$$đQ = dU + p\,dV \quad ; \quad U(V,T)$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

$$dS = \frac{đQ}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

S is a state fn, dS must be exact

Recall if $df = A\,dx + B\,dy$

exact $\Rightarrow$ $\dfrac{\partial A}{\partial y} = \dfrac{\partial B}{\partial x}$

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

exactness $\Longrightarrow$

$$\frac{\partial}{\partial V}\left(\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_T + p\right\}\right]$$

$$\cancel{\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \cancel{\frac{1}{T}\frac{\partial^2 U}{\partial T \partial V}} - \frac{1}{T^2}p + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V$$

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

We had already checked, for ideal gas

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

Internal energy for a real gas

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

one mole of van der Waals gas

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\partial}{\partial T}\left[\frac{RT}{V-b} - \frac{a}{V^2}\right] - \frac{RT}{V-b} + \frac{a}{V^2} \, .$$

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

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

integrate

$$U = a\int \frac{dV}{V^2} + f(T).$$

$$U(V,T) = -\frac{a}{V} + f(T)$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_v.$$

$$U = \int C_v\,dT + g(V)$$

$$\boxed{U(V,T) = \int C_v\,dT - \frac{a}{V}}$$

Try $U(V,T)$ for radiation gas.

$$p = \frac{1}{3}u = \frac{1}{3}\frac{U}{V}$$

Thermodynamic Potentials

State fns V, T, P, U, S ; Can we find other state fns systematically? Changing dependent variables may prove convenient for analyzing different problems.

If a state fn $f(x,y)$ depends on x, y

$$df = u\,dx + v\,dy \quad \text{—} \quad (1)$$

say want to choose independent variables u, y, and find new state fn $g(u,y)$. Systematic way of construction through Legendre transform

$$g \equiv f - ux$$

$$dg = df - u\,dx - x\,du = \cancel{u\,dx} + v\,dy - \cancel{u\,dx} - x\,du$$

$$\boxed{dg = v\,dy - x\,du}$$

Use this procedure to define new thermo state fns.

$$dU = -p\,dV + T\,dS \quad \text{— (2)}; \qquad U(V, S).$$

we want to change to P, S, $H(P, S)$ ⟶ enthalpy.

$$H(P, S) = U + PV \quad \text{— (3)}$$

dimensions of energy

$$dH = \underbrace{dU + p\,dV} + V\,dp.$$

$$\boxed{dH = T\,dS + V\,dp} \quad \text{— (4)}$$

Next change variables to T, V

$$dU = TdS - p\,dV \qquad U(\underbrace{S,V}_{\to\, T,V})$$

Through L transform $F(T,V)$ Helmholtz potential/free energy

$$F = U - TS \quad \text{--- (5)}$$

$$dF = -SdT - p\,dV \quad \text{--- (6)}$$

Change variables $\longrightarrow P, T$.

$$dH = TdS + VdP$$

L transform, $G(P,T) = H - ST$ Gibbs potential/free energy

$$= U + PV - TS \quad \text{--- (7)}$$

$$dG = VdP - SdT \quad \text{--- (8)}$$

$$dU = -PdV + TdS \quad \text{(i)}$$

$$dH = VdP + TdS \quad \text{(ii)}$$

$$dF = -PdV - SdT \quad \text{(iii)}$$

$$dG = VdP - SdT \quad \text{(iv)}$$

Potential energy in mech. $-\frac{\partial U}{\partial x} = \text{Force}$ from (i)

for example,

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_S = -P \qquad \left(\frac{\partial U}{\partial S}\right)_V = T}$$