

## Lecture 6. Fundamentals of atmospheric chemistry: Part 1

Objectives:

1. Chemical bonding: polar and nonpolar covalent bonds, ionic bond.  
Molecular structure of some common gases.
2. Valency and oxidation number.
3. The mechanics of chemical reactions.
4. Reaction rate, reaction rate constant, order of reactions.

Readings: Turco: p.68-77 ; Brimblecombe: p. 42-47

### 1. Chemical bonding.

The world around us is composed almost entirely of compounds and mixtures of compounds: rocks, coal, trees, and human bodies are all complex mixtures of chemical compound in which different kinds of atom are bound together.

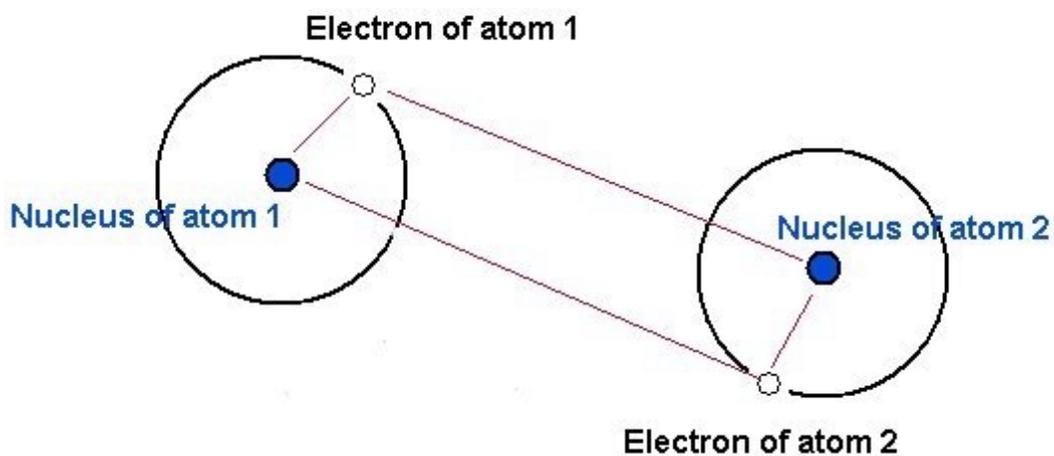
The forces that hold atoms together in compounds are called chemical bonds.

In isolated atom each electron is under the influence of the nuclear charge and the charges of all of the other electrons present. When atoms coming together forming compounds, a rearrangement of electrons occur such that electrons of one atom are influenced by the nucleus of another atom, thus electrons are *shared* or *transferred*. If this rearrangement produces an energetically stable condition then bond formation can occur.

The type of interaction, in which atoms share electrons, is called a **covalent bond**.

Example: a bond between two hydrogen atom, H

Figure 6.1 Schematic of the bond formation between two hydrogen atoms.



Through the ***covalent bond***, each hydrogen atom gets to ‘use’ an electron from other atom as well as its own, thus obtaining a filled outer level. The shared pair of electron arrangement in the bond can be represented in several different ways:

- **using Lewis symbols:** H : H ( here dots indicate electrons);
- **by the chemical formula:** H<sub>2</sub>
- **by the structural formula:** H - H

**Chemical formula** gives the number and kind of atoms in a molecule.

**Structural formula** shows individual bonds in a molecule.

Table 6.1 Diatomic molecules.

Element	Chemical formula	Structural formula	Type of bond
Hydrogen	H <sub>2</sub>	H-H	single
Fluorine	F <sub>2</sub>	F-F	single
Chlorine	Cl <sub>2</sub>	Cl-Cl	single
Bromine	Br <sub>2</sub>	Br-Br	single
Iodine	I <sub>2</sub>	I-I	single
Oxygen	O <sub>2</sub>	O=O	double
Nitrogen	N <sub>2</sub>	N - - - N	triple

Oxygen, O<sub>2</sub>, has a **double bond** because oxygen atom has six outer electrons ( $2s^2 2p^4$ ) and it need two more electrons to complete the outermost level to eight electrons (*octet rule*).

Nitrogen, N<sub>2</sub>, has five outermost electrons ( $2s^2 2p^3$ ) per atom. Thus, it requires three more electrons to fill the outermost level. Therefore, a nitrogen molecule is very strong. Because our bodies cannot break down the strong triple bond, we cannot use the nitrogen gas in the atmosphere although four-fifths of the atmosphere consists of N<sub>2</sub>.

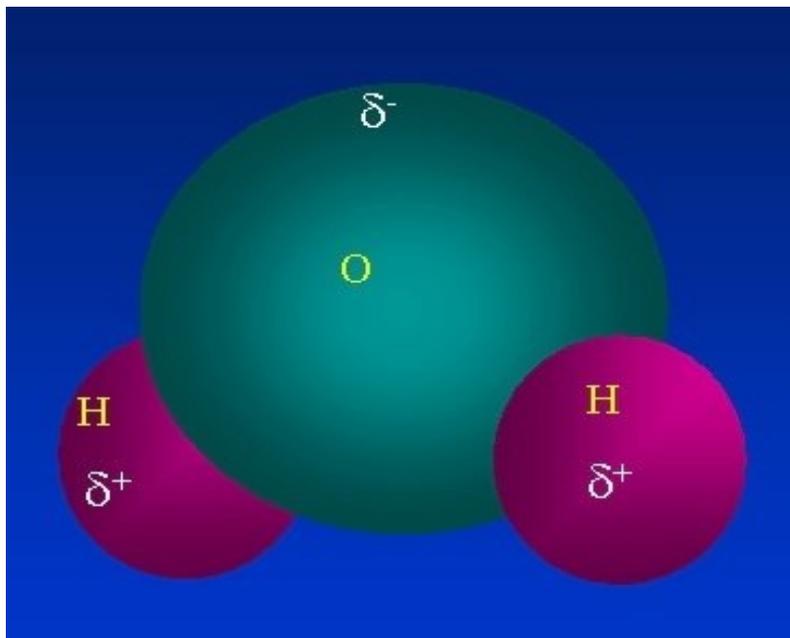
**Octet rule** states that atoms tend to combine in such a way that each obtains a filled outermost level of EIGHT electrons upon forming a chemical bond.

**Covalent bond** generally forms between of nonmetals. Here electrons are shared equally between identical atoms. This type of bond is also known as a **nonpolar covalent bond**. The type of **unequal** sharing of electrons is called a **polar covalent bond**.

**Example:** The polar covalent bond in a hydrogen chloride H - Cl creates a *dipole*. Hydrogen chloride is called a **polar molecule** because it contains a *dipole*.

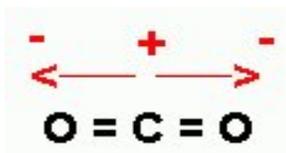
Dipole is a pair of equal but opposite charges that are separated by a small distance.

Figure 6.2 Polarity of water molecule.



Molecules are called **nonpolar** if they contain no dipole.

**Example:** CO<sub>2</sub> is nonpolar molecule because two dipoles of this molecule point in opposite directions and cancel each other



**Electronegativity** is a measure of the ability of an atom to attract to itself the electrons in a chemical bond.

- In the periodic table, across the period, electronegativity increases because the nucleus becomes more and more positively charged. Down a group, it decreases because the electron in the outermost orbitals are farther away from the nucleus of the atom. Thus the most electronegative elements are the nonmetals at the upper right of the periodic table. Fluorine is the most electronegative element, followed by oxygen and chlorine.

**Bound energy** is the amount of energy required to pull the bonded atoms apart.

**Bond length** is the distance between the atoms in a molecule.

- When *metals* form bonds with *nonmetals*, the differences in electronegativity between the atoms is so great that it become difficult to describe the bonding as simple as sharing of electrons. While in covalent bonds electrons of individual atoms in a molecule are considered to be shared between atoms, **ionic bonds** form when one or more electrons from one atom are completely transferred to a second atom.

**Ionic bonds** results from the attraction between appositely charged *ions*, namely *cation* and *anions*.

**Ions** are electrically charged atoms. **Cation** is a positively charged ion. A *cation* consists of a positive nucleus surrounded by electrons that are too few to balance the charges of all its protons. *Cations* are formed by a process called **oxidation**, which means the loss of one or more electrons.

**Anion** is a negatively charged ion. An *anion* consists of a positively nucleus surrounded by more than enough electrons to balance the charge of its protons. *Anions* are formed by **reduction**, which means the gain of one or more electrons.

- The elements most easily **oxidized** are the *metals*. The more metallic an element (the lower its electronegativity), the easier its atoms **oxidized** to become cations.
- The elements **reduced** more easily are the *nonmetals*. The more nonmetallic an element (the greater its electronegativity), the easier it is **reduced** to form an anion.

Table 6.2 Examples of metal elements.

Group number	Outer electron configuration	Number of outer electrons	Charge of cation	Example
1A	$s^1$	1	1+	$\text{Na}^+$
2A	$s^2$	2	2+	$\text{Ca}^{2+}$
3A	$s^2p^1$	3	3+	$\text{Al}^{3+}$

Table 6.3 Examples of nonmetal elements.

Group number	Outer electron configuration	Number of outer electrons	Number of electrons needed to complete level	Charge of anion	Example
5A	$s^2p^3$	5	3	3-	$\text{N}^{3-}$
6A	$s^2p^4$	6	2	2-	$\text{O}^{2-}$
7A	$s^2p^5$	7	1	1-	$\text{Cl}^-$

### Example of ionic bond formation:

Sodium chloride, NaCl, consists of the cation  $\text{Na}^+$  and the anion  $\text{Cl}^-$

Sodium is oxidized losing an electron.	$1s^2 2s^2 2p^6 3s^1$ <i>sodium atom, Na</i>	$1s^2 2s^2 2p^6$ <i>sodium ion, <math>\text{Na}^+</math></i>
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Chlorine is reduced gaining an electron	$1s^2 2s^2 2p^6 3s^2 3p^5$ <i>chlorine atom, Cl</i>	$1s^2 2s^2 2p^6 3s^2 3p^6$ <i>chloride, <math>\text{Cl}^-</math></i>
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The sodium cation and the chloride anion have opposite charges and therefore attract each other.

Magnesium chloride,  $\text{MgCl}_2$ , consists of the cation  $\text{Mg}^{2+}$  and two anions  $\text{Cl}^-$

Magnesium is oxidized losing **two** electrons:

$1s^2 2s^2 2p^6 3s^2$	$1s^2 2s^2 2p^6$
<i>magnesium atom, Mg</i>	<i>magnesium ion, <math>\text{Mg}^{2+}</math></i>

Chlorine is reduced gaining one electron. Therefore, two chlorine atoms are needed for each magnesium atom.

**Polyatomic ions** are groups of atoms that are covalently bonded and have a positive or negative charge.

Example: The hydroxide ion,  $\text{OH}^-$ , is an ion composed of one hydrogen atom and one oxygen atom.  $\text{OH}^-$  goes into bonding as an ion with charge  $1^-$  (for instance, NaOH sodium hydroxide).

**Examples** of polyatomic ions:

$\text{NH}_4^+$  ammonium ion;  $\text{NO}_3^-$  nitrate ion;  $\text{NO}_2^-$  nitrite ion;  $\text{CO}_3^{2-}$  carbonate ion  
 $\text{SO}_3^{2-}$  sulfite ion;  $\text{SO}_4^{2-}$  sulfate ion;  $\text{HSO}_4^-$  hydrogen sulfate ion (bisulfate ion)

## **2. Valency and oxidation number.**

The term **valence** describes the number of electrons which an atom utilizes in bonding.

**Oxidation number (or state)** is defined as the charge on the atom in a given compound or ion, after bonding electrons have been allocated according to the general rules.

**General rules to assign the oxidation numbers:**

1. The oxidation number of hydrogen is +1 (except in metallic hydrides when it is -1 and in hydrogen gas when it is 0).

For instance, it is +1 in hydrochloric acid  $\text{HCl}$ , ammonia  $\text{NH}_3$ , water  $\text{H}_2\text{O}$ , methane  $\text{CH}_4$ , but it is -1 in  $\text{LiH}$

2. The oxidation number of fluorine is always -1 and it never forms more than one bond. Similarly, the oxidation number of all halogens is -1 (except when they are combined with more electronegative elements).

For instance, it is -1 in  $\text{HI}$ , but it is +1 in  $\text{ICl}$ .

3. The oxidation number of oxygen is -2 (except in peroxides, for instance  $\text{H}_2\text{O}_2$ , when it is -1 and in oxygen gas  $\text{O}_2$  when it is 0).

For instance, it is -2 in  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ .

4. The oxidation number of an atom in an element is 0.

For instance, it is 0 in  $\text{Na(s)}$ ,  $\text{Hg(l)}$ ,  $\text{O}_2(\text{g})$ ,  $\text{O}_3(\text{g})$ ,  $\text{N}_2(\text{g})$ .

5. The oxidation number of monatomic ions is the charge of the ion

For instance,  $\text{Na}^+ \rightarrow +1$ ;  $\text{Cl}^- \rightarrow -1$

6. In any molecule or ion, the sum of the oxidation numbers of all atoms present is equal to the net charge on molecule or ion. If there is no any charge the sum of oxidation numbers is equal to 0.

For instance, the sum of oxidation numbers for the hydrogen and oxygen in water,  $\text{H}_2\text{O}$ , is 0.

For instance, the sum of the oxidation number for the carbon and oxygen atoms in  $\text{CO}_3^{2-}$  is -2 because the oxidation state for O is -2 and for C is +4.

- **The oxidation numbers (states)** are not actual *charges*. Actual charge is given as  $n^-$  or  $n^+$ , in turn oxidation number is given as  $-n$  or  $+n$ . For example, for  $\text{NO}_3^-$ , the overall charge is  $1^-$ ; the oxidation state for **N** is  $+5$  and for **O** is  $-2$ .
- The concept of **oxidation states (numbers)** provides a way to keep track of electrons in oxidation-reduction reactions which are very important in atmospheric chemistry (see Lecture 7).
- ◆ Some elements (such as nitrogen, carbon, sulfur) can exist in the environment in a wide range of oxidation states.

Table 6.4 Oxidation states of nitrogen and some typical compounds.

Oxidation states	Name of compound	Formula
<b>-3</b>	<b>ammonia</b>	<b><math>\text{NH}_3</math></b>
	<b>ammonium ion</b>	<b><math>\text{NH}_4^+</math></b>
	<b>amino acid, e.g. glycine</b>	<b><math>\text{H}_2\text{NCH}_2\text{CO}_2\text{H}</math></b>
<b>-2*</b>	<b>hydrazine</b>	<b><math>\text{N}_2\text{H}_4</math></b>
<b>-1*</b>	<b>hydroxylamine</b>	<b><math>\text{NH}_2\text{OH}</math></b>
<b>0</b>	<b>dinitrogen</b>	<b><math>\text{N}_2</math></b>
<b>+1</b>	<b>nitrous oxide</b>	<b><math>\text{N}_2\text{O}</math></b>
<b>+2</b>	<b>nitric oxide</b>	<b><math>\text{NO}</math></b>
<b>+3</b>	<b>nitrite ion</b>	<b><math>\text{NO}_2^-</math></b>
<b>+4</b>	<b>nitrogen dioxide</b>	<b><math>\text{NO}_2</math></b>
<b>+5</b>	<b>nitrate ion</b>	<b><math>\text{NO}_3^-</math></b>

\*Compounds with  $-2$  and  $-1$  states are not normally found in the natural environment.

### 3. The mechanics of chemical reactions.

**Chemical reaction** is the transformation of two or more interacting reactants through the intermediary phase of an activated complex, in which existing chemical bonds are broken and new bonds are formed, in which the chemical bonds define the species before and after the reaction.

**Chemical equation** is representation of a chemical reaction showing the relative numbers of reactants and products.

For instance,  $A + B \rightarrow C + D$

where A and B are the reactants; C and D are the products.

Example:

$NO + O_3 \rightarrow NO_2 + O_2$  (reactants: NO and  $O_3$ ; products:  $NO_2$  and  $O_2$ )

$NO_2 + h\nu \rightarrow NO + O$  (reactants:  $NO_2$ ; products: NO and O)

- In a chemical reaction atoms are neither created nor destroyed.
- Atoms, and therefore mass, are conserved in a chemical reaction.

NOTE: In this Lecture the gas-phase reactions are considered. Aqueous-phase reactions are discussed in Lecture 13.

Two major types of the gas-phase reactions:

**thermal (or kinetic) reactions** : reactions proceeding primarily due to the kinetic energy of reacting species (i.e., due to thermal agitation of species).

For instance,  $A + B \rightarrow \text{products}$

**photochemical reactions** : reactions proceeding due to an energy input in the form of light. For instance,  $A + h\nu \rightarrow \text{products}$

Figure 6.3 (a, b, c) The fundamental mechanisms of chemical and photochemical processes.

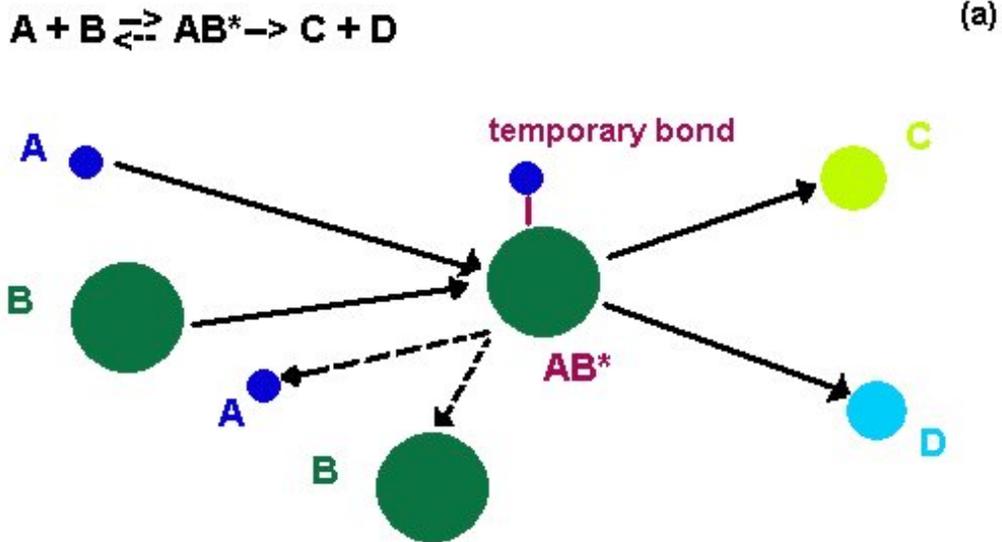


Figure 6.3a. Illustrates a binary, two-bodies, reaction between reactant molecules A and B yielding the product C and D.  $AB^*$  is an intermediate activated complex.

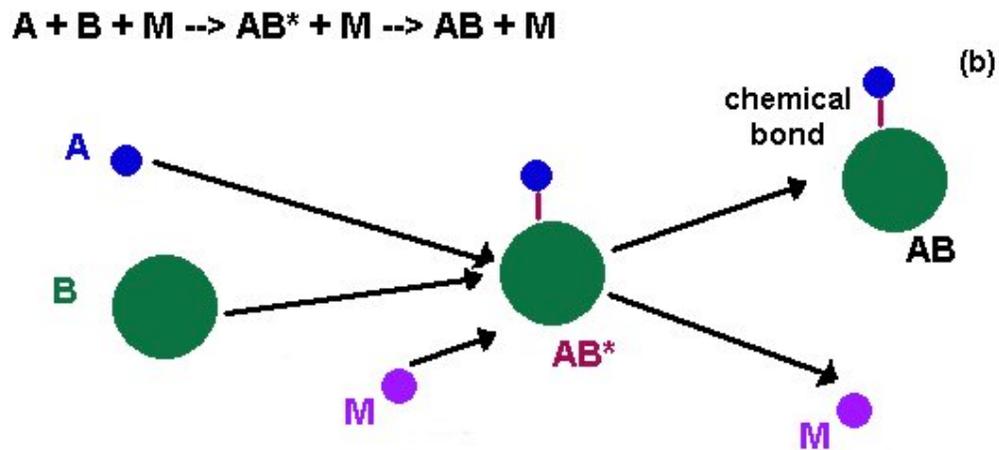
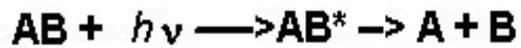


Figure 6.3b. Illustrates a ternary, three-bodies, reaction between reactant molecules A and B forming  $AB^*$  a three-way collision with another air molecule, M .



(c)

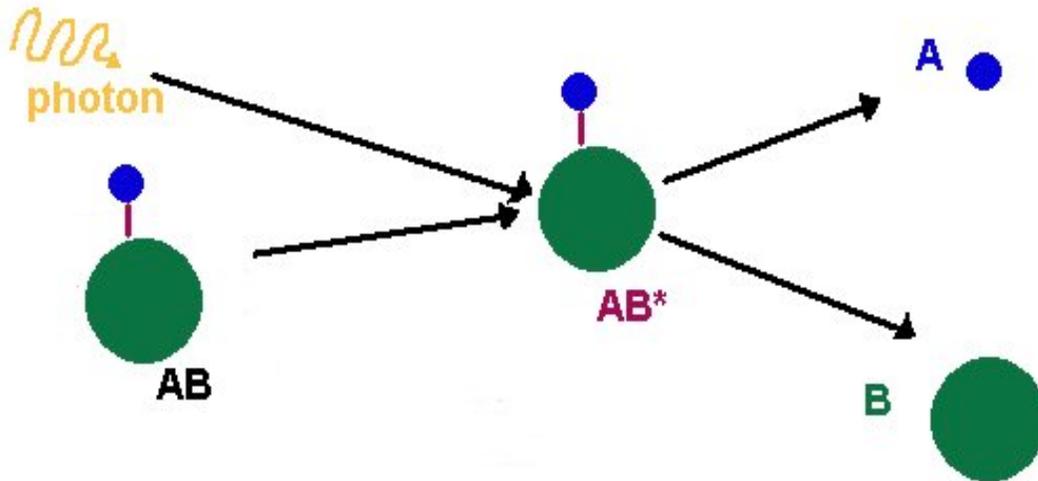
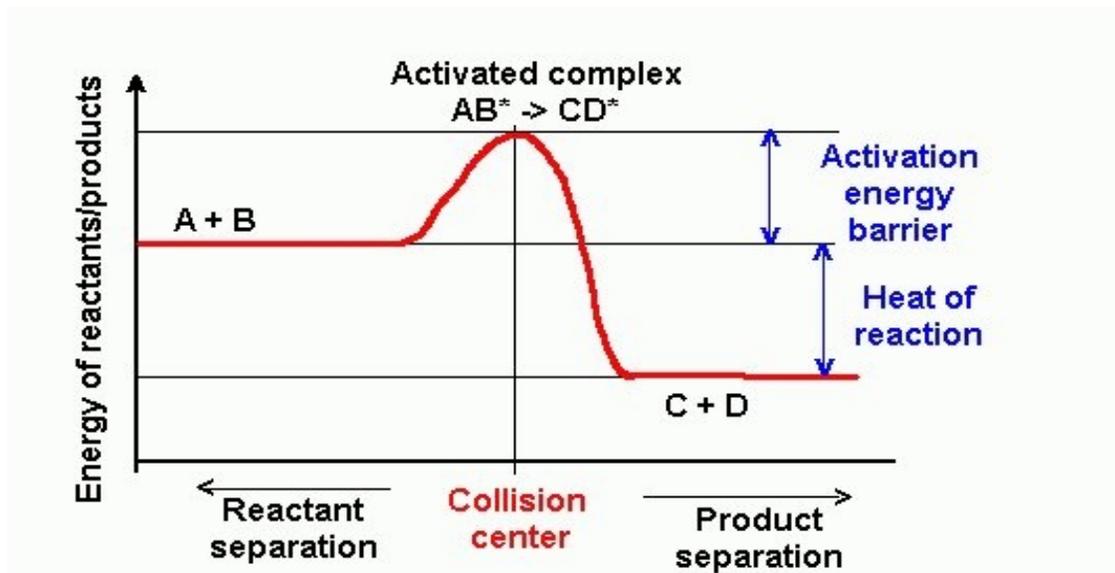


Figure 6.3c. The photodissociation of molecule AB into the products, following the absorption of a photon of radiation.

- Every molecule of a given species has the same *potential energy*, which is known or readily measurable. In any mixture of different gases, chemical and physical interactions between the gases work to minimize the total potential energy of the system.

Figure 6.4 The potential energy diagram for a binary reaction  $A+B \rightarrow C+D$



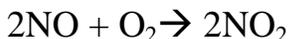
The **activation energy** is the minimum amount of energy needed for colliding species to react.

The **heat of reaction** is the potential energy difference between the reactants and products.

- The reaction is said to be **exothermic** if heat is generated during the reaction. The reaction is said to be **endothermic** if heat must be absorbed from the environment to make the reaction go.

Most chemical reactions occur by a series of steps called the reaction mechanism.

For example, for the reaction



the mechanism is thought to involve the following steps:



Each of these steps is called an **elementary step (or elementary reaction)**. The substance  $\text{NO}_3$  (highly reactive nitrate radical) is known as a **reactive intermediate**.

- An intermediate is formed in one step and consumed in a subsequent step and so it never seen as a product.

**Molecularity** is defined as the number of species that must collide to produce the reaction indicated by that step. A reaction involving one molecule is called a **unimolecular reaction**. Reactions involving the collision of two and three species are termed **bimolecular** and **termolecular**, respectively.

Example:

unimolecular reaction: decomposition of peroxyacetyl nitrate (PAN) gives peroxyacyl radical and nitrogen dioxide



#### 4. Reaction rate, reaction rate constant, order of reactions.

- The **rate** of a reaction describes how rapidly a chemical change takes place.

Example: consider an elementary reaction  $A + B \rightarrow C + D$

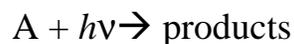
$$\text{Rate} = - d[A]/dt = - d[B]/dt = d[C]/dt = d[D]/dt$$

where [ ] means concentration of the species, t is time. Here negative signs denote loss of species A and B.

NOTE:  $d[A]/dt$  means {concentration of species A at time  $t_2$  - concentration of species A at time  $t_1$ }/  $t_2 - t_1$

The rate of an kinetic or photolytic reaction equals a **rate coefficient (or rate constant)** multiplied by the concentrations of each of the reactants.

- The rate of photochemical reaction



is defined as

$$\text{Rate} = J [A]$$

where **J** is the photolysis rate coefficient for species A.

NOTE: detailed discussion of the photochemical reactions is given in Lecture 7.

- The rates of unimolecular (one-body) , bimolecular (two-body), and termolecular (three-body) elementary reaction:

**unimolecular (one-body):**  $A \rightarrow \text{products}$

(reactions caused by *thermal decomposition*)

$$\text{Rate}_1 = - d[A]/dt = k_1 [A]$$

**bimolecular (two-body):**  $A + B \rightarrow \text{products}$

(any two chemically-active species that collide)

$$\text{Rate}_2 = - d[A]/dt = - d[B]/dt = k_2 [A] [B]$$

**termolecular (three-body):**  $A + B + C \rightarrow \text{products}$  (fairly rare reactions)

$$\text{Rate}_3 = - d[A]/dt = - d[B]/dt = - d[C]/dt = k_3 [A] [B] [C]$$

- In general, the **rate** of a hypothetical *elementary* reaction



is defined as

$$\text{Rate} = k [A]^a [B]^b [C]^c$$

where **k** is the **rate constant** (or **rate coefficient**), **[A]**, **[B]**, and **[C]** are

**concentrations** of reactants A, B, and C, respectively; and **n = a+b+c** is the **order of reaction**.

NOTE: Important to remember that for an elementary reaction, the rate equation follows directly from the molecularity of this reaction (based on the law mass action). Thus a unimolecular reaction is always first order, a bimolecular reaction is always second order, and so on. On the other hand, for an overall reaction containing several elementary steps, experimental determination of the rate is the only means of determining reaction orders.

- Many important atmospheric chemistry reactions are **pseudo first order**. This means that although they are truly second order reactions, the concentration of one component is essentially constant.

Example: nitric acid formation in air via reaction of nitrogen dioxide with the hydroxyl radical:  $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

$d[\text{HNO}_3]/dt = k_2 [\text{NO}_2] [\text{OH}] = k^* [\text{NO}_2]$  because concentration of OH may be considered constant over some time intervals (hours, but not days). Here  $k^*$  is called pseudo first order rate constant, and  $k^* = k_2 [\text{OH}]$ .

**Reaction rate coefficient:** ( $k_1, k_2, k_3$ )

Each kinetic reaction has a *rate coefficient* associated with it. The *rate coefficient* is a constant for a given temperature, pressure, and set of reactants, and relates the gas concentrations to the rate of reaction. Such *rate coefficients* are determined experimentally.

Most reaction *rate coefficients* are temperature dependent as given by the **Arrhenius equation**:

$$k = A_r \exp ( - E_r / R T ) ,$$

where  $A_r$  is the collisional prefactor (also known as *pre-exponential, or frequency factor, may depend on T*),  $E_r$  is the *activation energy*,  $R$  is the **universal gas constant**.

Activation energy is defined as the smallest amount of energy required for reacting species to form an activated complex or transition state before products are formed (see Fig. 6.4 for an illustration).

**Units** in reaction rates (used in atmospheric chemistry):

- concentration of reactants (gases) is in [ $\text{molec. cm}^{-3}$ ]
- the rate of reaction (regardless of whether it is unimolecular, bimolecular, or termolecular) is in [ $\text{molec. cm}^{-3} \text{ s}^{-1}$ ]
- the reaction rate coefficients (depend on type of reaction):
  - for unimolecular reaction is in [ $\text{s}^{-1}$ ];
  - for bimolecular reaction is in [ $\text{cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ ];
  - for termolecular reaction is in [ $\text{cm}^6 \text{ molec.}^{-2} \text{ s}^{-1}$ ].

NOTE: these units are related to units often used in chemistry (e.g., concentration of reactants [ $\text{mol L}^{-1}$ ]; rate of reaction is in [ $\text{mol L}^{-1} \text{ s}^{-1}$ ], etc.)