

Subject	Chemistry
Paper No and Title	10, Physical Chemistry- III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface chemistry, Fast kinetics)
Module No and Title	5, Joule Thomson effect
Module Tag	CHE_P10_M5

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CHEMISTRY

Paper No. 10: Physical Chemistry- III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface chemistry, Fast kinetics)

Module No. 5: Joule Thomson effect

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CHEMISTRY

Paper No. 10: Physical Chemistry- III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface chemistry, Fast kinetics)

Module No. 5: Joule Thomson effect

1. Learning Outcomes

After studying this module you shall be able to:

- Know about Throttling process
- Learn why Joule Thomson effect is known as isenthalpic process
- Differentiate between Joule Thomson coefficient of an ideal gas and Joule Thomson coefficient of real gas.
- Derive Joule Thomson coefficient

2. Introduction

In thermodynamics, the effect called Joule Thomson effect was discovered in 1852. This effect was named after two physicists James Prescott Joule (1818-1889) and William Thomson (1824-1907). This effect describes the change in temperature of a real gas or liquid when it is forced to pass through porous plug or valve while it is kept insulated so that exchange of heat with the environment is not possible. This process is called throttling process or Joule Thomson effect. This effect is mainly used in thermal machines such as refrigerators, heat pumps and air conditioners. This effect is discussed in detail in the next section.

3. Joule Thomson effect

Let the stream of gas which is at high pressure is allowed to expand by passing through porous plug into region of low pressure or vacuum. The gas gets cool under adiabatic conditions. But hydrogen and helium are exceptions as they get warmed up under similar circumstances. The temperature below which a gas becomes cooler on expansion is known as the **inversion temperature**. For example, the inversion temperature of hydrogen is -48°C while that of helium is -242°C . Thus **Joule-Thomson effect** can be defined as the phenomenon of temperature change produced when a gas is allowed to expand adiabatically from a region of high pressure to a region of extremely low pressure. This cooling of the gas is basically due to the decrease in the kinetic energy of the gaseous molecules as some part of this kinetic energy is utilized in overcoming intermolecular van der Waals force of attraction during expansion. The Joule-Thomson effect is very small when a gas approaches ideal behavior. Thus for an ideal gas, Joule Thomson effect is zero. Therefore, no absorption or evolution of heat takes

place when expansion of an ideal gas occurs i.e. $q = 0$. This is because in an ideal gas there are no intermolecular van der Waals forces of attraction thus there is no expenditure of energy in overcoming these forces during expansion. Further, when expansion of ideal gas occurs in vacuum then no work is done since pressure against which it expands is zero. From the first law equation we can say that ΔU is also equal to zero. Thus, when an ideal gas undergoes expansion under adiabatic conditions in vacuum, no change takes place in its internal energy. In other words, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume, i.e., $(\partial U / \partial V)_T = 0$.

An ideal gas may, therefore, be defined thermodynamically by the following two equations:

(i) $PV = \text{constant}$, at constant temperature

(ii) $(\partial U / \partial V)_T = 0$

The quantity $(\partial U / \partial V)_T$ is called the internal pressure and it is zero for ideal gas.

4. Joule Thomson Coefficient ($\mu_{J.T.}$)

Joule and Thomson derived the relationship between fall of pressure of gas on expansion and resulting lowering of temperature by performing the following technique:

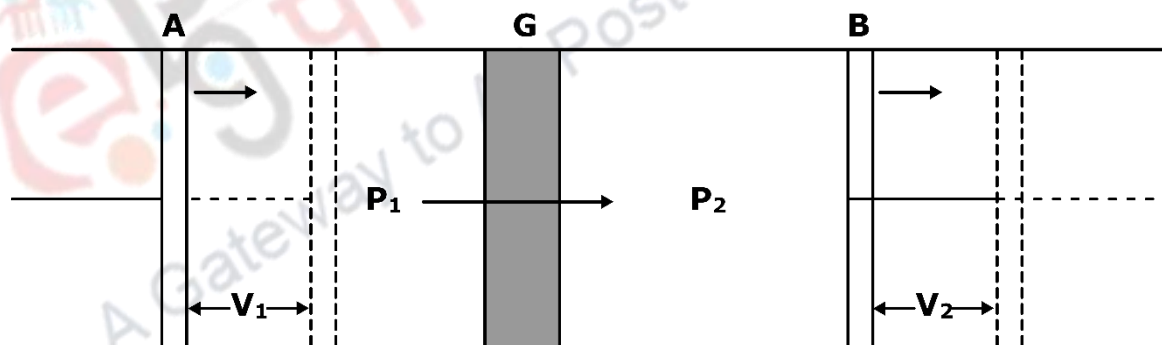


Fig. 1 The porous experiment

A tube made of a non-conducting material is fitted with a porous plug G in the middle and two pistons A and B on the sides, as shown. The tube is thoroughly insulated to ensure adiabatic conditions. Let the volume of gas enclosed between the piston A and the porous plug G at pressure P_1 is V_1 . This volume is forced to pass through porous plug by moving the piston A

inwards. At the same time the volume of gas enclosed between porous plug G and piston B i.e. V_2 is allowed to expand at a lower pressure P_2 by moving the piston B outward, as shown.

Therefore, work done on the system at the piston A = $+P_1V_1$

and work done by the system at the piston B = $-P_2V_2$

Then, net work done by the system = $-P_2V_2 + P_1V_1$

Since the expansion of the gas is done adiabatically i.e. no exchange of heat takes place between the system and surroundings. Thus the work is done by the system at the expense of internal energy only. Let the internal energy of the system changes from U_1 to U_2 .

$$\therefore -P_2V_2 + P_1V_1 = U_2 - U_1 \quad \dots(1)$$

$$\text{Or } U_2 + P_2V_2 = U_1 + P_1V_1$$

$$\text{or } H_2 = H_1$$

$$\text{or } H_2 - H_1 = 0 \text{ i.e. } \Delta H = 0 \quad \dots(2)$$

This states that the Joule-Thomson expansion of a real gas occurs with constant enthalpy and not with constant internal energy. According to this the process is known as **isenthalpic process**.

Taking enthalpy as the function of temperature and pressure, then the total differential of the enthalpy H can be written as

$$dH = (\partial H / \partial P)_T dP + (\partial H / \partial T)_P dT \quad \dots(3)$$

$$\text{But } (\partial H / \partial T)_P = C_P \quad \dots(4)$$

Substituting equation (4) in (3) we get,

$$dH = (\partial H / \partial P)_T dP + C_P dT$$

Since for adiabatic expansion, $dH = 0$, hence $(\partial H / \partial P)_T dP + C_P dT = 0$

Rearranging the above equation,

$$\frac{dT}{dP} = \frac{(\partial H / \partial P)_T}{C_P} \quad \dots(5)$$

$$\text{i.e., } (\partial T / \partial P)_H = -(\partial H / \partial P)_T / C_P \quad \dots(6)$$

The quantity $(\partial T / \partial P)_H$ is called **Joule-Thomson coefficient** and it is denoted as $\mu_{J.T.}$

For small pressure range the equation 6 can also be written as

$$\Delta T = -\frac{(\partial H / \partial P)_T}{C_P} \Delta P \quad \dots(7)$$

In the above equation ΔT is the fall of temperature and ΔP is fall of pressure.

4.1 Joule-Thomson Coefficient for an Ideal Gas.

Since $H = U + PV$, substituting this in equation 6 we get,

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T.} &= -\frac{1}{C_P} \left(\frac{\partial(U + PV)}{\partial P}\right)_T \\ &= -\frac{1}{C_P} \left[\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T \right] \\ &= -\frac{1}{C_P} \left[\left(\frac{\partial U}{\partial V} \times \frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T \right] \quad \dots(8) \end{aligned}$$

As the internal energy of an ideal gas at constant temperature is independent of its volume i.e. for an ideal gas, $(\partial U / \partial V)_T$ is zero, therefore

$$(\partial U / \partial V)_T (\partial V / \partial P)_T = 0 \quad \dots(9)$$

Also, PV is independent of temperature in the case of ideal gas i.e. $\left(\frac{\partial(PV)}{\partial P}\right)_T = 0$. Hence, Eq.

8 becomes $\mu_{J.T.} = 0$. This shows that the Joule-Thomson coefficient for an ideal gas is zero.

4.2 Joule-Thomson Coefficient for a Real Gas

There is no Joule Thomson effect for ideal gas but real gas do have Joule Thomson effect. So we can conclude that the Joule Thomson effect depends internal energy is dependent on change in volume. $(\partial U / \partial V)_T$ is positive for real gas. This can be explain as follows:

Consider the expansion of real gas in vacuum. In such expansion no external work is done since the external pressure is zero. But some work will definitely be done in separating the gas molecules against the intermolecular forces of attraction (the van der Waals forces). This work is stored in the gas in the form of potential energy, In other words, the potential energy of the gas increases and hence kinetic energy decreases by an equivalent amount if no heat is exchanged between the system and the surroundings. Due to this temperature of the gas falls.

But, in the present case, temperature is kept constant by the absorption of heat from outside. Therefore, the kinetic energy remains constant. Thus, during isothermal expansion of a real gas there is net increase in the energy of the gas (in the form of its potential energy). Hence, $(\partial U / \partial V)_T$ is positive. But the factor $(\partial V / \partial P)_T$ in Eq. 8 is negative because at constant temperature, as the pressure of a gas increases then volume of the gas decreases. Hence, the factor $[(\partial U / \partial V)_T (\partial V / \partial P)_T]$ is negative.

It is observed that at **ordinary temperatures** and when **the pressure is not very high**, the value of PV decreases as the pressure increases (except for H₂ and He), i.e., $(\partial(PV) / \partial P)_T$ is **negative**. Thus, under such condition, both the terms within the brackets of Eq. 8 are negative. Since the heat capacity is always positive, it states that the Joule-Thomson coefficient, $(\partial T / \partial P)_H$ is positive for real gases at ordinary temperatures and at low and moderate pressures. Thus, if ΔP is negative then ΔT is also negative, i.e., if there is fall in the pressure of the gas then temperature of gas also falls. In other words, the temperature of a gas falls as a result of its throttled expansion. Now considering the **high pressure** conditions, it is observed that with the increase of pressure of the gas, the value of PV for all gases also increases i.e., $(\partial(PV) / \partial P)_T$ **becomes positive**. The factor $[(\partial U / \partial V)_T (\partial V / \partial P)_T]$ in this case remains almost constant. Thus, in equation 8, one of the term within the brackets is negative and practically constant while the other term is positive and its magnitude increases with increase in pressure. Therefore, with the increase of pressure the magnitude of Joule—Thomson coefficient goes on decreasing and finally becomes zero when these two terms become equal in magnitude. Further if the pressure goes on increasing, the magnitude of the positive term exceeds that of the negative term. In such case Joule—Thomson coefficient becomes negative. Therefore if ΔP is negative then ΔT is positive, i.e. if the pressure of the gas falls then the temperature increases.

5. Derivation of Joule Thomson coefficient and Inversion temperature

The Joule-Thomson coefficient can be calculated with the help of the van der Waals equation. Considering the van der Waals equation i.e.

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad \dots(10)$$

In this equation, both terms a and b are small, hence the term ab/V^2 can be neglected when the pressure of the system is low. By rearranging this equation and neglecting the term ab/V^2 we get,

$$PV = RT - a/V + bP \quad \dots(11)$$

Substituting V by RT/P (approximation) we have

$$PV = RT - aP/RT + bP \quad \dots(12)$$

Dividing the whole equation by P, we get

$$V = RT/P - a/RT + b \quad \dots(13)$$

Differentiating with respect to temperature at constant pressure, we get

$$(\partial V / \partial T)_P = R/P + a/RT^2 \quad \dots(14)$$

Rearranging Eq. 12, we have

$$RT = P(V - b) + aP/RT \quad \dots(15)$$

Dividing both sides of the above equation by PT, we get

$$\frac{R}{P} = \frac{V - b}{T} + \frac{a}{RT^2} \quad \dots(16)$$

Replacing the value of R/P from Eq. 16 in Eq. 14, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} - \frac{b}{T} + \frac{2a}{RT^2} \quad \dots(17)$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b \quad \dots(18)$$

Now using the thermodynamic relation

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_P \quad \dots(19)$$

Then Eq. 18 may be written as

$$-\left(\frac{\partial H}{\partial P}\right)_T = \frac{2a}{RT} - b \quad \dots(20)$$

From Equations (6) and (20) we have

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right] \quad \dots(21)$$

From the above expression we conclude that Joule Thomson coefficient will be positive when $2a/RT$ is greater than b . It will become zero when $2a/RT$ is equal to b and negative if $2a/RT$ is less than b . Since a , b and R are constants, therefore magnitude and sign of Joule Thomson coefficient will be dependent only on the temperature at which the expansion of the gas occurred.

The temperature at which the sign of the Joule-Thomson coefficient changes is known as the inversion temperature. At this temperature, $\mu_{J.T.}$ is zero. Thus equation (21) will be zero when term inside the parenthesis will be zero so we get,

$$2a / RT_i = b \text{ or } T_i = 2a / Rb \quad \dots(22)$$

where T_i stands for the inversion temperature. Thus, the inversion temperature is dependent on the van der Waals constants a and b of the gas.

$$\mu_{J.T.} = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right]$$

6. Summary

- The temperature below which a gas becomes cooler on expansion is known as the **inversion temperature**.
- Thus **Joule-Thomson effect** can be defined as the phenomenon of temperature change produced when a gas is allowed to expand adiabatically from a region of high pressure to a region of extremely low pressure.
- Joule-Thomson expansion of a real gas occurs with constant enthalpy and not with constant internal energy and thus is also known as isenthalpic process.
- Joule Thomson coefficient is given by $(\partial T / \partial P)_H = -(\partial H / \partial P)_T / C_P$
- Joule Thomson coefficient for ideal gas is zero
- Joule Thomson coefficient for real gas is given by $\left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right]$