Chapter 14

Section 14.1 You should know that the photochemical reactions that follow the reaction between nitrogen and oxygen in vehicle engines ultimately lead to smog, a major air pollutant in urban areas. Familiarity with **reaction rates** or **chemical kinetics** is important in understanding how natural processes and those caused by human activity occur.

Section 14.2 You should know that the rate of a reaction can be measured by determining the rate of change in the concentration of reactants or products and that it can be expressed as either an **average rate** or an **instantaneous rate.** It is important to understand that the rates of disappearance of reactants and appearance of products are related by the stoichiometry of the reaction and are typically expressed in molarity per unit time. Reaction rates can be known only from experimental measurements and that in most reactions, the reaction rate decreases with increasing reaction time.

Section 14.3 You should know that the rate of a reaction, such as $a\mathrm{A} + \mathrm{b}B \rightarrow cC$, depends on the concentrations of A and B as determined experimentally and expressed in the **rate law** for the reaction: rate = $k[\mathrm{A}]^m[\mathrm{B}]^n$ where the power *m* and *n* are the **order of reaction** with respect to A and B, respectively and *k* is the **rate constant.** You need to be aware that the units of a rate constant depend on the **overall reaction order,** which is the sum of the reaction orders with respect to individual reactants. The order of a reaction and rate law can be determined from differences in the **initial rates** of a reaction observed in reaction mixtures with different concentrations of reactants or from the results of single kinetics experiments where reactant concentrations are plotted versus time (an **integrated rate law**). The **half-life ($t_{1/2}$)** of a reaction is the time required for the concentration of a reactant to decrease to one-half of its starting concentration.

Section 14.4 You should know that increasing the temperature increases the rate of a chemical reaction and that a reaction's **activation energy (E_a)** is a barrier that separates the sum of the internal energies of the reactants from the energies of the products. The top of the energy barrier is the **transition state** related to the internal energy of a short-lived **activated complex.** Reactions with large activation energies are usually slow. Measuring the rate constant (*k*) of a reaction at different temperatures allows the calculation of activation energies using the **Arrhenius equation.**

Section 14.5 You should know that the study of rates gives insight into **reaction mechanisms** and what is happening at a molecular level. The mechanism of a chemical reaction consists of one or more **elementary steps** that describe on a molecular level how the reaction takes place. The balanced overall reaction is the sum of these elementary steps. Elementary steps that involve one, two, or three molecules are said to be **unimolecular, bimolecular,** and **termolecular,** respectively. The rate law for a reaction applies to the slowest elementary step, which is called the **rate-determining step**. The proposed mechanism for any reaction must be consistent with the observed rate law and stoichiometry of the overall reaction.

Section 14.6 You should know that **Catalysts** increase the rates of reactions by decreasing the activation energy by changing the mechanism of a reaction. **Homogeneous catalysts** are in the same phase as the reactants, whereas **heterogeneous catalysts** (for example catalytic converters in vehicles) are in a separate phase from that of the reactants.