S. S. College. Jehanabad (Magadh University)

Department : Physics

Subject : Thermodynamics

Class : B.Sc(H) Physics Part I

Topic: Application of Maxwell’s Thermodynamical Relation

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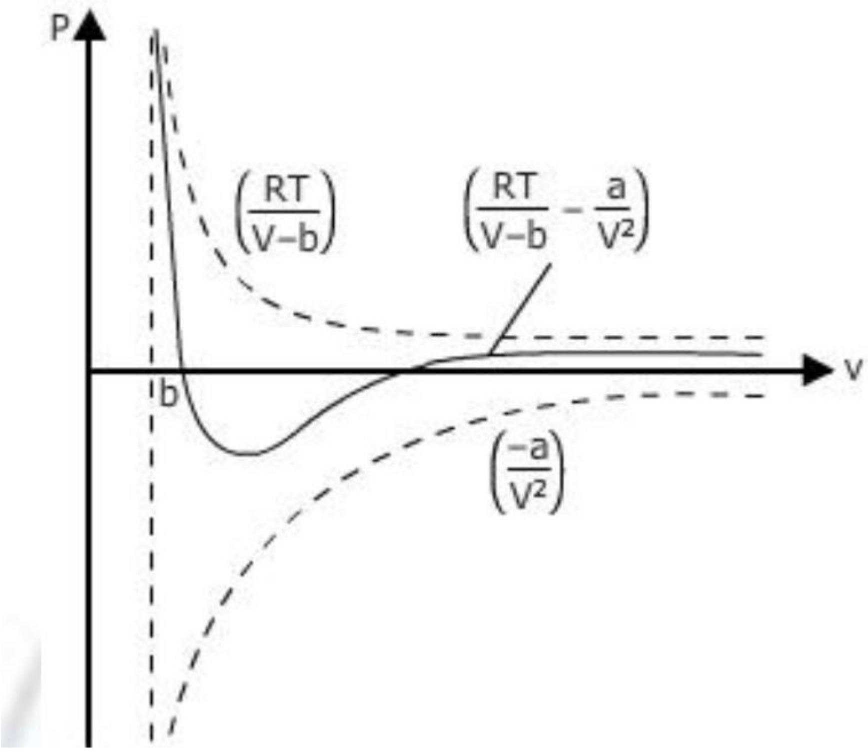
Continued……

(b) **Van der Waals :**



The equation of state for a Van der Waals gas is

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

where *a* and *b* are constants.

From the Van der Waals equation, we get

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

Differentiating the equation with respect to *T* at constant volume, we have

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

and differentiating with respect to T at constant pressure we have

$$0 - \frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{R}{(V-b)}$$

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

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\left[\frac{R}{(V-b)}\right]}{\left[\frac{RT}{(v-b)^2} - \frac{2a}{V^3}\right]}$$

Substituting the value of $\left(\frac{\partial P}{\partial T}\right)_V$ *and* $\left(\frac{\partial V}{\partial T}\right)_P$ in equation (1), we have

$$C_P - C_V = \frac{T\left(\frac{R}{V-b}\right)\left(\frac{R}{V-b}\right)}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]}$$

$$= \frac{R}{1 - \frac{2a}{V^3}\cdot\frac{(V-b)^2}{RT}}$$

Neglecting b in comparison to V *as b is much smaller than V*

$$C_P - C_V = \frac{R}{1 - \frac{2a}{V^3} \cdot \frac{V^2}{RT}}$$

$$= \frac{R}{1 - \frac{2a}{VRT}}$$

$$= R\left(1 - \frac{2a}{VRT}\right)^{-1}$$

Expanding binomially the above equation and neglecting higher powers of a as a is very small in comparison to V, we have

$$C_P - C_V = R\left(1 + \frac{2a}{VRT}\right)$$

2. To show

$$C_P - C_V = TE\,\alpha^2 V$$

where T is the absolute temperature

E is the isothermal elasticity of the gas,

α is the coefficient of volume expansion and

V *is* the specific volume of the gas.

From Maxwell's second thermodynamical relation

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

from the definition of C_P *and* C_V we have

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P$$

$$= T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

$$= T\left(\frac{\partial S}{\partial T}\right)_V$$

Taking $S = f(T,V)$, we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

dividing the above equation by dT and then carrying out the process at constant pressure we have

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right) + \left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

But from the maxwell's relation , we have

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

$$T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad \text{..................} \ (2)$$

taking the general equation of state for a gas as $P = f(V, T)$

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

Dividing the above equation by dT , we have

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

At constant pressure

$$dP = 0$$

the above equation becomes

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

Substituting the value in equation *(2)*

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 \quad \text{.............} \ (3)$$

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \quad \text{………. (4)}$$

modulus of elasticity at constant temperature is given by

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

and the coefficient of volume expansion is given by

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

Substituting these values in equation *(4)* we have

$$C_p - C_V = -TE\alpha^2 V \quad \text{……………… (5)}$$