

## Lecture No: 7

### 4. Molecular Motions

Each atom in a molecule is described by 3 coordinates. A molecule containing N atoms has 3N coordinates. Therefore, there are 3N independent modes of motion. We call this number "degrees of freedom".

Molecular motions are of three kinds;

- Translational motion
- Rotational motion
- Vibrational motion

#### 4.1 Translational Motion

Translational motion is the motion of the molecule as a whole along the three mutually perpendicular axis passing through its center of mass. Each molecule has 3 translational modes of motion. Due to this motion, the molecule gains kinetic energy only. Kinetic energy may be written as a sum of three components;

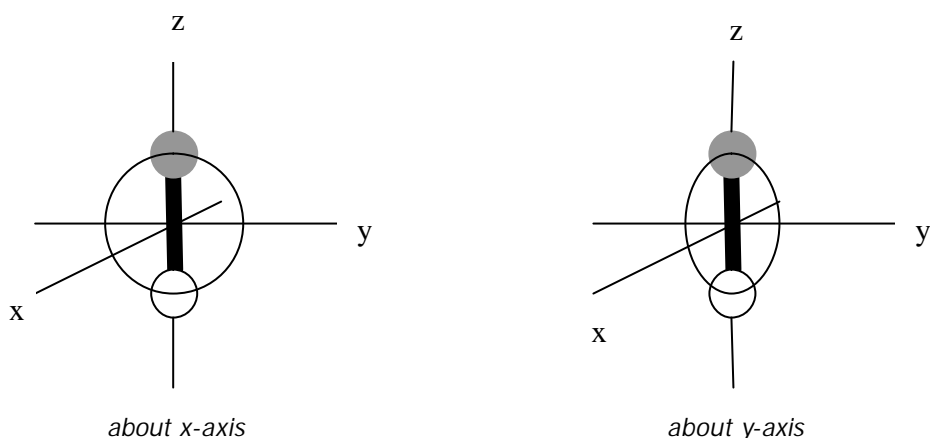
$$E_{trans} = (E_{tr})_x + (E_{tr})_y + (E_{tr})_z$$
$$E_{trans} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

Each of these terms contains the square of the velocity component. Therefore, each contributes  $\frac{1}{2} k_B T$  to the energy of the molecule. So, it may be concluded that every molecule spends 3 degrees of freedom for the translational motion and gains energy equal to  $\frac{3}{2} k_B T$ .

#### 4.2 Rotational Motion

Rotational motion is the motion of the molecule as a whole around the three main axes passing through its center of mass. This motion depends upon the geometry of the molecule. If the molecule is linear, then the molecular axis coincides with one of the main axes, then the molecule can rotate about the two

remaining axes. Two modes of rotation are possible. Linear molecules have 2 rotational modes of motion, but nonlinear molecules can rotate about the three main axes.



Molecules gain kinetic energy only due to the rotational motion.

$$E_{rot} = \frac{1}{2} \omega_x^2 I_x + \frac{1}{2} \omega_y^2 I_y \dots\dots\dots \text{linear}$$

$$E_{rot} = \frac{1}{2} \omega_x^2 I_x + \frac{1}{2} \omega_y^2 I_y + \frac{1}{2} \omega_z^2 I_z \dots\dots\dots \text{nonlinear}$$

In these equations,  $\omega$  s are angular velocities and  $I$  s are moments of inertia about the three main axes. Since each term is proportional to the square of the velocity component, each contributes  $\frac{1}{2} k_B T$  to the energy. Thus, linear molecules spend their 2 degrees of freedom for the rotational motion and gain a kinetic energy equal to  $k_B T$ . Nonlinear molecules spend their 3 degrees of freedom for the rotational motion and gain  $\frac{3}{2} k_B T$ .

### 4.3 Vibrational Motion

Molecules spend their remaining degrees of freedom for their vibrational motions. Vibrational motions are internal motions. The atoms in the molecule change their positions periodically with respect to each other. Vibrational coordinates are bond distances and bond angles. There are two types of vibrational motions;

- **Stretching motions** : are the vibrations along the bonds.

- **Bending vibrations** : change the magnitude of the bond angles.

The energy for each vibrational mode may be written as;

$$E_v = \frac{1}{2} m \left( \frac{dr}{dt} \right)^2 + \frac{1}{2} k (r - r_0)^2$$

In this equation,  $\mu$  is the reduced mass,  $k$  is the force constant,  $r$  is the coordinate,  $r_0$  is the equilibrium value of the coordinate and  $t$  is the time. The molecule gains kinetic and potential energy for each vibrational mode. Since each term is proportional to the square of the coordinate and the velocity each contributes  $\frac{1}{2} k_B T$  to the energy. Thus, contribution of each vibrational mode is  $k_B T$ . The vibrational energy is  $(3N-5)k_B T$  for linear molecules and  $(3N-6)k_B T$  for nonlinear molecules.

The total energy per molecule is;

$$E = \frac{3}{2} k_B T + \frac{2}{2} k_B T + (3N - 5) k_B T \dots \dots \dots \text{linear - molecules}$$

$$E = \frac{3}{2} k_B T + \frac{3}{2} k_B T + (3N - 6) k_B T \dots \dots \dots \text{nonlinear - molecules}$$

If we multiply these values by the Avagadro number, we obtain molar energies. By definition, the constant volume heat capacity is the derivative of the energy with respect to temperature at constant volume. Therefore, by differentiating the molar energies with respect to temperature, we obtain the molar heat capacities;

$$C_v = \frac{3}{2} R + \frac{2}{2} R + (3N - 5) R \dots \dots \dots \text{linear - molecules}$$

$$C_v = \frac{3}{2} R + \frac{3}{2} R + (3N - 6) R \dots \dots \dots \text{nonlinear - molecules}$$

**Example #1** :  $\gamma = C_p/C_v$  for ozone is 1.15. Assuming ideal gas behavior, is the molecule linear or nonlinear?

Solution :

If linear :

$$C_v = \frac{3}{2} R + \frac{2}{2} R + 4R = 6.5R$$

$$C_p = 6.5R + R = 7.5R$$

$$g = \frac{7.5}{6.5} = 1.15$$

If nonlinear :

$$C_v = \frac{3}{2}R + \frac{3}{2}R + 3R = 6R$$

$$C_p = 6R + R = 7R$$

$$g = \frac{7R}{6R} = 1.17$$

So, the molecule is linear.

**Example #2:** Substance X is an ideal gas containing n atoms per molecule.

- $C_p$  for X(g) and  $N_2$ (g) is the same at  $0^\circ\text{C}$ . (Consider the contribution of vibrational degrees of freedom to the heat capacity is negligible at  $0^\circ\text{C}$ ).
- The difference between the equipartition values of  $C_p$  for X and  $N_2$  is approximately  $6 \text{ cal.mol}^{-1}.\text{K}^{-1}$ . Show from the above information what can be concluded about n and any other aspects concerning the structure of X.

Solution :

For  $N_2$  :  $N=2$   
 $\Sigma\text{d.f.} = 3 \times 2 = 6$



3 translational + 2 rotational + 1 vibrational

$$C_v = 3/2 R + 2/2 R + R$$

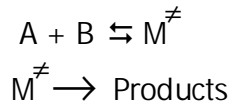
At  $0^\circ\text{C}$  only translational and rotational degrees of freedom are to be considered. Therefore, X has 2 rotational degrees of freedom, it is linear.

The difference between the heat capacities is due to the difference in the # of vibrational degrees of freedom. It corresponds to ~3 more vibrations, 1 more atom.

**X is a linear , triatomic molecule.**

## 5. Transition State Theory

In an elementary bimolecular reaction, the reactants produce the activated complex first, then it yields the products. The activated complex is that configuration of the atoms which corresponds to the top of the energy barrier.



The fundamental postulate of the theory is that the reactants are always in equilibrium with the reactants.

$$K^\ddagger = \frac{[M^\ddagger]}{[A][B]}$$

The activated complex is an aggregate of atoms. It is similar to an ordinary molecule, except it has one special vibration. If the frequency of this vibration is  $\nu$  then we may write;

$$\text{Rate} = \nu [M^\ddagger]$$

$$k = \nu \cdot K^\ddagger$$

If the equilibrium constant is written in terms of the molecular partition functions per unit volume and if the special vibration is factored out, we obtain the general expression giving the rate constant. This equation is known as Eyring Equation;

$$k = \frac{k_B T}{h} \frac{q^\ddagger}{q_A q_B} e^{-E_a/RT}$$

In this equation  $q^\ddagger$  is the partition function of the activated complex, but it is what remains after the special vibration is factored out.  $q_A$  and  $q_B$  are the molecular partition functions of the reactants.  $E_a$  is the activation energy and it is equal to the difference between the zero-point energies of the activated complex and the reactants.

The molecular partition function can be written as a product of partition functions for translation, rotation and vibration. For a diatomic linear molecule;

$$q = q_{trans}^3 \cdot q_{rot}^2 \cdot q_{vib}$$

For a nonlinear molecule with N atoms;

$$q = q_{trans}^3 \cdot q_{rot}^3 \cdot q_{vib}^{(3N-6)}$$

The Eyring equation may be written in a more convenient form for calculation;

$$k = \frac{k_B T}{h} K^\ddagger$$

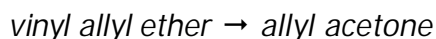
$$\ln K^\ddagger = -\frac{\Delta G^\ddagger}{RT} = -\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT}$$

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

$$E_a = \Delta H^\ddagger + nRT$$

In this equation, n is the molecularity of the reaction,  $\Delta G^\ddagger$  is the free energy of activation,  $\Delta H^\ddagger$  is the enthalpy of activation and  $\Delta S^\ddagger$  is the entropy of activation.

**Example #3 :** The gas-phase rearrangement reaction;



has a rate constant of  $6.015 \times 10^{-5} \text{ s}^{-1}$  at 420 K and a rate constant of  $2.971 \times 10^{-3} \text{ s}^{-1}$  at 470 K. Calculate the values of the Arrhenius parameters A and  $E_a$ . Calculate the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  at 420 K.

Solution :

We can write the Arrhenius equation for the two different temperatures and obtain;

$$E_a = R \left( \frac{T_1 T_2}{T_1 - T_2} \right) \ln \frac{k_1}{k_2}$$

$$E_a = (8.315) \left[ \frac{(420)(470)}{420 - 470} \right] \ln \frac{6.015 \times 10^{-5}}{2.971 \times 10^{-3}} = 128.0 \text{ kJ mol}^{-1}$$

Using this value with the rate constant at 420K;

$$6.015 \times 10^{-5} = A \cdot \exp \left[ -\frac{128000}{(8.315)(420)} \right]$$

$$A = 5.01 \times 10^{11} \text{ s}^{-1}$$

The reaction is unimolecular.

$$\Delta H^\ddagger = 128 - (8.315 \times 10^{-3})(420) = 124.5 \text{ kJ.mol}^{-1}$$

Using the modified Eyring equation;

$$A = \frac{e^2 k_B T}{h} \exp(\Delta S^\ddagger / R)$$

$$\Delta S^\ddagger = (8.315) \ln \frac{(5.01 \times 10^{11})(6.627 \times 10^{-34})}{e^2 (1.381 \times 10^{-23})(420)} = -40.4 \text{ J.mol}^{-1} . \text{K}^{-1}$$