 1 atm pressure and 298K.

Molar Entropies

- Molar entropies for elements are not zero like ΔH.
- The molar entropies are greater for gases than for liquids and solids.
- Molar entropies generally increase with increasing molar mass.
- Molar entropies generally increase with an increasing number of atoms in the formula of a substance.

Molar Entropy

$$\Delta S^{o} = \Sigma S^{o}_{(\text{products})} - \Sigma S^{o}_{(\text{reactants})}$$



Sample Exercise 19.5

- Calculate ΔS^o for the synthesis of ammonia from $N_{2(g)}$ and $H_{2(g)}$ at 298K:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

Practice Exercise

- Calculate the standard entropy change, ΔS^o, for the following reaction at 298K:

$$Al_2O_{3(s)} + 2H_{2(g)} \rightarrow 2Al_{(s)} + 3H_2O_{(g)}$$

Entropy and the Surroundings

- For an isothermal process, the entropy change is

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

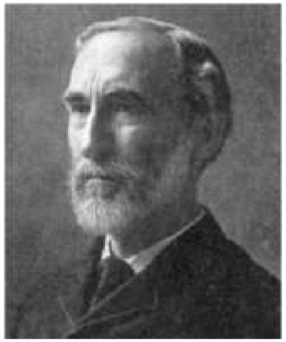
- For a reaction at constant pressure, entropy is

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

Section 19.5 – Gibbs Free Energy

- Spontaneous processes that decrease entropy are always exothermic.
- Spontaneity involves both enthalpy and entropy.
- Gibbs free energy is an equation used to determine spontaneity:

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



Gibbs Free Energy

- If temperature and pressure are constant then the sign of ΔG means the following:

1. If ΔG is negative, the reaction is spontaneous.
2. If ΔG is positive, the reaction is nonspontaneous, but the reverse is spontaneous.
3. If ΔG is zero, the reaction is at equilibrium.

Sample Exercise 19.6

- Calculate the standard free energy change for the formation of $NO_{(g)}$ from $N_{2(g)}$ and $O_{2(g)}$ at 298K:

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

given that $\Delta H^o = 180.7kJ$ and $\Delta S^o = 24.7$ J/K. IS the reaction spontaneous under these circumstances?

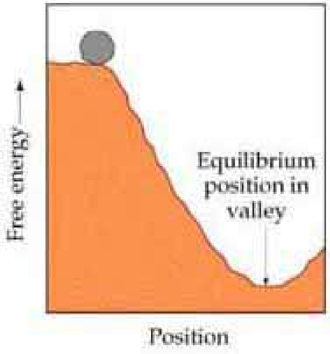
Practice Exercise

- A particular reaction has ΔH^o = 24.6kJ and ΔS^o = 132 J/K at 298K. Calculate ΔG^o. Is the reaction spontaneous under these conditions?

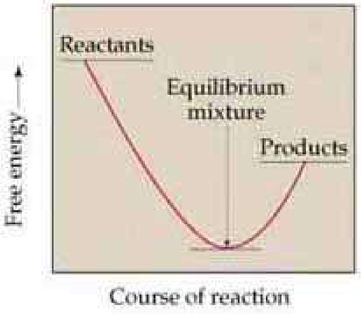
Standard Free Energy of Formation

- The standard free energy of formation is the free energy associated with the formation of a substance at standard conditions.
- For solutions, standard state is 1M.

$$\Delta G^{o} = \Sigma \Delta G_{f}^{o}(\text{products}) - \Sigma \Delta G_{f}^{o}(\text{reactants})$$



(a)



(b)

Sample Exercise 19.7

a. Calculate the standard free-energy change for the following reaction at 298K:

$$P_{4(g)} + 6Cl_{2(g)} \rightarrow 4PCl_{3(g)}$$

b. What is the ΔG^o for the reverse of the above reaction?

Practice Exercise

- Calculate the ΔG^o at 298K for the combustion of methane:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Sample Exercise 19.8

a. Without using data from Appendix C, predict whether ΔG^o for this reaction is more negative or less negative than ΔH^o.

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)}$$

$$\Delta H^o = -2220 kJ$$

Practice Exercise

- Consider the combustion of propane to form $CO_{2(g)}$ and $H_2O_{(g)}$ at 298K:

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

Would you expect ΔG^o to be more negative or less negative than ΔH^o?

Section 19.6 – Free Energy and Temperature

- Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	ΔG	S or NS
-	+	-	-	S
+	-	+	+	NS
-	-	+	+ or -	S at low T
+	+	-	+ or -	S at high T

Sample Exercise 19.9

- The Haber process for the production of ammonia involves the equilibrium

$$N_{2(g)} + 3H_{2(g)} \leftarrow\rightarrow 2NH_{3(g)}$$

Assume that ΔH^o and ΔS^o for this reaction do not change with temperature.

a. Predict the direction in which ΔG^o for this reaction changes with increasing temperature?

Sample Exercise 19.9 con't

b. Calculate the values of ΔG^o for the reaction at 25^oC and 500^oC.

Practice Exercise

a. Using standard enthalpies of formation and standard entropies, calculate ΔH^o and ΔS^o at 298K for the following reaction:

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

b. Using the values obtained in part a, estimate ΔG^o at 400K.

Section 19.7 – Free Energy and the Equilibrium Constant

- There is a relationship between ΔG and the reaction quotient.

$$\Delta G = \Delta G^{o} + RT\ln Q$$

$R = 8.31$ J/mol·K

Sample Exercise 19.10

- 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, $CCl_{4(l)}$.

Sample Exercise 19.10 con’t

b. What is the value of ΔG^o for the equilibrium in part a?

c. Estimate the normal boiling point of CCl_4.

Practice Exercise

- Estimate the normal boiling, in K, for elemental bromine, $Br_{2(l)}$.

Sample Exercise 19.11

- Calculate the ΔG at 298K for a reaction mixture that consists of 1.0 atm N_2, 3.0 atm H_2, and 0.5 atm NH_3.

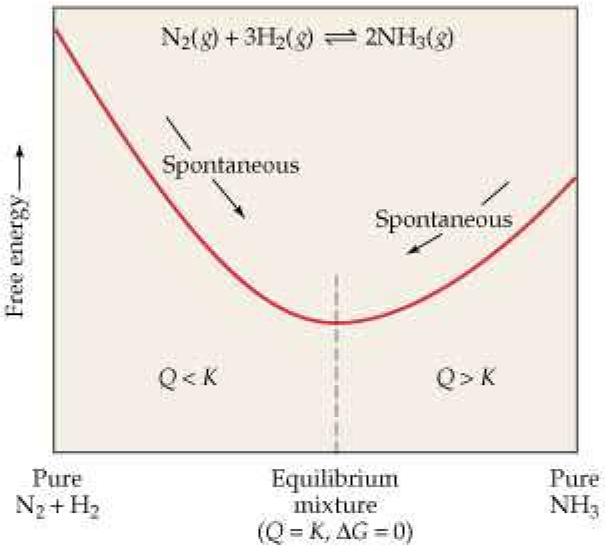
Gibbs Free Energy

$$\Delta G^o = -RT\ln K$$

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

The more negative ΔG^o is, the larger the value for K.

If ΔG^o is positive, then K is less than one.



Sample Exercise 19.12

- Use standard free energies of formation to calculate the equilibrium constant, K, at 25^oC for the reaction invovled in the Haber process:

$$N_{2(g)} + 3H_{2(g)} \leftarrow\rightarrow 2NH_{3(g)}$$

The standard free-energy change for this reaction was calculated in Smaple Exercise 19.9: ΔG^o = -33.3 kJ/mol.

Practice Exercise

- Calculate the standard free-energy change, ΔG^o, and the equilibrium constant, K, at 298K for the reaction

$$H_{2(g)} + Br_{2(l)} \leftarrow\rightarrow 2HBr_{(g)}$$

Sample Integrative Exercise

- Consider the simple salts $NaCl_{(s)}$ and $AgCl_{(s)}$. We will examine the equilibria in which these salts dissolve in water to form aqueous solutions of ions:

$$NaCl_{(s)} \leftarrow\rightarrow Na^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$$

$$AgCl_{(s)} \leftarrow\rightarrow Ag^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$$

a. Calculate the value of ΔG^{o} at 298K for each of the preceding reactions.

Sample Integrative Exercise con’t

b. The two values from part a are very different. Is this difference primarily due to the enthalpy term or the entropy term of the standard free-energy change?

c. Use the values of ΔG^o to calculate the K_{sp} values for the two salts at 298K.

Sample Integrative Exercise con’t

d. Sodium chloride is considered a soluble salt, whereas silver chloride is considered insoluble. Are these descriptions consistent with the answers to part c?

e. How will ΔG^o for the solution process of these salts change with increasing T? What effect should this change has on the solubility of the salts?

THE END