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B.Sc. (Hons) Thermal Physics

Chapter - 7, 8

7. Molecular Collisions

8. Real Gases

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Chapter - 7
Molecular Collisions

> **Molecular Collisions**: Mean Free Path. Collision Probability. Estimation of Mean Free Path. Transport Phenomenon in Ideal Gases: (1) Viscosity, (2) Thermal Conductivity

**Que1: Define mean free path for a molecule/particle.**

Ans: In physics, the mean free path is the average distance traveled by a moving particle (such as an atom, a molecule, a photon) between successive impacts (collisions), which modify its direction or energy or other particle properties**.**

Que2: Derive an expression for number of collisions for a gas molecule in a given volume.

Ans:

Number of collisions per unit area per second (*flux*)

Consider a volume of gas with concentration n and mean velocity v and lets see how many molecules will pass through an area A per unit time. We further split our velocity in three components one of which is perpendicular to area A (we done this before in kinetic theory). Then in time t about 1/6 of the molecules in the volume vtA will pass through A and hence flux j:

$$l = \bar{v}t$$

$$V = lA = \bar{v}tA$$
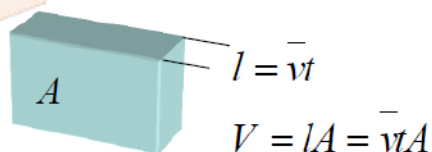
$$j = \frac{1}{6}\frac{n\bar{v}At}{At} = \frac{1}{6}n\bar{v}$$
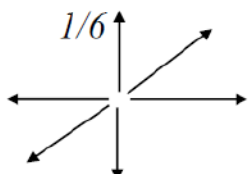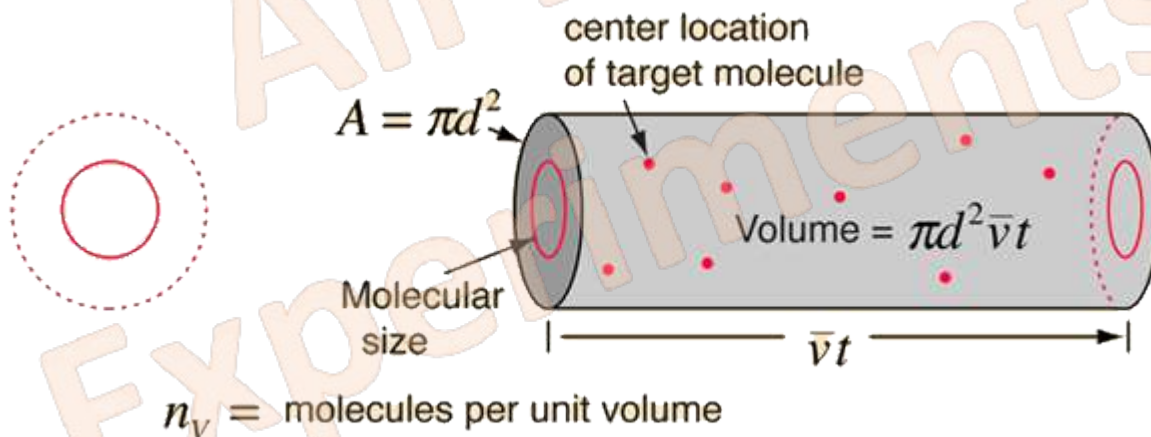
Que3 : Estimate Mean Free Path using Kinetic Theory of gases.

Ans: The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory. Serway's approach is a good visualization - if the molecules have diameter d, then the effective cross-section for collision can be modeled by

The effective collision area is

$$A = \pi d^2$$
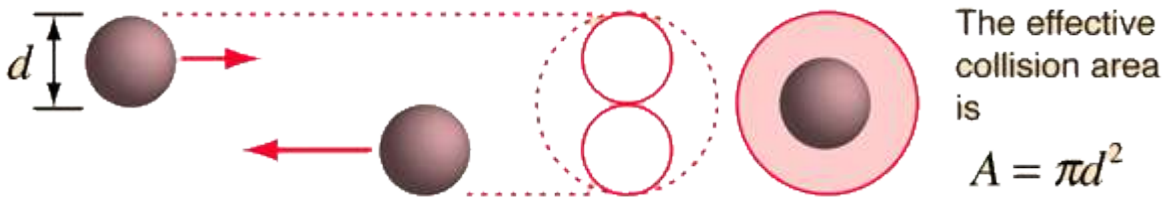
using a circle of diameter 2d to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume

$$A = \pi d^2$$

center location of target molecule

Volume = $\pi d^2 \bar{v} t$

Molecular size

$\bar{v} t$

$n_V = $ molecules per unit volume

The mean free path could then be taken as the length of the path divided by the number of collisions.

Distance traveled

Mean distance per collision

$$\text{Mean free path estimate} = \frac{\bar{v} t}{\pi d^2 \bar{v} t \, n_V} = \frac{1}{\pi d^2 n_V}$$

Volume of interaction

Number of molecules per unit volume

The problem with this expression is that the average molecular velocity is used, but the target molecules are also moving. The frequency of collisions depends upon the average relative velocity of the randomly moving molecules.

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which revises the expression for the effective volume swept out in time t

Effective volume of targets swept $\pi d^2 \sqrt{2}\, \bar{v} t$

The number of collisions is $\sqrt{2}$ times the number with stationary targets.

The resulting mean free path is

$$n_V = \frac{nN_A}{V} = \frac{nN_A}{\frac{nRT}{P}} = \frac{N_A P}{RT}$$

Mean free path

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

Que4 : Explain Diffusion, Viscosity and Thermal conductivity in gases and derive the mathematical expressions.
**Ans:**

Diffusion

Now if we consider gas with a concentration gradient it should be clear that molecules will move from the more concentrated to the less concentrated regions via a process of collision/random walk. This is diffusion process. If over distance dx concentration change is dn the concentration gradient is dn/dx. The number of molecules crossing A normal to gradient per second can then be written as:

$$\frac{dN}{dt} = -D\frac{dn}{dx}A \qquad \left(j = \frac{dN}{Adt} = -D\frac{dn}{dx}\right) \qquad \text{Fick's Law}$$

Where D is called the coefficient of self-diffusion and the negative sign implies flow in the direction of smaller concentration.

Consider the following situation:
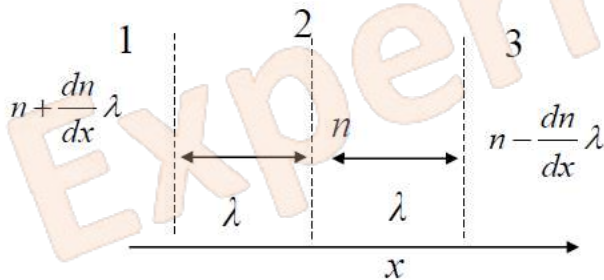
We would then have the number of molecules per second crossing from 1

$$= \frac{1}{6}\left(n + \frac{dn}{dx}\lambda\right)\bar{v}A$$

and from 3

$$= \frac{1}{6}\left(n - \frac{dn}{dx}\lambda\right)\bar{v}A$$

There will also be molecules leaving on each side of 2 of number $= \frac{1}{6}n\bar{v}A$

So the net transfer is then

$$-\frac{1}{6}\left(n + \frac{dn}{dx}\lambda\right)\bar{v}A + \frac{1}{6}\left(n - \frac{dn}{dx}\lambda\right)\bar{v}A - \frac{1}{6}n\bar{v}A + \frac{1}{6}n\bar{v}A = -\frac{1}{3}\frac{dn}{dx}\lambda\bar{v}A = -D\frac{dn}{dx}A$$

hence

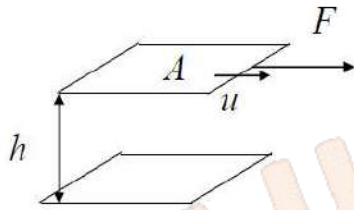$$D = \frac{\bar{\lambda v}}{3} = \frac{\bar{v}}{3\pi n \sigma^2}$$

For air at STP $\sigma = 0.3$nm, $\lambda \approx 100$nm, $v = 450$m/s, $n \approx 3 \times 10^{25}$m^{-3} which gives D of order 10^{-2} m^2/s

also

$$\bar{v} = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$
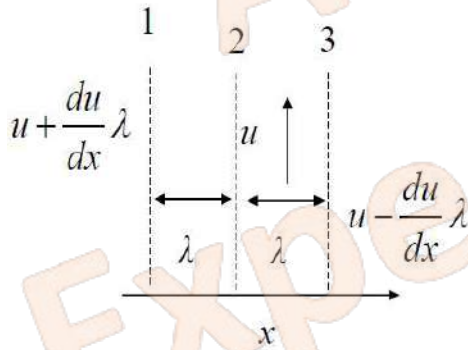
hence D can be related with macroscopic T and also P and V through n

Viscosity

F must be applied to maintain constant flow. F is proportional to A and u/h.

$$F = \eta A \frac{du}{dx}$$

We further assume: (i) $u \ll v$, (ii) the only molecules reaching 2 are those that just made their collision at a distance λ. Thus the number of molecules crossing A is $\frac{1}{6}\bar{nv}A$ per second and from 3 this molecules bring to 2 net horizontal momentum

$$m\left(u - \frac{du}{dx}\lambda\right)\frac{\bar{nv}}{6}A$$
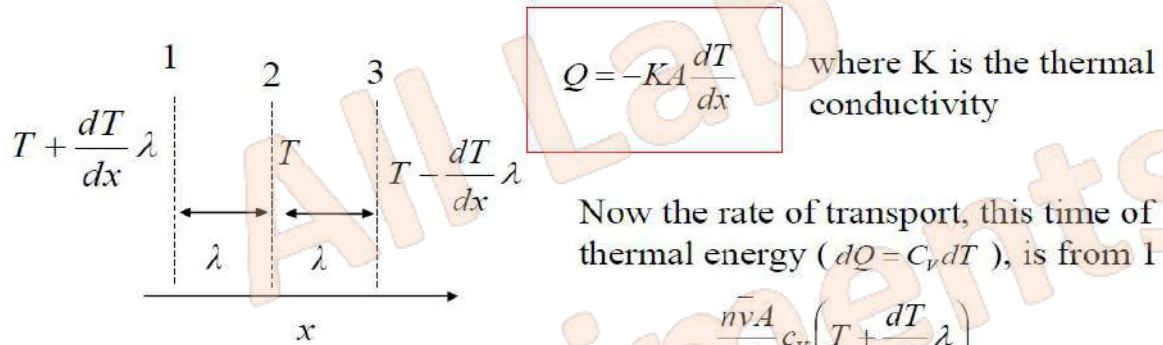
Similarly fro 1 to 2 $m\left(u + \frac{du}{dx}\lambda\right)\frac{\bar{nv}}{6}A$

But 2 sends $\frac{1}{6}\bar{nv}A$ both ways too

Thus the total momentum transfer per second (i.e. force) is

$$F = \frac{m\lambda \bar{nv}}{3}A\frac{du}{dx} \Rightarrow \eta = \frac{1}{3}m\lambda \bar{nv} = \frac{1}{3}\frac{m\bar{v}}{\pi\sigma^2}$$

Thermal conductivity

$$Q = -KA \frac{dT}{dx}$$ where K is the thermal conductivity

$$T + \frac{dT}{dx}\lambda$$

$$T$$

$$T - \frac{dT}{dx}\lambda$$

$$\lambda \qquad \lambda$$

$$x$$

Now the rate of transport, this time of thermal energy ($dQ = C_V dT$), is from 1

$$\frac{\overline{nv}A}{6} c_v \left(T + \frac{dT}{dx}\lambda \right)$$

from 3 $$\frac{\overline{nv}A}{6} c_v \left(T - \frac{dT}{dx}\lambda \right)$$ so the net transfer at 2 is $$\frac{\overline{nv}A}{3} c_v \left(\frac{dT}{dx}\lambda \right)$$

hence $$Q = -\frac{\overline{nv}A}{3} c_v \lambda \frac{dT}{dx} \Rightarrow K = \frac{\overline{nv}\lambda}{3} c_v$$

Chapter – 8
Real Gases

Real Gases: Behavior of Real Gases: Deviations from the Ideal Gas Equation. Andrew's Experiments on CO_2 Gas. Virial Equation. Critical Constants. Continuity of Liquid and Gaseous State. Vapour and Gas. Boyle Temperature. van der Waal's Equation of State for Real Gases. Values of Critical Constants. Law of Corresponding States. Comparison with Experimental Curves. p-V Diagrams. Free Adiabatic Expansion of a Perfect Gas. Joule-Thomson Porous Plug Experiment. Joule-Thomson Effect for Real and van der Waal Gases. Temperature of Inversion. Joule-Thomson Cooling.   **(10 Lectures)**

Que1: Distinguish between Ideal and Real Gases.

Ans: A gas which obeys the ideal gas equation, PV = nRT under all conditions of temperature and pressure is called an '**ideal gas**'. However, there is no gas which obeys the ideal gas equation under all conditions of temperature and pressure. Hence, the concept of ideal gas is only theoretical or hypothetical. The gases are found to obey the gas laws fairly well if the pressure is low or the temperature is high. Such gases are, therefore, known as '**Real gases.**' All gases are real gases. However, it is found that gases which are soluble in water or are easily liquefiable, e. g. CO_2, SO_2, NH_3 etc. show larger deviations than the gases like H_2, O_2, N_2 etc.

Differences between Ideal Gas and Real Gas

Ideal Gases obey all gas laws under all conditions of temperature and pressure.	Real Gases obey gas laws only at low pressures and high temperature.
The volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.	The volume occupied by the molecules is not negligible as compared to the total volume of the gas.
The force of attraction among the molecules are negligible.	The force of attraction are not negligible at all temperatures and pressures.
Obeys ideal gas equation PV = nRT	Obey Van der Waals equation $(P + an^2/V^2)(V - nb) = nRT$

Que2: Explain the causes of deviation from Ideal gas behavior.

Ans: Causes of Deviation from Ideal Behaviour
As stated above, the real gases obey ideal gas equation (PV = nRT) only if the pressure is low the temperature is high. However, if the pressure is high or the temperature is

low, the real gases show marked deviations from ideal behaviour. The reasons for such a behaviour shown by the real gases have been found to be as follows:

The derivation of the gas laws (and hence of the ideal gas equation) is based upon the Kinetic Theory of Gases which in turn is based upon certain assumptions. Thus, there must be something wrong with certain assumptions. A careful study shows that at high pressure or low temperature, two assumptions of Kinetic Theory of Gases are fails:

- When compared to the total volume of the gas, the volume occupied by the gas molecules is negligible.
- The forces of attraction or repulsion between the gas molecules are negligible.

The above two assumptions are true only if the pressure is low or the temperature is high so that the distance between the molecules is large. However, if the pressure is high or the temperature is low, the gas molecules come close together. Hence, under these conditions:

- The forces of attraction or repulsion between the molecules.
- The volume occupied by the gas may be so small that the volume occupied by the molecules may not be negligible.

## Que3: Explain the van der Waals Equation of State for Real gases.

Ans: The ideal gas law treats the molecules of a gas as point particles with perfectly elastic collisions. This works well for dilute gases in many experimental circumstances. But gas molecules are not point masses, and there are circumstances where the properties of the molecules have an experimentally measurable effect. A modification of the ideal gas law was proposed by Johannes D. van der Waals in 1873 to take into account molecular size and molecular interaction forces. It is usually referred to as the van der Waals equation of state.

The constants a and b have positive values and are characteristic of the individual gas. The van der Waals equation of state approaches the ideal gas law PV=nRT as the values of these constants approach zero. The constant a provides a correction for the intermolecular forces. Constant b is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

Que4: Explain the deviation of Real gases using PV diagrams.

Ans: To understand the deviations from ideal behaviour, let us first see how the real gases show deviations from Boyle's law. According to Boyle's law, PV = constant, at constant temperature. Hence, at constant temperature, plot of PV vs. P has to be a straight line which is parallel to x-axis. However, the real gases do not show such a behaviour as shown in figure no. 1 below.

From the plots, we observe that for gases like H_2 and He, PV increases continuously with increase of pressure whereas for gases like CO, CH_4 etc. PV first decreases with increase of pressure and reaches a minimum value and then increases continuously with increase of pressure.
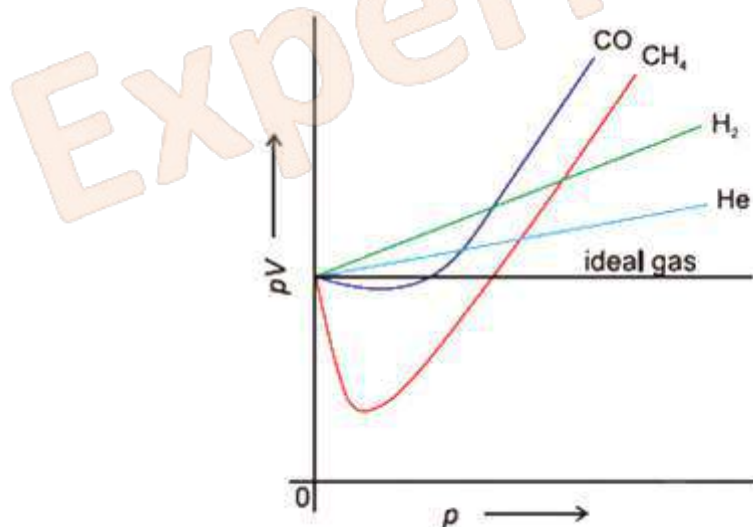
From above graph, we observe that at higher pressure, volume which is observed is higher than that of calculated volume. At lower pressures, the observed and the calculated volumes approach each other.

Que5: Explain the deviation of Real gases from Idea gas equation using compressibility factor.

Ans: Extent upto which a real gas deviates from ideal behaviour can be studied using the terms of a quantity 'Z' which is known as the compressibility factor, and defined as:

$$Z = \frac{V_{real}}{V_{ideal}}$$

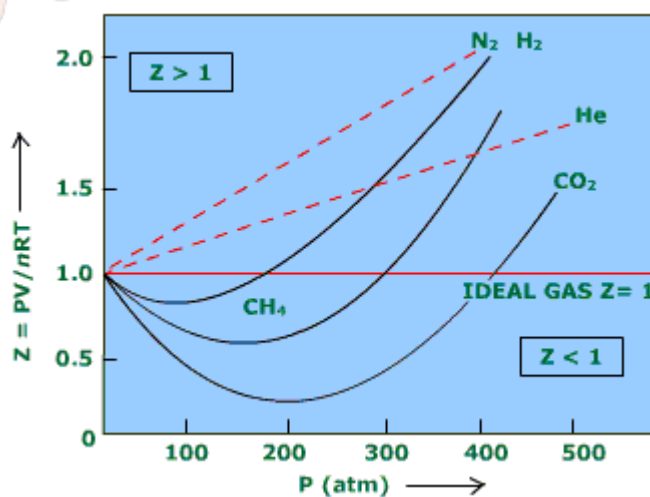(i) For an ideal gas, as PV = nRT, Z = 1

(ii) For a real gas, as PV ≠ nRT, Z ≠ 1.

Hence,   two   cases   arise:
(a) When Z < 1, (**For Example:** for CH_4, CO_2 etc.) The gas is said to show negative deviation. Therefore, gas will show more compression than expected from ideal behaviour.
This is caused by predominance of attractive forces among the molecules of these gases.
(b) When Z > 1, the gas is said to show positive deviation. This implies that the gas will show less compression than expected from ideal behaviour.
This is caused by the predominance of the strong repulsive forces among the molecules. Greater the departure in the value of Z from unity, greater are the deviations from ideal behaviour.

At the same temperature and pressure, the extent of deviation depends upon the nature of the gas, as shown in figure below. Thus, at intermediate pressures, CO_2 shows much larger negative deviation than H_2 or N_2.

Que6: Explain Virial equation.

Ans:

The compressibility factor of a gas Z is defined as $Z = pV/(nRT) = pV_m/(RT)$, where the subscript on V indicates that this is a molar quantity. Obviously, for an ideal gas, $Z = 1$ always. For real gases, additional corrections have to be introduced. Virial equations are expressions in which such corrections can be systematically incorporated. For example,

$$Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \ldots$$

We may substitute for V_m in terms of the ideal gas law and get an expression in terms of pressure, which is often more convenient to use:

$$Z = 1 + \frac{B}{RT}p + \frac{C}{(RT)^2}p^2 + ...$$
$$1 + B'(T)p + C'(T)p^2 + ...$$

The constants B, C' etc., have to be found experimentally for each gas.

Que7: Define Critical Point of a Real gas.

Ans: Liquid and gas can coexist only within the regions indicated by the green-shaded area in the diagram above. As the temperature and pressure rise, this region becomes more narrow, finally reaching zero width at the critical point. The values of P, T, and V at this juncture are known as the critical constants P_c, T_c, and V_c. The isotherm that passes through the critical point is called the critical isotherm. Beyond this isotherm, the gas and liquids become indistinguishable; there is only a single fluid phase, sometimes referred to as a supercritical liquid (Figure below).
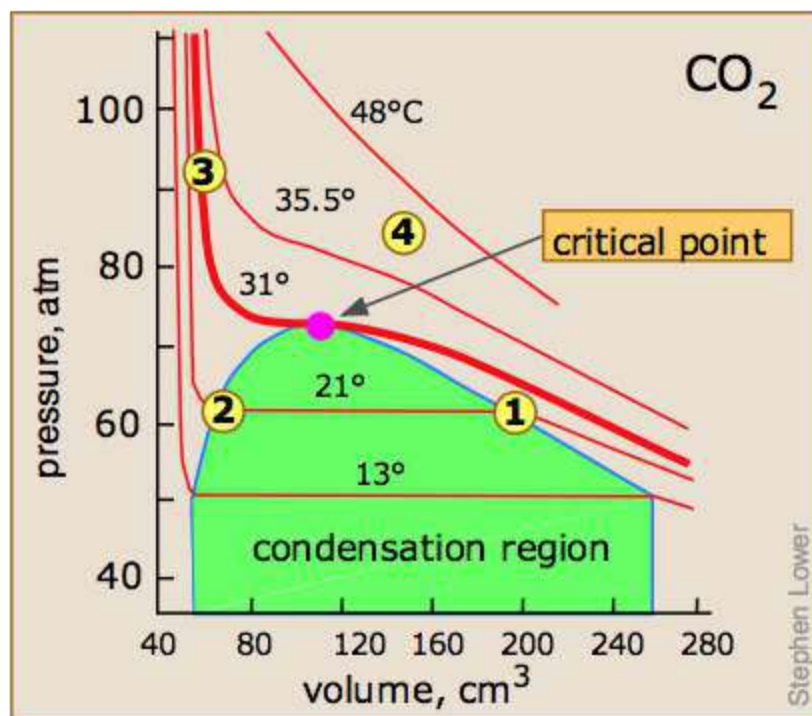
At temperatures below 31°C (the critical temperature), CO_2 acts somewhat like an ideal gas even at a rather high pressure. Below 31°, an attempt to compress the gas to a smaller volume eventually causes condensation to begin. Thus at 21°C, at a pressure of about 62 atm , the volume can be reduced from 200 cm³ to about 55 cm³ without any

further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared, the pressure rises very rapidly because now all that remains is an almost incompressible liquid. Above this isotherm, CO_2 exists only as a supercritical fluid.

Que8: Calculate critical constants for a Real gas.

Ans: Van der Waals equation of state for real gas is given as

$$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=\left(p+a\left(\frac{n}{V}\right)^2\right)\left(\frac{V}{n}-b\right)=RT$$

In order to find the relationship between the critical parameters p_k, V_k and T_k and the van der Waals constants a and b, one considers the shape of the critical isotherm that has an inflection point at the critical point. At this point the critical isotherm has both a horizontal tangent $\partial p/\partial V_m{}_T=0$ and a vanishing second derivative $\partial^2 p/\partial V_m^2{}_-=0$. The partial derivatives are:

$$\left(\frac{\partial p}{\partial V_m}\right)_T=-\frac{RT_k}{(V_{mk}-b)^2}+\frac{2a}{V_{mk}^3}=0$$

$$\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T=\frac{2RT_k}{(V_{mk}-b)^3}-\frac{6a}{V_{mk}^4}=0$$

With the van der Waals state equation the critical point can be evaluated as:

$$p_k=\frac{a}{27b^2},\quad T_k=\frac{8a}{27Rb},\quad V_{mk}=3b$$

or

$$a=\frac{27R^2T_k^2}{64p_k},\quad b=\frac{RT_k}{8p_k}.$$

Que9: Define Boyle temperature or Boyle point.

Ans: The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point.

Que10: Give an Explanation of the Behaviour of Real Gases by van der Waals Equation.

Ans:

- **At Very Low Pressures**, V is very large. Hence, the correction term a/V^2 is so small that it can be neglected, Similarly, the correction term 'b' can also be neglected in comparison to V. Thus, van der Waals equation reduces to the form PV = RT. This explains why at very low pressures, the real gases behave like ideal gases.
- **At Moderate Pressures**, V decreases. Hence, a/V^2 increases and cannot be neglected. However, is still large enough in comparision to 'b' so that 'b' can be neglected. Thus, van der Waals equation becomes

$$\left(P + \frac{a}{v^2}\right)V = RT \ \text{ or } \ RV + \frac{a}{V} = RT \ \text{ or } \ PV = \ RT - \frac{a}{V}$$

$$\text{OR} \quad \frac{PV}{RT} = 1 - \frac{q}{RTV}$$

$$\text{OR} \quad Z = 1 - \frac{a}{RTV}$$

Thus, compressibility factor is less than 1. So at when at constant temperature, pressure is increased, V decreases so that the factor a/RTV increases. This explains why initially a dip in the plot of Z versus P is observed.

- **At High Pressures**, V is so small that 'b' cannot be neglected in comparison to V. The factor a/V^2 is no doubt large but as P is very high, a/V^2 can be neglected in comparison to P. Thus, van der Waals equation reduces to the form:

$$P(V - b) = RT \ \text{ or } \ PV = RT + Pb$$

$$\text{OR} \quad \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$\text{OR} \quad Z = 1 + \frac{Pb}{RT}$$

Thus, compressibility factor is greater than 1. As P is increased (at constant T), the factor Pb/RT increases. This explains why after minima in the curves, the compressibility factor increases continuously with pressure.

- **At High Temperatures:** V is very large (at a given pressure) so that both the correction factors (a/V^2 and b) become negligible as in case (i). Hence, at high temperature, real gases behave like ideal gas.

Que11: Explain Free adiabatic expansion of a perfect gas.

Ans: Free expansion is an irreversible process in which a gas expands into an insulated evacuated chamber. It is also called Joule expansion.
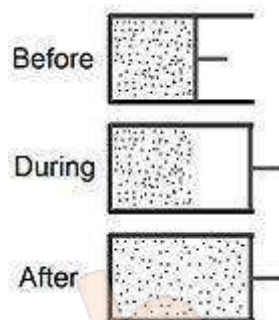
Real gases experience a temperature change during free expansion. For an ideal gas, the temperature doesn't change.

Adiabatic free expansion of a perfect gas

For an adiabatic free expansion of an ideal gas, the gas is contained in an insulated container and then allowed to expand in a vacuum. Because there is no external pressure for the gas to expand against, the work done by or on the system is zero. Since this process does not involve any heat transfer or work, the first law of thermodynamics then implies that the net internal energy change of the system is zero. For an ideal gas, the temperature remains constant because the internal energy only depends on temperature in that case. Since at constant temperature, the entropy is proportional to the volume, the entropy increases in this case, therefore this process is irreversible.

Que12: Explain Joule-Thomson effect for Ideal and Real gases.

Ans:

By the **Joule-Thomson effect** we refer to a change in the temperature of a gas which occurs during adiabatic expansion of gas through a throttle from high pressure p_1 to lower pressure p_2. We will now calculate this change in temperature. Similar to the Joule effect, this is an irreversible process.

Assume that before the expansion, the gas occupies volume V_1, after the expansion - V_2. We can think of the system as having two pistons, one at each side of the throttle, that keeps the pressures p_1 and p_2 constants (see Figure 4).
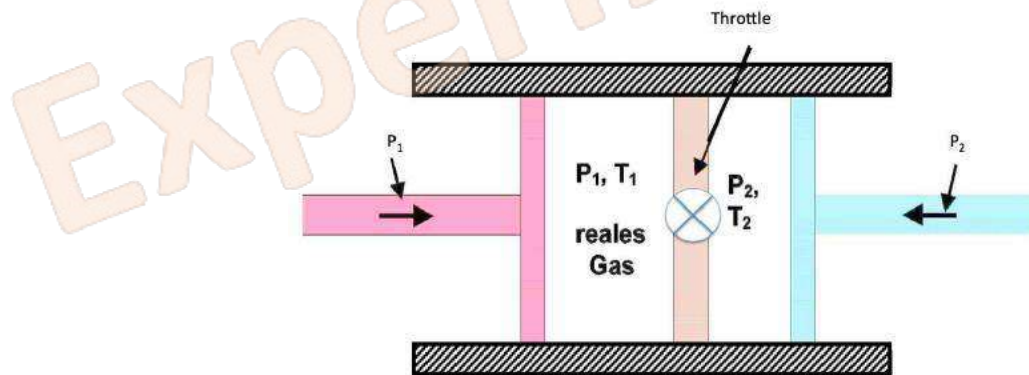

Fig. 4.— The Joule-Thomson expansion through a throttle. The two pistons ensure constant pressures on the two sides of the throttle.

The work done on the gas by the pistons is

$$W = - \int_{V_1}^{0} p_1 dV - \int_{0}^{V_2} p_2 dV = -p_1(0 - V_1) - p_2(V_2 - 0) = p_1 V_1 - p_2 V_2$$

The device is thermally isolated. Thus, from the first law $\Delta E = Q + W = W$, or

$$E_2 - E_1 = p_1 V_1 - p_2 V_2$$
$$E_2 + p_2 V_2 = E_1 + p_1 V_1.$$

Recall the definition of the Enthalpy, $H \equiv E + pV$; Equation 42 is simply $H_1 = H_2$. Thus, the Joule-Thomson process conserves the enthalpy - it is an **isenthalpic** process.

We can now repeat similar calculations to those used in calculating the temperature in the Joule effect (Equations 30 - 36), but with H replacing E and p replacing V. We use $dH(T, p) = 0$; The temperature T and the pressure p change during the process, and so

$$\left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = 0.$$

we can define the **Joule-Thomson coefficient,**

$$\alpha_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}.$$

The denominator in above equation is

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_p,$$

from which

$$\alpha_{JT} = -\frac{1}{C_p}\left[\left(\frac{\partial E}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial p}\right)_T\right].$$

We can write the numerator using the fundamental relation:

$$
\begin{aligned}
dE &= TdS - pdV \\
dS &= \tfrac{1}{T}dE + \tfrac{p}{T}dV \\
&= \tfrac{1}{T}dH - \tfrac{V}{T}dp.
\end{aligned}
$$

Let us substitute in:

$$
\begin{aligned}
dS &= \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT \\
dH &= \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT.
\end{aligned}
$$

Equating coefficients of dT, dp, one gets

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p ;$$
$$\left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right].$$

cross-differentiate $(\partial^2 S/(\partial p \partial T) = \partial^2 S/(\partial T \partial p))$ and simplify, one gets

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p,$$

from which we obtain

$$\alpha_{JT} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$$

For an ideal gas, $\alpha_{JT} = 0$; thus, the temperature of the gas doesn't change. However, even for non-ideal gas, $\alpha_{JT} = 0$ provided that

$$T\left(\frac{\partial V}{\partial T}\right)_p = V$$

Equation above defines a curve in the T − p plane (see Figure 5): this curve is known as inversion   curve.
Also plotted in the figure are **isenthalps**, curves of constant enthalpy.

Inside the inversion curve, T increases with p along isenthalp, and thus $\alpha_{JT} = (\partial T/\partial p)_H > 0$: the gas cools in expansion. Outside the inversion curve, $\alpha_{JT} < 0$, and so the gas *warms up* in expansion. Above a certain temperature, T_i, known as the **inversion temperature**, the gas is always outside the inversion curve, and thus it is always warmed in Joule-Thomson expansion. For most gases, T_i is above room temperature.
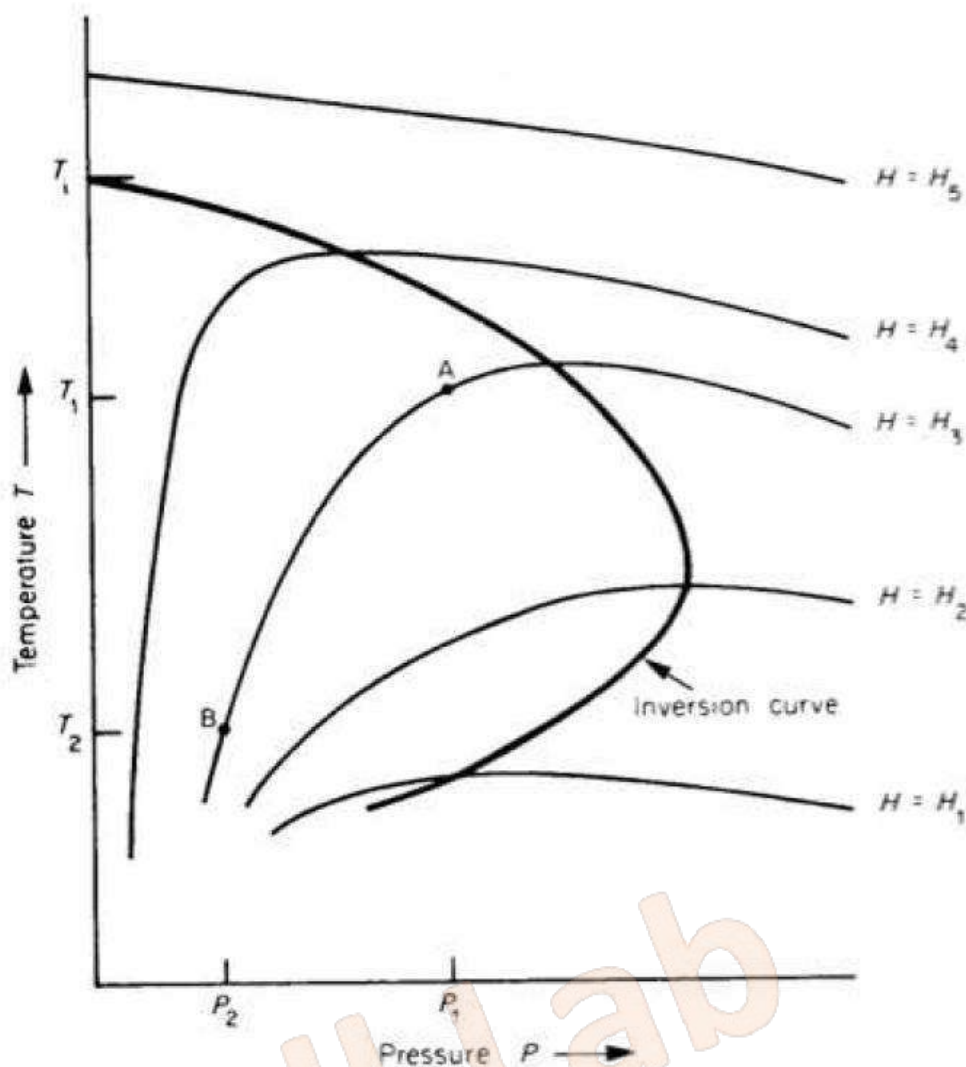
Fig. 5.— Inversion curve in the T-p plane is shown in bold. The solid lines are isenthalps (=curves of constant enthalpy, $H(p, T) = Const$). Inside the inversion curve, T increases with p along isenthalp, while outside it decreases.

Calculation of temperature change during Joule-Thomson expansion is done using

$$\Delta T = T_2 - T_1 = \int_{p_1}^{p_2} \left(\frac{\partial T}{\partial p} \right)_H dp$$

This is difficult to evaluate analytically, since non-ideal gases often do not have a simple relation between T and p. But this equation can easily be solved numerically.