

19: Chemical Thermodynamics

OVERVIEW OF THE CHAPTER

19.1 Spontaneous Processes

Review: Activation energy (14.5); chemical equilibrium (15.1); first law of thermodynamics (5.2); concept of rate of reaction (14.1).

Learning Goals: You should be able to:

1. Define the terms spontaneous and spontaneity and apply them in identifying spontaneous processes.
2. Define the terms reversible and irreversible and apply them to identifying reversible and irreversible processes.
3. Define the term isothermal.

19.2, 19.3, 19.4, 19.5 Entropy and Second and Third Laws of Thermodynamics

Review: Properties of gases, liquids, and solids (10.1, 11.1); solution processes (13.1); thermodynamic state functions (5.2, 5.3).

Learning Goals: You should be able to:

1. Define the term entropy.
2. Describe how entropy is related to the total number of microstates in a thermodynamic system.
3. Describe how the number of microstates is related to the ideas of randomness of positions of particles and dispersion of kinetic energy.
4. State the second law of thermodynamics.
5. Predict whether the entropy change in a given process is positive, negative, or near zero.
6. State the third law of thermodynamics.
7. Describe how the entropy of a substance changes with increasing temperature and during a phase change.
8. Calculate ΔS° for any reaction from tabulated absolute entropy values, S° .

19.5, 19.6, 19.7 Gibbs Free Energy and the Equilibrium State

Review: Enthalpy (5.3); standard state and heat of formation (5.7); equilibrium constant (15.2); reaction quotient (15.6).

Learning Goals: You should be able to:

1. Define Gibbs free energy.
2. Explain the relationship between the sign of the free-energy change, ΔG and whether a process is spontaneous in the forward direction, at equilibrium, or the reverse process is spontaneous.
3. Calculate the standard free-energy change at constant temperature and pressure, ΔG° , for any process from tabulated values for the standard free energies of reactants and products.
4. List the usual conventions regarding standard states in setting the values for standard free energies.
5. Calculate ΔG° from K and perform the reverse operation.

6. Describe the relationship between ΔG and the maximum work that can be derived from a spontaneous process, or the minimum work required to accomplish a nonspontaneous process.
7. Calculate the free-energy change under nonstandard conditions.

19.6

The Dependence of Gibbs Free Energy on Temperature

Review: Melting and freezing processes (11.4).

Learning Goals: You should be able to:

1. predict how ΔG changes with temperature, given the signs for ΔH and ΔS .
2. Estimate ΔG° at any temperature, given ΔS° and ΔH° .