

Chapter 11

Phase Transition and Low Temperature Physics

1. Third Law of Thermodynamics and Attainable of Low Temperature

The third law of thermodynamics is some time stated as follows:

It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its zero point value in a finite number of operations.

Properties of material at low temperature

At $T \rightarrow 0$

$$C_p = C_v = 0$$

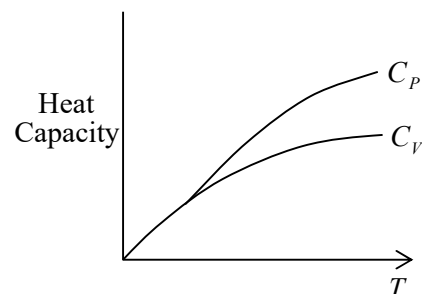
At $T \rightarrow 0$

$$S \rightarrow 0$$

At $T \rightarrow 0$

$$\text{Thermal expansion coefficient } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = 0$$

$$\alpha = 0$$



Production of Low Temperature: The Joule – Kelvin Expansion:

The Joule – Kelvin Expansion is essentially a continuous steady – state flow process in which a compressed gas is made to expand adiabatically irreversibly through a porous plug and do work.

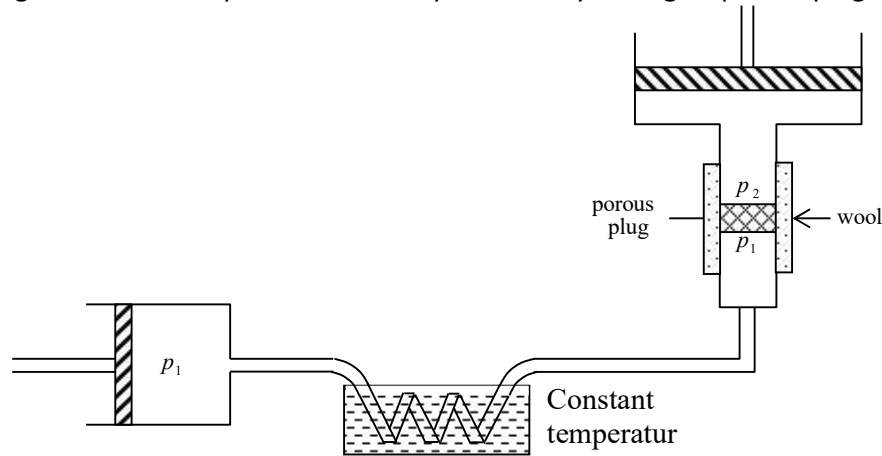


Fig: A schematic diagram of the porous-plug experiment for Joule-Kelvin

Let us assume that we start off with a gas of internal energy U_1 and volume V_1 . After passing through the porous plug let find internal energy and volume of the gas by U_2 and V_2 . No heat enters the system.

So this work has to performed at the expense of internal energy

$$U_1 + P_1V_1 = U_2 + P_2V_2$$

$$H_1 = H_2$$

Joule – Kelvin expansion is isenthalpic process

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

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

$$dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad dH = TdS + VdP$$

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

$$dH = C_p dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP$$

Hence H does not change $dH = 0$

The μ is defined $\left(\frac{\partial H}{\partial P}\right)_H$

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu = \frac{1}{C_p} \left(T \left(\frac{\partial V}{\partial T} \right)_P - V \right) = \frac{T^2}{C_p} \left(\frac{\partial}{\partial T} \left(\frac{V}{T} \right)_P \right)$$

where μ is known as the Joule – Kelvin Coefficient.

The equation defines a curve in the (T, P) plane and is known as the inversion curve when $\mu = 0$.

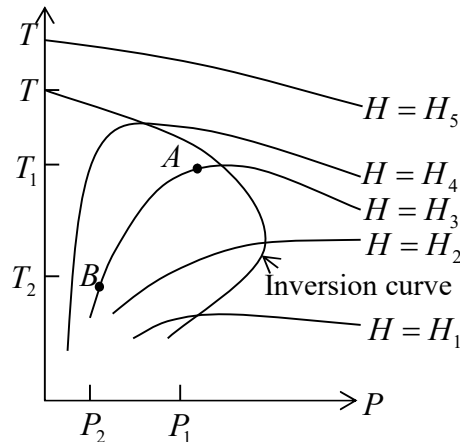


Figure: Curves of constant enthalpy. The bold curve is the inversion curve. Inside it, the gas is cooled on expansion. The temperature change $\Delta T = T_2 - T_1$ produced in a finite pressure

A series of isoenthalps, i.e. curve with $H(T, P) = \text{constant}$.

At $T = T_i$ $\mu = 0$ known as inversion temperature.

$T < T_i$ and $\mu = \text{Positive}$. There is heating effect of gases i.e. temperature and pressure move in same direction.

$T > T_i$ $\mu = \text{Negative}$. There is cooling effect i.e. temperature and pressure move in opposite direction.

Example: (a) For van der Waals gas. Prove that inversion temperature $T_i = \frac{2a}{Rb}$ where a and b are parameter used in van der Waals gas.

(b) Why Hydrogen and helium shows heating effect as pressure increased at constant enthalpy.

Solution: (a) $\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p} \left(T \left(\frac{\partial V}{\partial T} \right)_P - V \right)$

For van der Waals gas

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

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{(V-b)}{T\left(1 - \frac{2a(V-b)^2}{RTV^3}\right)}$$

since $b \ll V$

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

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

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

For inversion temperature, $\mu = 0 \Rightarrow \frac{2a}{RT_i} = b \quad T_i = \frac{2a}{Rb}$

(b) Since inversion temperature of Hydrogen and Helium is very small. For cooling effect initial temperature must be smaller than inversion temperature, but for Helium and Hydrogen inversion temperature is very small

So, it is not possible to achieve initial condition lower than inversion temperature so Helium and Hydrogen give heated effect.

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right) \quad dT = \frac{1}{C}\left(\frac{\partial V}{\partial T}\right)_p dP - VdP$$

$$\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 \quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{-1}{\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T} = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_p dP = -\left(\frac{\partial P}{\partial T}\right)_V dV$$