

Ques :- What is meant by Joule-Kelvin effect? Derive an expression for the Joule-Thomson cooling of a gas. What is inversion temperature?

or

Derive an expression for the change in the temperature of a gas undergoing Joule-Thomson expansion. Discuss the role of inversion temperature in it.

Ans :- When a gas is allowed to pass through a porous plug from the region of constant high pressure to the region at constant low pressure, it undergoes a change in temperature. This phenomenon is called Joule-Thomson effect or Joule-Kelvin effect. The change in temperature depends upon the nature of the gas and the initial temperature.

In case of Vander Waal's gas, the attractive forces between the molecules of the gas are equivalent to an internal pressure i.e. $p = \frac{a}{V^2}$.

When the gas expands from V_1 to V_2 , the work done is against the inter-molecular attractions.

$$W = \int_{V_1}^{V_2} p \, dV$$

$$W = \int_{V_1}^{V_2} \frac{a}{V^2} \, dV$$

$$w = \left(-\frac{a}{v_2} + \frac{a}{v_1} \right)$$

If one gm. mole of a real gas expands through porous plug from a pressure P_1 and volume V_1 to a pressure P_2 and volume V_2 .

$$\text{The external work done by the gas} = (P_2 V_2 - P_1 V_1)$$

Hence the total work done by the gas

$$W = (P_2 V_2 - P_1 V_1) + w \\ = (P_2 V_2 - P_1 V_1) - \frac{a}{v_2} + \frac{a}{v_1} \quad \text{--- (1)}$$

From Vander waal's equation of state

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

$$Pv + \frac{a}{v} - bP - \frac{ab}{v^2} = RT$$

$$Pv = RT + bP - \frac{a}{v} \quad \left[\frac{ab}{v^2} \text{ is negligible} \right]$$

$$\text{--- (2)}$$

Putting (2) in (1)

$$W = \left[RT + bP_2 - \frac{a}{v_2} \right] - \left[RT + bP_1 - \frac{a}{v_1} \right] - \frac{a}{v_2} + \frac{a}{v_1}$$

$$= b(P_2 - P_1) + 2a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

$$\text{But } v_1 = \frac{RT}{P_1} \text{ and } v_2 = \frac{RT}{P_2}$$

$$W = b(P_2 - P_1) + 2a \left(\frac{P_1}{RT} - \frac{P_2}{RT} \right)$$

$$= -b(P_1 - P_2) + \frac{2a}{RT} (P_1 - P_2)$$

$$= (P_1 - P_2) \left(\frac{2a}{RT} - b \right) \quad \text{--- (3)}$$

Let the fall in temperature is δT

$$W = JH \\ = JM C_p \delta T \quad \text{--- (4)}$$

Where M is the gram-molecular weight of gas.

$$\therefore JM C_p \delta T = (P_1 - P_2) \left(\frac{2a}{RT} - b \right)$$

$$\boxed{\delta T = \left[\frac{P_1 - P_2}{JM C_p} \right] \left(\frac{2a}{RT} - b \right)} \quad \text{--- (5)}$$

Special Cases -

(i) $P_1 - P_2$ is +ve

δT will be +ve if $\left(\frac{2a}{RT} - b \right)$ is +ve

$$\text{i.e. } \frac{2a}{RT} > b \quad \text{or} \quad \frac{2a}{Rb} > T \quad \text{or} \quad T < \frac{2a}{Rb}$$

Therefore, cooling takes place if the temperature of the gas is less than $\frac{2a}{Rb}$.

(ii) δT will be zero if $\frac{2a}{RT} - b = 0$

$$\text{i.e. } T = \frac{2a}{Rb}$$

This temperature is called the temperature of inversion and is represented by T_i

$$\boxed{T_i = \frac{2a}{Rb}}$$

At this temperature, there is neither cooling nor heating of the gas.

(iii) δT will be negative, if $\left(\frac{2a}{RT} - b \right)$ is -ve

$$\text{i.e. } b > \frac{2a}{RT}$$

$$\text{or } T > \frac{2a}{Rb}$$

$$\text{or } T > T_i$$

In this case, heating will take place if the temperature of the gas is more than the temperature of inversion. ✓

Results :- (i) If the gas is at the temperature of inversion then no cooling or heating is observed when it is passed through the porous plug.

(ii) If the gas is at a temperature lower than the temperature of inversion, cooling will take place when it is passed through the porous plug. This is called regenerative cooling or Joule-Kelvin cooling or Joule Thomson cooling. This principle has been used in the liquefaction of the so-called permanent gases like nitrogen, oxygen, hydrogen and helium.

(iii) If the gas is at a temperature higher than the temperature of inversion, instead of cooling, heating is observed when the gas is passed through the porous plug.

Relation between Boyle temperature, inversion temperature and critical temperature

$$T_i = \frac{2a}{Rb} \quad \text{--- (i)}$$

$$T_B = \frac{a}{Rb} \quad \text{--- (ii)}$$

$$T_c = \frac{8a}{27Rb} \quad \text{--- (iii)}$$

From (i) and (ii)

$$T_i = 2T_B \quad \text{--- (iv)}$$

From (i) and (iii)

$$\frac{T_i}{T_c} = \frac{2a}{Rb} \cdot \frac{27Rb}{8a} = \frac{27}{4}$$

$$\frac{T_i}{T_c} = 6.75$$

The experimental value of $\frac{T_i}{T_c}$ for actual gases is just less than 6.