Thermodynamic Potentials

abstract concept
isolated system → not applicable to expt!

more typical case: system connected to reservoir

- energy, particles, etc can flow system ⟷ reservoir and reservoir properties unchanged

much larger system

<u>note</u>: entropy of system may increase or decrease, all we know for sure is

no subscript (system)

$$\Delta S_{composite} = \Delta S + \Delta S_{reservoir} \geq 0$$

we want to identify properties of the system that are a maximum/minimum

- energy can be transferred between system & reservoir

$$\Delta S_{reservoir} = \frac{-Q}{T_{reservoir}}$$

Then,

$$\Delta S_{composite} = \Delta S - \frac{Q}{T_{reservoir}}$$

1st law

$\Delta E = Q + W$

$$= \Delta S - \frac{\Delta E - W}{T_{reservoir}}$$

$W = -P_{reservoir} \Delta V$

work done on system due to reservoir

$$= \Delta S - \frac{\Delta E + P_{reservoir} \Delta V}{T_{reservoir}} \geq 0$$

$$\Delta E + P_{reservoir} \Delta V - T_{reservoir} \Delta S \leq 0$$

Let's examine typical experimental situations, and define relevant functions that depend only on the properties of the system

1. Assume V, N are fixed, $T = T_{reservoir}$

$$\Delta E + \cancel{P_{reservoir} \Delta V}^{\,0} - \underbrace{T_{\cancel{reservoir}}}_{}^{\,T} \Delta S \leq 0$$

$$\underbrace{\Delta E - T \Delta S}_{\Delta F} \leq 0$$

Helmholtz free energy

$$\boxed{F \equiv E - TS}$$

We see that $\Delta F \leq 0$

$\rightarrow$ if constraint removed,

F will decrease or remain the same

$\Rightarrow$ F is a minimum at equillibrium (fixed V, N, T)

What are the natural variables for F?

$$dF = \underbrace{dE}_{TdS - PdV + \mu dN} - TdS - SdT$$

$$= \cancel{TdS} - PdV + \mu dN - \cancel{TdS} - SdT$$

$$\boxed{dF = -SdT - PdV + \mu dN}$$

Thus, natural variables for F are $\underline{T, V, N}$, and

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

(2) Assume volume can now vary N fixed, $T = T_{reservoir}$, $P = P_{reservoir}$

$$\Delta E + P_{\cancel{reservoir}}^{\;P} \Delta V - T_{\cancel{reservoir}}^{\;T} \Delta S \leq 0$$

$$\underbrace{\Delta E + P \Delta V - T \Delta S}_{\Delta G} \leq 0$$

Gibbs free energy

$$\boxed{G = E - TS + PV}$$

→ G is similarly a minimum at equilibrium

(fixed N, T, P)

$$dG = dE - TdS - SdT + PdV + VdP$$

$$= \cancel{TdS} \cancel{-PdV} + \mu dN - \cancel{TdS} - SdT \cancel{+PdV} + VdP$$

$$\boxed{dG = -SdT + VdP + \mu dN}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

(3) enthalpy $\quad H = E + PV \quad$ (fixed S, P, N)

$$dH = dE + PdV - VdP$$

$$= TdS - \cancel{PdV} + \mu dN + \cancel{PdV} - VdP$$

$$\boxed{dH = TdS - VdP + \mu dN}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$$

$$V = -\left(\frac{\partial H}{\partial P}\right)_{S,N}$$

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$$

Note: $\quad \Delta E + P_{reservoir}\Delta V - \cancelto{0}{T_{reservoir}}\Delta S \leq 0$

$\Delta H = \Delta E + P\Delta V \quad$ minimum in equilibrium (fixed S)

Maxwell Relations

- all thermodynamic measurements expressed in terms of partial derivatives

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

→ its important to be explicit about which variables are independant (natural variables / potential) and what is being held constant

→ it is often very useful to relate various derivatives to each other

assume N fixed

<u>ex</u>: $dE = TdS - PdV + \cancel{\mu dN}$

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

<u>recall</u>: order of differentiation is irrelevant

for any function $f(x,y)$, $\dfrac{\partial^2 F}{\partial x \partial y} = \dfrac{\partial^2 F}{\partial y \partial x}$

Thus,
$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S$$

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

There are many of these!