

## Enthalpy $H(S, p, N)$

use pressure instead of volume

$$E(S, V, N), \quad p = -\left(\frac{\partial E}{\partial V}\right)_{S, N}$$

$$H(S, p, N) \equiv E + pV$$

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

$$dH = TdS + Vdp + \mu dN$$

Since  $E = TS - pV + \mu N$

$$H = E + pV = TS + \mu N$$

## Gibbs Free Energy $G(T, p, N)$

use temperature and pressure instead of entropy and volume

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

$$G(T, p, N) = E - TS + pV$$

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

$$dG = -SdT + Vdp + \mu dN$$

$$\text{Since } E = TS - pV + \mu N$$

$$G = E - TS + pV = \mu N$$

$$\text{or } \boxed{\frac{G}{N} \equiv g = \mu}$$

The chemical potential is the Gibbs free energy per particle

$$\text{From } G = \mu N \text{ we get } dG = \mu dN + N d\mu$$

$$\text{Combining with } dG = -SdT + Vdp + \mu dN$$

$$\cancel{\mu dN} + N d\mu = -SdT + Vdp + \cancel{\mu dN}$$

$$\Rightarrow SdT - Vdp + N d\mu = 0$$

we regain the Gibbs-Duhem relation

Note: If we are dealing with a system with more than one species of particles,  $N_1, N_2, \dots$  then

$$G(T, p, N_1, N_2, \dots) = \mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3 + \dots$$

$$\text{where } \mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T, p, N_j \neq i}$$

## Grand potential $\Sigma(T, V, \mu)$

use temperature and chemical potential instead of entropy and particle number

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

$$\Sigma(T, V, \mu) = E - TS - \mu N$$

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

$$d\Sigma = -SdT - pdV - Nd\mu$$

Since  $E = TS - pV + \mu N$

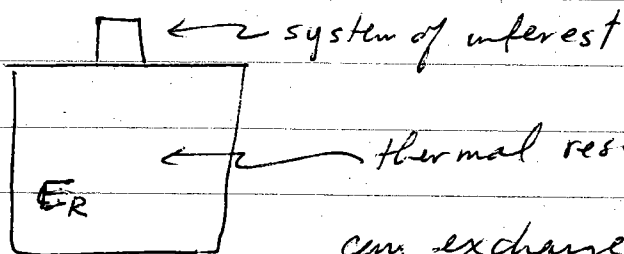
$$\Sigma = E - TS - \mu N = -pV$$

$$-\frac{\Sigma}{V} = p$$

the pressure is (-) the grand potential per unit volume.

## Extremum Principles for Free Energies

Concept of a thermal reservoir



can exchange only heat between system and reservoir

$$\left(\frac{\partial E_R}{\partial S_R}\right)_{V,N} = T_R$$

Suppose we add heat  $dQ = T dS$  to the reservoir.

The change in the reservoirs temperature  $T_R$  will be

$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R}\right) dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) dS$$

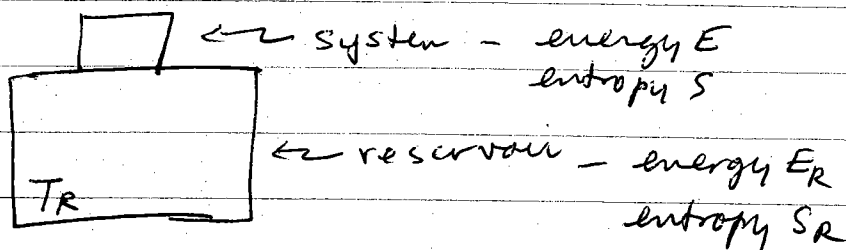
Since  $E_R$  and  $S_R$  are both extensive variables, they scale with the number of particles in the reservoir  $N_R$ .

So

$$\left(\frac{\partial^2 E_R}{\partial S_R^2}\right) \sim \frac{1}{N_R} \rightarrow 0 \quad \left. \begin{array}{l} \text{for infinitely large reservoir} \\ \Rightarrow \Delta T_R \rightarrow 0 \end{array} \right\}$$

Formally, a thermal reservoir is a system so large that its temperature does not change when it exchanges heat with the system of interest.

Consider a system in contact with a thermal reservoir  
 Only energy can be exchanged between system + reservoir  
 Temperature  $T_R$  of reservoir is const by definition



Since system is in equilib with reservoir, the system temp  $T = T_R$

If an internal constraint in the system is relaxed, what determines the new equilib state?

Use entropy formulation - total energy is conserved  $E = E_R + E^{\text{tot}}$   
 total entropy is maximized

$$S^{\text{tot}} = S_R(E_R) + S(E)$$

$$= S_R(E^{\text{tot}} - E) + S(E)$$

Since  $E \ll E^{\text{tot}}$  (as  $E_R \gg E$  by def of reservoir)  
 we can expand

$$S^{\text{tot}} \approx S_R(E^{\text{tot}}) - \left( \frac{\partial S_R}{\partial E_R} \right) E + S(E)$$

$$= S_R(E^{\text{tot}}) - \frac{E}{T_R} + S(E)$$

$$= S_R(E^{\text{tot}}) - (E - T_R S) / T_R$$

$$T_R = T$$

$$= \underbrace{S_R(E^{\text{tot}})}_T - \underbrace{A}_{\uparrow} / T_R$$

↑  
system temp

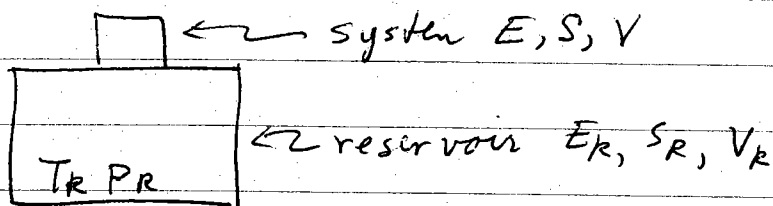
constant Helmholtz free energy

$S^{\text{tot}}$  maximized  $\Rightarrow$   $A$  minimized

$\Rightarrow$  the equilib state of a system in contact with a thermal reservoir will be the one that minimizes the Helmholtz free energy  $A(T, V, N)$

Now consider a system in contact with a thermal + pressure reservoir

pressure reservoir always has fixed pressure  $p_R$



total energy conserved  $E^{\text{tot}} = E_R + E = \text{constant}$

total volume conserved  $V^{\text{tot}} = V_R + V = \text{const}$

system in equilib with reservoir  $\Rightarrow T = T_R, p = p_R$

$$S^{\text{tot}} = S_R(E_R, V_R) + S(E, V)$$

$$= S_R(E^{\text{tot}} - E, V^{\text{tot}} - V) + S(E, V)$$

$$\approx S_R(E^{\text{tot}}, V^{\text{tot}}) - \left(\frac{\partial S_R}{\partial E_R}\right) E - \left(\frac{\partial S_R}{\partial V_R}\right) V + S(E, V)$$

$$= \text{constant} - \frac{E}{T_R} + \frac{P_R}{T_R} V + S$$

$$= \text{const} - (E + PV - ST) / T = \text{const} - G / T$$

$S^{\text{tot}}$  maximized  $\Rightarrow$   $G$ , Gibbs Free Energy is minimized

⇒ the equilib state of a system in contact with a thermal & pressure reservoir will be the one that minimizes the Gibbs free energy  $G(T, P, N)$

Similarly - the equilib state of a system in contact with a pressure reservoir will be the one that minimizes the enthalpy  $H(S, p, N)$

and - the equilib state of a system in contact with a thermal and a particle reservoir (a particle reservoir can exchange particles with the system, but is so large that its chemical potential  $\mu_p$  stays constant) will be the one that minimizes the grand potential  $\Sigma(T, V, \mu)$

## Maxwell Relations

Follow from 2<sup>nd</sup> derivatives of the thermodynamic potentials  
Energy:

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

$$\text{so } \left(\frac{\partial^2 E}{\partial S \partial V}\right)_N = \left(\frac{\partial T}{\partial V}\right)_{S, N}$$

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

$$\text{so } \left(\frac{\partial^2 E}{\partial V \partial S}\right)_N = -\left(\frac{\partial P}{\partial S}\right)_{V, N}$$

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

Can do the same for any thermodynamic potential  
Helmholtz free energy

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

$$\text{so } -\left(\frac{\partial^2 A}{\partial T \partial V}\right)_N = \left(\frac{\partial S}{\partial V}\right)_{T, N}$$

$$\text{but: } -\left(\frac{\partial A}{\partial V}\right)_{T, N} = P(T, V, N)$$

$$\text{so } -\left(\frac{\partial^2 A}{\partial V \partial T}\right)_N = \left(\frac{\partial P}{\partial T}\right)_{V, N}$$

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



or Gibbs free energy

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

$$\text{so } \left( \frac{\partial^2 G}{\partial p \partial N} \right)_T = \left( \frac{\partial V}{\partial N} \right)_{T, p}$$

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

$$\text{so } \left( \frac{\partial^2 G}{\partial N \partial p} \right)_T = \left( \frac{\partial \mu}{\partial p} \right)_{T, N}$$

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

These equivalences, which follow from the independence of the order of taking 2nd derivatives, are called the Maxwell Relations

See Callen Chpt 7 for a complete list