

Udai Pratap (Autonomous) College, Varanasi**E-learning Material**

Module/ Lecture	09
Topic	Joule-Thomson Effect
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Joule-Thomson Effect

When a gas under a constant higher pressure is made to pass through an insulated porous plug to a region of lower constant pressure, it suffers a change in temperature. This is known as Joule-Thomson Effect and the process is known as Joule-Thomson throttling process.

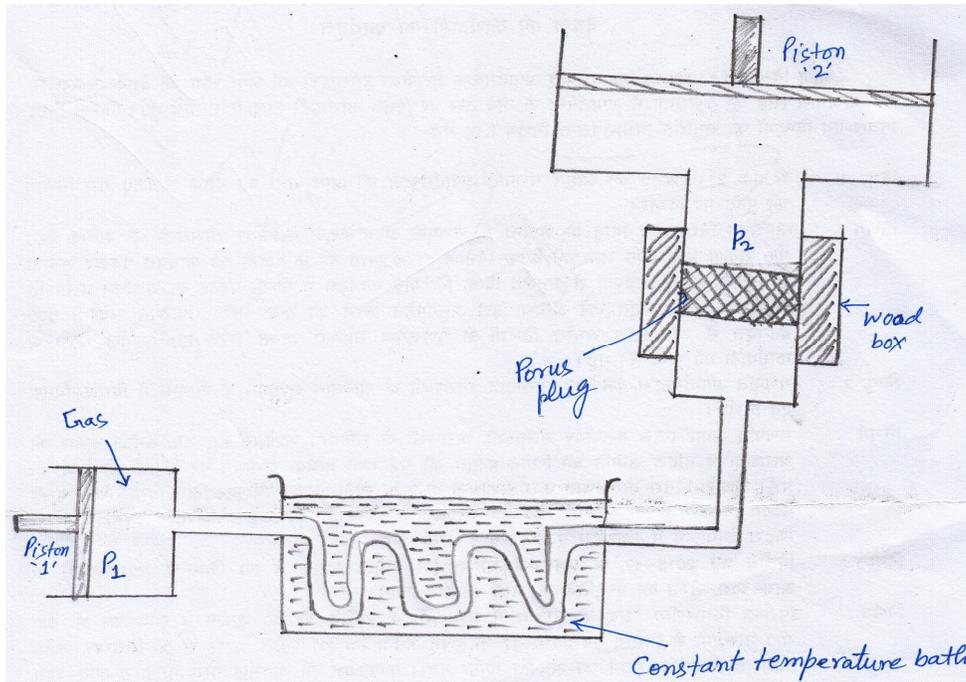


Fig. 1

A schematic diagram of the apparatus used to measure the change in temperature using Joule-Thomson expansion is shown in the fig. 1. In the experiment the porous plug is fitted in cylindrical wood box containing cotton wool in order to avoid loss or gain of heat from surroundings.

Suppose that the pressures on the two sides of the porous plug are kept at constant values p_1 and p_2 (with $p_2 < p_1$) (This can be done by moving pistons at appropriate rate). Let us start the experiment with a gas between piston '1' and porous plug having temperature T_1 , volume V_1 and internal energy U_1 . At the end of the experiment all of the gas has been pushed through the porous plug and volume of gas between piston '1' and porous plug becomes zero. After passing through the porous plug, let temperature volume internal energy become T_2 , V_2 and U_2 respectively. The curious result of this experiment is that careful measurement

shows that T_2 is not equal to T_1 . Under some conditions it is higher, under others it is lower.

The net work done by the gas on the piston is

$$\begin{aligned}\delta W &= \int_{V_1}^0 p_1 dV + \int_0^{V_2} p_2 dV \\ &= p_2 V_2 - p_1 V_1\end{aligned}\quad (1)$$

Since system is isolated completely, thus $\delta Q = 0$. Therefore 1st law of thermodynamics $\delta Q = \delta W + dU$ gives

$$\delta W + dU = 0 \quad (2)$$

Also, $dU = U_2 - U_1$ (3)

Hence from Eqns. (1, 2 & 3) we have

$$U_2 - U_1 + p_2 V_2 - p_1 V_1 = 0$$

i.e. $U_1 + p_1 V_1 = U_2 + p_2 V_2$ (4)

or $H_1 = H_2$ (5)

i.e. enthalpy is conserved. Thus the Joule-Thomson expansion process is **isenthalpic**.

The Joule-Thomson Coefficient

In Joule-Thomson expansion experiment enthalpy of the gas remains constant.

i.e.

$$H = U + pV = \text{constant}$$

i.e. $dH = dU + pdV + Vdp = 0$ (1)

But from 1st and 2nd laws of thermodynamics

$$dU = TdS - pdV$$
 (2)

From Eqns. (1 & 2) we have,

$$TdS + Vdp = 0$$
 (3)

Let $S = S(p, T)$

thus $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$ (4)

Substituting the value of dS from Eq. (4) in Eq. (3),

$$T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp + Vdp = 0$$
 (5)

Since $T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_p = \text{Molar specific heat at constant pressure}$

From Maxwell's relation, $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

Thus from Eq. (5) becomes

$$C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p \right] dp = 0$$

i.e. $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[T\left(\frac{\partial V}{\partial T}\right)_p - V \right]$ (6)

The change in temperature with the change in pressure at constant enthalpy is known as the **Joule-Thomson coefficient** and is denoted by μ . Thus

i.e. $\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[T\left(\frac{\partial V}{\partial T}\right)_p - V \right]$ (7)

since $p_2 < p_1$, i.e. $dp = -ve$, thus from Equation (7) we see that

- (i) if Joule-Thomson Coefficient $\mu = +ve$ then $dT = -ve$ i.e. cooling will be produced after Joule-Thomson expansion

(ii) if Joule-Thomson Coefficient $\mu = +ve$ then $dT = +ve$ i.e. heating will be produced after Joule-Thomson expansion

(iii) if Joule-Thomson Coefficient $\mu = 0$ then $dT = 0$, i.e. temperature will remain constant. Neither cooling nor heating will be produced after Joule-Thomson expansion.

The Joule-Thomson Coefficient for Perfect and real gases

1. For perfect Gas: For 1 mole of a perfect gas

$$pV = RT$$

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

hence from equation (7)

$$\begin{aligned} \mu &= \frac{1}{C_p} \left[T \frac{R}{p} - V \right] \\ &= 0 \end{aligned} \tag{8}$$

Which means that the Joule-Thomson effect disappears for perfect gas after the Joule-Thomson expansion i.e. for perfect gas the Joule-Thomson effect cannot be observed.

Equation (4) is known as Mayer's relation.

2. For real Gas: For 1 mole of perfect a real gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{9}$$

Differentiating (9) with respect to T at constant p, we get

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

or
$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_p &= \frac{R}{\left[\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)\right]} \\ &= \frac{R}{\left(\frac{RT}{(V - b)} - \frac{2a}{V^3}(V - b)\right)} \\ &= \frac{R(V - b)}{\left(RT - \frac{2a}{V^3}(V - b)^2\right)} \end{aligned}$$

Thus
$$T \left(\frac{\partial V}{\partial T} \right)_p = \frac{RT(V-b)}{\left(RT - \frac{2a}{V^3}(V-b)^2 \right)}$$

Since $b \ll V$, we can neglect it in comparison $(V-b)^2$, thus

$$\begin{aligned} T \left(\frac{\partial V}{\partial T} \right)_p &= \frac{(V-b)}{\left(1 - \frac{2a}{RTV} \right)} \\ &= (V-b) \left(1 - \frac{2a}{RTV} \right)^{-1} \end{aligned}$$

Using binomial expansion of 2nd term and neglecting the terms containing a^2 and higher order of a .

$$\begin{aligned} T \left(\frac{\partial V}{\partial T} \right)_p &= (V-b) \left(1 + \frac{2a}{RTV} \right) \\ &= V - b + \frac{2a}{RT} - \frac{2ab}{RTV} \end{aligned}$$

Neglecting last term, which is multiplication of two small quantities a & b in numerator, we get

$$T \left(\frac{\partial V}{\partial T} \right)_p \approx V - b + \frac{2a}{RT} \quad (10)$$

hence from equation (7)

$$\mu = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \quad (11)$$

Equation (11) gives joule-Thomson Coefficient for a real gas. We see that

- (i). If $\left[\frac{2a}{RT} - b \right]$ is positive, μ will also be positive i.e. final temperature after Joule-Thomson expansion will reduced and we get cooling effect. This happen if initial temperature is given by $T < \frac{2a}{Rb}$.

(ii). If $\left[\frac{2a}{RT} - b\right]$ is negative, μ will also be negative i.e. final temperature after Joule-Thomson expansion will increased and we get heating effect. This happen if initial temperature is given by $T > \frac{2a}{Rb}$.

(iii). If $\left[\frac{2a}{RT} - b\right] = 0$, i. e. $T = \frac{2a}{Rb}$ and $\mu = 0$ and therefore there is no change in temperature after Joule-Thomson expansion. The temperature $T = \frac{2a}{Rb}$ is known as inversion temperature and is denoted by T_i . Thus the temperature of the gas remains unaffected in the Joule-Thomson expansion if its initial temperature is equal to the inversion temperature $T_i = \frac{2a}{Rb}$.

Temperature $T_i = \frac{2a}{Rb}$ is called inversion temperature due to the fact that on passing through this temperature Joule-Thomson Coefficient μ changes in sign.