

Chemical Thermodynamics 05

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Calculations of –

- i) Law of equipartition of energy
- ii) Degrees of freedom & molecular basis of heat capacities.

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Law of Equipartition of Energy (1)

The average translational KE of a gas molecule,

$$E_{tr} = \frac{1}{2} m \bar{c}^2 = \frac{3}{2} kT$$

It depends only on the temp. \therefore is independent of the mass and nature of the molecule (Ex. in a mixture of He and Hg vapour, in a ratio masses of 1:50, the average KE of translational energy of two species is the same)

When C_x, C_y, C_z are the components of velocity c in three \perp directions, we ~~know~~ know —

$$\bar{c}^2 = \bar{c}_x^2 + \bar{c}_y^2 + \bar{c}_z^2 \text{ and } \bar{c}_x^2 = \bar{c}_y^2 = \bar{c}_z^2$$

$$\text{hence, } \frac{1}{2} m \bar{c}_x^2 = \frac{1}{2} m \bar{c}_y^2 = \frac{1}{2} m \bar{c}_z^2$$

$$\begin{aligned} \therefore E_{tr} &= \frac{1}{2} m \bar{c}^2 \\ &= \frac{1}{2} m \bar{c}_x^2 + \frac{1}{2} m \bar{c}_y^2 + \frac{1}{2} m \bar{c}_z^2 \\ &= E_x + E_y + E_z \end{aligned}$$

Where E_x, E_y or E_z are translational KE associated with each component of velocity

$$\therefore \epsilon_{tr} = 3 \epsilon_x = \frac{3}{2} kT$$

$$\Rightarrow \epsilon_x = \frac{1}{2} kT$$

That is, the translational KE is made up of three equal parts corresponding to velocity components in three 1r directions.

That the average KE of translational along each direction would be $\frac{1}{2} kT$ is a consequence of Maxwell Distribution Law.

$$dn_x = n f(c_x) dc_x ; \text{ where } f(c_x) = A e^{-bc_x^2}$$

c_x may have +ve or -ve value, we can write for the mean square of the velocity components c_x as —

$$c_x^2 = \frac{1}{n} \int_{-\infty}^{\infty} c_x^2 \cdot n \cdot A \cdot e^{-bc_x^2} dc_x$$

$$= 2A \cdot \frac{1}{4} \sqrt{\frac{\pi}{b^3}} \quad (\text{standard value})$$

$$= 2 \cdot \left(\frac{m}{2\pi kT}\right)^{1/2} \cdot \frac{1}{4} \cdot \pi^{1/2} \cdot \left(\frac{2kT}{m}\right)^{3/2}$$

$$= \frac{2kT}{m}$$

$$\therefore \bar{E}_x = \frac{1}{2} m \bar{c}_x^2 = \frac{1}{2} m \cdot \frac{kT}{m} = \frac{1}{2} kT.$$

It is obvious that, \bar{E}_y and \bar{E}_z would also equal to $\frac{1}{2} kT$.

It shows that translational energy is equally distributed among the three independent components of motion along the three $\perp r$ directions. Each independent component that must be specified to determine the energy of the molecule is called Degree of Freedom. A molecule has thus

three translational degrees of freedom. It is seen that the translational energy is equally divided among the three degrees of freedom.

$$\text{Thus, } E = \frac{1}{2} m c_x^2 + \frac{1}{2} m c_y^2 + \frac{1}{2} m c_z^2$$

Maxwell & Boltzmann enunciated as - The total KE of a molecule is equally distributed bet. the various degrees of freedom. This is known as Principle of Equipartition of energy.

Heat Capacity :-

The amount of heat required to raise the temp^r of one gm. of a substance by 1°K is called its specific heat. The heat input required to raise by 1°K the temp^r of one mole of the substance is called its molar heat capacity or simply "heat capacity" which is denoted by C .

If dQ heat is required for dT increase in temp^r for one mole of the substance, then,

$$C = \frac{dQ}{dT}$$

But dQ is a path function, so we can place certain restriction to obtain precise value of heat capacity. The usual restriction are at constant vol^m and constant press^r. So that we have,

$$C_v = \frac{dQ_v}{dT}$$

$$C_p = \frac{dQ_p}{dT}$$

But we have, $dU = dQ_v \Rightarrow dH = dQ_p$

Hence, $C_v = \left(\frac{dU}{dT}\right)_v \rightarrow (1)$

$\Rightarrow C_p = \left(\frac{dH}{dT}\right)_p \rightarrow (2)$

Again for finite process, at const. volⁿ →
 at const. Press^r

$$\Delta U = C_V \Delta T \longrightarrow (3)$$

$$\Delta H = C_P \Delta T \longrightarrow (4)$$

It is assuming that both the C_V and C_P are practically unaltered in the temp^r range of integration.

Relation between C_P & C_V :-

We know, $U = f(V, T)$

$$\Delta U = \left(\frac{\partial U}{\partial T}\right)_V \Delta T + \left(\frac{\partial U}{\partial V}\right)_T \Delta V$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{Then, } C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \quad \left. \begin{array}{l} \because H = U + PV \\ P = \text{Const.} \end{array} \right\}$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial T}\right)_P$$

For a gm. mole of ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$\therefore C_p - C_v = P \left(\frac{\partial V}{\partial T}\right)_P$$

$$= P \cdot \frac{R}{P}$$

$$\boxed{C_p - C_v = R}$$

$$\Rightarrow \frac{\partial}{\partial T} \cdot \frac{RT}{P}$$

$$\because PV = RT$$

$$\therefore V = \frac{RT}{P}$$

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