30/09/20

HW

adiabatic free expansion

$C_p - C_v = R$

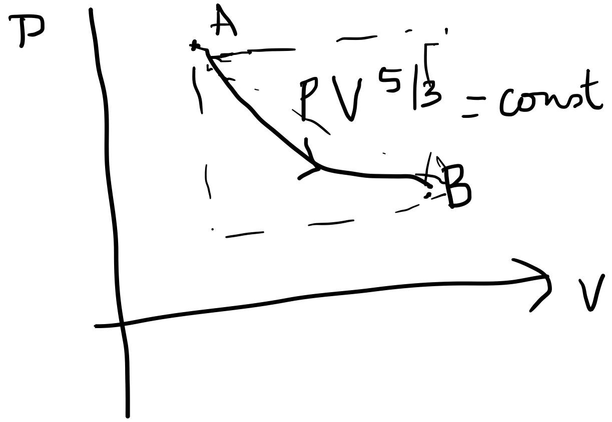
$PV^\gamma = \text{const}$ X

$T_1 = T_2$ $\Delta U = 0$

derive $\left(\frac{\partial U}{\partial T}\right)_P = C_p - PV\beta$

$\text{đ}Q = dU \cancel{+} - \text{đ}W$

some wrote $\left(\frac{\partial Q}{\partial T}\right)_P$, $\left(\frac{\partial W}{\partial T}\right)_P$ X $\left(\frac{\text{đ}Q}{dT}\right)_P$



$$PV^{5/3} = \alpha$$

$$\downarrow$$

$$PV^{\gamma} = \text{const} \qquad \frac{C_p}{C_v} = 5/3$$

$$U(B) - U(A) = -\int_A^B \underbrace{p\,dV}_{\text{adiabatic}}$$

$$\left.\begin{cases} dU = -PdV + TdS \\ dH = VdP + TdS \\ dF = -PdV - SdT \\ dG = VdP - SdT \end{cases}\right\} \longrightarrow \left(\frac{\partial U}{\partial V}\right)_S = -P \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

Physical Significance of potentials

In purely mechanical system, external work performed by system

$$\Delta U = -W$$

for thermo

$$-W = \Delta U - Q$$

Let us suppose that system is in contact with an environment at const T ($W <$ or $> -\Delta U$ depending whether heat is absorbed or given up)

$A \longrightarrow B$

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A).$$

temp const

$$\frac{1}{T} \int_A^B dQ \leq S(B) - S(A)$$

$$Q = \int_A^B dQ \leq T\left(S(B) - S(A)\right)$$

↳ upper limit on how much heat can be received from env.

$$Q \leq T\left[S(B) - S(A)\right]$$

$$\Delta U + W \leq T\left[S(B) - S(A)\right]$$

$$U(B) - U(A) + W \leq T\left[S(B) - S(A)\right]$$

$$W \leq U(A) - U(B) + T\left[S(B) - S(A)\right]$$

Recall $F = U - TS$

$$W \leq F(A) - F(B) = -\Delta F$$

$$\boxed{W \leq -\Delta F}$$

; Contrast with $W = -\Delta U$

$$W \leq F(A) - F(B)$$

maximum work $= F(A) - F(B) \longrightarrow$ upper limit on work extractible from system

$\Longrightarrow$ free energy : energy free for doing work

Helmholtz free energy.

Now consider dynamical isolation of system $\equiv$ no exchange of work with environment (clamped piston)

$$0 \leq F(A) - F(B).$$

$$\boxed{F(B) \leq F(A)}$$

free energy cannot increase

free energy minimum $\longrightarrow$ stable equilibrium

$G \equiv$ Gibbs free energy/potential.

situation : pressure and temp do not change.

isothermal, isobaric transform

$$W = P[V(B) - V(A)]$$

+isothermal $W \leq F(A) - F(B)$

$$P[V(B) - V(A)] \leq F(A) - F(B).$$

Recall, $G = F + PV$.

$$\boxed{G(B) \leq G(A)}$$

Gibbs potential cannot increase.

$G_{min} \rightarrow$ stable equilibrium.

Maxwell's Relations

$$dU = -PdV + TdS \quad (1)$$
$$dH = VdP + TdS \quad (2)$$
$$dF = -PdV - SdT \quad (3)$$
$$dG = VdP - Sdt \quad (4)$$

$\rightarrow$ exact differentials

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

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

from (1)

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \quad (5)$$

from (2)

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad (6)$$

from 3

$$-\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T \quad (7)$$

from (4)

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad (8)$$

- Provide relationships between measurable quantities and those that cannot be measured

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \longrightarrow -\beta V$$

$$\left(\frac{\partial S}{\partial P}\right)_T \begin{cases} > 0 & \text{if } \beta < 0 \\ < 0 & \text{if } \beta > 0 \end{cases}$$