

Chapter 18 Summary

Key Learning Outcomes

Chapter Objectives	Assessment
Predict the Sign of Entropy Change (18.4)	<ul style="list-style-type: none"> Example 18.1 For Practice 18.1 Exercises 27, 28, 35, 36, 37, 38, 41, 42
Calculate ΔS for a Change of State (18.4)	<ul style="list-style-type: none"> Example 18.2 For Practice 18.2 Exercises 31, 32, 33, 34
Calculate Entropy Changes in the Surroundings (18.5)	<ul style="list-style-type: none"> Example 18.3 For Practice 18.3 For More Practice 18.3 Exercises 37, 38, 40
Calculate Gibbs Free Energy Changes and Predicting Spontaneity from ΔH and ΔS (18.6)	<ul style="list-style-type: none"> Example 18.4 For Practice 18.4 Exercises 43, 44, 45, 46, 47, 48
Calculate Standard Entropy Changes $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$ (18.4)	<ul style="list-style-type: none"> Example 18.5 For Practice 18.5 Exercises 55, 56, 57, 58
Calculate the Standard Change in Free Energy for a Reaction Using $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$ (18.7)	<ul style="list-style-type: none"> Examples 18.6, 18.7 For Practice 18.6, 18.7 Exercises 59, 60, 61, 62, 65, 66
Calculate $\Delta G_{\text{rxn}}^{\circ}$ from Standard Free Energies of Formation (18.7)	<ul style="list-style-type: none"> Example 18.8 For Practice 18.8 For More Practice 18.8 Exercises 63, 64
Determine $\Delta G_{\text{rxn}}^{\circ}$ for a Stepwise Reaction (18.7)	<ul style="list-style-type: none"> Example 18.9 For Practice 18.9 Exercises 67, 68
Calculate ΔG_{rxn} under Nonstandard Conditions (18.8)	<ul style="list-style-type: none"> Example 18.10 For Practice 18.10 Exercises 69, 70, 71, 72, 75, 76
Relate the Equilibrium Constant and $\Delta G_{\text{rxn}}^{\circ}$ (18.9)	<ul style="list-style-type: none"> Example 18.11 For Practice 18.11 Exercises 73, 74, 77, 78, 79, 80, 81, 82

Key Terms

Section 18.2

spontaneous process

Section 18.3

entropy (S)

macrostate

microstate

second law of thermodynamics

Section 18.4

reversible process

Section 18.6

Gibbs free energy (G)

Section 18.7

standard entropy change for a reaction ($\Delta S_{\text{rxn}}^\circ$)

standard molar entropies (S°)

third law of thermodynamics

allotropes

Section 18.8

standard change in free energy ($\Delta G_{\text{rxn}}^\circ$)

free energy of formation (ΔG_f°)

Section 18.9

free energy change of a reaction under nonstandard conditions (ΔG_{rxn})

Key Concepts

Nature's Heat Tax: You Can't Win and You Can't Break Even (18.1)

- The first law of thermodynamics states that energy can be neither created nor destroyed.
- According to the second law of thermodynamics, in every energy transaction, some energy is lost to the surroundings; this lost energy is nature's heat tax.

Spontaneous and Nonspontaneous Processes (18.2)

- Both spontaneous and nonspontaneous processes can occur, but only spontaneous processes can take place without outside intervention.
- Thermodynamics is the study of the *spontaneity* of reactions, *not* to be confused with kinetics, the study of the *rate* of reactions.

Entropy and the Second Law of Thermodynamics (18.3)

- The second law of thermodynamics states that for *any* spontaneous process, the entropy of the universe increases.
- Entropy (S) is proportional to the number of energetically equivalent ways in which the components of a

- Entropy (S) is proportional to the number of energetically equivalent ways in which the components of a system can be arranged and is a measure of energy dispersal per unit temperature.

The Entropy Changes Associated with Changes of State (18.4)

- The entropy of a substance increases as it changes state from a solid to a liquid and when it changes from a liquid to a gas.
- The change in entropy for a system undergoing a reversible change in state is $\Delta S = q_{\text{rev}}/T$.

Heat Transfer and Changes in the Entropy of the Surroundings (18.5)

- For a process to be spontaneous, the total entropy of the universe (system plus surroundings) must increase.
- The entropy of the surroundings increases when the change in *enthalpy* of the system (ΔH_{sys}) is negative (i.e., for exothermic reactions).
- The change in entropy of the surroundings for a given ΔH_{sys} depends inversely on temperature—the greater the temperature, the smaller the magnitude of ΔS_{surr} .

Gibbs Free Energy (18.6)

- Gibbs free energy, G , is a thermodynamic function that is proportional to the negative of the change in the entropy of the universe. A negative ΔG represents a spontaneous reaction, and a positive ΔG represents a nonspontaneous reaction.
- We can calculate the value of ΔG for a reaction from the values of ΔH and ΔS for the *system* using the equation $\Delta G = \Delta H - T\Delta S$.

Entropy Changes in Chemical Reactions: Calculating $\Delta S_{\text{rxn}}^{\circ}$ (18.7)

- We calculate the standard change in entropy for a reaction similarly to the way we calculate the standard change in enthalpy for a reaction: by subtracting the sum of the standard entropies of the reactants multiplied by their stoichiometric coefficients from the sum of the standard entropies of the products multiplied by their stoichiometric coefficients.
- Standard entropies are *absolute*; an entropy of zero is established by the third law of thermodynamics as the entropy of a perfect crystal at absolute zero.
- The entropy of a substance at a given temperature depends on factors that affect the number of energetically equivalent arrangements of the substance; these include the state, size, and molecular complexity of the substance.

Free Energy Changes in Chemical Reactions: Calculating $\Delta G_{\text{rxn}}^{\circ}$ (18.8)

- There are three ways to calculate $\Delta G_{\text{rxn}}^{\circ}$: (1) from ΔH° and ΔS° , (2) from free energies of formations (only at 25 °C), and (3) from the ΔG° values of reactions that sum to the reaction of interest.
- The magnitude of a negative $\Delta G_{\text{rxn}}^{\circ}$ represents the theoretical amount of energy available to do work, while a positive $\Delta G_{\text{rxn}}^{\circ}$ represents the minimum amount of energy required to make a nonspontaneous process occur.

Free Energy Changes for Nonstandard States: The Relationship between $\Delta G_{\text{rxn}}^{\circ}$ and ΔG_{rxn} (18.9)

- The value of $\Delta G_{\text{rxn}}^{\circ}$ applies only to standard conditions, and most real conditions are not standard.
- Under nonstandard conditions, we can calculate ΔG_{rxn} from the equation $\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln Q$.

Free Energy and Equilibrium: Relating $\Delta G_{\text{rxn}}^{\circ}$ to the Equilibrium Constant (K) (18.10)

- Under standard conditions, the free energy change for a reaction is directly proportional to the negative of

the natural log of the equilibrium constant, K ; the more negative the free energy change (i.e., the more spontaneous the reaction), the larger the equilibrium constant.

- We can use the temperature dependence of $\Delta G_{\text{rxn}}^{\circ}$, as given by $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$, to derive an expression for the temperature dependence of the equilibrium constant.

Key Equations and Relationships

The Definition of Entropy (18.3)

$$S = k \ln W \quad k = 1.38 \times 10^{-23} \text{ J/K}$$

Change in Entropy (18.3, 18.4)

$$\begin{aligned} \Delta S &= S_{\text{final}} - S_{\text{initial}} \\ \Delta S &= q_{\text{rev}}/T \text{ (isothermal, reversible process)} \end{aligned}$$

Change in the Entropy of the Universe (18.5)

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

Change in the Entropy of the Surroundings (18.5)

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \text{ (constant } T, P)$$

Change in Gibbs Free Energy (18.6)

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

The Relationship between Spontaneity and ΔH , ΔS , and T (18.6)

ΔH	ΔS	Low Temperature	High Temperature
–	+	Spontaneous	Spontaneous
+	–	Nonspontaneous	Nonspontaneous
–	–	Spontaneous	Nonspontaneous
+	+	Nonspontaneous	Spontaneous

Standard Change in Entropy (18.7)

$$\Delta S_{\text{rxn}}^{\circ} = \sum n_p S^{\circ} (\text{products}) - \sum n_r S^{\circ} (\text{reactants})$$

Methods for Calculating the Free Energy of Formation ($\Delta G_{\text{rxn}}^{\circ}$) (18.8)

1. $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$
2. $\Delta G_{\text{rxn}}^{\circ} = \sum n_p \Delta G_f^{\circ} (\text{products}) - \sum n_r \Delta G_f^{\circ} (\text{reactants})$
3. $\Delta G_{\text{rxn}}^{\circ} (\text{overall}) = \Delta G_{\text{rxn}}^{\circ} (\text{step 1}) + \Delta G_{\text{rxn}}^{\circ} (\text{step 2}) + \Delta G_{\text{rxn}}^{\circ} (\text{step 3}) + \dots$

The Relationship between $\Delta G_{\text{rxn}}^{\circ}$ and ΔG_{rxn} (18.9)

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \quad R = 8.314 \text{ J/mol} \cdot \text{K}$$

The Relationship between $\Delta G_{\text{rxn}}^{\circ}$ and K (18.10)

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K$$

The Temperature Dependence of the Equilibrium Constant (18.10)

$$\ln K = \frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left(\frac{1}{T} \right) + \frac{\Delta S_{\text{rxn}}^{\circ}}{R}$$
$$\ln \frac{K_2}{K_1} = \frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Not for Distribution

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