

## Chapter 16 - Spontaneity, Entropy, and Free Energy

### 16.1 Spontaneous Processes and Entropy

#### A. First Law

1. "Energy can neither be created nor destroyed"
2. The energy of the universe is constant

#### B. Spontaneous Processes

1. Processes that occur without outside intervention
2. Spontaneous processes may be fast or slow
  - a. Many forms of combustion are fast
  - b. Conversion of diamond to graphite is slow

#### C. Entropy (S)

1. A measure of the randomness or disorder
2. The driving force for a spontaneous process is an increase in the entropy of the universe
3. Entropy is a thermodynamic function describing the number of arrangements that are available to a system
  - a. Nature proceeds toward the states that have the highest probabilities of existing

#### D. Positional Entropy

1. The probability of occurrence of a particular state depends on the number of ways (microstates) in which that arrangement can be achieved

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

### 16.2 Entropy and the Second Law of Thermodynamics

#### A. Second Law of Thermodynamics

1. "In any spontaneous process there is always an increase in the entropy of the universe"
2. "The entropy of the universe is increasing"
3. For a given change to be spontaneous,  $\Delta S_{\text{univ}}$  must be positive

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

### 16.3 The Effect of Temperature on Spontaneity

#### A. Direction of Heat Flow

1. Entropy changes in the surroundings are primarily determined by heat flow
  - a. Exothermic reactions in a system at constant temperature increase the entropy of surroundings
  - b. Endothermic reactions in a system at constant temperature decrease the entropy of surroundings
  - c. The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures

### 16.4 Free Energy (G), also called "Gibbs Free Energy"

#### A. Calculating Free Energy Change (constant temperature and pressure)

1.  $\Delta G = \Delta H - T\Delta S$ 
  - a. H is enthalpy
  - b. T is Kelvin temperature

## B. Free Energy and Spontaneity

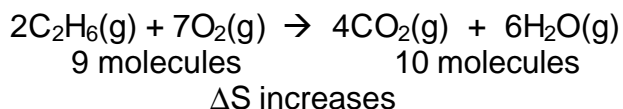
- Reactions proceed in the direction that lowers their free energy ( $-\Delta G$ )

Value of $\Delta H$	Value of $T\Delta S$	Value of $\Delta G$	Spontaneity
Negative	Positive	Negative	Spontaneous
Positive	Negative	Positive	Nonspontaneous
Negative	Negative	???	Spontaneous if the absolute value of $\Delta H$ is greater than the absolute value of $T\Delta S$ (low temperature)
Positive	Positive	???	Spontaneous if the absolute value of $T\Delta S$ is greater than the absolute value of $\Delta H$ (high temperature)

## 16.5 Entropy Changes in Chemical Reactions

### A. Constant Temperature and Pressure

- Reactions involving gaseous molecules
  - The change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products



### B. Third Law of Thermodynamics

- "The entropy of a perfect crystal at 0 K is zero" (NO disorder, since everything is in perfect position)

### C. Calculating Entropy Change in a Reaction

$$\Delta S_{\text{reaction}}^0 = \sum n_p S_{\text{products}}^0 - \sum n_r S_{\text{reactants}}^0$$

- Entropy is an extensive property (a function of the number of moles)
- Generally, the more complex the molecule, the higher the standard entropy value

## 16.6 Free Energy and Chemical Reactions

### A. Standard Free Energy Change

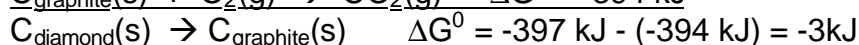
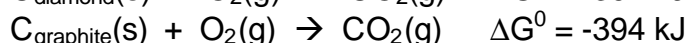
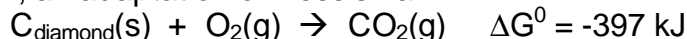
- $\Delta G^0$  is the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states
- $\Delta G^0$  cannot be measured directly
- The more negative the value for  $\Delta G^0$ , the farther to the right the reaction will proceed in order to achieve equilibrium
  - Equilibrium is the lowest possible free energy position for a reaction

### B. Calculating Free Energy Change

- Method #1, for reactions at constant temperature:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

- Method #2, an adaptation of Hess's Law:



(Complete example is on page 798)

3. Method #3, using standard free energy of formation ( $\Delta G_f^0$ )

- Standard Free Energy of Formation is the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states
- $\Delta G_f^0$  of an element in its standard state is zero

$$\Delta G^0 = \sum n_p \Delta G_{f(\text{products})}^0 - \sum n_r \Delta G_{f(\text{reactants})}^0$$

## 16.7 The Dependence of Free Energy on Pressure

### A. Enthalpy, H

- enthalpy is not pressure dependent

### B. Entropy, S

- entropy depends on volume, so it also depends on pressure

$$S_{\text{large volume}} > S_{\text{small volume}}$$

$$S_{\text{low pressure}} > S_{\text{high pressure}}$$

- $G = G^0 + RT \ln(P)$

- $G^0$  is the free energy of the gas at a pressure of 1 atm
- $G$  is the free energy of the gas at a pressure of P atm
- $R$  is the universal gas constant,  $T$  is Kelvin temperature

- $\Delta G = \Delta G^0 + RT \ln(Q)$

- $Q$  is the reaction quotient (from the law of mass action, section 13.5)
- $R$  is the gas constant (8.3145 J/K·mol)
- $\Delta G^0$  is the free energy change for the reaction with all reactants and products at a pressure of 1 atm
- $\Delta G$  is the free energy change for the reaction for the specified pressures of reactants and products

## 16.8 Free Energy and Equilibrium

### A. Thermodynamic View of Equilibrium

- Equilibrium point occurs at the lowest value of free energy available to the reaction system
- At equilibrium,  $\Delta G = 0$  and  $Q = K$   

$$\Delta G^0 = -RT \ln(K)$$

$\Delta G^0$	$K$
$\Delta G^0 = 0$	$K = 1$
$\Delta G^0 < 0$	$K > 1$
$\Delta G^0 > 0$	$K < 1$

### B. Temperature Dependence of K

- $\Delta G^0 = -RT \ln(K) = \Delta H^0 - T\Delta S^0$

- $$\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} = -\frac{\Delta H^0}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^0}{R}$$

so  $\ln(K) \propto 1/T$

## 16.9 Free Energy and Work

### A. Relationship to Work

1. The maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy  
("Free energy" is energy "free" to do work)

$$w_{\max} = \Delta G$$

2. The amount of work obtained is always less than the maximum

### B. Henry Bent's First Two Laws of Thermodynamics

1. First law: You can't win, you can only break even
2. Second law: You can't break even

The amount of available free energy of our system (Earth) is decreasing.