

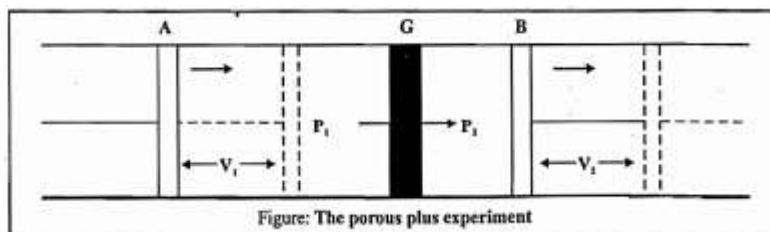
Study Notes on Joule Thomson Effect



Joule – Thomson Effect

Porous Plug Experiment: When any gas is subjected from a region of higher pressure to a lower pressure through a porous plug adiabatically, cooling takes place except for H₂ and He. At the same conditions of temperature and pressure when these gases are subjected from a higher-pressure region to a lower pressure region through a porous plug adiabatically, heating takes place.

This effect is known as Joule-Thomson effect'. It is an isenthalpic and adiabatic process.



As Joule – Thomson effects is an adiabatic Process, therefore,

$$dQ = dU + dW$$

$$0 = dU + dW$$

$$-dW = dU \quad (\because dQ = 0) \quad \dots(1)$$

From the above expression, it can be said that the work done by the gas is equal to the change in internal energy.

$$-PdV = dU$$

$$-P(V_2 - V_1) = U_2 - U_1$$

$$-PV_2 + PV_1 = U_2 - U_1$$

$$U_1 + PV_1 = U_2 + PV_2$$

$$H_1 = H_2$$

$$H_2 - H_1 = 0$$

$$\Delta H = 0 \quad \Rightarrow dH = 0$$

$$H = \text{constant}$$

So, Joule – Thomson effect is an isenthalpic process.

Joule Thomson Coefficient:

$$H = H(T, P)$$

$$\Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\Rightarrow 0 = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad [\because \text{In Joule – Thomson effect } dH = 0]$$

$$\Rightarrow 0 = C_p dT + \left(\frac{\partial H}{\partial P} \right)_T dP \Rightarrow C_p dT = - \left(\frac{\partial H}{\partial P} \right)_T dP \Rightarrow \left(\frac{\partial T}{\partial P} \right)_H = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

$$\Rightarrow \left[\left(\frac{\partial T}{\partial P} \right)_H = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T \right]$$

$\left(\frac{\partial T}{\partial P} \right)_H$ is known as Joule – Thomson coefficient and is denoted as $\mu_{J.T.}$ (Joule Thomson Coefficient)

From thermodynamics square:

$$dH = TdS + VdP$$

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

Again,

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

$$\therefore \mu_{J.T} = - \frac{1}{C_p} \left[-T \left(\frac{\partial V}{\partial T} \right)_P + V \right]$$

$$\boxed{\mu_{J.T} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]} \quad \dots (2)$$

Joule – Thomson Coefficient and Ideal gas equation of state:

The expression of Joule-Thomson coefficient can be expressed as:

$$\begin{aligned} \mu_{J.T} &= \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] = \frac{1}{C_p} \left[T \left(\frac{\partial}{\partial T} \frac{RT}{P} \right)_P - V \right] = \frac{1}{C_p} \left[\frac{R}{P} T \left(\frac{\partial T}{\partial T} \right)_P - V \right] \\ &= \left[\frac{T R}{C_p P} - \frac{V}{C_p} \right] = \frac{V}{C_p} - \frac{V}{C_p} = \frac{1}{C_p} (V - V) \end{aligned}$$

$$\therefore \boxed{\mu_{J.T} = 0} \text{ for ideal gas.}$$

Joule – Thomson Coefficient and Vander Waal equation of state:

The expression for Joule – Thomson coefficient can be expressed as:

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

Now, determine the value of $\left(\frac{\partial V}{\partial T} \right)_P$ for real gas and put it into above equation:

$$\begin{aligned}
 & \quad \quad \quad \text{I} \quad \quad \quad \text{II} \quad \quad \quad \text{I} \quad \quad \quad \text{II} \\
 & \frac{\partial}{\partial T} \left[\left(P + \frac{a}{V^2} \right) (V - b) \right]_p = \frac{\partial}{\partial T} (RT)_p \\
 \Rightarrow & \quad \left(P + \frac{a}{V^2} \right) \frac{\partial}{\partial T} (V - b)_p + (V - b) \frac{\partial}{\partial T} \left(P + \frac{a}{V^2} \right)_p = R \left(\frac{\partial T}{\partial T} \right)_p + T \left(\frac{\partial R}{\partial T} \right)_p \\
 \Rightarrow & \quad \left(P + \frac{a}{V^2} \right) \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial b}{\partial T} \right)_p + (V - b) \left[\left(\frac{\partial P}{\partial T} \right)_p + \left(\frac{\partial}{\partial T} \frac{a}{V^2} \right)_p \right] = R \\
 \Rightarrow & \quad \left(P + \frac{a}{V^2} \right) \left[\left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial b}{\partial T} \right)_p \right] + (V - b) \left[\left(\frac{\partial P}{\partial T} \right)_p + \left(\frac{\partial a}{\partial T V^2} \right)_p \right] = R \\
 \Rightarrow & \quad \left(P + \frac{a}{V^2} \right) \left[\left(\frac{\partial V}{\partial T} \right)_p - 0 \right] + (V - b) \left[0 + \frac{-2a}{V^3} \left(\frac{\partial V}{\partial T} \right)_p \right] = R \\
 \Rightarrow & \quad \left(P + \frac{a}{V^2} \right) \left(\frac{\partial V}{\partial T} \right)_p + (V - b) - \frac{2a}{V^3} \left(\frac{\partial V}{\partial T} \right)_p \Rightarrow \left(\frac{\partial V}{\partial T} \right)_p \left[\left(P + \frac{a}{V^2} \right) - \frac{2a}{V^3} (V - b) \right] = R \\
 \Rightarrow & \quad \left(\frac{\partial V}{\partial T} \right)_p \left[\frac{RT}{V - b} - \frac{2a(V - b)}{V^3} \right] = R \quad \left[\left(P + \frac{a}{V^2} \right) = \frac{RT}{(V - b)} \right] \\
 & \quad \left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{\frac{RT}{(V - b)} \left[1 - \frac{2a(V - b)^2}{V^3 RT} \right]} \quad \dots (2)
 \end{aligned}$$

Substitute the value of equation (2) in equation (1):

$$\begin{aligned}
 \mu_{J,T} &= \frac{1}{C_p} \left[\frac{TR}{\frac{RT}{V - b} \left[1 - \frac{2aV^2}{V^3 RT} \right]} - V \right] = \frac{1}{C_p} \left[V + \frac{2aV}{RTV} - b - \frac{2ab}{RTV} - V \right] \\
 & \quad \quad \quad \downarrow \text{neglected} \\
 \mu_{J,T} &= \frac{1}{C_p} \left[(V - b) \left(1 - \frac{2a}{RTV} \right)^{-1} - V \right] \quad \left(\frac{2ab}{RTV} \text{ is very small may be neglected} \right) \\
 & \quad \quad \quad \left[\text{so, } \left(1 - \frac{2a}{RTV} \right)^{-1} = \left(1 + \frac{2a}{RTV} \right) \right] \\
 \mu_{J,T} &= \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]
 \end{aligned}$$

Inversion temperature (T_i):

The temperature at which the value of $\mu_{J,T}$ becomes zero which means neither heating nor cooling takes place and gas behaves ideally is called inversion temperature.

$$\mu_{J,T} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$$

If $\mu_{J,T} = 0$, $T = T_i$

$$\Rightarrow 0 = \frac{1}{C_p} \left[\frac{2a}{RT_i} - b \right] \Rightarrow \frac{2a}{RT_i} - b = 0 \Rightarrow \frac{2a}{RT_i} = b$$

$$\boxed{T_i = \frac{2a}{Rb}} \quad \dots (3)$$

During J.T. effect:

$$dP = -ve \quad \therefore \quad \mu_{J,T} = \left(\frac{\partial T}{\partial P} \right)_H$$

If $\mu_{J,T}$ = positive then ∂T should negative, $T_2 < T_1$

Thus, cooling takes place.

In experimental condition:

$$\mu_{J,T} = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \quad \text{If } \mu_{J,T} = +ve \text{ means } \mu_{J,T} > 0$$

$$\Rightarrow 0 < \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]; \left(\frac{2a}{RT} - b \right) > 0; \left(\frac{2a}{RT} - b \right) > 0; \frac{2a}{Rb} > T$$

$$\boxed{T_i > T}$$

Hence, experimental temperature should be less than the inversion temperature of a gas for cooling

If,

$\mu_{J,T}$ = negative:

Thus, ∂T should be positive.

$\therefore T_2 - T_1 > 0$; $T_2 > T_1$ (Heating takes place)

In experimental condition:

$$0 > \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \Rightarrow \frac{2a}{RT} < b \Rightarrow \frac{2a}{Rb} < T \Rightarrow T_i < T \quad [T = \text{experimental temperature}]$$

If experimental temperature is greater than T , heating takes during J.T. experiment.

Note: H₂ and He gases have a very low T_i (-80°C and -240°C). This temperature will always remain below the experimental condition temperature; thus, heating happen.

Joule-Thomson Coefficient for a Real gas:

Joule-Thomson coefficient maybe positive or negative or zero depending upon the temperature and pressure of the gas. Since the change in pressure, dp, in Joule-Thomson experiment is always negative, it follows that dT will be negative when μ_{JT} is positive, and vice-versa.

Experimental result	μ_{JT}	$\left(\frac{\partial H}{\partial P}\right)_T$	Comments
dT negative, i.e. Cooling	(+)	(-)	Most gases, H ₂ and He at low temperature.
dT zero, i.e. Neither heating nor cooling	Zero	Zero	Ideal gas, real gas at inversion temperature
dT positive i.e., Heating	(-)	(+)	Most gases at high temperature H ₂ and He at ordinary temperature

Calculation of various thermodynamic relation for Vander Waal's relation:

(1). Expression of W:

$$dW = -p_{\text{ext}} \cdot dv$$

For reversible change in volume,

$$P_{\text{ext}} = P_{\text{int}} \pm dP \approx P_{\text{int}}$$

$$dw = -P_{\text{int}} dv \Rightarrow \int dw = -\int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2} \right) dV$$

$$W = -nRT \ln \frac{V_2 - nb}{V_1 - nb} - n^2a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

(2). Expression of ΔU :

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

For Vander Waal gas,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V-nb}$$

$$\therefore \left(\frac{\partial U}{\partial V} \right)_T = \frac{nRT}{V-nb} - P = \frac{nRT}{(V-nb)} - \left(\frac{nRT}{(V-nb)} - \frac{n^2a}{V^2} \right) = \frac{n^2a}{V^2} \Rightarrow \left(\frac{\partial U}{\partial V} \right)_T = \frac{n^2a}{V^2}$$

$$\therefore U = f(T, V)$$

$$\therefore dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

For Isothermal change,

$$dT = 0$$

$$\therefore dU = \left(\frac{\partial U}{\partial V} \right)_T dV \Rightarrow \int dU = \int_{V_1}^{V_2} \frac{n^2 a}{V^2} dV$$

$$\Rightarrow \boxed{\Delta U = -n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)}$$

Similarly,

$$q = \Delta U - w$$

$$\Rightarrow \boxed{q = nRT \ln \frac{V_2 - nb}{V_1 - nb}}$$

(3). Expression of ΔH :

$$\therefore \Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = -n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) + \Delta \left[\left(\frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \right) V \right]$$

$$\Delta H = -n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) + nRT \left(\frac{V_2}{V_2 - nb} - \frac{V_1}{V_1 - nb} \right) - n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$\boxed{\Delta H = -2n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) + nRT \left(\frac{V_2}{(V_2 - nb)} - \frac{V_1}{(V_1 - nb)} \right)}$$

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