

# JOULE THOMSON EFFECT:

(2)

The cooling is produced when a gas is allowed to expand through a narrow orifice containing porous plug is called Joule-Thomson effect.

This porous plug experiment was performed by Joule and Thomson in 1852 in which a gas undergoes a change in temperature during adiabatic expansion process.

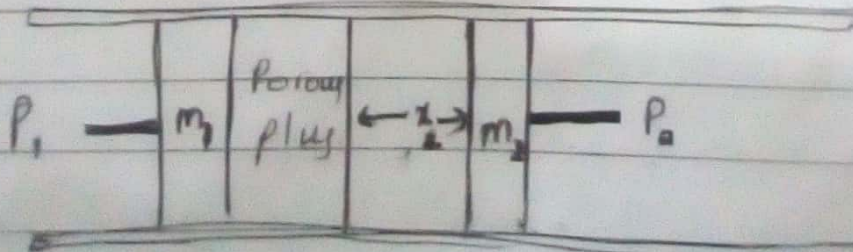
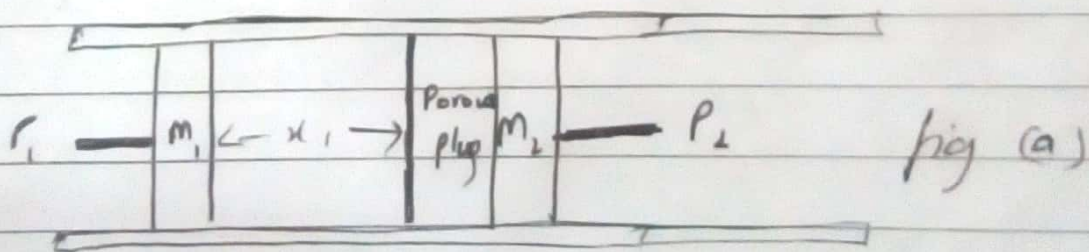
## Experimental arrangement:

The apparatus of experiment is provided by cylinder of non conducting walls and provided with piston  $m_1$  &  $m_2$  such that each having cross-sectional area 'A'.

A porous plug is placed at a distance  $x_1$  from piston  $m_1$ .

The volume of gas b/w porous plug and piston  $m_1$  is  $V_1$ .

The distance b/w porous plug & piston  $m_2$  is zero.



Important:



WORKING:

The gas is highly compressed to pressure  $P_1$  and on the other side ~~side~~ of plug is  $P_2$  as shown in diagram

The gas flows through the pores of porous plug due to this large difference of pressure-

The escape of gas tends to decrease in pressure  $P_1$ .

Now piston  $m_1$  is slowly move inward so that pressure  $P_1$  remain constant

The piston  $m_2$  will move outward slowly to keep the pressure  $P_2$  constant.

The piston  $m_2$  move through a distance  $x_2$  when all the gas is passed through porous plug.

Now volume of gas b/w porous plug by piston  $m_2$  is  $V_2$

Work done by the piston  $m_1$  on the gas  
 $= F_1 x_1$

Work done by  $g = (P_1 A) x_1$   
 $= P_1 V_1$

Similarly, work done by the gas on the piston  $m_2$   
 $= F_2 x_2$   
 $= P_2 A x_2$   
 $= P_2 V_2$

The net work done by the gas is given as

Important:  ~~$P_2 V_2$~~   $dW = P_2 V_2 - P_1 V_1$



The net heat transfer is zero bcz system is well insulated.

The internal energy of the molecules of gas before passing the porous plug is  $U_1$ , internal energy of molecules of gas after passing the porous plug is  $U_2$ .

The change in internal energy is given as

$$dE_{int} = U_1 - U_2$$

The first law of thermodynamic gives

$$dE_{int} = dQ + dW$$

$$U_1 - U_2 = 0 + (P_2 V_2 - P_1 V_1)$$

$$U_1 - U_2 = P_2 V_2 - P_1 V_1$$

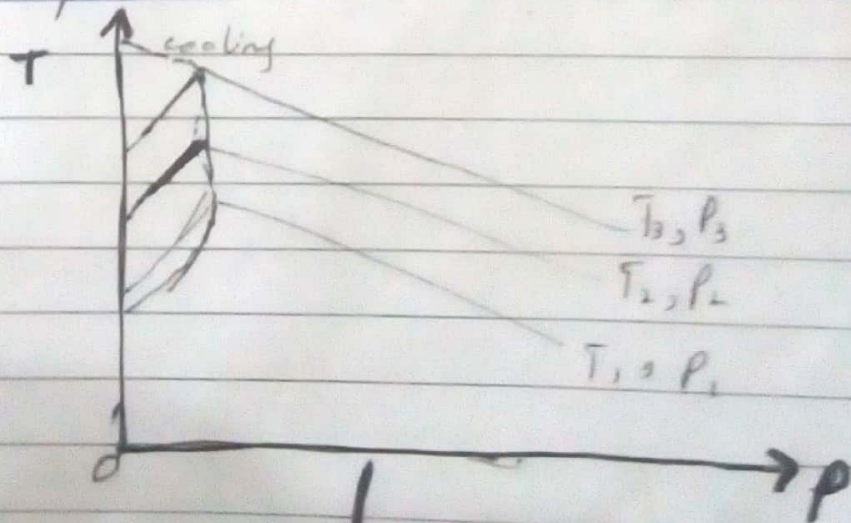
$$U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$$U + PV = \text{constant}$$

$$\text{or } H = \text{constant}$$

where  $H$  is called enthalpy of gas

$H$  shows that enthalpy of a gas suffering a throttling process remains constant.



The pressure-temperature diagram is

Important form isenthalpic curve. The family



of curve corresponding to different constant value of enthalpy are shown. Each curve pass through maximum called inversion point

→ The maximum slope of an isenthalpic curve on T-P diagram at any point is called Joule kelvin coefficient and written as

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

The value of  $\mu$  is zero at inversion point. The region inside the inversion curve is called cooling region.  $\mu$  is +ve inside this region. The value of  $\mu$  is -ve outside this region, called region of heating.

The enthalpy of system is defined as

$$H = U + PV$$

differentiating above we get.

$$dH = dU + PdV + VdP$$

$$dH = dQ + VdP \quad \text{1st law of the}$$

$$dH = Tds + VdP \quad \text{--- (1) } \because ds = \frac{dQ}{T}$$

Consider that entropy of system is function of temperature and pressure, written as

$$S = S(T, P)$$

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP \quad \text{--- (2)}$$

Important:

pathy (1) in (1)

$$\begin{aligned}
 dH &= T \left[ \left( \frac{\partial S}{\partial T} \right) dT + \left( \frac{\partial S}{\partial P} \right) dP \right] + V dV \\
 &= T \left( \frac{\partial S}{\partial T} \right)_P dT + T \left( \frac{\partial S}{\partial P} \right)_T dP + V dP \\
 &= C_p dT + \left[ T \left( \frac{\partial S}{\partial P} \right)_T + V \right] dP \quad \text{--- (3)}
 \end{aligned}$$

using Maxwell fourth eq

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

$dH = 0$  because  $H$  is constant  
using this in eq (3)

$$\begin{aligned}
 0 &= C_p dT + \left[ -T \left( \frac{\partial V}{\partial T} \right)_P + V \right] dP \\
 + C_p dT &= + \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right] dP \\
 \frac{dT}{dP} &= \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right] \quad \text{--- (4)}
 \end{aligned}$$

$$\mu = \frac{V}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - 1 \right]$$

This is called thermodynamical expression  
for joule thomson (kelvin) coefficient

We shall now derive the thermodynamic  
expression for joule thomson (kelvin)  
coefficient when gases are real.



The first law of thermodynamics is  
 $dQ = dU + dW$   
 $dQ = dU + PdV$  — (1)

The 2nd law of thermodynamics in terms of entropy

$dQ = Tds$  — (2)  
 comparing eq (1) & (2)  
 $Tds = dU + PdV$

As

$d(PV) = PdV + vdf$   
 or  $PdV = d(PV) - vdf$   
 putting in above eq

$Tds = dU + d(PV) - vdf$

$T \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial U}{\partial P} \right)_T + \left( \frac{\partial(PV)}{\partial P} \right)_T - v \left( \frac{\partial P}{\partial P} \right)_T$

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

$-T \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\partial U}{\partial P} \right)_T + \left( \frac{\partial(PV)}{\partial P} \right)_T - v$

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

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

$\gamma C_p = - \left( \frac{\partial U}{\partial P} \right)_T - \left( \frac{\partial(PV)}{\partial P} \right)_T$  (from eq 3)

Important:  $\gamma = - \frac{1}{C_p} \left( \frac{\partial U}{\partial P} \right)_T - \frac{1}{C_p} \left( \frac{\partial(PV)}{\partial P} \right)_T$

The first term from R.H.S accounts for ~~the~~ deviation from Joules law &  
2nd term accounts for deviation from Boyle's law for real gas.

For ideal gas both terms on R.H.S of eq reduce to zero. It means ideal gas shows no cooling or heating effect on suffering a throttling process.

## THE THERMODYNAMIC POTENTIAL:

The four quantities called thermodynamic potential are used in chemical thermodynamics of reactions and noncyclic process.

They are

- (1) Internal energy
- (2) Enthalpy
- (3) Helmholtz
- (4) Gibbs free energy

### ① INTERNAL ENERGY:

It is defined as energy associated with random, disordered motion of molecules.

It is separated in scale from the macroscopic ordered energy associated with moving objects.

It refers to the invisible microscopic energy on the atomic & molecular scale.