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Lesson: Joule Thomson Effect

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Table of contents:

Chapter 3:	Joule Thomson Effect			
1	3.1 Introduction			
100	3.2 Free adiabatic expansion of a gas			
	3.3 Pours plug experiment			
13/	3.4 Joule Thomson coefficients 3.4.1 for ideal gas 3.4.2 for van der Waal's gas			
	3.5 Temperature of inversion 3.5.1 inversion curve			
668 USA	3.6 Summary			
A SHELL	3.7 Exercises			
	3.8 Glossary			
100	3.9 References			

Learning Objectives:

After studying this lesson, you will be able to;

- ✓ obtain the expression for Joule Thomson Coefficient.
- understand the distinction between perfect gas and real gas in terms of Joule Thomson Coefficient.
- ✓ understand temperature of inversion.
- ✓ find the conditions for cooling produced in terms of pressure.
- \checkmark analyze the conditions for liquefaction of a gas in terms of inversion temperature.

3.1 Introduction

Joule performed an experiment to study the intermolecular forces of the gas molecules. The experimental result showed no change in temperature after free adiabatic expansion of the gas hence it is of not much practical use for cooling of the gases. This experiment suggests that there is no force of attraction between the ideal gas molecules which may be the cause for no change in temperature of the gas. But the low temperature produced in Joule Thomson experiment played an important role in the study of liquefaction of gases and other properties. This experiment is extremely useful as the cooling is produced by expansion under certain conditions of pressure and temperature. Porous plug experiment confirms the existence of inter molecular attraction in real gases.

3.2 Free adiabatic expansion of a gas

If a vessel which contains a gas is connected with another evacuated vessel with a stopcock connection and the whole system is enclosed with a thermal insulation as depicted in Figure (3.1), a sudden opening of the stopcock will enable the gas to expand freely in vacuum. This is free adiabatic expansion.

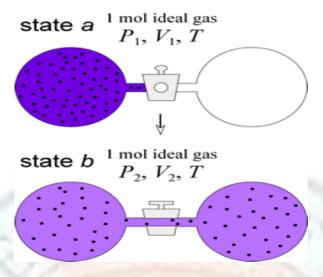


Figure 3.1: Free adiabatic expansion of a gas

Joule's experiment:

Joule designed an apparatus to study the inter-molecular attraction between the gas molecules with the variation of pressure and volume. There are two vessels 'A' and 'B' [See Figure (3.2)]. A is filled with a gas at high pressure and B is evacuated. These two vessels are connected with a tube fitted with a stopcock. The whole arrangement is thermally isolated and kept in water bath. A sensitive thermometer is used to measure the temperature.

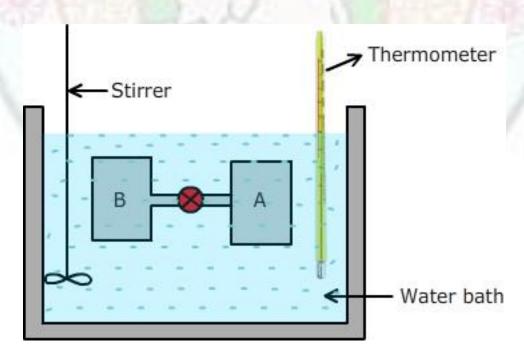


Figure 3.2: Joule's experimental arrangement

Stop cock is opened so that gas from A rushes to B adiabatically (there is no exchange of heat). This is 'adiabatic free expansion' as discussed earlier. After the expansion, the pressure was same in both the vessels but no change in temperature was observed.

Double click on the following icon to see the working of Joule's experiment.



According to first law of thermodynamics;

$$\delta Q = dU + \delta W - - - - - - - - - (3.1)$$

Since the process is adiabatic, $\delta Q = 0$.

The gas is perfect one. So no work is done during the expansion in the evacuated chamber.

Therefore, $\delta W = 0$

Thus the internal energy remains unchanged as long as temperature remains constant i.e. dU=0

Hence the internal energy (U) of the gas depends on its temperature (T) only. i.e. U = f(T). This is known as Joule's law.

Internal energy of the system does not change with volume or pressure as long as the temperature remains constant. Also the change in internal energy per degree rise of temperature is the same no matter whether the pressure or the volume is kept constant during the process.

Therefore,
$$\left(\frac{\delta U}{\delta V}\right)_T = 0$$
; $\left(\frac{\delta U}{\delta P}\right)_T = 0$ and $\left(\frac{\delta U}{\delta T}\right)_V = \left(\frac{\delta U}{\delta T}\right)_P$.

Joule's expansion is an irreversible process (as the gas that goes into B cannot come back to A)

3.3 Porous plug experiment

James Joule and William Thomson (later Lord Kelvin) had devised an experiment known as 'porous plug experiment'. This experiment was quite sensitive to detect the existence of change in temperature and subsequently the existence of inter-molecular forces in real gases.

In their experimental arrangement, a gas is allowed to pass through a porous plug from constant higher pressure region to a constant lower pressure region.

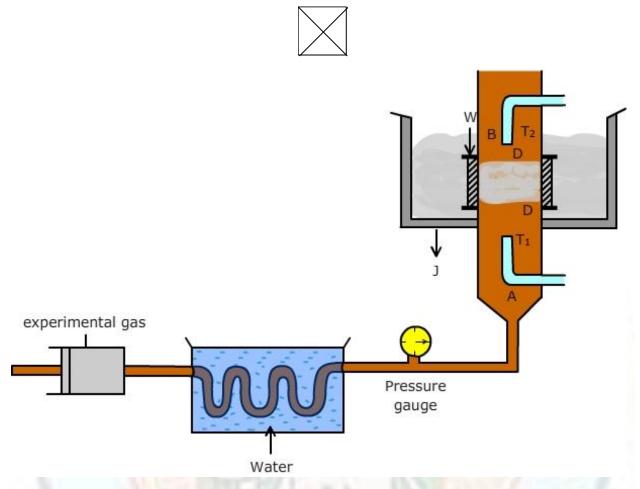


Figure 3.3: Porous plug experiment

A **porous plug** consists of silk fiber or cotton wool packed in a space between two perforated brass discs (DD) and has a number of fine holes such that heat cannot flow smoothly through it and this process is considered to be adiabatic. Thus, porous plug maintains a constant pressure difference on the opposite sides of the plug.

This plug is fitted in a cylindrical non conducting tube W, separating it into two parts. This arrangement is surrounded by a vessel (J) containing cotton wool to avoid any loss or gain of heat from the surroundings. The lower end of this tube is connected to a pump through a long spiral tube. $`T_1'$ and $`T_2'$ are two platinum resistance thermometers to measure the temperature of incoming and outgoing gas respectively. The gas is compressed to a high pressure with the help of a piston and it is passed through the spiral tube immersed in a water bath maintained at a constant temperature. If there is any heating of the gas due to compression, this heat is taken away by the circulating water in the water bath. A pressure gauge is used to measure the pressure of the inlet gas. The upper portion of the tube `C' is open. Thus, the pressure of this side $`P_2'$ is maintained at atmospheric pressure.

In this process gas flows through a large number of narrow orifices in the porous plug. The molecules of the gas are gradually pulled apart and the gas expands slowly from a constant higher pressure to a constant lower pressure state. This process is termed as **throttling process.** Due to this reason a porous plug is also called as throttled valve.

Double click on the following icon to see the animation on the Porus plug experiment.



The behavior of large number of gases has been studied after passing through the porous plug at various inlet temperatures and the following conclusions were drawn:

- 1. All of the gases show change in temperature, proving existence of molecular attraction between the molecules and that no gas is perfect one.
- 2. At ordinary temperature all gases show cooling effect except hydrogen and helium which show heating effect.
- 3. At sufficiently low temperature all gases show cooling effect.
- 4. The fall in temperature is directly proportional to the pressure differences on the two sides of the porous plug. *i.e.* $\delta T \propto \delta P$
- 5. For a given pressure difference, the fall in temperature is more if the initial temperature is less.
- 6. There is a particular inlet temperature for every gas at which gases show no change in temperature when they are passed through the porous plug. This temperature is called as the **'temperature of inversion** (*T_i*)'. Below this temperature gases show cooling effect while above this temperature, they show heating effect.

Theory of Porus Plug experiment:

The simplified arrangement of the above experimental process can be shown in Figure (3.4). The gas is allowed to pass through the porous plug from higher pressure side to the lower pressure side. Let P_1 , V_1 , T_1 and P_2 , V_2 , T_2 represent the pressure, volume and temperature on the two sides of the porus plug. When the piston A is moved through a certain distance, the piston B also moves through the same distance.

The work done on the gas by the piston A, $W_1 = P_1V_1$.

The work done by the gas on the piston B, $W_2 = P_2V_2$.

Thus the net work done by the gas, $\delta W = W_2 - W_1$



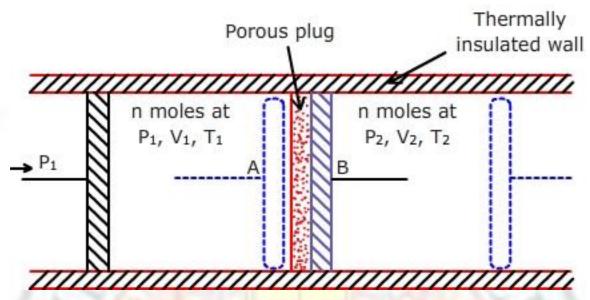


Figure 3.4: Simplified diagram of porous plug experiment

The dotted lines in the figure indicate the final position of the piston.

Since the system is thermally isolated, we can apply the law of conservation of energy. The work done by the gas on the piston is:

$$\delta W = P_2 V_2 - P_1 V_1$$

Since no heat enters the system, this work has to be performed at the cost of its internal energy.

According to first law,

$$\delta Q = dU + \delta W \ (from \ equation \ 3.1)$$
 Here,
$$\delta Q = 0 \quad [\text{Adiabatic process}]$$

$$\delta W = P_2 \, V_2 - P_1 \, V_1 \quad [\text{Work done on the piston}]$$
 And
$$dU = U_2 - U_1 \, [\text{Change in internal energy}]$$

Here $U_1 \& U_2$ represent the internal energy of the gas on the two sides of the porous plug.

From equation (3.1), $0 = (U_2 - U_1) + (P_2V_2 - P_1V_1)$

Or,
$$U_1 + P_1V_1 = U_2 + P_2V_2 - - - - - - - - - (3.2)$$

Here $H_1 \& H_2$ are the enthalpy on the two sides of the porous plug.

Thus we conclude that the **enthalpy** is conserved. So, in the throttling process, enthalpy remains constant. This process is known as Joule Thomson or Joule Kelvin expansion which is **'quasistatic isenthalpic'** in nature.

Equation (3.2) leads to the following conclusions:

- (i) If the gas is perfect, obeying Boyle's law i.e. $P_1V_1 = P_2V_2$, then $U_1 = U_2$. The internal energy remains unchanged at a constant temperature, thus proving Joule's law for a perfect gas.
- (ii) If $P_2V_2 > P_1V_1$, we get $U_1 > U_2$ i.e. internal energy of the gas decreases, so is the temperature. Hence there will be a cooling effect.
- (iii) If $P_2V_2 < P_1V_1$, then $U_1 < U_2$. That means internal energy of the gas increases after throttling process, showing heating effect.

3.4 Joule Thomson coefficients

Joule Kelvin coefficient (μ) is the ratio of change in temperature to the change in pressure at constant enthalpy. i.e.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{H}$$

If we take enthalpy (H) as a function of temperature (T) and pressure (P),

So that we can rewrite equation (3.5) as,

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP - - - - - - - - - - (3.6)$$

But,
$$dH = T. ds + V. dP - - - - - - - - - - - - - (3.7)$$

Or,
$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V$$

Using Maxwell's relation,

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

Or,
$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P + V - - - - - - (3.8)$$

On combining equation (3.6) and (3.8) we have,

$$dH = C_P dT + \left(V - T \left(\frac{\partial V}{\partial T}\right)_P\right) dP - - - - - - (3.9)$$

Since enthalpy does not change (dH = 0) in Joule Thomson expansion, which is both irreversible and adiabatic, the change in temperature with pressure is given by:

$$C_P dT = -\left\{V - T(\frac{\partial V}{\partial T})_P\right\} dP$$

Therefore, the Joule- Kelvin coefficient,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{H} = \frac{1}{C_{P}} \left\{ T \left(\frac{\partial V}{\partial T}\right)_{P} - V \right\} - - - - - - - (3.10)$$

We also have another form of the same expression as follows:

$$\mu = \frac{T^2}{C_P} \left[\frac{\partial}{\partial T} \left(\frac{V}{T} \right)_P \right] - - - - - - - - - - - (3.11)$$

Since final pressure is less than the initial pressure $(P_1>>P_2)$, dP will be negative. So, a positive value of μ implies that final temperature is negative, that means cooling will be produced. Similarly, a negative value of μ implies heating effect and μ equal to zero implies neither heating nor cooling. The physical relation for this may be understood from the following relation:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{H} = \left(\frac{\partial T}{\partial H}\right)_{P} \left(\frac{\partial H}{\partial P}\right)_{T}$$
$$= \frac{1}{C_{P}} \left(\frac{\partial H}{\partial P}\right)_{T}$$

Since enthalpy, H = U + PV

Therefore, $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left\{\left(\frac{\partial}{\partial P}\right)(PV)\right\}_T$

So,
$$\mu = \frac{1}{c_P} \left\{ \left(\frac{\partial U}{\partial P} \right)_T + \frac{\partial}{\partial P} (PV)_T \right\} - - - - - - - - - (3.12)$$

The first term of this equation on the R.H.S is a measure of deviation from Joule's law, whereas, the second term gives deviation from Boyle's law. For a perfect gas, both these terms are zero. From this, we may conclude that if Joule-Kelvin coefficient vanishes for a gas, it may be regarded as perfect. For the real gas, first term always contributes to cooling but the second term may contribute to heating and cooling depending upon the temperature and pressure of the gas. So the net result of Joule Thomson expansion is determined by the interplay of these two terms and can have either sign. It will vanish when cooling due to deviation from Joule's law exactly cancels heating due to deviation from Boyle's law i.e. $\left(\frac{\partial U}{\partial P}\right)_T + \frac{\partial}{\partial P}(PV)_T = 0$ [from equation (3.12)]

3.4.1 Joule Thomson coefficient for an ideal gas

Ideal gas equation for one mole of a gas

$$PV = RT$$

Differentiating above equation with respect to T at constant P,

We get,
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Since
$$\mu = \frac{1}{c_P} \left\{ T \left(\frac{\partial V}{\partial T} \right)_P - V \right\} - - - - - - - [from equation (3.10)]$$

Substituting $\left(\frac{\partial V}{\partial T}\right)_{P}$ for an ideal gas

We get,
$$\mu = \frac{1}{C_P} \left(T \frac{R}{P} - V \right) = \frac{1}{C_P} \left(\frac{PV}{P} - V \right) = 0$$

Therefore,

$$\mu = 0 - - - - (3.13)$$

3.4.2 Joule Thomson coefficient for Van Der Waal's gas

Van der Waal's gas equation is given as:

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

Differentiating above equation with respect to T at constant P,

Multiplying numerator as well as denominator on the R.H.S. of this equation by (V-b) and simplifying the result, we get

$$\left(\frac{\partial V}{\partial T}\right)_{P} = \frac{R(V-b)}{\left(P + \frac{a}{V^{2}}\right)(V-b) - \frac{2a}{V^{3}}(V-b)^{2}}$$

$$= \frac{R(V-b)}{RT - \frac{2a(V-b)^{2}}{V^{3}}}$$

$$= \frac{V}{T}\left(1 - \frac{b}{V}\right)\left(1 - \frac{2a}{RTV}\right)^{-1} - - - - - - - - - - (3.15)$$

$$= \left(\frac{V-b}{T}\right)\left(1 - \frac{2a}{RTV}\right)^{-1}$$

$$= \frac{V}{T\left(1 - \frac{2a}{RTV}\right)} - \frac{b}{T\left(1 - \frac{2a}{RTV}\right)^{-1}}$$

$$= \frac{V}{T}\left(1 - \frac{2a}{RTV}\right)^{-1} - \frac{b}{T}\left(1 - \frac{2a}{RTV}\right)^{-1}$$

$$= \frac{V}{T}\left(1 - \frac{b}{V}\right)\left(1 - \frac{2a}{RTV}\right)^{-1}$$

For b << V, we can write the above expression using binomial expansion,

$$\left(\frac{\partial V}{\partial T}\right)_{P} = \frac{V}{T}\left(1 - \frac{b}{V}\right)\left(1 + \frac{2a}{RTV}\right) - - - - - - - (3.16)$$

Here, we have neglected terms containing products of Van der Waal's constants and their higher powers. By rearranging equation (3.16) we can write:

$$T\left(\frac{\partial V}{\partial T}\right)_P = (V - b) + \frac{2a}{RT}$$

Or, $T\left(\frac{\partial V}{\partial T}\right)_{P} - V = \frac{2a}{RT} - b - - - - - - - - (3.17)$

Substituting this result in equation (3.10), we get

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{H} = \frac{1}{C_{P}}\left(\frac{2a}{RT} - b\right) - - - - - - - (3.18)$$

This is the expression for Joule Kelvin coefficient for van der Waal's gas.



Let us solve the following problem using ideal gas equation

Problem: Calculate the drop in temperature produced by adiabatic throttling process in the case of oxygen when the pressure is reduced by 40 atmospheres. Initial temperature of the gas obeys van der Waal's equation. The values of few constants are given as,

 $a=1.3\times10^{12}$ cm⁴ dynes/mole², b=31.2 cm³/mole, $C_P=7$ Cal/mole-K

Solution: Using equation (3.10),
$$\left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right]$$

 $\partial P = 40$ atmospheres

$$= 40x76x13.6980 \text{ dynes}/cm^2$$

$$C_P = 7 \frac{cal}{mole - K}$$

$$= \frac{7X4.2X10^7 ergs}{mole - K}$$

$$T = 30^0 C = 303 K$$

$$R = \frac{8.32X10^7 ergs}{mole - K}$$

$$\partial T = \left[\frac{40X76X13.6X980}{7X4.2X10^7} \right] \left[\frac{2X1.32X10^{12}}{8.31X10^7X303} - 31.2 \right]$$

 $= 10.16^{\circ}C = 10.16 K$

3.5 Temperature of inversion

From equation (3.18) we can write,

$$\mu = \frac{1}{C_P} \left(\frac{2a}{RT} - b \right)$$

Now we consider three cases for above expression;

Case I: If $\left(\frac{2a}{RT} - b\right)$ is zero, then the intermolecular forces are negligible and there will be neither heating nor cooling.

Here T_i is the **inversion temperature**



Let us calculate T_i for the following case:

Problem: The constants a and b for a Van der Waal's gas are $1.39 \times 10^2 \text{ lit}^2$ and $3.92 \times 10^2 \text{ lit}$ mol⁻¹ respectively. If the value of the gas constant R=0.082 lit-atm deg⁻¹ mol⁻¹. Calculate the value of the inversion temperature for the gas.

Solution:
$$T_i = \frac{2a}{Rb} = \frac{2X1.39X10^2}{0.082X3.92X10^2} = \frac{2.78X1000}{82X3.92} = 8.64K$$

Case II: If $\left(\frac{2a}{RT}-b\right)$ is positive, then a>>b and μ is also positive which means that the intermolecular forces are strong. The final temperature after expansion is reduced and we get a cooling effect. This happens when the initial temperature T is given by

$$\frac{2a}{RT} > b$$
or, $T < \frac{2a}{Rb}$
or, $T < T_i$

Case III: If $\left(\frac{2a}{RT}-b\right)$ is negative, then a<
b and μ is also negative which means that the intermolecular forces are weak. The final temperature after expansion is reduced and we get a heating effect.

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

or, $T > \frac{2a}{RT}$
or, $T > T_i$

The temperature of inversion is the temperature at which if the gas is allowed to expand adiabatically through porous plug, the gas shows neither cooling nor heating effect. But, if the gas is below temperature of inversion and is passed through porous plug, it will show cooling effect and if the inlet temperature of the gas is more than that of temperature of inversion, it will show heating effect.

This is the temperature of the gas at which the Joule Kelvin coefficient changes its sign. Below temperature of inversion it is positive, above negative and when it is equal to T_i , the value is zero.

The above discussion can be summarized in the following table:

Inlet temperature o the gas	Joule- Thomson coefficient	Change in pressure	Change in temperature	Final effect
Below temperature o inversion	Positive	Always negative	Negative	Cooling
Above temperature o inversion	Negative	Always negative	Positive	Heating

Table 3.1

Relation between Boyle's temperature (T_B) , critical temperature (T_C) and temperature of inversion (T_i) :

From equation (2.33),(2.18) and (3.19) we can write,

$$T_B = \frac{a}{Rb}$$

$$T_C = \frac{8a}{27Rb}$$

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

Dividing T_i by T_B we get,

$$\frac{T_i}{T_B} = \left(\frac{2a}{Rb}\right) \left(\frac{Rb}{a}\right) = 2$$

Or,

$$T_i = 2 T_B$$

Dividing T_i by T_C we get,

$$\frac{T_i}{T_C} = \left(\frac{2a}{Rb}\right) \left(\frac{27Rb}{8a}\right) = \frac{27}{4}$$

Or,

$$T_i = \frac{27}{4} T_C = 6.25 T_C$$

Therefore,

$$T_i > T_B > T_C$$

The following table shows the temperature of inversion for four different gases:

Gas	He	H ₂	N ₂	O ₂

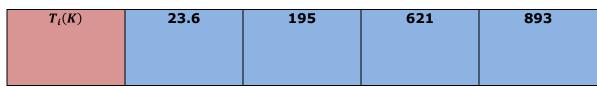


Table 3.1

In case of hydrogen and helium, instead of cooling, heating was observed at room temperature because it was at a temperature far higher than their temperature of inversion.

3.5.1 Inversion curve

The locus of points at μ =0 where the isenthalps (curves of constant enthalpy) are maximum on the T-P plane is called the inversion curve.

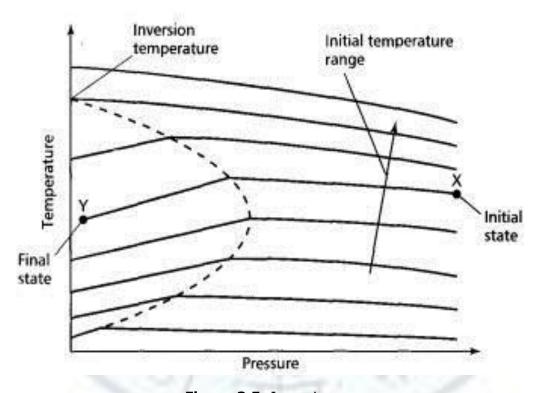


Figure 3.5: Inversion curve

At $\mu=0$, from equation (3.11)

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{H} = \frac{1}{C_{P}} \left\{ T \left(\frac{\partial V}{\partial T}\right)_{P} - V \right\}$$
$$T \left(\frac{\partial V}{\partial T}\right)_{P} - V = 0$$

or,
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}$$

This equation defines inversion curve in the T-P plane. The curve is plotted in figure 3.5. The gradients of the lines of constant enthalpy change sign when they cross the inversion curve. Cooling is produced for the gradients of the isenthalp to be positive in this diagram.

In the Joule Thomson experiment the gas is expanded isenthalpic ally through porous plug and the slope of the curve on the T-P plane is Joule Thomson coefficient and its value is zero.



Liquefied gases are used in refrigerants, fire extinguisher, fuel (LPG), medicine for cancer and research field.

3.6 Summary

- ✓ Joule Thomson effect signifies the change in temperature of a gas on being throttled through a porous plug from a region of constant high pressure to that of a constant low pressure.
- ✓ Joule Kelvin coefficient is the change in temperature per unit change in pressure across the porous plug. It is given by, $\mu = \left(\frac{\partial T}{\partial P}\right)_{\mu}$
- ✓ Sign of " μ " is opposite to that of the change in temperature.
- \checkmark The temperature at which $\mu=0$ is known as temperature of Inversion.
- ✓ Adiabatic throttling can result in either heating or cooling of the gas depending whether the initial temperature of the gas is higher or lower than the inversion temperature.
- ✓ Joule Thomson expansion is a steady flow process in which enthalpy is conserved.
- ✓ This experiment played an important role in the study of real gases.
- ✓ Cooling produced in this experiment provides a means of liquefying gases.

3.7 Exercises

I. Fill in the blanks:		
1) Adiabatic throttling of a gas is a of through a	expansion from a region of to tha	эt
 Gas expands against a constant pressure process. 	e in expansion which is a	
3) Cooling or heating is produced dependingor than the	· ·	
4) Joule Thomson expansion results in between molecules.	for gases because of th	e

- 5) Joule Thomson experiment played an important role in the study of ______
- 6) In a throttling process the initial and the final -----are equal.

II. State true /false for each of the following statements:

- 1) Joule Thomson experiment is a reversible process.
- 2) Intermolecular attraction does not play an important role in case of real gases.
- 3) No liquefaction can occur above critical temperature how high the pressure may be.
- 4) In Joule's free expansion the gas expands in vacuum
- 5) No real gas behaves perfectly.

III. Short answer:

- 1) Why temperature was constant in Joule's experiment?
- 2) What is the difference between adiabatic expansion and Joule's Thomson expansion?
- 3) Why all gases except H_2 and He show cooling effect at room temperature?
- 4) What is the difference between critical temperature and inversion temperature?
- 5) Why Joule Thomson coefficient is zero for a perfect gas?
- 6) Can we consider Joule Thomson coefficient to be a measure of departure of a gas from an ideal gas?

3.8 Glossary

Throttling process: It is a restricted process in which molecules of a fluid are gradually pulled apart and the expansion occurs slowly from a constant high pressure to a constant low pressure at constant enthalpy.

Adiabatic process: The process in which there is no exchange of heat from the system and its surroundings.

Irreversible process: A process which cannot be retraced back to its original state.

Critical temperature: The temperature above which a gas cannot be liquefied by applying pressure alone.

Boyle's temperature: The temperature at which Boyle's Law is obeyed.

Enthalpy: The amount of heat that flows in a system at constant pressure.

Quasistatic process: A thermodynamic process that occurs infinitely slowly and remains in equilibrium throughout the process.

Isenthalpic process: The process in which enthalpy remains constant.

Internal Energy: It is the sum of potential energy (associated with the relative positions of molecules) and kinetic energy (associated with the interaction between the molecules) of a system. It is the total energy content of a system.

Specific heat at constant pressure (C_P): The amount of heat to raise the temperature of one gram of a substance through one degree centigrade at constant pressure.

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