Paper - VII

Physical chemistry

Unit - II

From Dr A K Gupta (chemistry)

Linear Harmonic Oscillator

Simple harmonic motion (vibration or Oscillation) is a back-and-forth motion along the same path in which the displacement from an equilibrium position varies periodically with time.

An harmonic Oscillator obey's Hooke's law which states that restoring force is directly proportional to the amount of displacement of mass from an equilibrium position i.e.

$$f \propto x$$

or $$f = -K \cdot x$$

where K is called proportionality Constant called the force Constant of the bond. The -ve sign indicates that the direction of 'f' is opposite to that in which 'x' increases.

K is the measure of stiffness of the bond. A strong bond has a large K and vice-versa.

As the bond moves up and down periodically, the variation of the displacement 'x' with time 't'.

Thus,

$$x = A \cos 2\pi \nu_0 t$$

The term 'A' is the amplitude of the vibration. Every time 't' increases by $1/\nu_0$, the $2\pi\nu_0 t$ increases by 2π and Cosine function Completes a cycle. ν_0 is the vibration of frequency.

Since $$f = m \cdot \frac{d^2x}{dt^2} \quad \left(\text{where } \frac{d^2x}{dt^2} = \text{acceleration}\right)$$

So, $$-K \cdot x = m \cdot \frac{d^2x}{dt^2}$$

or $$-K \cdot (A \cos 2\pi \nu_0 t) = m \cdot \frac{d^2}{dt^2}(A \cos 2\pi \nu_0 t)$$

(2)

or, $-K(A \cos 2\pi \nu_0 t) = m(-4\pi^2 \nu_0^2 A \cos 2\pi \nu_0 t)$

or $$\nu_0 = \frac{1}{2\pi}\sqrt{K/m} \quad \text{—— (1)}$$

for a diatomic harmonic Oscillator,

$$\nu_0 = \frac{1}{2\pi}\sqrt{K/\mu} \quad \text{—— (2)}$$

Where,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass.}$$

* Potential Energy (U)

In streatching a bond, a force must be exerted in opposition to the restoring force of the spring. The work done in this process increases the potential energy of the system. If the potential energy for the equilibrium length of the bond is taken to be zero, then

$$U = \int_0^x Kx\,dx = \frac{1}{2}Kx^2 \quad \text{—— (3)}$$

where, K is the distortion from the equilibrium length.

on compairing eq^n - (2) and eq^n - (3), we get-

$$U = 2\pi^2 \nu_0^2 \mu x^2 \quad \text{—— (4)}$$

At the limit i.e. x = amplitude A, there is no kinetic energy and all its energy must be potential energy. So,

$$\text{Vibrational energy} = 2\pi^2 \nu_0^2 \mu \cdot A.$$

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