Heat and Thermodynamics

Heat and thermodynamics is a fundamental branch of physics, that deals with the relationship between heat, energy and work basically. For an engineering student, understanding thermodynamics is essential for designing and analysing system that involves the transfer of heat and energy. This also includes engines, power plants, refrigeration system, heat and cooling system. It also plays a critical role in understanding the performance and efficiency of these systems. Understanding the environmental impact for developing sustainable energy solution is also essential.

3.1 Quantity of Heat

3.1.1 Calorific Value

Calorific value of food and fuel is the quantity of heat produced when a unit quantity of substance is completely burnt. It is used to measure quality of foods and fuels. It is measured in calorie/gm or joule/kg. The different experimental samples will be bread, biscuits, rice, drinks etc. in foods and fuel will be coal, petrol, diesel, oils, wood etc.

The quality is important not only for researchers but also for food producers as well as fuel consumers. A healthy person needs normally 2256 calories (WHO-2022) everyday for his normal activities. An engine requires petrol or diesel with proper calories. Before eating food, one should care, what amount of energy or calorie does it provide and should have an idea that which food provide proper calorific values for our body. In the same way a driver of vehicle should also think whether the petrol or

diesel supplied to the vehicle is pure or not. A pure petrol or diesel only provides proper calorie for the engine.

The calorific value of foods and fuels is determined easily and accurately by differential scanning calorimeter. It is a sophisticated computer-controlled instrument measurement and characterization of thermal properties of the samples. The simple type of differential scanning calorimeter is a Bomb Calorimeter.

Bomb Calorimeter

A bomb calorimeter consists of a steel or gun metal vessel D inside of bowl a platinum crucible B is suspended. E is sample of fuel or food in the form of powder. A heating wire is immersed in the fuel and its ends are connected to the terminals T_1 and T_2. R is a regulating valve for the fuel supply of oxygen inside D, which is closed with air tight lid. The whole system is immersed in a calorimeter C containing water.

When current is supplied through the heater wire, the fuel is ignited. The heat produced due to the combustion of the fuel is taken by the surrounding water in the calorimeter. So, the heat produced = $(m+w)(T_1 - T_2)$

Figure 3.1 Bomb Calorimeter

If M be the mass of the sample, then the calorific value will be

$$C = \frac{(m+w)(T_1 - T_2)}{M}$$

Where m is mass of water, w is heat capacity of calorimeter and vessel, T_1 and T_2 are initial and final temperatures of water.

Example 3.1

A petrol engine consumes 25 litres of petrol per hour. The calorific value of petrol is 4.788×10^7 J litre. The output of the engine is 35 kW. Calculate the efficiency of the engine.

Solution:

Here, the total heat produced by the petrol in one hour = 119.7×10^7 J
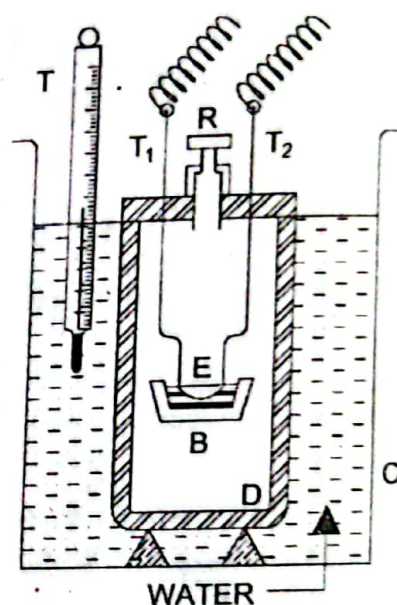
Heat produced per second $= \frac{119.7 \times 10^7}{3600} W = 332.5 \times 10^3 W$

Hence, the efficiency of the engine $= \frac{output}{input} \times 100\% = \frac{35}{332.5} \times 100\% = 10.5\%$

3.1.2 Specific Heat of Solid

The specific heat of a substance is defined as the heat required to raise the temperature of one gram mole of the substance through 1°C. Hence, the specific heat is

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

The specific heat of gas may be at constant pressure and at constant volume. The former is always greater than the latter according to first law of thermodynamics.

In solid, most of the supplied heat is used up to increase the internal energy which occurs in two ways:

(a) rigorous vibration on increasing temperature which results lattice specific heat.

(b) electrons are excited thermally to higher states and contribute electronic specific heat.

So, in solid or metal the specific heat is the sum of both i.e.,

$C_{solid} = C_{lattice} + C_{elec}.$

Here, we mainly concentrate on lattice heat capacity.

Classical Theory of Heat Capacity of Solid

The classical theory of solid was first developed by Dulong and Petit in 1819 on the basis of classical energy oscillator with Maxwell-Boltzmann distribution of atoms. The assumptions of this theory are

- Each atom in the crystal vibrates freely constitutes a 3D harmonic oscillator and vibrate independent to each other.
- Each vibrational degree can be regarded as a one-dimensional harmonic oscillator,
- Each harmonic oscillator vibrates with is natural frequency (ω).

- The total energy of a one-dimensional harmonic oscillator of mass is the sum of kinetic and potential energy i.e.,

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \qquad \ldots 3.1$$

Now, the average energy of the oscillator, according to classical statistics is

$$\hat{E} = \frac{\int E e^{-E/KT} dE}{\int e^{-E/KT} dE} \qquad \ldots 3.2$$

Substituting the value of E from equation 3.1 and using standard integration, we get

$$\hat{E} = KT$$

Now, total vibrational energy in 3N one dimensional oscillator is

$$U = 3NKT$$

So, the specific heat capacity or simply called heat capacity is

Figure 3.2

$$C_v = \left(\frac{dU}{dT}\right)_v = 3NK = 3R = 5.96 \ cal/mol.K = 24.93 \ J/mol.K \qquad \ldots 3.3$$

R is universal gas constant for a gram atom and R = 1.9856 cal. per gram atom = 8.31 J/mol.K.

This is Dulong and Petits value of heat capacity which reveals the independency with temperature. This is, however, contrary to the experimentally observed facts. It has been found by experiments that the specific heat of all substances varies with temperature.

Einstein's Quantum Theory of Heat Capacity of Solid

The discrepancy between experimental results and theoretical prediction leads to development of new theory. Einstein in 1911, attempted to resolve the drawbacks of classical theory using Planck's quantum theory. The assumptions of this theory are:
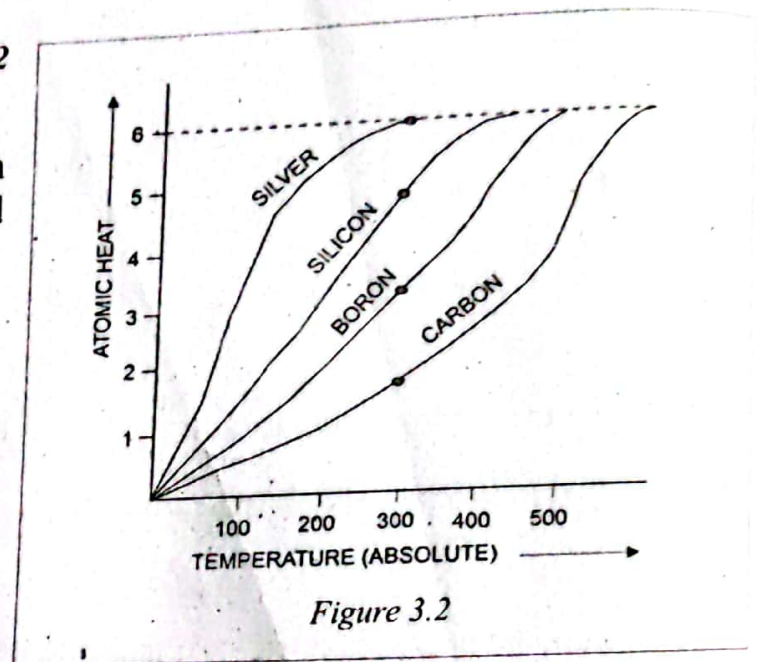
- A crystal of solid consists of atoms which may be regarded as identical and independent harmonic oscillator.
- The solid consists N atoms is equivalent 3N one dimensional harmonic oscillator.
- Due to identical environment of each, all oscillator vibrates with same natural frequency.
- The oscillators are quantum oscillators having discrete energy obeying Maxwell-Boltzmann distribution of energy, which is

$$E_n = n\hbar\omega = nhf \qquad \qquad \ldots 3.4$$

Where $n = 0, 1, 2, \ldots\ldots\ldots$

Now, the average energy according to statistical distribution

$$\hat{E} = \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/KT}}{\sum_{n=0}^{\infty} e^{-E_n/KT}}$$

Substituting the value of E_n from equation 3.4 and using

$$x = \frac{\hbar\omega}{KT}, \text{ we get}$$

$$\hat{E} = \frac{\hbar\omega}{e^{-\hbar\omega/KT} - 1} \qquad \ldots 3.5$$

Figure 3.3 Experimental curve between atomic heat and temperature

Thus, the internal energy of the solid is

$$U = 3N\hat{E} = \frac{3N\hbar\omega}{e^{-\hbar\omega/KT} - 1} \qquad \qquad \ldots 3.6$$

Let us suppose Einstein's temperature θ_E, i.e.,

$$\theta_E = \frac{\hbar\omega}{K} \qquad \qquad \ldots 3.7$$
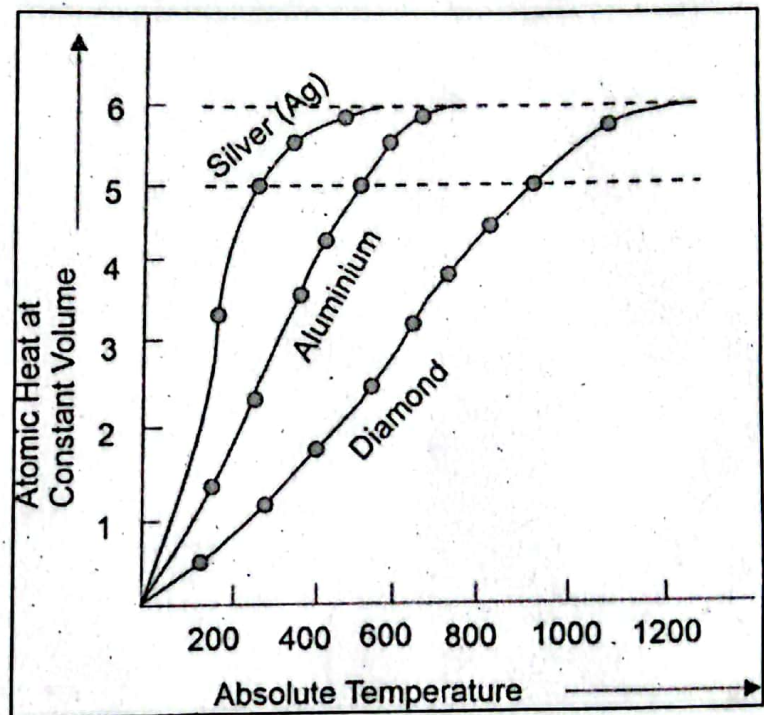
Hence, the heat capacity of the solid is

$$C_v(T) = \left(\frac{dU}{dT}\right)_v = \frac{3R\left(\frac{\theta_E}{T}\right)^2 e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2} \qquad \dots 3.8$$

At high temperature $C_v = 3R$, which is same as classical theory but at low temperature obeying experimental values as shown in figure.

Example 3.2

If Einstein's temperature of a solid is 373 K, calculate the frequency of the Einstein's oscillator.

Solution:

We have,
$$\theta_E = \frac{\hbar\omega}{K} = \frac{\hbar 2\pi f}{1.38 \times 10^{-23}} = \frac{hf}{1.38 \times 10^{-23}}$$

or,
$$373 = \frac{6.64 \times 10^{-34} f}{1.38 \times 10^{-23}}$$

$$f = 7.8 \times 10^{12} \text{ Hz}$$

Example 3.3

If a solid has Einstein's temperature 473 K, calculate its specific heat at 373 K.

Solution:

We know the specific heat relation

$$C_v(T) = \frac{3R\left(\frac{\theta_E}{T}\right)^2 e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2}$$

$$= \frac{3 \times 8.31 \left(\frac{473}{373}\right)^2 e^{\frac{473}{373}}}{\left(e^{\frac{473}{373}} - 1\right)^2} = \frac{24.93 \times 161 \times 3.554}{(3.554-1)^2} = \frac{142.648}{6.523} = 21.87 \text{J/mol. K}$$

Which is approximately equal to the high temperature value of heat capacity.

3.2 Nature of Heat

3.2.1 Degree of Freedom and Maxwell's Law of Equipartition of Energy

A molecule in a gas can move along any of the three coordinate axes. It means, it has three degree of freedom. Degree of freedom is the number of independent variables that must be known to describe the state or the position of the body completely. A monoatomic gas molecule has three degree of freedom. A diatomic gas molecule has 3 degree of freedom of translation and 2 degree of freedom of rotation i.e., it has in all five degree of freedom.

$$I = \frac{2}{5}mr^2$$

In general, the number of degree of freedom of a system of particles may be found by subtracting the number of relations among coordinates from the total number of coordinates required to completely specify the configuration of the dynamic system. If a system consists n - particles and there are l - independent relations among their coordinates, then the number of degree of freedom of the system will be

$$f = 3n - l$$

$$\ldots 3.9$$

A rigid body has 3 translational motion and 3 rotational motions. Thus, its degree of freedom is 6. In case of gas, the degree of freedom is determined by the translational, rotational and some-times vibrational motion also.

According to kinetic theory of gases, the mean kinetic energy of a molecules at temperature T is

$$\frac{1}{2}mv^2 = \frac{3}{2}KT = \frac{1}{2}m\,(v_x^2 + v_y^2 + v_z^2)$$

For a gas in thermal equilibrium at temperature T, the mean value of velocity along the three axes are equal i.e., $v_x^2 = v_y^2 = v_z^2$

$$\therefore \qquad \frac{1}{2}mv_x^2 = \frac{1}{2}mv_y^2 = \frac{1}{2}mv_z^2$$

i.e., $\qquad \frac{1}{2}mv^2 = 3 \times \frac{1}{2}mv_x^2 = \frac{3}{2}KT$

i.e., $\qquad \frac{1}{2}mv_x^2 = \frac{1}{2}KT, \qquad\qquad \frac{1}{2}mv_y^2 = \frac{1}{2}KT \qquad$ and $\qquad \frac{1}{2}mv_z^2 = \frac{1}{2}KT$

Hence, the total kinetic energy of a gas is thermal equilibrium is equally distributed among all degree of freedom and the kinetic energy associated with each degree of freedom is $\frac{1}{2}KT$.

This is also called Maxwell's law of equipartition of energy.

3.2.2 Atomicity of Gases

Ideal gas molecules do not interact and they do not possess potential energy. Thus, the total energy of ideal gas is wholly kinetic.

(i) Monoatomic Gas:

A molecule of a monoatomic gas like *He, Ne, Ar*, contains one atom only. Therefore, it may be treated as a point mass. It has translatory motion only, so its degree of freedom f with no independent relation is $f = 3 \times 1 - 0 = 3$

According to law of equipartition of energy, the mean kinetic energy for each degree of freedom is $\frac{1}{2}KT$ and kinetic energy per molecule $= 3 \times \frac{1}{2}KT = \frac{3}{2}KT$

The energy associated with each mass of a gas

$$U = N_A \times \frac{3}{2}KT = \frac{3}{2}(N_A K)T = \frac{3}{2}RT$$

Where $N_A = 6.023 \times 10^{23}/mol$ is Avogadro's number.

Thus, the molar specific heat of monoatomic gas at constant volume is

$$C_V = \left(\frac{dU}{dT}\right)_v = \frac{3}{2}R$$

Similarly, the specific heat at constant pressure is

$$C_P = C_V + R = \frac{5}{2}R$$

∴ The adiabatic exponent

$$\gamma = \frac{C_P}{C_v} = \frac{5}{3} = 1.67$$

(ii) Diatomic Gas:

A molecule of a diatomic gas like H_2, O_2, N_2 etc has two atoms which are bound together by attractive forces. Each molecule may be supposed as a system of two-point masses connected by one independent relation. So, $l = 1$

∴ $f = 2n - 1 = 3 \times 2 - 1 = 5$

Thus, the degree of freedom associated with diatomic molecule is 3 + 2 i.e., 3 due to translational motion and 2 due to rotational motion. But, at very high temperature greater than 500 K, vibrational motion is also executed with more 2 degree of freedom. then the total number of degree of freedom will be 7.

Thus, the kinetic energy associated per molecule $= \frac{5}{2} KT$

The kinetic energy associated per mole of internal energy is $= \frac{5}{2} (N_A K)T = \frac{5}{2} RT$

The molar specific heat of diatomic gas at constant volume is thus

$$C_V = \left(\frac{dU}{dT}\right)_v = \frac{5}{2} R$$

and $\quad C_P = C_V + R = \frac{7}{2} R$

∴ The adiabatic exponent

$$\gamma = \frac{C_P}{C_v} = \frac{7}{5} = 1.40$$

(iii) Triatomic Gas:

A molecule of triatomic gas like CO_2, H_2O, NO_2 etc. has three atoms. These are two types of triatomic gas.

(a) Linear triatomic molecule: In this case all the three atoms are related by 2 independent relations. So, its degree of freedom is $f = 3n - 1 = 3 \times 3 - 2 = 7$.

(b) Non-linear triatomic molecule: In this case the three atoms are arranged at the vertices of a triangle, so the number of independent relations in their positions will be 3.

∴ $\quad f = 3n - 1 = 3 \times 3 - 3 = 6$.

Thus, for triatomic gas with 7 degree of freedom has

$$C_V = \frac{7}{2} R \text{ and } C_P = \frac{9}{2} R$$

and $\quad \gamma = \frac{9}{7} = 1.28$

Similarly, for 6 degree of freedom has

$$C_V = 3R \text{ and } C_P = 4R$$

and $\gamma = \frac{4}{3} = 1.33$

Now, in general

$$\left. \begin{array}{l} C_v = \frac{f}{2} R \\ C_P = \left(\frac{f}{2} + 1\right) R \\ \gamma = \frac{f+2}{f} \end{array} \right\}$$

... 3.10

Example 3.4

Calculate the kinetic energy of one mole of (i) oxygen and (ii) argon at 127°C.

Solution:

(i) Oxygen is diatomic molecule, having 5 degree of freedom. Its kinetic energy will be

$$KE = \frac{f}{2} RT = \frac{5}{2} R \times 400 = 8.31 \times 10^3 \, J$$

(ii) Argon is monoatomic gas. So, its degree of freedom is 2 only. The kinetic energy of the gas is

$$KE = \frac{f}{2} RT = \frac{3}{2} R \times 400 = 4.98 \times 10^3 \, J$$

Example 3.5

Find the translational kinetic energy of one mole of a monoatomic gas at normal temperature and pressure. What will be its value at 273°C?

Solution:

The monoatomic gas has wholly translational energy only and 3 degree of freedom. So,

$$KE = \frac{3}{2} RT = \frac{3}{2} \times 8.31 \times 273 = 3.4 \times 10^3 J$$

At 273°C, $KE = \frac{3}{2} \times 8.31 \times 546 = 6.8 \times 10^3 J$

3.2.3 Vander-Waal's Equation of Real Gas

While deriving the perfect gas equation $PV = RT$, on the basis of kinetic energy, it was assuming that (i) size of the molecules of the gas is negligible and (ii) the force of inter-molecular attraction is absent. But, in actual practice, at high pressure the size of the molecules of the gas becomes significant and cannot be neglected in comparison with the volume of the gas. Also, at high pressure the molecules become closer and the forces of intermolecular attraction are appreciable. Thus, correction should be applied to derive the gas equation for real gas.

(a) Correction for pressure:

A molecule in the interior of a gas experiences forces of attraction in all direction and the resultant cohesive force is zero. A molecule near the walls of the container experiences a resultant force inward is away from the wall. Due to this reason the observed pressure of the gas is less than the actual pressure. The correction of pressure depends on (i) number of molecules striking unit area of the walls of the container per second and (ii) the number of molecules present in the given volume. Both of these factors depend on density of gas. So, the correction for pressure $p \propto \rho^2 \propto \frac{1}{V^2}$

$$\therefore p = \frac{a}{V^2} \qquad \qquad \text{... 3J1}$$

Where a is constant and V is the volume of the gas.

$$\therefore \text{Corrected pressure} = (P + p) = (P + \frac{a}{V^2}) \qquad \qquad \text{... 3J2}$$

(b) Correction for volume:

Kinetic molecular theory assumes that an individual molecule in a gas occupies no volume and moves about in a vacant space. But, in fact that molecule has finite size and shows that the actual space for the movement of the molecule is less than the volume of the vessel.

Now, let the radius of a single molecule be r of which volume be $x = (4/3)\pi r^3$.

For two non-compressible spherical molecules in contact, separated by a distance $2r$ (Figure 3.2), the volume of sphere of influence of each molecule $s = (4/3)\pi(2r)^3 = 8x$.

If V be the volume of the container and molecules are inserted one by one.

The volume available for the first molecule $= V$

The volume available for the second molecule $= V - 8x = V - s$

The volume available for the third molecule $= V - 2s$

Similarly, the volume available for nth molecule $= V - (n-1)s$

∴ Average space available for each molecule =

$$\frac{V + (V - s) + (V - 2s) + \ldots\ldots\ldots\ldots\ldots\ldots\ldots + \{V - (n-1)s\}}{n}$$

$$= \frac{nV}{n} - \frac{s}{n}\{1 + 2 + 3 + \ldots\ldots\ldots\ldots. + (n+1)\}$$

$$= V - \frac{s}{n} \cdot \frac{(n-1)n}{2} = V - \frac{ns}{2} + \frac{s}{2}$$

Here, $\frac{s}{2}$ is very small in comparison to V. So, average space available for each molecule

$$= V - \frac{ns}{2} = V - n(4x) \qquad \ldots 3.13$$
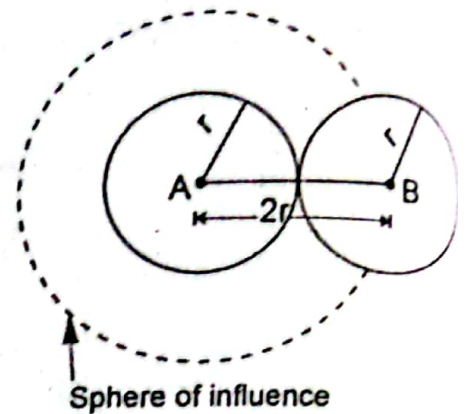

Sphere of influence

Figure 3.4

Let us suppose $b = 4 (nx) =$ four times the actual volume of the molecule.

Hence, the corrected kinetic gas equation will be

$$(P + \frac{a}{V^2})(V - b) = RT \qquad \ldots 3.14$$

This is known as Van der Waals equation for real gas, where a and b are Van der Waal constants.

Critical Constants

From Vander-Waal's equation of state, we have

$$(P + \frac{a}{V^2})(V - b) = RT$$

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \qquad \ldots 3.15$$

Now, plotting a graph between P with V, we get the nature of the curve as shown in figure 3.5 for CO_2 at temperatures 13.1°C, 21.5°C and 31.1°C for three roots.
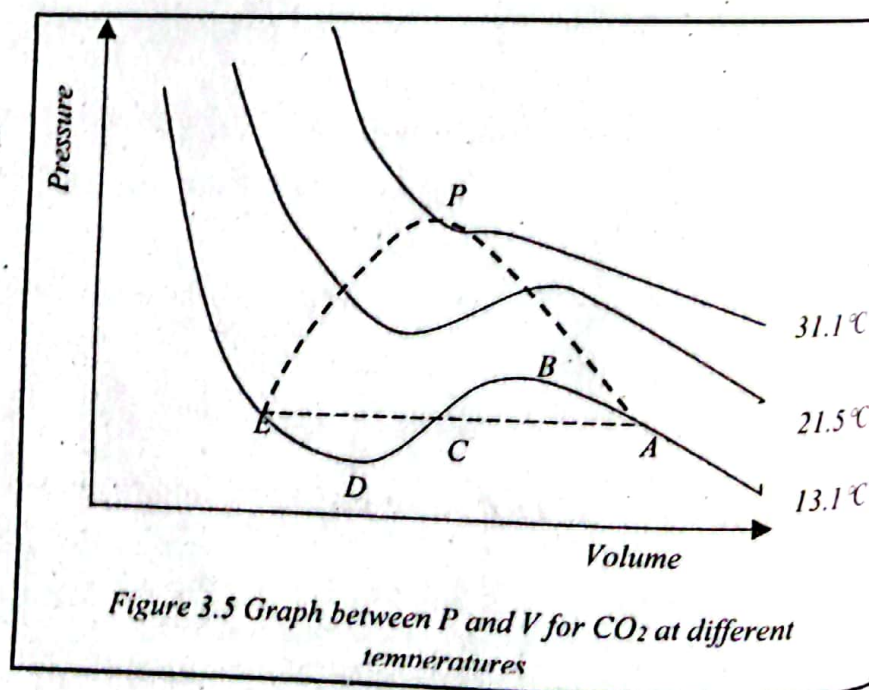

Figure 3.5 Graph between P and V for CO_2 at different temperatures

In the graph at low temperature, horizontal portion is absent, instead the curve ABCDE is obtained. This does not agree with the experimental isothermals of CO_2 as obtained by Andrews. In this case, AB represents the super-cooling of the vapour and ED due to the super-heating of the liquid. But, the curve BCD cannot be explained, because it shows decrease in volume with decrease in pressure. At higher temperature, theoretical and experimental values are similar. In such curve there are three volumes with the single value of pressure. We also find that with the increase of pressure volume will decrease. At point P three roots of Vander Waals equation will identical i.e., volume of liquid will be equal to the volume of substance as gas, i.e., there is no difference between liquid and gaseous state, called critical state or critical condition. The volume, pressure and temperature are critical corresponding to this point.

At critical point, the rate of change of pressure with volume, also called point of inflexion i.e. $\frac{dP}{dV} = 0$.

Thus, differentiating equation 3.15 with respect to V and equating to zero, we get

$$\frac{dP}{dV} = 0 = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} \qquad \ldots 3.16$$

Now, at this point $T = T_C$ and $V = V_C$, we get

$$\frac{2a}{V_C^3} = \frac{RT_C}{(V_C-b)^2} \qquad \ldots 3.17$$

Again, differentiating equation 3.16 and setting $\frac{d^2P}{dV^2} = 0$, we get

$$\frac{3a}{V_C^4} = \frac{2RT_C}{(V_C-b)^3}. \qquad \ldots 3.18$$

Now, dividing equation 3.17 by equation 3.18, we get

$$\left. \begin{array}{l} V_C = 3b \\[2mm] T_C = \dfrac{8a}{27Rb} \\[2mm] P_C = \dfrac{a}{27b^2} \end{array} \right\} \qquad \ldots 3.19$$

These are Van der Waals critical constants. The Van der Waals coefficients are also determined in terms of critical constants from equation 3.19 i.e.,

$$a = \frac{27}{64}\left(\frac{R^2 T_C^2}{P_C}\right)$$

$$\text{and } b = \frac{V_C}{3} = \frac{RT_C}{8P_C}$$

... 3.20

The ratio of RT_C and $P_C V_C$ is always constant for all gases and is called critical coefficient.

i.e., $\qquad \frac{RT_C}{P_C V_C} = \frac{8}{3}$ $\qquad\qquad$ ... 3.21

Example 3.6

If the dry air has $T_C = 132K$, $P_C = 37.2$ atmospheres. Calculate the Van der Waals constants.

Solution:

Here, $\quad P_C = 37.2$ atmospheres $= 37.2 \times 1.01 \times 10^5 \ N/m^2$

$\qquad R = 8.31 \ J/mol.K$

$\qquad T_C = 132K$

We know, $a = \frac{27}{64}\left(\frac{R^2 T_C^2}{P_C}\right)$

$\qquad a = \frac{27}{64}\left(\frac{8.31^2 \times 132^2}{37.2 \times 1.01 \times 10^5}\right) = 13.51 \times 10^{-2} \ N/m^2 \, m^6$

$\qquad b = \frac{RT_C}{8P_C} = \frac{8.31 \times 132}{8 \times 37.2 \times 1.01 \times 10^5} = 3.65 \times 10^{-5} \ m^3.$

Example 3.7

Calculate the critical constants of a gas if Van der Waals coefficients are $a = 13.31 \times 10^5$ atmospheres cm³ and $b = 36.42 \, cm^3$ and $R = 82.07 \, cm^3$ atoms K.

Solution:

We know, the critical constants of the gas at critical point are

$\qquad V_C = 3b = 109.23 \ cm^3$

$\qquad T_C = \frac{8a}{27Rb} = \frac{8 \times 13.31 \times 10^5}{27 \times 82.07 \times 36.42} = 132K$

$\qquad P_C = \frac{a}{27b^2} = \frac{13.31 \times 10^5}{27 \times (36.41)^2} = 37.2 \ atoms$

3.3 Thermodynamics

3.3.1 Laws of Thermodynamics

In the early stages, thermodynamics was concerned with the relationship between mechanical and heat energy only. Further, development turned thermodynamics into a science that is concerned with heat and all kinds of energy such as chemical, electrical