

## Chapter 13

**Section 13.1** Students should know that **entropy (S)** is a thermodynamic property that measures the distribution of energy in a system at a specific temperature; changes in entropy ( $\Delta S$ ) are the basis for understanding spontaneity. Make sure you understand that according to the **Second Law of Thermodynamics**, processes that are **spontaneous** occur without a constant input of energy and result in an increase in entropy of the universe, whereas **nonspontaneous** processes require continuous energy input in order to occur. Forming a gas from a solid or a liquid, converting a solid into a liquid, or dissolving a solid in a liquid are processes accompanied by an increase in the system entropy. Most exothermic reactions are spontaneous, but endothermic reactions may also be spontaneous. All particles in a system can occupy one of a large number of **energy states**, or **energy levels**. Each different arrangement of particles is called a **microstate**. The entropy of a system increases as the number of available microstates increases and is generally highest for gases.

**Section 13.2** Students should know that phase changes of pure substances take place over a constant temperature and are **isothermal** processes. For a spontaneous process such as ice melting at room temperature, the entropy change of the universe must be positive:  $\Delta S_{\text{univ}} > 0$ . The entropy change of the universe equals the sum of the entropy change of the system and the entropy change of the surroundings:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ . Reversible processes are ideal processes that take place in very small steps and very slowly. No change in entropy takes place in a reversible process. This concept enables us to calculate maximum efficiency, which is the most work available from a given quantity of energy. If  $\Delta S_{\text{sys}} < 0$  in a spontaneous process, then  $\Delta S_{\text{surr}} > 0$  and  $\Delta S_{\text{surr}}$  must be large enough to insure that  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ . If  $\Delta S_{\text{sys}} > 0$ , then  $\Delta S_{\text{surr}}$  must have a value so that  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ .

**Section 13.3** Students should know that according to the **Third Law of Thermodynamics** perfect crystals of a pure substance have zero entropy at absolute zero. All substances have positive entropies at temperatures above absolute zero; **Standard Molar Entropies ( $S^\circ$ )** are entropy values under standard state conditions. The entropy of a system increases with increasing molecular complexity and temperature.

**Section 13.4** Students should know that the entropy change in a reaction under standard conditions can be calculated from the standard entropies of the products and reactants and their coefficients in the balanced chemical equation. If we study isothermal processes carried out reversibly, we can calculate the entropy change of the surroundings by dividing the heat exchanged ( $q_{\text{rev}}$ ) by the temperature at which the process occurs. We can then also calculate the entropy change of the universe and determine whether the process is spontaneous by noting the sign of  $\Delta S_{\text{univ}}$ .

**Section 13.5** Students should know that the **Free-Energy change ( $\Delta G$ ; Gibbs Free Energy)** in a process is a state function giving *the maximum useful work the system can do on its surroundings*. You need to remember that **spontaneous processes have negative  $\Delta G$  values** and reversing a process changes the sign of  $\Delta G$ . Also, you should know that for a system at equilibrium,  $\Delta G = 0$ . The standard  $\Delta G^\circ$  free-energy change in a process can be calculated from the **standard free energies of formation ( $\Delta G_f^\circ$ )** of the products and reactants or from the

enthalpy and entropy changes. Values for  $\Delta G_f^\circ$  refer to standard state conditions, and for the formation of elements,  $\Delta G_f^\circ = 0$ . The temperature range over which a process is spontaneous depends on the values of  $\Delta H$  and  $\Delta S$ .

**Section 13.6** Students should know that **Exergonic** reactions are spontaneous and **Endergonic** processes are not spontaneous. Many important biochemical processes, including **glycolysis** and **phosphorylation**, are made possible by coupled exergonic and endergonic reactions. The free energy released in such processes (such as the hydrolysis of ATP to form ADP) is used in our bodies to drive endergonic processes.