Chapter 10
Entropy and the Second Law of Thermodynamics

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Spontaneity: Natures Arrow

- A spontaneous process takes place without continuous intervention, according to thermodynamics.
  - Spontaneous processes are not necessarily rapid processes (time is not a factor).

$$C_{(diamond)} \xrightarrow[\text{spontaneous}]{\text{v. slow}} C_{(graphite)}$$

- Some spontaneous reactions only occur once they are initiated.
  - The combustion of gasoline is a spontaneous reaction but only occurs when the reaction is initiated with a spark.

$$C_8H_{18}(g) + 12½\ O_2(g) \xrightarrow[\text{spontaneous}]{\text{v. fast}} 8CO_2(g) + 9H_2O(g)$$

- Nonspontaneous reactions only occur with a continual input of energy.

Example Problem

On the basis of your experience, predict which of the following reactions are spontaneous:

(a) $CO_2(s) \rightarrow CO_2(g)$ at 25 ºC — spontaneous

(b) $NaCl(s) \rightarrow NaCl(l)$ at 25 ºC — Non-spontaneous

(c) $2\ NaCl(s) \rightarrow 2\ Na(s) + Cl_2(g)$ — Non-spontaneous

(d) $CO_2(s) \rightarrow C(s) + O_2(g)$ — Non-spontaneous

Practice 10.10, 10.11, 10.13

Judging Entropy Changes in Processes

- Entropy can be tentatively defined as a measurement of the randomness, or disorder, of a system.
- Certain types of changes will result in increased entropy.
  a) Certain phase changes.

solid $\xrightarrow{\text{melting}}$ **liquid** $\xrightarrow{\text{boiling}}$ **gas**

entropy increases $\rightarrow$

  b) An increase in the number of particles present.

$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(g)$ **entropy increases**

$CO(g) + 2\ H_2(g) \longrightarrow CH_3OH(l)$ **entropy decreases**

  c) An increase in the temperature of a substance.

Practice 10.23, 10.26, 10.27

Exam Questions

Without doing a calculation, predict the entropy change of these process?

(a) $2\ HNO_3(l) + NO(g) \longrightarrow 3\ NO_2(g) + H_2O(l)$ increase

(b) $CO_2(s) \longrightarrow CO_2(g)$ at 25 ºC increase

(c) $CO(g) + 2\ H_2(g) \longrightarrow CH_3OH(l)$ decrease

(d) $2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$ increase

(e) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ decrease

A) Certain phase changes.

B) An increase in the number of particles present.

Exam Questions

If a 5.0 L flask holds 0.125 moles of nitrogen at STP, what happens to the entropy of the system upon cooling the gas to -75 ° C?

The entropy decreases

C) An increase in the temperature of a substance.

The Second Law of Thermodynamics

- The second law of thermodynamics: in any spontaneous process, the total entropy change of the universe is positive ($\Delta S_u > 0$); entropy increase.

$$\Delta S_u = \Delta S_{sys} + \Delta S_{surr} > 0$$

  - ΔS_u = entropy of the universe
  - ΔS_{sys} = entropy of the system
  - ΔS_{surr} = entropy of the surroundings

The Third Law of Thermodynamics

- The third law of thermodynamics states that the entropy of a perfect crystal of any pure substance approaches zero as the temperature approaches absolute zero (0 K).

- The entropy of one mole of a chemical substance under standard conditions is the standard molar entropy, S° (1 atm, 298 K).

- The 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.

$$\Delta S^\circ = \sum_i \nu_i S^\circ(\text{product})_i - \sum_j \nu_j S^\circ(\text{reactant})_j$$

Practice 10.47, 10.53. 10.55

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.

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

$\Delta G < 0$ spontaneous

Sign of ΔH	Sign of ΔS	Implications for Spontaneity
–	+	Spontaneous at all temperatures
+	–	Never spontaneous
–	–	Spontaneous only at low temperatures
+	+	Spontaneous only at high temperatures

Exam Questions

The sign of ΔH_{rxn} and ΔS_{rxn} for several reactions are given. Determine the spontaneity of these processes.

(a) $\Delta H_{rxn} < 0$; $\Delta S_{rxn} < 0$ — Spontaneous at low T

(b) $\Delta H_{rxn} < 0$; $\Delta S_{rxn} > 0$ — Always spontaneous

(c) $\Delta H_{rxn} > 0$; $\Delta S_{rxn} < 0$ — Always nonspontaneous

(d) $\Delta H_{rxn} > 0$; $\Delta S_{rxn} > 0$ — Spontaneous at high T

(e) $\Delta H_{rxn} = \Delta S_{rxn}$

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

Example Problem

Confirm that the reaction below would be spontaneous, or nonspontaneous at 25°C, by calculating the standard free energy change using the values from ΔH^o and ΔS^o.

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$$

$\Delta H_{rxn}^o = -283.0$ kJ $\Delta S_{rxn}^o = -86.6$ J/K

$$\Delta G_{rxn}^o = \Delta H_{rxn}^o - T\Delta S_{rxn}^o$$

$$\Delta G_{rxn}^o = -283.0\ \mathbf{kJ} - 298\ K \times \frac{-86.6\ \mathbf{J}}{K} \times \frac{\mathbf{kJ}}{1000\ \mathbf{J}}$$

= -283.0 kJ + 25.8 kJ

= -257 kJ spontaneous **Practice 10.59, 10.65**

Exam Questions

When magnesium sulfite decomposes, the solid transforms into magnesium oxide and sulfur dioxide.

$$MgSO_3(s) \rightarrow MgO(s) + SO_2(g)$$

At what temperature will this reaction be spontaneous according to Gibb's Energy?

ΔH_f^o in kJ/mol for: $MgSO_3(s)$ = −1068, $MgO(s)$ = −601.8, $SO_2(g)$ = −296.8
S^o in J/mol K for: $MgSO_3(s)$ = 121, $MgO(s)$ = 27, $SO_2(g)$ = 248.1

$$\Delta H^o_{rxn} = \sum_i \nu_i \Delta H^o_f(\textbf{products})_i - \sum_j \nu_j \Delta H^o_f(\textbf{reactants})_j$$

$$\Delta S^\circ = \sum_i \nu_i S^\circ(\text{product})_i - \sum_j \nu_j S^\circ(\text{reactant})_j$$

$$\Delta G = \Delta H - T\Delta S \quad \text{When } \Delta G = 0,\ T = \frac{\Delta H}{\Delta S}$$

Free Energy and Chemical Reactions

- The standard Gibbs free energy change, ΔG^o, can be calculated from Gibbs free energies of formation, ΔG_f^o.

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

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

$$\Delta H_{rxn}^o = \sum_i \nu_i \Delta H_f^o(\textbf{products})_i - \sum_j \nu_j \Delta H_f^o(\textbf{reactants})_j$$

- $\Delta H_f^o = 0$ for elements in their free standard state.

Example Problem

For which of the following is $\Delta H_f^o = 0$; $\Delta G_f^o = 0$?

X **a) Al(g)** Not the standard state

X **b) $MgCO_3(aq)$** Not an element

√ **c) C (graphite)** the standard state

√ **d) $Cl_2(g)$** the standard state

X **e) $CO_2(g)$** Not an element

Example Problem

- Confirm that the reaction below would be spontaneous, or nonspontaneous at 25°C, by calculating the standard free energy change, $\Delta G°$, using values for $\Delta G_f°$.

$$2C_2H_4(g) + H_2(g) \rightarrow C_4H_{10}(g)$$

$\Delta G°_f$ (kJ/mol)	68.12	0	-15.71

$$\Delta G° = \sum_i \nu_i \Delta G_f°(\text{product})_i - \sum_j \nu_j \Delta G_f°(\text{reactant})_j$$

$$\Delta G° = \Delta G_f°[C_4H_{10}(g)] - 2\Delta G_f°[C_2H_4(g)] - \Delta G_f°[H_2(g)]$$

$$= (-15.71\ \text{kJ}) - 2(68.12\ \text{kJ}) - (0) = -151.95\ \text{kJ}$$

Reaction is spontaneous **Practice 10.69, 10.70**

Chapter 11
Chemical Kinetics

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Rates of Reaction

- The reaction rate is the ratio of the change in concentration to the elapsed time.

$$\text{Rate} = \frac{\text{change in concentration}}{\text{elapsed time}} = \frac{\Delta[\text{substance}]}{\Delta t}$$

  - Concentration is measured in M, or mol L^{-1}, and designated with square brackets, [ ].
  - Time in measured in s.
  - The unit for rate is mol L^{-1} s^{-1}.

$$\text{Rate} = \frac{\Delta[\text{product}]}{\Delta t}$$

$$\text{Rate} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

Stoichiometry and Rate

- The change in the concentrations of the product and reactant are not necessarily equal.

$$2O_3 \rightarrow 3O_2$$

  - To ensure that the same reaction rate is obtained when using either the reactants or the products, the stoichiometric coefficient, ν, is included in the denominator of the rate expression.

$$\text{Rate} = \frac{\Delta[\text{product}]}{\nu_{\text{prod}}\Delta t} = -\frac{\Delta[\text{reactant}]}{\nu_{\text{react}}\Delta t}$$

$$a\,\mathbf{A} + b\,\mathbf{B} \longrightarrow c\,\mathbf{C} + d\,\mathbf{D}$$

$$\text{Rate of reaction} = +\frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = +\frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t}$$

Practice 11.16, 11.17

Example Problem

Q. Based on the reaction below

$$2HBr(g) \longrightarrow H_2(g) + Br_2(g)$$

a) Express the rate of the reaction in terms of the change in concentration of each of the reactant and products

$$\text{Rate of reaction} = +\frac{\Delta[H_2]}{\Delta t} = +\frac{\Delta[Br_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[HBr]}{\Delta t}$$

b) In the first 25 s, [HBr] decreased from 0.60 M to 0.51 M. What is the rate of the reaction during the first 25 s?

$$\text{Rate of reaction} = -\frac{1}{2}\frac{(0.51-0.60)}{25\ s}$$

$= 1.8\times10^{-3}$ M/s

The Rate Law

- For a reaction between substances A and B, the rate of the reaction can be described by an equation of the form:

$$a\,\mathbf{A} + b\,\mathbf{B} \longrightarrow c\,\mathbf{C} + d\,\mathbf{D}$$

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n$$

  - k is the rate constant
  - [A] and [B] are the reactant concentrations
  - m and n are typically either integers or half integers and **must** be determined experimentally.

The Rate Law $\text{Rate} = k[\text{A}]^m[\text{B}]^n$

- The experimentally determined exponents (m, n) are referred to as the order of the reaction.
  - If $m = 0$, the reaction is said to be zero order.
  - If $m = 1$, the reaction is said to be first order.
  - If $m = 2$, the reaction is said to be second order.
  - Exponents greater than 2 are unusual.

- For reactions where the rate depends on more than one reactant concentration:
  - The exponent on each reactant is the order with respect to that reactant.
  - The sum of the exponents (m + n) is the overall order of the reaction.

Determination of the Rate Law

- For a reaction with only one reactant, A, the rate of the reaction is rate = $k[A]^n$.
- The common possible orders with respect to A are 0, 1, 2.
- If the concentration of A is doubled experimentally, the rate of the reaction will change in a simple and predictable way.

  - If $n = 0$, doubling [A] does not change the reaction rate.
  - If $n = 1$, doubling [A] doubles the reaction rate.
  - If $n = 2$, doubling [A] quadruples the reaction rate.

$2^0=1$, $2^1=2$, $2^2=4$, $2^3=8$,…

Practice 11.23, 11.26

Exam Questions

Based on the generic rate law, which of the followings are correct?

$$\text{Rate of reaction} = k[\text{A}]^m\,[\text{B}]^n$$

(a) The experimentally determined exponents (m, n) are referred to as the order of the reaction with respect to A and B, respectively. **Y**

(b) If $m = 1$, the reaction is first order with respect to B. **N**

(c) If $m = 0$, the reaction is independent of the concentration of A. **Y**

(d) If $n = 2$, the reaction is second order with respect to B. **Y**

(e) The overall order of the reaction = m $\times$ n **N**

Determination of the Rate Law

- For a reaction with two reactants, A and B, the rate of the reaction is rate = $k[A]^m[B]^n$.
- To separate the influence of one reactant concentration from the other, one reactant concentration is held constant while changing the other to determine its effect on the rate.
- To determine the order with respect to A and B, at least three experiments must be carried out.

Example Problem

Q. Consider the following data for the reaction shown. Determine the rate law and rate constant for this reaction at the temperature of these experiments.

$$NO + O_2 \rightarrow NO_2 + O$$

Expt	[NO] (mol L^{-1})	[O_2] (mol L^{-1})	Rate (mol L^{-1} s^{-1})
1	0.002	0.005	8.0×10^{-17}
2	0.002	0.010	1.6×10^{-16}
3	0.006	0.005	2.4×10^{-16}

$$\text{Rate} = k[\text{NO}]^m[\text{O}_2]^n \qquad \frac{Rate_x}{Rate_y} = \frac{[NO]_x^m[O_2]_x^n}{[NO]_y^m[O_2]_y^n}$$

Practice 11.29, 11.33, 11.35

Example Problem

$$\text{Rate} = k[\text{NO}]^m[\text{O}_2]^n$$

Use expts 1 and 2 to determine the value of n

$$\frac{\textbf{expt 2}}{\textbf{expt 1}} = \left(\frac{\textbf{0.010}}{\textbf{0.005}}\right)^n = \left(\frac{1.6\times10^{-16}}{8.0\times10^{-17}}\right)$$

$2^n = 2$ **n = 1**

Use expts 1 and 3 to determine the value of m

$$\frac{\textbf{expt 3}}{\textbf{expt 1}} = \left(\frac{\textbf{0.006}}{\textbf{0.002}}\right)^m = \left(\frac{2.4\times10^{-16}}{8.0\times10^{-17}}\right)$$

$3^m = 3$ **m = 1**

$$\text{Rate} = k[\text{NO}]^1[\text{O}_2]^1$$

Example Problem

Use expt 1 information to solve for k

$$\text{Rate} = k[\text{NO}][\text{O}_2]$$

$$8.0\times10^{-17}\ \text{mol L}^{-1}\ \text{s}^{-1} = k(0.002\ mol\ L^{-1})(0.005\ mol\ L^{-1})$$

$$k = \frac{8.0\times10^{-17}\ \cancel{\text{mol L}^{-1}}\ \text{s}^{-1}}{(0.002\ \cancel{mol\ L^{-1}})(0.005\ mol\ L^{-1})}$$

$k = 8.0\times10^{-12}\ \text{L mol}^{-1}\ \text{s}^{-1}$

$k = 8.0\times10^{-12}\ \text{M}^{-1}\ \text{s}^{-1}$

Zero-Order Integrated Rate Law

- For a zero-order reaction, the rate law is:

$$\text{rate} = k[\text{A}]^0 = k. \qquad \text{differential rate law}$$

- The zero-order integrated rate law.

$$[\text{A}]_t = [\text{A}]_o - kt \qquad \text{integrated rate law}$$

- If a plot of [A] versus time is linear, the overall order is zero order and the slope equals $-k$.

$$[\text{A}]_t = -kt + [\text{A}]_0$$

$$y = mx + b$$

First-Order Integrated Rate Law

- For a first-order reaction, the rate law is:

$$\text{rate} = k[\text{A}]^1$$ differential rate law

- The first-order integrated rate law.

$$\ln\frac{[\text{A}]_\text{t}}{[\text{A}]_\text{o}} = -kt \quad \text{or} \quad [\text{A}]_t = [\text{A}]_0 e^{-kt}$$

integrated rate law

- If a plot of ln [A] versus time is linear, the overall order is first order and the slope equals -k.

Example Problem

- The photodissociation of ozone by ultraviolet light in the upper atmosphere is a first-order reaction with a rate constant of 1.0 x 10^{-5} s^{-1} at 10 km above the planet's surface.

$$O_3 + h\nu \rightarrow O + O_2$$

- Consider a laboratory experiment in which a vessel of ozone is exposed to UV radiation at an intensity chosen to mimic the conditions at that altitude. If the initial O_3 concentration is 5.0 mM, what will the concentration be after 1.0 day?

$$K = 1.0 \times 10^{-5}\ s^{-1}$$

$$[O_3] = [O_3]_0 e^{-kt}$$

Practice 11.39

Example Problem

$K = 1.0 \times 10^{-5}\ s^{-1}$

$[O_3]_0 = 5.0\ mM$ t = 1.0 day

$$1.0\ \text{day}\left(\frac{24\ \text{h}}{1\ \text{day}}\right)\left(\frac{60\ \text{min}}{1\ \text{h}}\right)\left(\frac{60\ \text{s}}{1\ \text{min}}\right) = 8.6 \times 10^4\ \text{s}$$

$$[O_3] = [O_3]_0 e^{-kt}$$

$$= 5.0\ \text{mM}\ (e^{-(1.0\times10^{-5}\ \text{s}^{-1})\,(8.6\times10^4\ \text{s})})$$

$$= 2.1\ \text{mM}$$

Half-Life

- The half-life, $t_{1/2}$, of a reactant is the time it takes for its concentration to fall to one-half its original value.
  - When a reaction has proceeded for one half-life, the concentration of the reactant must be $[A]_t = 0.5[A]_0$.

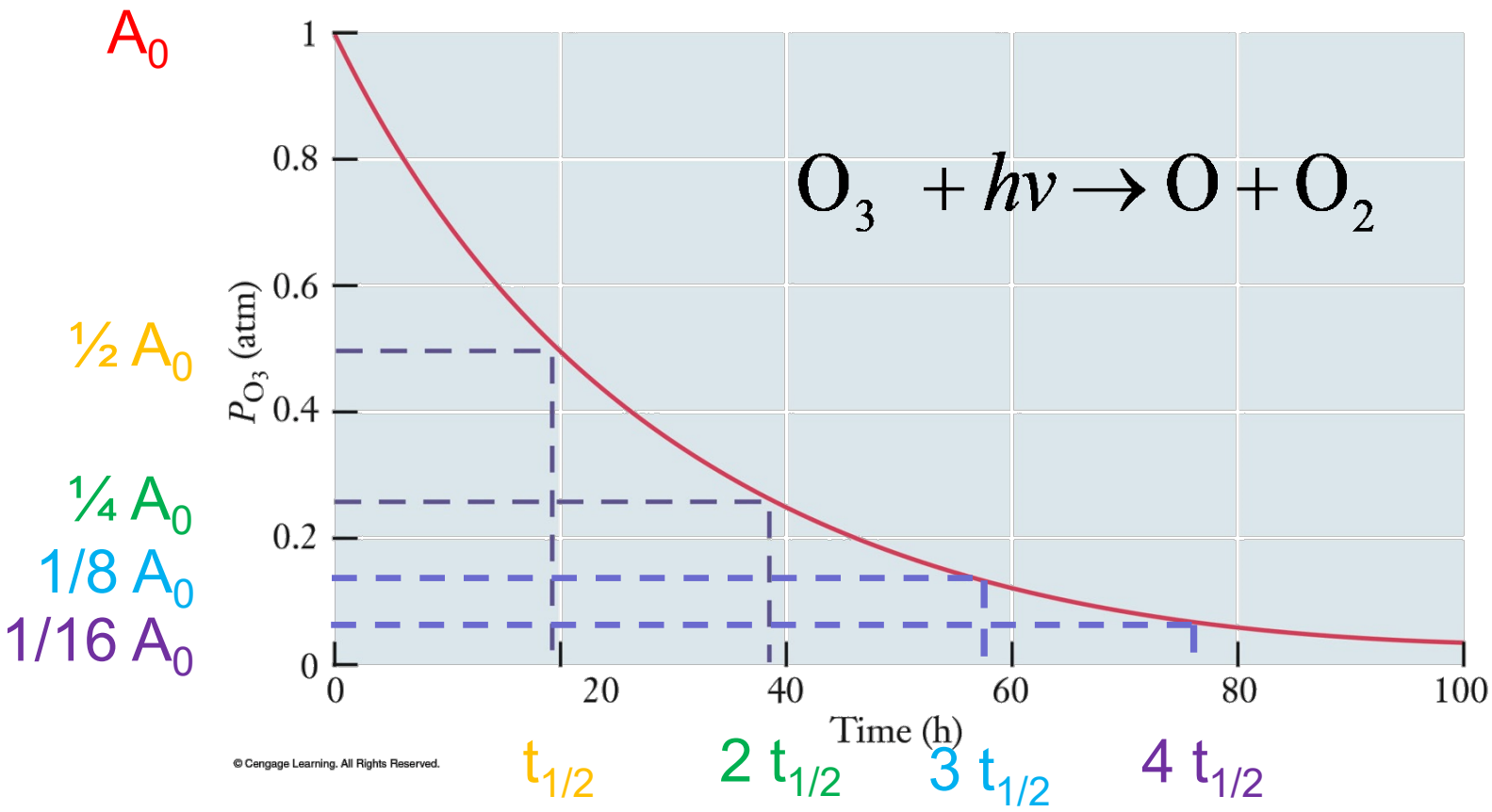
- Substituting $[A]_t = 0.5[A]_0$ into the first-order integrated rate expression, $t_{1/2}$ can be evaluated.

$$\ln\frac{0.5[A]_0}{[A]_0} = -kt_{1/2} = \ln\frac{1}{2} = \ln 1 - \ln 2 \qquad t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

- Other half-life equations can be constructed for zero-order and second-order reactions using the same method.

Practice 11.43, 11.45

Half-Life



- Ozone pressure as a function of time in an experiment designed to model the destruction of ozone in the stratosphere.
  - The ozone pressure falls by a factor of 0.5 every 19 hours.
  - Thus, $t_{1/2}$ is 19 hours.

Exam Questions

If the initial concentration of the reactant A in a first-order reaction, A → B + C, is 0.96 mol/L and the half-life is 30.0 s, what's the concentration of A after reacting for a certain time?

(a) 30.0 s 0.48 mol/L

(b) 60.0 s 0.24 mol/L

(c) 90.0 s 0.12 mol/L

(d) 120.0 s 0.060 mol/L

(e) 150.0 s 0.030 mol/L

Temperature and Kinetics

- There is a temperature dependence for the rate of reaction.
    - The rate of reaction decreases as the temperature of the reaction is decreased.
- For two molecules to react, they must first collide.
- The collision between reactant molecules must be sufficiently energetic before reaction will occur.
- For a given minimum kinetic energy, as temperature increases, the fraction of molecules with the minimum kinetic energy increases and the rate of reaction increases.

Reaction Mechanisms

- A reaction mechanism is a collection of one or more molecular steps that account for the way reactants become products.

  - A reaction mechanism is composed of a series of individual steps called elementary steps.

$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$$

$$ClO\cdot + O_3 \rightarrow Cl\cdot + 2\ O_2$$

$$\text{Net:} \qquad 2\ O_3 \rightarrow 3\ O_2$$

Elementary Steps and Reaction Mechanisms

- Only three types of elementary steps may occur.
  - Unimolecular steps have one reactant.
  - Bimolecular steps have two reactants.
  - Termolecular steps have three reactants.
    - Reactions involving the collision of three reactants are uncommon.

Elementary Steps and Reaction Mechanisms

Table 11.1

Summary of molecularity of elementary reactions

Type of Elementary Reaction	Molecularity	Rate Law
$A \rightarrow$ products	Unimolecular	Rate $= k[A]$
$A + B \rightarrow$ products	Bimolecular	Rate $= k[A][B]$
$2\,A \rightarrow$ products		Rate $= k[A]^2$
$A + B + C \rightarrow$ products	Termolecular	Rate $= k[A][B][C]$
$2\,A + B \rightarrow$ products		Rate $= k[A]^2[B]$
$A + B + C + D \rightarrow$ products	Not observed	

Elementary Steps and Reaction Mechanisms

- Two important characteristics of a reaction mechanism:
  - A chemical species generated in one step and consumed in a later step is called a reactive intermediate, such as the ClO· shown below.

$$Cl\cdot + O_3 \rightarrow \boxed{ClO\cdot} + O_2$$

$$\boxed{ClO\cdot} + O_3 \rightarrow Cl\cdot + 2\ O_2$$

$$\text{Net:} \qquad 2\ O_3 \rightarrow 3\ O_2$$

  - When the steps of the mechanism are properly summed, they give the observed stoichiometry of the overall reaction.

Practice 11.69, 11.71

Example Problem

- The decomposition of N_2O_5 is given by the equation:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

- The following mechanism is proposed for this reaction:

$$N_2O_5 \rightarrow NO_2 + NO_3$$

$$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$$

$$NO + NO_3 \rightarrow 2NO_2$$

  - Does this mechanism as written provide the correct stoichiometry? If not, how does it need adjustment?
  - Identify all intermediates in the mechanism.
  - Identify the molecularity of each step in the mechanism.

Practice 11.69, 11.71

Example Problem

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

(a) $N_2O_5 \rightarrow NO_2 + NO_3$

$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ $\qquad$ $N_2O_5 + NO_3 \rightarrow O_2 + 3\ NO_2$

$NO + NO_3 \rightarrow 2\ NO_2$

$2\ N_2O_5 \rightarrow 2\ NO_2 + 2\ NO_3$

$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ $\qquad$ $2\ N_2O_5 \rightarrow O_2 + 4\ NO_2$

$NO + NO_3 \rightarrow 2\ NO_2$

(b) The intermediates in this case are NO_3 and NO.

(c) The first step is unimolecular, whereas steps two and three are bimolecular.