APPLICATIONS OF THERMODYNAMIC RELATIONS

CLAUSIUS – CLAPEYRON EQUATION

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

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

$$\{T\,\partial S = \partial Q\}$$

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

$$\partial V = V_2 - V_1 \qquad \therefore \partial Q = L$$

$$\frac{L}{V_2 - V_1} = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow \boxed{\frac{\partial P}{\partial T} = \frac{L}{T(V_2 - V_1)}} \quad \text{— } (2)$$

Clausius Clapeyron's Latent heat Eqn

TDS EQUATIONS

T & V

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

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial v}\right)_V dv$$

$$T\left(\frac{\partial s}{\partial T}\right) = C_V$$ for reversible isochoric process

Maxwell's third relation $\left(\frac{\partial s}{\partial V}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V$

$$\Rightarrow \boxed{Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV} \quad -(1)$$

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

$$\Rightarrow T\,dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\underline{\underline{\left(\frac{\partial S}{\partial P}\right)_T}}\, dP$$

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

$\underline{\underline{4^{th}}}$ $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \boxed{T\,dS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP} \quad \text{--- } (2)$$

THE ENERGY EQUATIONS

$$dU = TdS - PdV$$

$$\frac{dU}{dV} = T\frac{dS}{dV} - P$$

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

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

First energy Eq^n

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \quad \text{—} \; (1)$$

$$du = Tds - Pdv$$

$$\frac{du}{dP} = T\frac{ds}{dP} - P\frac{dv}{dP}$$

$$\left(\frac{\partial u}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T$$

4th relation $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$

$$\Rightarrow \boxed{\left(\frac{\partial u}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T} \quad -(2)$$

2nd Energy Eq^n

(a) For a perfect gas

$$PV = RT$$

$$\Rightarrow \frac{\partial P}{\partial T} = \frac{R}{V}$$

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

$$= \frac{RT}{V} - \frac{RT}{V}$$

$$= 0$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$$

(b)

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

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

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

$$\Rightarrow \boxed{\left(\frac{\partial u}{\partial V}\right)_T = \frac{a}{V^2}}$$

THANKYOU