

### Joule-Thomson Expansion

In 1852, Lord Kelvin Thomson in collaboration with Joule devised an experiment, usually known as the *porous plug experiment*. In this experiment, a highly compressed gas is being continuously forced at constant pressure through a porous plug. The plug consists of a porous material, say cotton-wool, silk, etc., having a number of fine holes or pores and is thus equivalent to a number of narrow orifices in parallel. The gas during its passage through the pores becomes throttled or wire-drawn, viz., the molecules of the gas are drawn further apart from one another. The gas thus suffers a volume expansion.

**Figure 6** (a) Principle of Joule - Thomson Expansion. (b) Apparatus for J-T expansion.

The apparatus used by Joule and Thomson is shown in figure 6. A continuous flow of gas at a much higher pressure  $p_1$  and higher temperature  $T_1$  is forced through a porous plug in a tube, from which it emerges at a lower pressure  $p_2$  and a lower temperature  $T_2$ , since the plug offers great resistance to the flow of the gas. The plug is surrounded by a nonconducting jacket so that the process is adiabatic. Therefore this process is known as *Joule-Thomson expansion* or *adiabatic throttling*.

*“The change in temperature of a gas when it is allowed to expand through a narrow orifice or porous plug from a region of constant high pressure to a region of constant low pressure is called **Joule-Thomson effect**.”*

#### Theory of Joule-Thomson Expansion

Suppose that the pressure on the two sides of the porous plug are kept constant at values  $p_1$  and  $p_2$ , where  $p_2 < p_1$ . Let us assume that before the process starts the gas on one side has internal energy  $U_1$ . After expanding through porous plug let the internal energy of the gas on other side be  $U_2$ .

If the piston A (shown in figure 7) is slowly moved towards plug so as to keep the pressure constant at  $p_1$  as the gas escapes, then the piston B will move slowly outward to keep the pressure on the other side constant at  $p_2$ . If  $x_1$  and  $x_2$  be the distances through which the piston A and B move respectively and  $a$  the area cross section of the piston, then the force acting at A is equal to  $p_1 a$  and work done by this force upon the gas is  $p_1 a x_1 = p_1 V_1$ . Similarly, the work done by the gas in forcing the piston B is  $p_2 a x_2 = p_2 V_2$ . Therefore, the net work done by the gas is

$$W = p_2 V_2 - p_1 V_1$$

Since the device is thermally insulated  $\delta Q = 0$ , and from the first law of thermodynamics, the work done by the system is equal to the decrease in its internal energy,  $U_1 - U_2$ , i.e.

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

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$$\text{or, } U_1 + p_1 V_1 = U_2 + p_2 V_2$$

$$\text{or, } H_1 = H_2 \quad (17)$$

Hence, the enthalpy  $H = U + pV$  remain constant in the throttling process, i.e.,  $dH = 0$ .

Figure 7 (a) Initial State

(b) Final State.

### Thermodynamics of Joule-Thomson Expansion

The Joule-Thomson expansion can be regarded as a quasistatic isenthalpic process for the sake of thermodynamic analysis. Let us calculate the change in temperature due to Joule-Thomson expansion. We write  $H$  as a function of temperature and pressure;

$$H = H(T, p)$$

$$\text{so that, } dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad (18)$$

By definition of enthalpy, heat capacity at constant pressure is

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \quad (19)$$

so that we can rewrite eq. (18) as

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad (20)$$

We also know by definition of enthalpy, that

$$dH = TdS + Vdp$$

so that, on differentiating it with respect to pressure at constant temperature, we get

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = -T\left(\frac{\partial V}{\partial p}\right)_T + V \quad (21)$$

where we used Maxwell's relation. On substituting eq. (21) into (20), we get

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

Since the enthalpy  $H = U + pV$  remain constant in the throttling process, i.e.,  $dH = 0$ , the change in temperature with respect to pressure is given by

$$\mu = \left(\frac{dT}{dp}\right)_H = \frac{1}{C_p} \left[ T\left(\frac{\partial V}{\partial T}\right)_p - V \right] \quad (22)$$

where  $\mu$  is known as the *Joule-Thomson coefficient*.

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Since  $p_2 < p_1$ ,  $dp$  will be negative. So a positive value of  $\mu$  implies that  $dT$  is negative, i.e., cooling is produced. Similarly, a negative value of  $\mu$  implies that Joule-Thomson expansion leads to heating and  $\mu = 0$  means that there is no heating or cooling.

### Joule-Thomson Expansion of Ideal Gas

The equation of state for a perfect gas is,  $pV = RT$

On differentiating it with respect to temperature at constant pressure, we get

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

Then,

$$\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] = \left[\frac{RT}{p} - V\right] = \left[\frac{pV}{p} - V\right] = 0$$

Therefore, from eq. (22), we get

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = 0 \quad (23)$$

The Joule Thomson coefficient is zero means *there is no change in temperature of a perfect gas*, if it is expand adiabatically across the porous plug.

### Joule-Thomson Expansion of Vander-Waals' Gas

The equation of state for Vander-Waals' gas is,

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

or

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

On differentiating it with respect to temperature at constant pressure, we get

$$0 - \frac{2a}{V^3} \left(\frac{\partial V}{\partial T}\right)_p = -\frac{RT}{(V - b)^2} \left(\frac{\partial V}{\partial T}\right)_p + \frac{R}{(V - b)}$$

or,

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

or,

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

Multiplying both sides by  $T$ , we get

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

As  $b \ll V$ , we may neglect  $b$  in the square term  $(V - b)^2$ . Then equation reduces to

$$T \left(\frac{\partial V}{\partial T}\right)_p = \frac{RT(V - b)}{RT - \frac{2a}{V}} = \frac{(V - b)}{1 - \frac{2a}{VRT}} = (V - b) \left(1 - \frac{2a}{VRT}\right)^{-1}$$

Using binomial theorem to expand and neglecting the higher order terms, we get

$$T \left( \frac{\partial V}{\partial T} \right)_p = (V-b) \left( 1 + \frac{2a}{VRT} \right) = V-b + \frac{2a}{RT} - \frac{2ab}{VRT}$$

neglecting last term because product of  $a$  and  $b$  is negligibly small. Thus

$$\left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right] = \frac{2a}{RT} - b$$

Putting this result in eq. (22) we get

$$\mu = \left( \frac{dT}{dp} \right)_H = \frac{1}{C_p} \left[ \frac{2a}{RT} - b \right] \quad (24)$$

This is the Joule Thomson coefficient for a Vander Waal's gas. As the pressure is lower on the emergent side of the porous plug therefore, the  $dp$  is necessarily a negative quantity.

### Estimates of Joule-Thomson Cooling

It is clear from the eq. (24) that for a given difference in pressure on two sides of plug,

1. If  $\frac{2a}{RT} > b$  or  $T < \frac{2a}{Rb}$  then right side term would be positive, hence  $dT$  will be negative or the gas will be *cooled down* on passing through porous plug.
2. If  $\frac{2a}{RT} < b$  or  $T > \frac{2a}{Rb}$  then right side term would be negative, hence  $dT$  will be positive or the gas will be *heated up* on passing through porous plug.
3. If  $\frac{2a}{RT} = b$  or  $T = \frac{2a}{Rb}$  then right side term would be zero, hence  $dT$  will be zero or the gas will be neither cooled nor warmed on passing through porous plug, i.e., *no change in temperature*. The temperature below which the gases shows cooling effect and above which shows heating effect is known as the *temperature of inversion*, and is written as

$$T_i = \frac{2a}{Rb} \quad (25)$$

This shows that Joule-Thomson expansion will necessarily cool a gas if its initial temperature is below its inversion temperature. We have given the inversion temperature for some gases of interest in Table.

**Table:** Inversion temperatures of few gases of interest.

Gas	He	H <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	Air
T <sub>i</sub> (K)	23.6	195	621	893	1500	603

For ordinary gases  $T_i$  is greater than the temperatures at which the J-T expansion was carried out, i.e., room temperature, hence a cooling effect was obtained. We note that but for hydrogen and helium, the inversion temperature is quite low than the room temperature, hence heating effect was found. This explains why these two gases (He and H<sub>2</sub>) could not be liquefied easily. As we know, these gases were not pre-cooled below their inversion temperature, pre-cooling has to be done with other liquids, then they showed cooling on J-T expansion.