

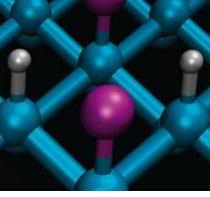


# Chapter 10

## Entropy and the Second Law of Thermodynamics

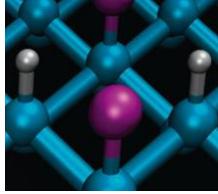


# Spontaneity: Nature's Arrow



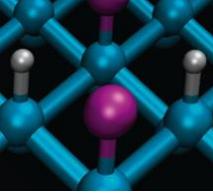
- Nature “knows” the correct direction for all processes
- Some processes or reactions proceed in only one direction
  - Gasoline reacts spontaneously with oxygen to form carbon dioxide and water, but water and carbon dioxide never spontaneously react to reform gasoline
- According to thermodynamics, a **spontaneous** process takes place without continuous intervention
  - Spontaneous processes are not necessarily rapid processes
  - The combustion of diamond is thermodynamically spontaneous, but diamonds are considered to last forever

# Spontaneous Processes



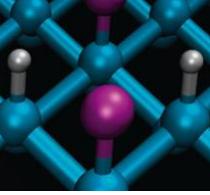
- Some reactions are spontaneous and can proceed without intervention, but require initiation
  - The combustion of gasoline is a spontaneous reaction but only occurs when the reaction is initiated with a spark
- Nonspontaneous reactions only occur with a continual input of energy

# Enthalpy and Spontaneity



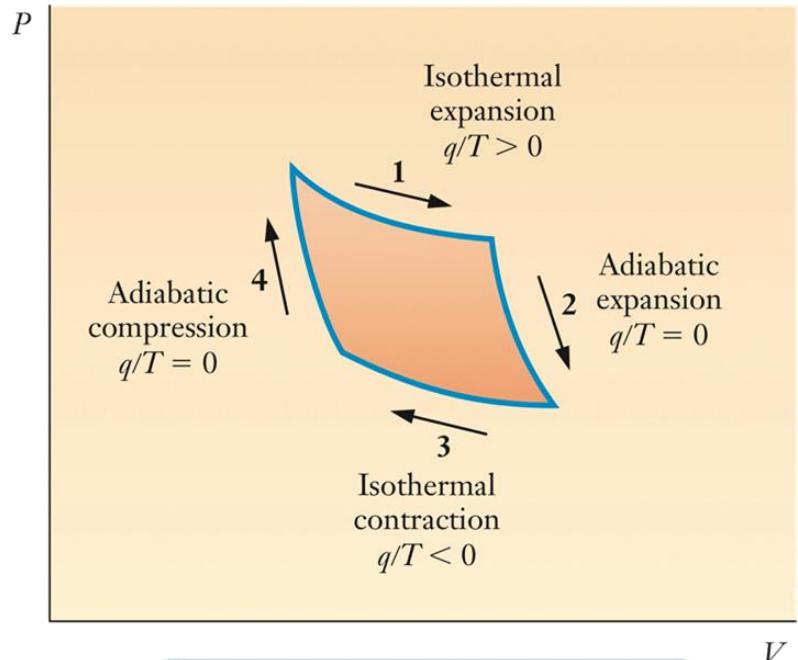
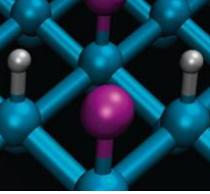
- Exothermic reactions are generally preferred over endothermic reactions
  - Melting ice is an endothermic process but occurs spontaneously
  - Enthalpy is not the exclusive determinant of spontaneity

# Entropy



- Thermodynamic state function
  - Was first introduced in considering the efficiency of steam engines
- The **Carnot cycle**
  - Uses a combination of **adiabatic** processes (no heat is exchanged) and **isothermal** processes (temperature is constant)

# Entropy

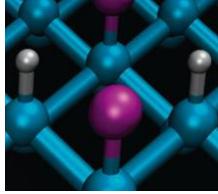


The sum of  $q/T$  around the cycle is zero, so there must be a state function that is given by this expression.

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- For the Carnot cycle, the sum of  $q/T$  around the closed path is equal to zero and therefore defines the state function
  - The new state function is known as **entropy**

# Probability and Spontaneous Change

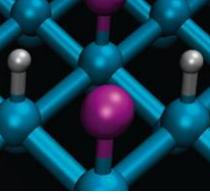


- The fundamentals of probability are explained using the rolling of dice
  - The probability of rolling a 4 for one die is 1 in 6
- As the number of dice increases, the probability of rolling all fours decreases

$$\text{Probability} = \left(\frac{1}{6}\right)^N$$

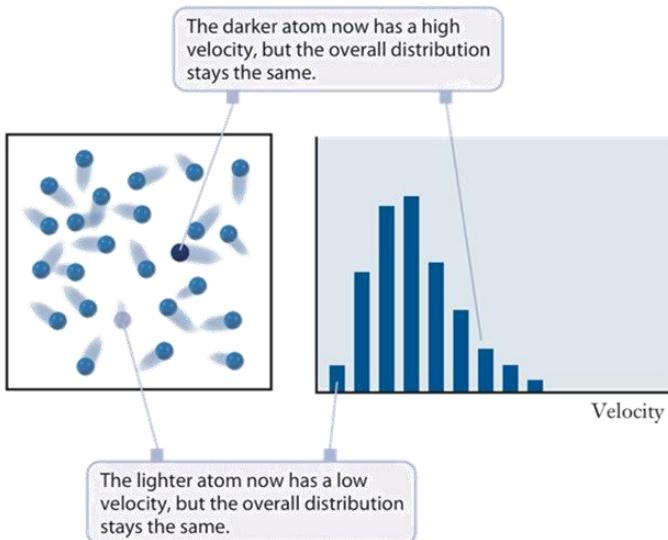
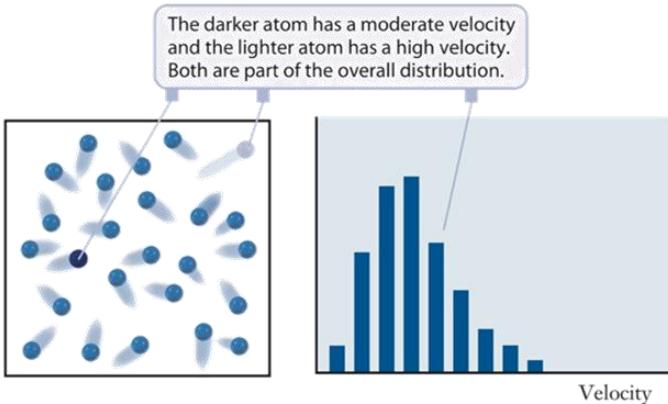
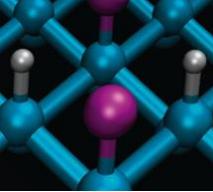
- $N$  is the number of dice being thrown
- The chances of rolling the same number with five dice in one roll are 1 in 1296

# Definition of Entropy



- Probability favors random arrangements for large numbers of particles
  - Based on this insight, entropy is tentatively defined as a measurement of the randomness or disorder of a system
  - Statistical mechanics, or statistical thermodynamics, provides a quantitative basis and a molecular perspective to entropy using probability
- For entropy, the probability of the number of ways in which particles can achieve the same energy is used
  - Way by which the collection of particles can assume a given energy is a **microstate**
    - Number of possible microstates is designated by  $\Omega$
    - Number of microstates increases as the “randomness” of the system increases

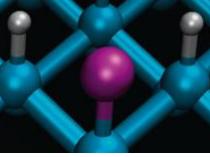
# Defining Entropy



- The **Maxwell-Boltzmann distribution** indicates the **overall** collection of molecular speeds but not the speed of individual particles
- Energy is exchanged during molecular collisions without disrupting the overall distribution of speeds

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# Definition of Entropy

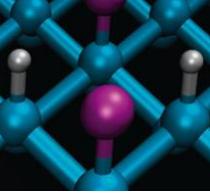


- As the number of microstates for a system increases, the entropy of the system increases
  - This relationship is defined by the equation:

$$S = k_b \ln \Omega$$

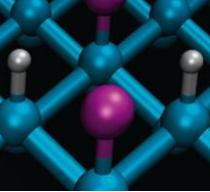
- $S$  is entropy
- $k_b$  is the Boltzmann constant
- $\Omega$  is the number of microstates

# Judging Entropy Changes in Processes



- When a solid melts to form a liquid, entropy increases
  - In solids, the particles are held in place rigidly, limiting the number of ways a specific energy can be obtained
  - In liquids, the particles move past each other, increasing the number of ways a specific energy can be obtained
  - The number of microstates increases during melting
- Certain other types of changes will also result in increased entropy
  - Increase in the number of particles present
  - Increase in the temperature of a substance

# The Second Law of Thermodynamics

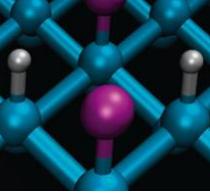


- Impossible to convert heat completely to work
- In any spontaneous process, the total entropy of the universe is positive
  - $(\Delta S_u > 0)$ 
    - $\Delta S_u$  = entropy of the universe
    - $\Delta S_{sys}$  = entropy of the system
    - $\Delta S_{surr}$  = entropy of the surroundings

$$\Delta S_u = \Delta S_{sys} + \Delta S_{surr}$$

- The entropy of the surroundings increases, and the total entropy change in the system and surroundings is positive

# The Second Law of Thermodynamics

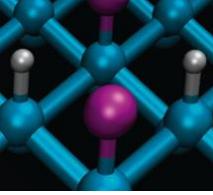


- The entropy change for the surroundings can be calculated from the heat flow from the system, which is equal to  $-\Delta H$

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

- For an exothermic reaction, the entropy of the surroundings increases

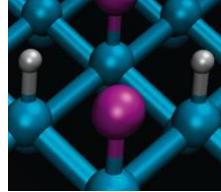
# Third Law of Thermodynamics



- States that the entropy of a perfect crystal of any pure substance approaches zero as the temperature approaches absolute zero
- Entropy of one mole of a chemical substance under standard conditions is the **standard molar entropy**,  $S^\circ$
- Entropy change for a reaction can be calculated from the standard molar entropies of the reactants and products
  - This law allows for the quantification of entropy

$$\Delta S^\circ = \sum_i v_i \Delta S^\circ(\text{products})_i - \sum_j v_j \Delta S^\circ(\text{reactants})_j$$

# Third Law of Thermodynamics



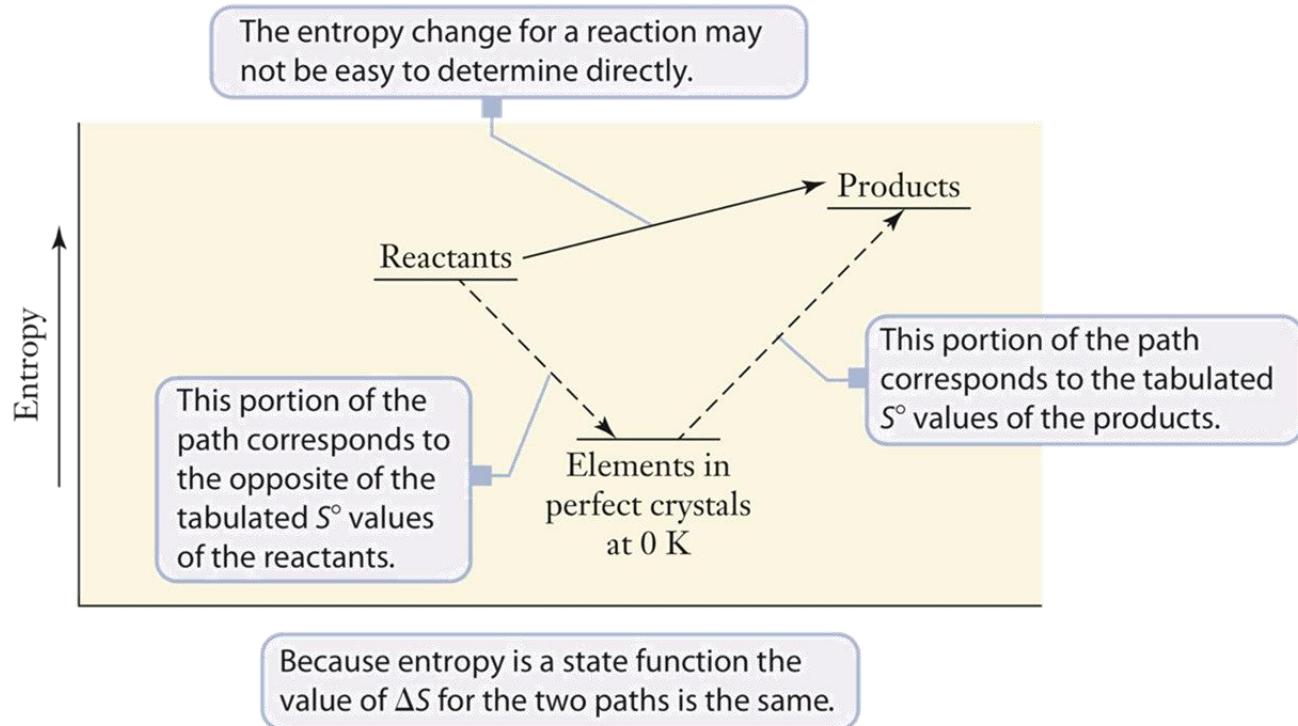
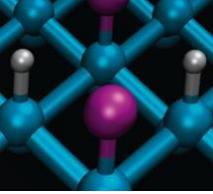
**Table 10.1** Standard molar entropy values

Standard molar entropies ( $S^\circ$ ) for selected substances. A much larger listing appears in Appendix E. Values of many compounds can also be found in the NIST chemistry WebBook at <http://webbook.nist.gov/chemistry>.

Compound	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Compound	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
H <sub>2</sub> (g)	130.6	CO <sub>2</sub> (g)	213.6
O <sub>2</sub> (g)	205.0	C <sub>4</sub> H <sub>10</sub> (g)	310.03
H <sub>2</sub> O(ℓ)	69.91	CH <sub>4</sub> (g)	186.2
H <sub>2</sub> O(g)	188.7	C <sub>2</sub> H <sub>4</sub> (g)	219.5
NH <sub>3</sub> (g)	192.3	C <sub>3</sub> H <sub>3</sub> N(ℓ)	178.91

- Standard molar entropies for selected substances

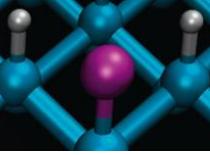
# Third Law of Thermodynamics



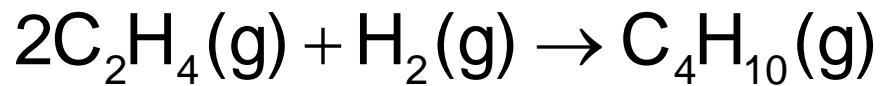
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- Entropy is a state function, so the value of  $\Delta S$  must be independent of the path taken from reactants to products

# Example Problem 10.1

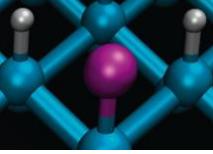


- Use data from Table 10.1 to calculate  $\Delta S$  for this reaction



$$\begin{aligned}\Delta S &= S_{\text{products}} - S_{\text{reactants}} \\ &= 310.03 - (2 \times 19.5 + 130.6) \\ &= -259.5 \text{ J/mol}\end{aligned}$$

# Gibbs Free Energy



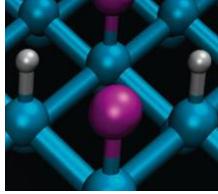
- The Gibbs free energy function,  $G$ , is defined as:

$$G = H - TS$$

- Changes in this function can predict whether or not a process is spontaneous under conditions of constant pressure and temperature

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

# Free Energy and Spontaneous Change

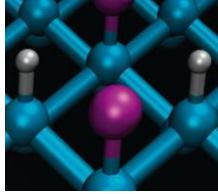


- For a spontaneous reaction, the Gibbs free energy change must be negative

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

- For a negative  $\Delta H$  and a positive  $\Delta S$ ,  $\Delta G$  will always be negative and the reaction will be spontaneous
- For a positive  $\Delta H$  and a negative  $\Delta S$ ,  $\Delta G$  will always be positive and the reaction will be nonspontaneous

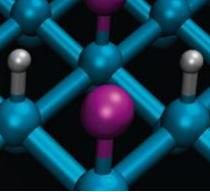
# Free Energy and Spontaneous Change



- For a positive  $\Delta H$  and a positive  $\Delta S$ , the value of  $\Delta G$  depends on temperature
- For a spontaneous reaction with a negative  $\Delta H$  and a negative  $\Delta S$ , the reaction only occurs at low temperature
  - These reactions are referred to as **enthalpy driven** because the negative value for the enthalpy is responsible for the negative value of the Gibbs free energy change
- For a negative  $\Delta H$  and a negative  $\Delta S$ , the value for  $\Delta G$  depends on the temperature
  - The temperature at which a reaction changes from spontaneous to nonspontaneous can be calculated

$$T = \frac{\Delta H}{\Delta S}$$

# Free Energy and Spontaneous Change



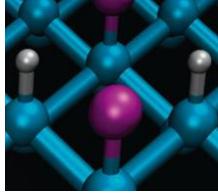
- The four possible combinations for the signs of  $\Delta H$  and  $\Delta S$  used to determine spontaneity of a chemical reaction

**Table 10.2** Effects of temperature on spontaneity

The four possible combinations for the signs of  $\Delta H$  and  $\Delta S$

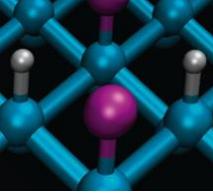
Sigh of $\Delta H$	Sign of $\Delta S$	Implications for Spontaneity
-	+	Spontaneous at all temperatures
+	-	Never spontaneous
-	-	Spontaneous only at low temperatures
+	+	Spontaneous only at high temperatures

# Free Energy and Spontaneous Change

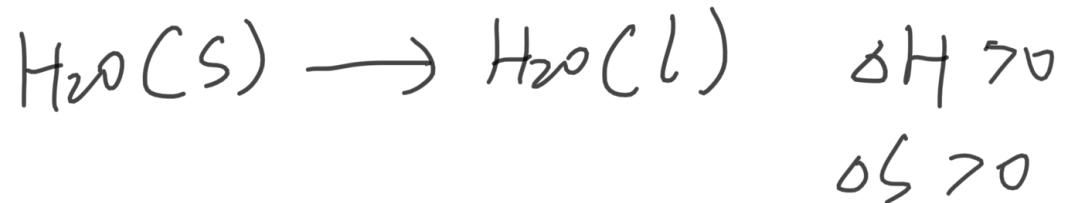


- For a spontaneous reaction with a positive  $\Delta H$  and a positive  $\Delta S$ , the reaction only occurs at high temperature
  - These reactions are referred to as **entropy driven** because the product of the positive entropy change and the absolute temperature is responsible for the negative value of the Gibbs free energy change

## Example Problem 10.2



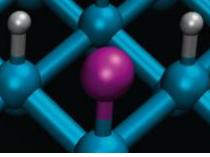
- Use the signs of  $\Delta H$  and  $\Delta S$  to explain why ice spontaneously melts at room temperature but not outside on a freezing winter day



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

So ice spontaneously melts at higher temperature

# Example Problem 10.3

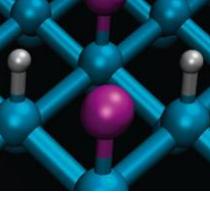


- The heat of fusion of polyethylene is approximately 7.7 kJ/mol, and the corresponding entropy is  $19 \text{ J mol}^{-1} \text{ K}^{-1}$ 
  - Use these data to estimate the melting point of polyethylene

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

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{7.7 \text{ kJ/mol}}{19 \text{ J/(mol}\cdot\text{K)}} = 405 \text{ K}$$

# Free Energy and Work

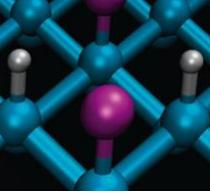


- Change in Gibbs free energy can be shown to be equal to the maximum useful work done by the system
- A minus sign in this expression is used to be consistent with the convention that *w is the work done on the system*

$$\Delta G = -W_{\max}$$

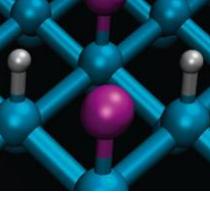
- Work is not a state function
- Maximum work realized only if the reaction or process is carried out along a very specific path

# Free Energy and Work



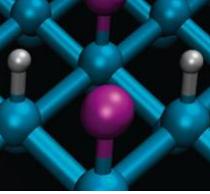
- A **reversible** path is the specific path required for maximum useful work
  - For a system with a reversible path, the system is near equilibrium and a small incremental change in a variable will bring the system back to its initial state
- In an **irreversible** change, a small incremental change in any variable does not restore the initial state
  - The amount of work available is always less than the maximum work for an irreversible change

# Free Energy and Work



- The Gibbs free energy change establishes the upper bound to the amount of work obtained from a given process
  - Actual work produced in any real application may be considerably less
- Reactant mixtures such as those for combustion reactions are generally very far from equilibrium
  - Systems that are far from equilibrium often change rapidly, and rapid changes tend to be irreversible

# Free Energy and Chemical Reactions



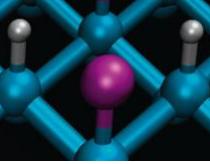
- The standard Gibbs free energy change,  $\Delta G^\circ$  can be calculated from Gibbs free energies of formation,  $\Delta G_f^\circ$ .

- $\Delta G_f^\circ = 0$  for elements in their free standard state

$$\Delta G^\circ = \sum_i \nu_i \Delta G_f^\circ(\text{products})_i - \sum_j \nu_j \Delta G_f^\circ(\text{reactants})_j$$

- This equation provides an alternative method to calculate  $\Delta G$ , without entropy or enthalpy

# Free Energy and Chemical Reactions



- Values of the free energy change of formation,  $\Delta G_f^\circ$ , for selected compounds

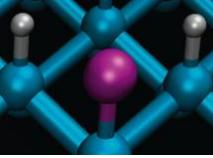
**Table 10.3** Free energy changes of formation

Values of the free change of formation,  $\Delta G_f^\circ$ , for Selected compounds.

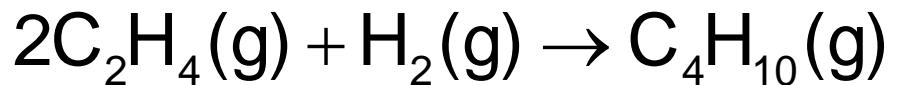
A much larger list appears in Appendix E.

Substance	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	Substance	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )
H <sub>2</sub> (g)	0	CO <sub>2</sub> (g)	-394.4
O <sub>2</sub> (g)	0	C <sub>4</sub> H <sub>10</sub> (g)	-15.71
H <sub>2</sub> O(ℓ)	-237.2	CH <sub>4</sub> (g)	-50.75
H <sub>2</sub> O(g)	-228.6	C <sub>2</sub> H <sub>4</sub> (g)	68.12
NH <sub>3</sub> (g)	-16.5	C <sub>3</sub> H <sub>6</sub> (g)	62.75

## Example Problem 10.4



- Confirm that the reaction below would be spontaneous by calculating the standard free energy change using values from Table 10.3

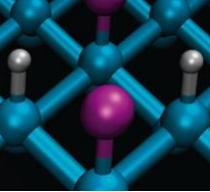


$$\Delta H < 0 \quad \Delta S < 0$$

So this reaction is spontaneous at high temperature

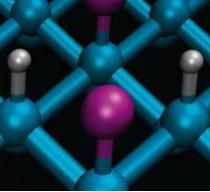
$$\begin{aligned}\Delta G &= (-15.71) - (2 \times 68.12 + 0) \\ &= -151.95 \text{ kJ/mol}\end{aligned}$$

# Implications of $\Delta G^\circ$ for a Reaction



- Gibbs free energy change ( $\Delta G^\circ$ ) indicates maximum useful work that can be obtained from a chemical reaction
- For the formation of PMMA at 298 K,  $\Delta H^\circ = -56 \text{ kJ}$  and  $\Delta S^\circ = -117 \text{ J/K}$ 
  - $\Delta G^\circ = -21 \text{ kJ}$  at 298K for the formation of PMMA
  - The negative value indicates that the formation of PMMA is spontaneous at 298 K

# Implications of $\Delta G^\circ$ for a Reaction



- The reverse reaction, the thermolysis of PMMA to form methyl methacrylate monomer, has  $\Delta G^\circ = +21 \text{ kJ}$  at 298 K
  - The positive value indicates that the thermolysis of PMMA is nonspontaneous at 298 K
- The temperature at which the thermolysis of PMMA becomes spontaneous is 480 K
  - The thermolysis of PMMA above 480 K is an entropy-driven process

$$T = \frac{\Delta H}{\Delta S} = \frac{-56 \text{ kJ}}{-0.117 \text{ kJ K}^{-1}} = 480 \text{ K}$$