LAW OF EQUIPARTITION OF ENERGY

For a gas in thermal equilibrium at temperature T (in 3 dimensions)

$$\frac{1}{2}mv_x^2+\frac{1}{2}mv_y^2+\frac{1}{2}mv_z^2=\left(\frac{3}{2}\right)k_BT$$

Since there is no preferred direction,

$$\frac{1}{2}mv_x^2=\left(\frac{1}{2}\right)k_BT,\ \frac{1}{2}mv_y^2=\left(\frac{1}{2}\right)k_BT,\ \frac{1}{2}mv_z^2=\left(\frac{1}{2}\right)k_BT$$

In thermal equilibrium

The average energy of each degree of freedom is **$\frac{1}{2} k_B T$**.

That is, in equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an average energy equal to ***$\frac{1}{2} k_B T$***. This is known as the **law of equipartition of energy**.

Vibrational mode

Since a vibrational mode has both kinetic and potential energy modes, each vibrational frequency contributes

$2 \times 1/2\, k_B\, T = k_B\, T$ to the Energy

SPECIFIC HEAT CAPACITY

Monatomic Gases

The molecule of a monatomic gas has only three translational degrees of freedom. Thus, the average energy of a molecule at temperature T is

$$(3/2)k_B T.$$

The total internal energy of a mole

U= $(3/2)k_B$ T x N_A = (3/2) R T since R = N_A k_B

The molar specific heat at constant volume, C_v

$$C_v = \frac{dU}{dT} = \frac{3}{2}R$$

For an ideal gas, $$C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R$$

The ratio of specific heats

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

Diatomic Gases (rigid)

A diatomic molecule treated as a rigid rotator, like a dumbbell, has 5 degrees of freedom: 3 translational and 2 rotational.

Using the law of equipartition of energy, average energy is **$5/2\ k_B T$** .

Then the total internal energy of a mole of such a gas is **$U = 5/2\ k_B T\ \ N_A = 5/2\ RT$**

The molar specific heats

$$C_v = \frac{dU}{dT} = \frac{5}{2}R$$

$$C_p = C_v + R = \frac{5}{2}R + R = \frac{7}{2}R$$

$$\gamma = \frac{C_p}{C_v} = \frac{7}{5}$$

Diatomic molecule (not rigid)

If the diatomic molecule is not rigid but has in addition a vibrational mode (both K E and PE), it has total 7 degrees of freedom (modes).

Then

$$U = \frac{7}{3} RT$$

$$C_v = \frac{dU}{dT} = \frac{7}{2} R$$

$$\gamma = \frac{C_p}{C_v} = \frac{9}{7}$$

$$C_p = C_v + R = \frac{7}{2} R + R = \frac{9}{2} R$$

Polyatomic molecule

In general a polyatomic molecule has 3 translational, 3 rotational degrees of freedom and a certain number (f) of vibrational modes.

According to Equipartition of Energy,

$$U=\left(\frac{3}{2}k_B T+\frac{3}{2}k_B T+f\,k_B T\right)N_A=\left(3+f\right)RT$$

Molar specific heats

$$C_v = \frac{dU}{dT} = (3+f)R$$

$$C_p = C_v + R = (4+f)R$$

$$\gamma = \frac{C_p}{C_v} = \frac{(4+f)}{(3+f)}$$

Specific Heat Capacity of Solids

Consider a solid of N atoms, each vibrating about its mean position.

Since Vibration has 2 modes of energy,

In One dimensions, average energy is **$2(\frac{1}{2})\ k_BT = k_BT$**

In Three dimensions, average energy is **$3\ k_BT$**

For One mole of solid,

$U = 3\,k_B T\,N_A = 3RT$

$$C = \frac{dQ}{dT} = \frac{dU}{dT} = 3R$$

Since there is no change in Volume

That is no work is done by the solid molecules

Specific Heat Capacity of Water

Since Water molecule has three atoms, two hydrogen and one oxygen, Internal Energy $U = 3 \times 3\ k_B T \times N_A = 9\ RT$

And

$$C = \frac{dQ}{dT} = \frac{dU}{dT} = 9\,R$$

MEAN FREE PATH

The average distance between two successive collisions, called the mean free path.