ADVANCED CHEMISTRY BLOC

(THERMODYNAMICS)

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Cyclic rule in thermodynamics has its own importance. Hardly, we see books showing its applications. This small article will show you the need of applications of cyclic rule. Also read this small article to discover the existence of two inversion temperatures for gases; which we generally ignore.

CYCLIC RULE

- **Applications of cyclic rule in thermodynamics and joule-thomson coefficient**

The cyclic rule in thermodynamics says

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial y}{\partial z}\right)_x=-1 \text{ for } f(x,\ y,\ z)=0$$

The applications of cyclic rule :

Irrespective of physics or chemistry, if we have to find out $\left(\frac{\partial P}{\partial T}\right)_V$ for a real gas.

We know that, for a real gas,

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

or, $$\left(P+\frac{an^2}{V^2}\right)=nRT(V-nb)^{-1}$$

or, $P = nRT(V - nb)^{-1} - an^2V^{-2}$

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

Now, Let's find out $\left(\frac{\partial P}{\partial V}\right)_T$ for the same real gas,

$$\left(\frac{\partial P}{\partial V}\right)_T=nRT(-1)(V-nb)^{-2}-an^2(-2)V^{-3}$$

or, $$\left(\frac{\partial P}{\partial V}\right)_T=\frac{-nRT}{(V-nb)^2}+\frac{2an^2}{V^3}$$

Now, if we have to find $\left(\frac{\partial V}{\partial P}\right)_T$ for the real gas. First we have to derive using $V=f(T, P)$ and then find $\left(\frac{\partial V}{\partial P}\right)_T$, surely will be difficult to find.

Now, by applying cyclic rule

$$\left(\frac{\partial V}{\partial P}\right)_T=\frac{1}{\left(\frac{\partial P}{\partial V}\right)_T}$$

Thus, $$\left(\frac{\partial V}{\partial P}\right)_T=\frac{(V-nb)^2V^3}{-nRTV^3+2an^2(V-nb)^2}$$

[Using the expression of $\left(\frac{\partial P}{\partial V}\right)_T$ as shown above]

Similarly, if we have to find $\left(\frac{\partial V}{\partial T}\right)_P$ for the real gas. Again the same difficult situation. First find $V=f(T, P)$ and then $\left(\frac{\partial V}{\partial T}\right)_P$

Alternatively, using cyclic rule

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

- **Thermal expansion coefficient and isothermal compressibility**

$$\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

β is the volumetric thermal expansion coefficient.

β has the unit K^{-1} and usually $\beta > 0$.

Similarly, $$\alpha=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

'α' has the unit bar^{-1} and $\alpha > 0$.

α is the isothermal compressibility. Questions on α and β are frequently observed in both physics and chemistry.

Before moving ahead, just imagine why volume has been divided into both α and β expressions. The reason is to make α and β extensive properties. Clearly, with dimension of K^{-1} for β and bar^{-1} for α, they are now extensive properties.

Now, another application of thermodynamics is :

For an ideal gas, $V = \frac{nRT}{P}$

$$\therefore \quad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}\cdot\frac{P}{nRT} = \frac{1}{T}$$

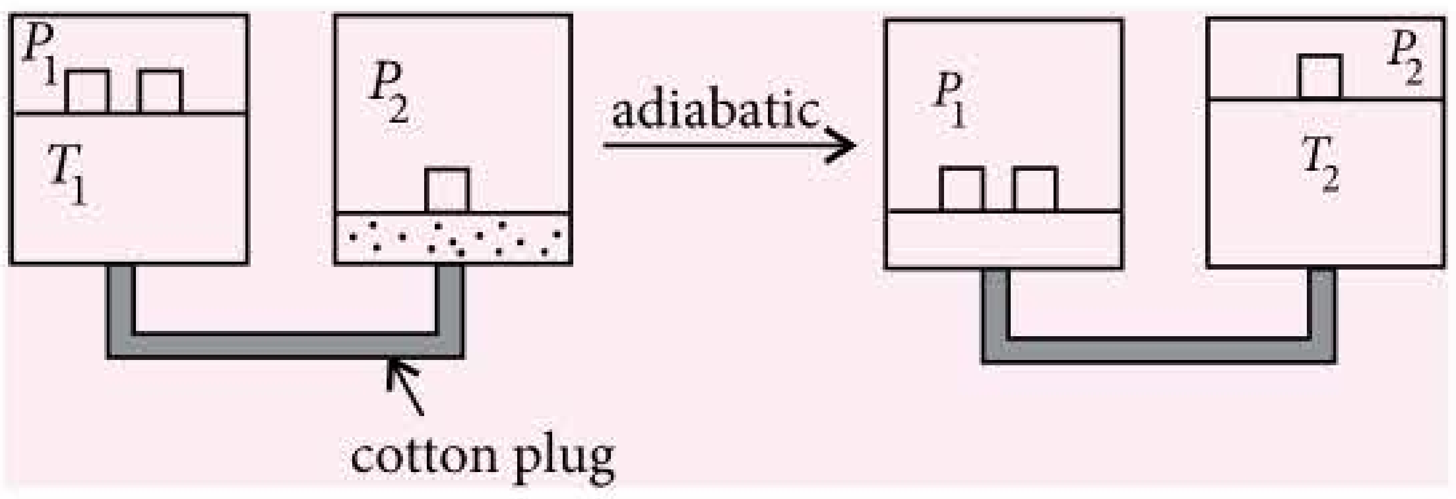
$$\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -(-)\frac{nRT}{P^2}\cdot\frac{P}{nRT} = \frac{1}{P}$$

Suppose if we have to measure $\left(\frac{\partial P}{\partial T}\right)_V$, it will be difficult to measure. Rather, it is obtained by applying the cyclic rule.

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = -\left(-\frac{1}{\alpha V}\right)\times\beta V = \frac{\beta}{\alpha}$$

Thus, $\left(\frac{\partial P}{\partial T}\right)_V$ is obtained as $\frac{\beta}{\alpha}$.

JOULE-THOMSON EXPERIMENT



A gas (may be ideal or real though ideal gases have $\mu_{J.T.} = 0$) is allowed to undergo adiabatic expansion through a porous plug from a region of high pressure to low pressure. A change in temperature is noted.

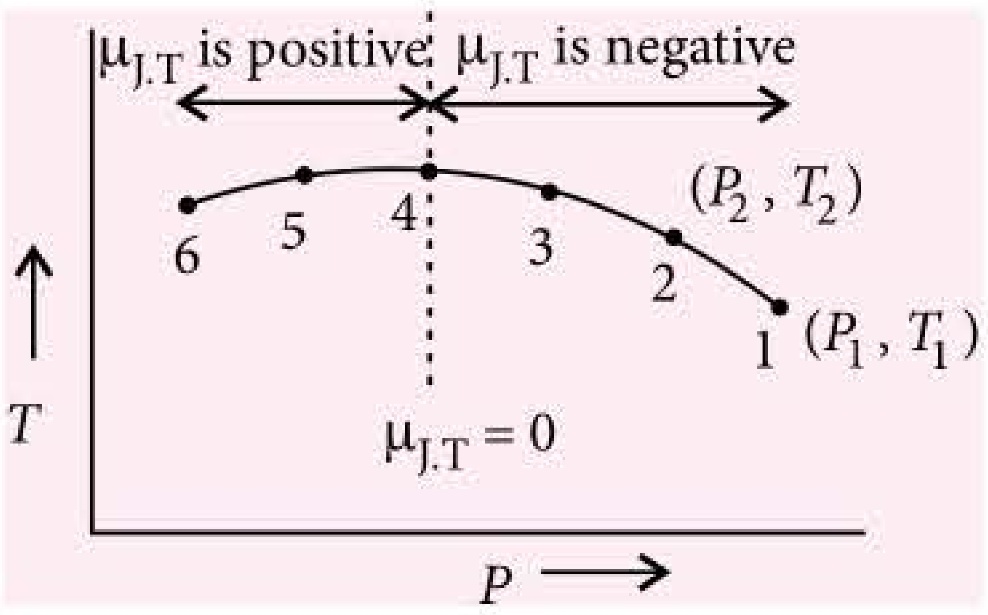
Joule-Thomson coefficient $(\mu_{J.T}) = \left(\frac{\partial T}{\partial P}\right)_H$

T and P both are intensive property. So the ratio $\mu_{J.T.}$ is also an intensive property. Like any other intensive property, it is a function of T and P and also depends on nature of the gas.

Assume that P_1 and T_1 are the initial pressure and temperature of the gas on the left hand side. Pressure on the right hand side is maintained at P_2. The temperature measured is T_2.

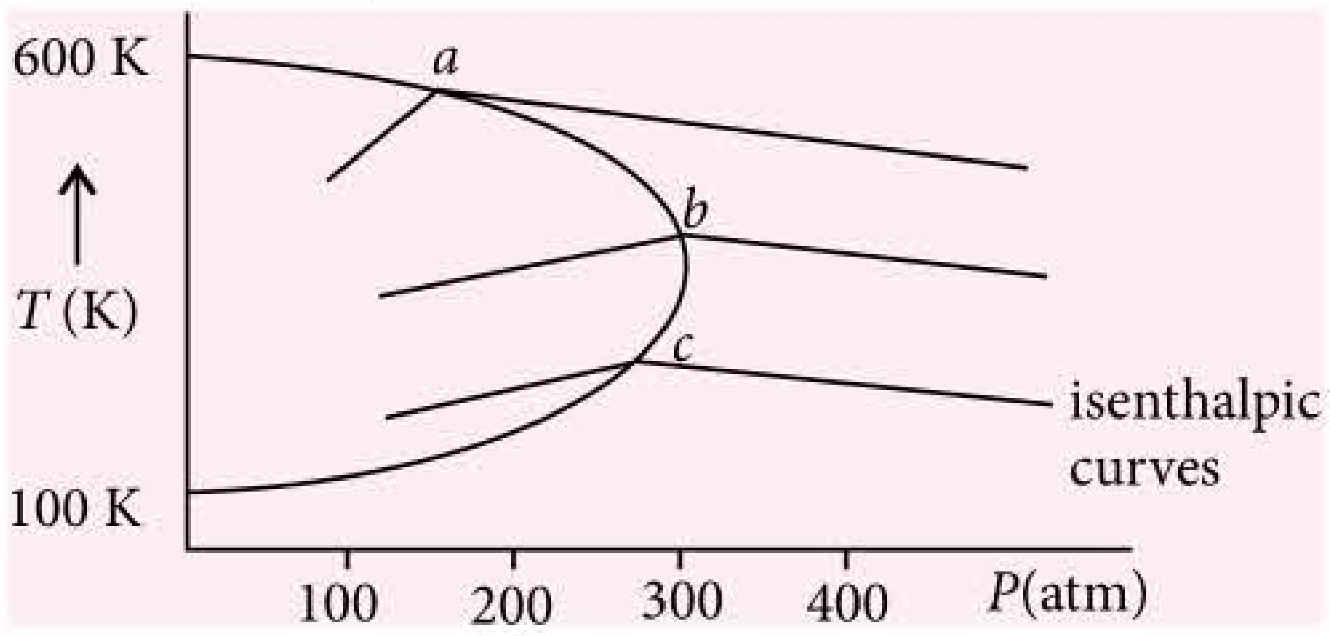
Note that $P_2 < P_1$. The two points (T_1, P_1) and (T_2, P_2) are shown by 1 and 2 in a T-P curve. The two states 1 and 2 have the same enthalpy H. The same experiment is now repeated with the same initial P_1, T_1 but different new values P_3, P_4 etc. maintained on the right hand side. The corresponding temperatures measured are T_3, T_4 etc. These points are shown as 3, 4 etc. in the diagram.

Initially, while moving from P_1 to P_2, you are moving in the direction of low pressure (as $P_2 < P_1$). So ΔP is –ve. If temperature increases then ΔT is +ve and $\mu_{J.T}$ is negative. As it can be seen from the isenthalpic curve, $\mu_{J.T}$ value changes sign from point G. This curve is called isenthalpic curve. Slope of this curve at any point gives $\mu_{J.T}$, as the slope of the line is $\left(\frac{\partial T}{\partial P}\right)_H$.



The temperature at which $\mu_{J.T}$ changes sign is called inversion temperature.

If different isenthalpic curves are drawn starting with different initial pressure.



For each curve there is a T_i (where $\mu_{J.T} = 0$). The different T_i are noted as a, b and c. On joining these points, an inversion curve for N_2 obtained. Thus, a gas typically have different inversion temperatures. For N_2, the maximum inversion temperature is 600 K and the minimum inversion temperature is 100 K (when $P \rightarrow 0$). For H_2 and He, the maximum upper T_i values are 204 K and 43 K respectively. Hydrogen and helium thus show heating effect in Joule-Thomson expansion when carried out at room temperature while other gases show cooling effect.

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