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Chapter-11. Concept of Real & Ideal gases

Concept of ideal and Real gases.

That types of gas which obeys gas law i.e. boyle's law, charle's law are known as ideal gas. Such gases have negligible mass and negligible attraction between two molecules.

That types of gas which doesnot obey the gas laws (PV = RT) at very high pressure and low temp^r. is known as real gases.

Joule-Thomson Expansion/porous plug experiment

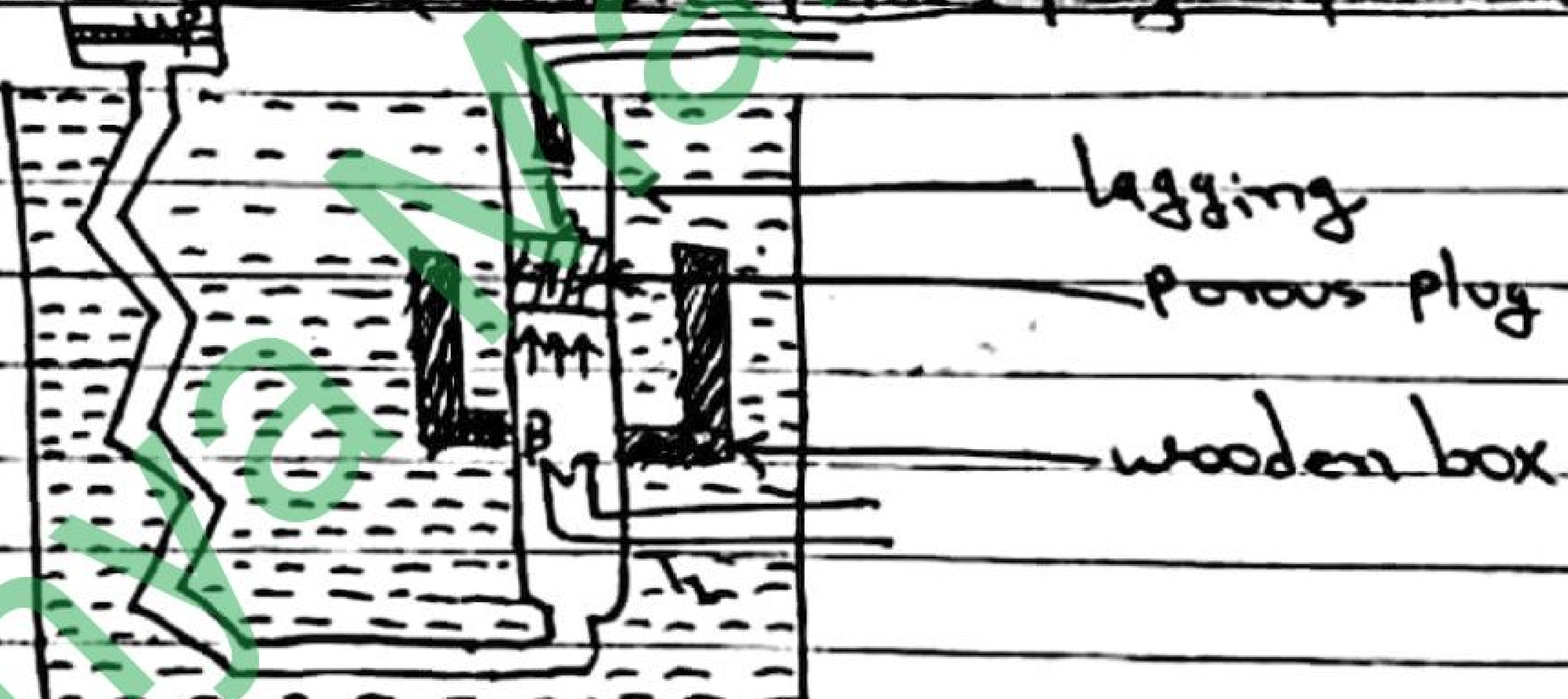

Fig:- Porous plug experiment.

Joule and Thomson devised a new technique which show the presence of intermolecular attraction. The gas under the experiment is compressed to a high pressure with the help of piston 'P' and is passed through a long spiral tube S immersed in a water bath 'w' maintained a constant temperature.

The compressed gas enters the tube B filled with a porous plug G of cotton, wool or silk fibre. The plug is contained between two pretorated brass disc DD'. when the gas ~~follows~~ flows through the plug, it suffers a large drop in pressure. When its flow ~~between~~ becomes steady, the temp. of gas on two sides of plug is measured with platinum resistance thermometer T_1 and T_2. Therefore the gas passing through the plug suffers a fall in temp. Since, a cooling of gas was actually demonstrated by Joule and Thomson in their famous porous plug experiment i.e. indicating the existence of intermolecular attraction and hence it is called ~~by~~ the Joule-Thomson or Joule Kelvin effect.

Constancy of Enthalpy (Theory of Joule-Thomson expansion)

⇒ Enthalpy is defined as the total heat content in the system. Mathematically $H = U + PV$.

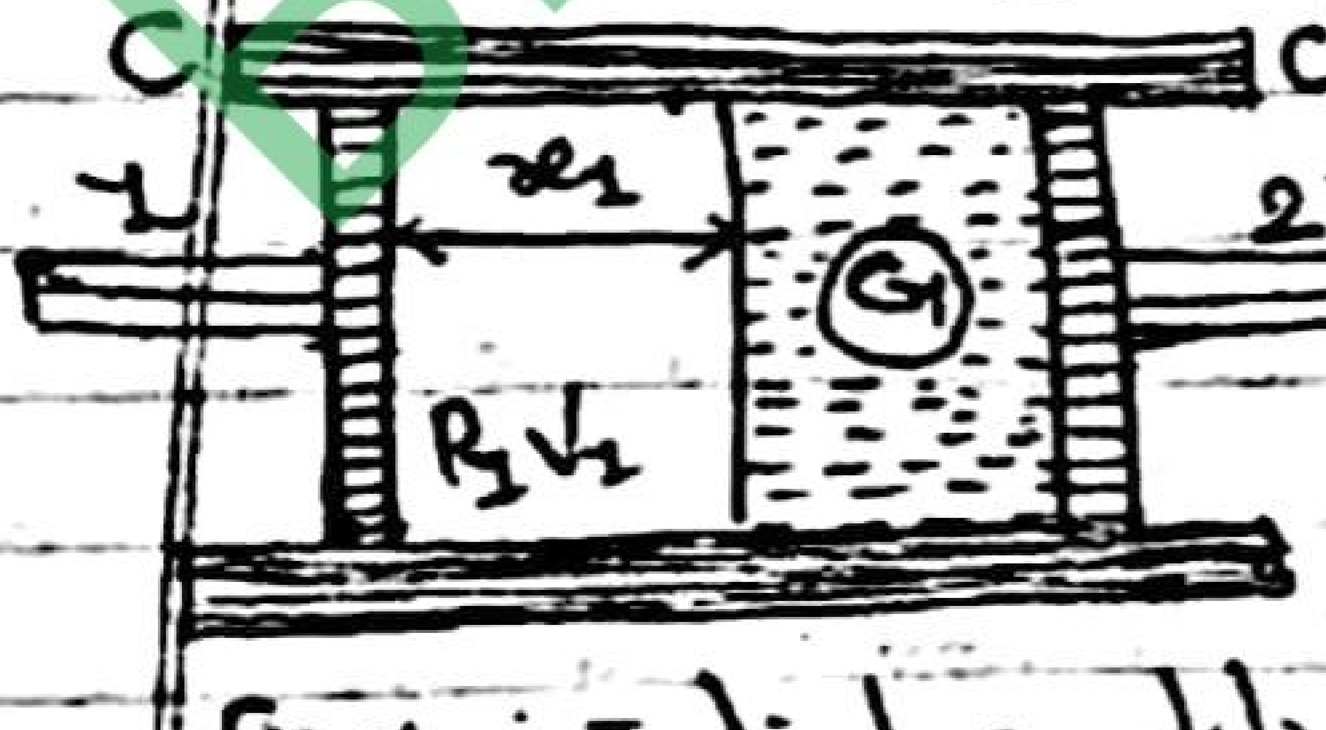

Fig. 1 : Initial condition for J-T

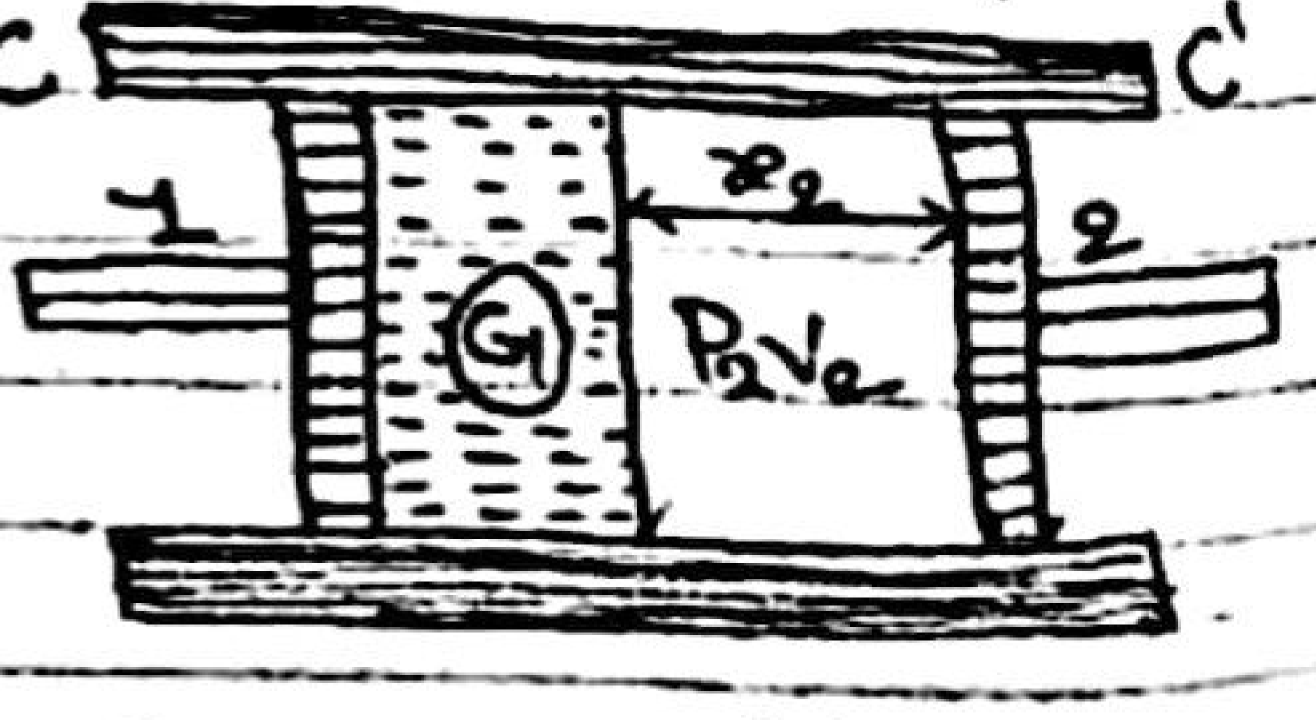

Fig. 2 : Final condition for J-T

The simple arrangement of the porous plug experiment is shown in figure. The gas is allowed to pass through porous plug from high pressure side to low pressure side.

CC' is a cylinder with non-conducting walls having porous plug G and fitted with two non-conducting piston 1 and 2. A fixed mass of gas having volume V_2 is filled in between the piston 1 and porous plug. Let ~~its~~ pressure P_1 and the pressure on other side P_2. Due to a large difference of pressure the gas flows through the porous plug and gets throttled.

Now let piston 1 be moved slowly inwards in such a way so as to keep a constant pressure P_1 on left of plug. The piston 2 ~~with~~ will move slowly outwards so as to keep a lower constant pressure P_2 on right side of plug. The gas will now occupy a greater volume say V_2. If x_1 and x_2 are the distance through which piston 1 and 2 move and A is the area of cross section of the piston then,

External workdone on the gas by piston 1

$= P_1 \times A \times x_1 = P_1V_1$ [$\because V_1 = A \times x_1$]

External workdone by the escaping gas on piston 2

$= P_2 \times A \times x_2 = P_2V_2$

∴ Net external workdone by the gas in passing through the plug $= P_2V_2 - P_1V_1$

As the cylinder is thermally insulated so no heat is exchanged between the gas and its surrounding. Also the net workdone by the gas = Change in internal energy.

If U_1 and U_2 be the intial and final internal energy, then

Change in internal energy $= U_1 - U_2$

$\therefore U_1 - U_2 =$ Net workdone by gas.

or, $U_1 - U_2 = P_2V_2 - P_1V_1$

or, $U_1 + P_1V_1 = U_2 + P_2V_2$

$\therefore H_1 = H_2 \quad [\because H = U + PV]$

The quantity U+PV which is conserved called enthalpy and denoted by H. Hence, in a throttling process the intial and final ~~enthalpie~~ enthalpies are equal.

Cases:

1. If $P_2V_2 > P_1V_1$ then $U_1 - U_2 > 0$
i.e. cooling is produced in J-T expansion and vice versa.

2. If $P_2V_2 = P_1V_1$ then $U_1 = U_2$
i.e. the gas is perfect and obey Boyle's law.

Vanderwaal's equation of gas

Joule's law is true for ideal gas only but experiment shows that real gas deviate from the perfect gas equation at high pressure. This deviations are due to finite size of molecules of and due to the mutual attraction of the molecules. At high pressure, the size of molecules of the gas becomes significant and neglected. Therefore Vander-waal's corrected the perfect gas equation allowing for molecular attractions and the finite volume occupied by molecules.

(1) Pressure correction :- A molecules in the interior of gas is attracted by other molecules in all directions and hence the net cohesive force on it is zero. But when a molecule strikes the walls of the container, it is pulled back by other molecules and hence the observed pressure of the gases on the walls of the container is less than the actual pressure within the body of the gas. This decrease in pressure is proportional to

a) the number of attracting molecules per unit volume and

b) The number of attracted molecules striking per unit area of the wall of the container per sec.

Both these factors depend upon the number of molecules per cc or the density (ρ) of the gas

$\therefore$ Decrease in pressure (p) $\propto \rho \propto \frac{1}{V^2}$

$\therefore p = \frac{a}{V^2}$

where 'a' is constant and V ~~be~~ is the volume of gas.

Hence, real pressure $= P + p$

$= P + \frac{a}{V^2}$

where P is observed pressure.

(2) <u>Volume correction</u> :- As the molecules have finite size, they occupy a space. Hence, the actual space for the movement is less than the observed volume 'V' of the container. Therefore, the volume in the eq^n of state be written as $(V-b)$, where b is constant for per unit mass of gas.

Now Vander-wall's eq^n for 1-mole of gas becomes

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

Critical constant of Vander-waal's gas

The vander-waal's eqⁿ. for 1-mole of gas is

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

or, $PV - Pb + \frac{aV}{V^2} - \frac{ab}{V^2} = RT$

or, $PV^3 - PbV^2 + aV - ab = RTV^2$

or, $PV^3 - V^2(Pb+RT) + aV - ab = 0$

Dividing both sides by P

or, $V^3 - V^2(b+\frac{RT}{P}) + \frac{a}{P}V - \frac{a}{P}b = 0 \longrightarrow (1)$

This is cubic eqⁿ in 'V'

Let $V = x$ then $V - x = 0$

$(V-x)^3 = 0$

or, $V^3 + 3Vx^2 - 3V^2x - x^3 = 0 \longrightarrow (2)$

Comparing eqⁿ (1) and (2), we get,

$3x = b + \frac{RT}{P} \longrightarrow (3)$

$3x^2 = \frac{a}{P} \longrightarrow (4)$

$x^3 = \frac{ab}{P} \longrightarrow (5)$

Dividing (5) by (4), we get

$\frac{x}{3} = b$

$\therefore x = 3b$

Critical volume, $V_c = 3b \longrightarrow (6)$

putting $x = 3b$ in eqⁿ (1) we get

$$3\cdot(3b)^2 = \frac{a}{P}$$

$$3\cdot 9b^2 = \frac{a}{P}$$

$$\therefore P = \frac{a}{27b^2}$$

Critical pressure $(P_c) = \frac{a}{27b^2} \longrightarrow (7)$

putting $x = 3b$ in eqⁿ (3) we get

$$3\cdot 3b = b + \frac{RT_c}{P_c}$$

$$9b = b + R\frac{T_c}{a/27b^2}$$

$$\therefore T_c = \frac{8a}{27Rb} \longrightarrow (8)$$

This is critical temperature.

Also,

$$\frac{P_cV_c}{T_c} = 3b \times \frac{a}{27b^2} \times \frac{27Rb}{8a}$$

$$= \frac{3}{8}R$$

$\therefore R = \frac{8}{3} \frac{P_cV_c}{T_c}$

$\therefore \frac{RT_c}{P_cV_c} = \frac{8}{3}$

The quantity $\frac{RT_c}{P_cV_c}$ is called the critical cofficient of gas and its value is same for all gases.

Vander-waal's constants :-

we have,

$V_c = 3b \longrightarrow (1)$

$P_c = \frac{a}{27b^2} \longrightarrow (2)$

$T_c = \frac{8a}{27Rb} \longrightarrow (3)$

From (1), (2) and (3) calculated 'a' and 'b',
we have,

$a = \frac{27}{64} \frac{R^2T_c^2}{P_c}$, $b = \frac{RT_c}{8P_c}$.

only this Chapter-12 → Production of very low Temp

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Vander-waal's gas in Joule-Thomson Effect

In Joule-thomson expansion in porous plug experiment suppose 1gm mole of a real gas is allowed to expand through a pressure P_1 and Volume V_1 to a pressure P_2 and Volume V_2. Suppose temperature also changes from T_1 to T_2. The net external workdone by the gas

$$= P_2V_2 - P_1V_1.$$

Now an internal work is also done by the gas in overcoming the force of molecular attraction. In case of a Vander waal's gas, the attractive force between the molecule of the gas is equivalent to an internal pressure $\frac{a}{V^2}$ a is constant.

When the gas expands from a volume V_1 to V_2 the internal workdone by it is given as

$$\int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{a}{V^2}\,dV$$

$$= a\int_{V_1}^{V_2} V^{-2}\,dV$$

$$= a\left(\frac{V^{-2+1}}{-2+1}\right)_{V_1}^{V_2}$$

$$= a\left(\frac{V^{-1}}{-1}\right)_{V_1}^{V_2}$$

$$= a\left(-\frac{1}{V}\right)_{V_1}^{V_2}$$

$$= a\left[-\frac{1}{V_2} - \left(-\frac{1}{V_1}\right)\right]$$

$$= a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

Hence the total workdone by gas

$$W = (P_2V_2 - P_1V_1) + \frac{a}{V_1} - \frac{a}{V_2} \longrightarrow (1)$$

The vander-waal's eqn. for 1-mole of gas is

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

or, $PV + \frac{aV}{V^2} - Pb - \frac{ab}{V^2} = RT$

or, $PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$

∴ $PV = RT + Pb - \frac{a}{V} \longrightarrow (2)$

[∵ neglecting $\frac{a}{V^2}$ being very small]

∴ $P_1V_1 = RT_1 + P_1b + \frac{a}{V_1} \longrightarrow (3)$

∴ $P_2V_2 = RT_2 + P_2b - \frac{a}{V_2} \longrightarrow (4)$

Using eqn (3) and (4), eqn (2) becomes

$$W = RT_2 + P_2 b - \frac{a}{V_2} - RT_1 - P_1 b + \frac{a}{V_1} + \frac{a}{V_1} - \frac{a}{V_2}$$

$$\therefore W = R(T_2 - T_1) + b(P_2 - P_1) + \frac{2a}{V_1} - \frac{2a}{V_2} \longrightarrow (5)$$

Since eqn (2), 'a' and 'b' are very small, so

$$PV = RT$$

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

$$\therefore V_1 = \frac{RT_1}{P_1} ; \quad V_2 = \frac{RT_2}{P_2}$$

putting this values of V_1 and V_2 in eqn (5), we get

$$W = R(T_2 - T_1) + b(P_2 - P_1) + \frac{2aP_1}{RT_1} - \frac{2aP_2}{RT_2} \rightarrow (6)$$

If T_1 and T_2 are very nearly equal then,

$T_1 - T_2 = dT$, and $T_1 = T_2 = T$,

eqn (6) becomes,

or, $$W = -RdT + b(P_2 - P_1) + \frac{2a}{RT}(P_1 - P_2)$$

$$\therefore W = (P_1 - P_2)\left(\frac{2a}{RT} - b\right) - RdT \longrightarrow (7)$$

If C_v is the specific heat of gas at constant volume, then heat lost by the gas to do the work 'W' is $C_v dT$ i.e. W is equivalent to $C_v dT$.

Hence,

$$C_v dT = (P_1-P_2)\left(\frac{2a}{RT}-b\right) - RdT$$

$$(C_v+R)dT = (P_1-P_2)\left(\frac{2a}{RT}-b\right)$$

$$C_p dT = (P_1-P_2)\left(\frac{2a}{RT}-b\right) \quad \left[\because C_p - C_v = R\right.$$

$$\therefore dT = \frac{(P_1-P_2)}{C_p}\left(\frac{2a}{RT}-b\right) \longrightarrow (8)$$

This shows that cooling at any temperature is directly proportional to the fall in the pressure.

$$\boxed{\therefore \frac{dT}{P_1-P_2} = \frac{1}{C_p}\left(\frac{2a}{RT}-b\right)}$$

Cases:-

(1) Here, $P_1 > P_2$ i.e. $P_1 - P_2$ is +ve, then dT will be +ve if $\frac{2a}{RT} - b$ is +ve i.e. $\frac{2a}{RT} > b$ or, $\frac{2a}{Rb} > T$ i.e.

cooling effect will take place if the intial tempr. of gas is less than $\frac{2a}{Rb}$.

(2) Here $P_1 - P_2$ is +ve then dT will be 0 if $\frac{2a}{RT} - b = 0$

$$\frac{2a}{RT} = b$$

$$T = \frac{2a}{Rb}$$

As $dT = 0$, so there will be no change in temp^r. so this value of temperature is called temp^r. of inversion and denoted by T_i

i.e. $T_i = \frac{2a}{Rb}$.

(3) Here $P_1 - P_2$ is +ve, dT will be -ve only when

$$\left(\frac{2a}{RT} - b\right) < 0$$

$$\frac{2a}{RT} < b$$

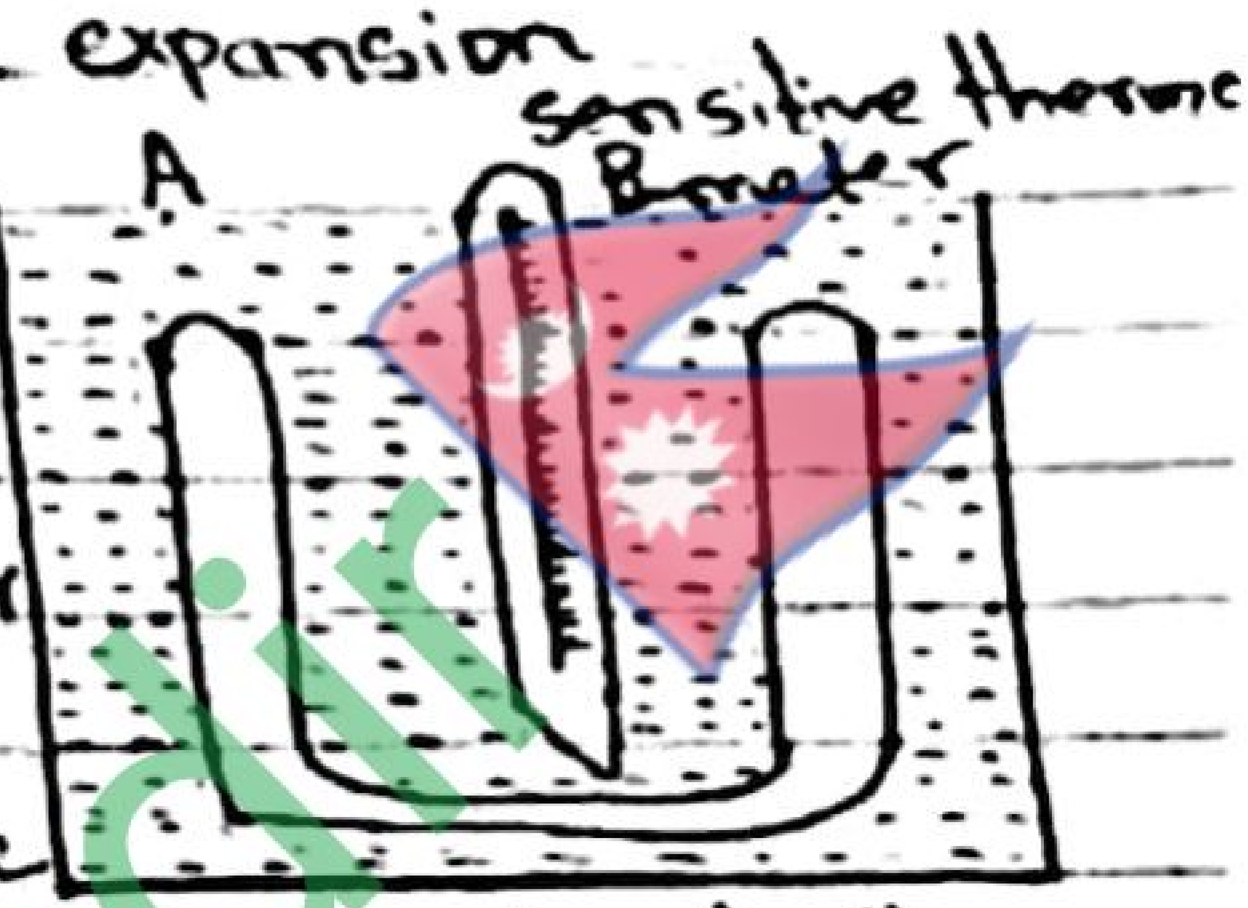
$$\frac{2a}{Rb} < T$$

Since, $T_i = \frac{2a}{Rb}$, so

$\therefore \boxed{T_i < T}$ i.e. heating effect will take place.

(Joule law for a perfect gas)

Joule expansion (free expansion):



Fg. Water bath

When a gas undergoes on expansion under adiabatic condition, the expansion is called free-expansion or Joule expansion.

If there exist intermolecular forces of attraction, the necessary work for the free expansion must be provided from the internal energy of the gas and there by decrease in temperature. Similarly if there exist intermolecular forces of repulsion, there must be increase in temperature. To predict these concussion Joule's performed an experiment under adiabatic condition. The experimental arrangement for Joule's expansion is shown in figure.

The experiment consists of two copper cylinders A and B connected by a stop clock 'S'. The cylinder A contains only air at high pressures and the cylinder B is evacuated. A sensitive thermometer is adjusted to measure the temperature. The whole arrangement is immersed into a water to achieve the condition of free expansion.

Now the dry air from cylinder A at high pressure is expanded into the cylinder B which is evacuated by opening the stop clock 's'. Then taking the measurement of temperature. Joule found that there is no change in temperature before and after the expansion. Then he concluded that there exist no inter molecular forces in gases molecules and the internal energy of gas is only the function of temperature. It doesn't get change whatever be the change in pressure and volume.

Mathematically, Joule's law can be expressed as

$$u = u(T)$$

And $\left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_p$ where u is internal energy.

$$\left(\frac{\partial u}{\partial V}\right)_T = \left(\frac{\partial u}{\partial p}\right)_T = 0.$$

Distinguish between Joule expansion, J-T expansion and adiabatic expansion

Joule's expansion	J-T expansion	Adiabatic expansion
1. The system is thermally as well as mechanically isolated from surrounding	1. The system is isolated thermally but not mechanically	1. The system is isolated thermally but not mechanically.
2. There is no external work done.	2. In this case external work done = $P_2V_2 - P_1V_1$	2. In this case the external done $dW = PdV$
3. There is neither cooling nor heating	3. There may be either cooling or heating	3. There always cooling.
4. There is no change in in temperature.	4. cooling is done to the work done in against to intermolecular forces of attraction	4. The cooling is due to the external work in against to the atmospheric Pressure.

P.T.O.

Difference between ideal and real gas

Ideal gas	Real gas
1. Molecules of ideal gas does not have finite volumes.	1. Molecules of real gas have finite volume.
2. Collision between the molecules of ideal gas is perfectly elastic.	2. Collision between the molecules of real gas is inelastic.
3. It obeys gases laws at all conditions of temperature and pressure	3. It obeys gases laws at low pressure and high temperature.
4. The equation of ideal gas is $PV = RT$	4. The eqn. of real gas is $(P + \frac{a}{V^2})(V-b) = RT$