THERMODYNAMIC POTENTIALS

- FOR AN <u>ISOLATED SYSTEM</u> THE "NATURAL" INDEPENDENT VARIABLES ARE $E, V, \vec{N}$ (BECAUSE THESE ARE THE VARIABLES WE CONTROL & THEY ARE FIXED).

  THE ENTROPY IS "NATURALLY" A FUNCTION OF THESE VARIABLES (dS DEPENDS ON dE, dV AND dN_i, USING CONSERVATION OF ENERGY).

  FOR AN ISOLATED SYSTEM, $S(E, V, \vec{N})$ DETERMINES THE DIRECTION OF SPONTANEOUS CHANGE IF WE REMOVE AN INTERNAL CONSTRAINT — CHANGE ONLY OCCURS IF S INCREASES.

- WE NEED TO BE ABLE TO DETERMINE THE DIRECTION OF SPONTANEOUS CHANGE FOR <u>OPEN</u> (i.e. NON-ISOLATED) SYSTEMS (SYSTEMS WHICH CAN INTERACT WITH THEIR ENVIRONMENT, WHERE ONE OR MORE OF $E, V, \vec{N}$ ARE NO LONGER FIXED).

- FOR <u>OPEN SYSTEMS</u> THE "NATURAL" INDEPENDENT VARIABLES (THE ONES WE ARE CONTROLLING) INCLUDE ONE OR MORE OF p, T, μ_i.

$$\boxed{\text{THE DIRECTION OF SPONTANEOUS CHANGE FOR OPEN SYSTEMS IS DETERMINED BY THE FACT THAT THE SYSTEM WILL SEEK A MAXIMUM OR MINIMUM FOR A CERTAIN THERMODYNAMIC POTENTIAL WHICH IS "NATURALLY" A FUNCTION OF THE "NATURAL VARIABLES"}}$$

- FOR <u>ISOLATED SYSTEMS</u>: THE NATURAL VARIABLES ARE $E, V, \vec{N}$ & THE THERMODYNAMIC POTENTIAL IS $S(E, V, \vec{N})$

OTHER THERMODYNAMIC POTENTIALS

1. THE (HELMHOLTZ) FREE ENERGY F

$$\boxed{F := E - TS}$$

FOR AN INFINITESIMAL CHANGE FROM ONE EQUILIBRIUM STATE TO ANOTHER

$$dF = dE - TdS - SdT$$

FOR A QUASISTATIC PROCESS, CONSERVATION OF ENERGY IS

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

$$\Rightarrow \quad dF = (\cancel{TdS} - pdV + \sum_i \mu_i dN_i) \cancel{- TdS} - SdT$$

$$\Rightarrow \quad \boxed{dF = -SdT - pdV + \sum_i \mu_i dN_i} \quad (1)$$

$\Rightarrow$ F IS "NATURALLY" A FUNCTION OF $T, V, \vec{N}$ SINCE THE CHANGE IN F IS COMPLETELY DETERMINED BY THE CHANGE IN THESE QUANTITIES (USING ONLY CONSERVATION OF ENERGY)

$$\Rightarrow \quad \boxed{F = F(T, V, \vec{N})}$$

USING THE DEFINITION OF THE DIFFERENTIAL

$$\boxed{dF(T,V,\vec{N}) = \frac{\partial F}{\partial T}\,dT + \frac{\partial F}{\partial V}\,dV + \sum_i \frac{\partial F}{\partial N_i}\,dN_i} \quad (2)$$

COMPARING (1) & (2)

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

$$\frac{\partial F(T,V,\vec{N})}{\partial V} = -p$$

$$\frac{\partial F(T,V,\vec{N})}{\partial N_i} = \mu_i$$

$\leftarrow$ 3 EQUATIONS OF STATE

2. THE GIBBS FREE ENERGY G

$$\boxed{G := E - TS + pV}$$

PRACTICE PROBLEM: COMPUTE dG USING THE EXPRESSION FOR dE FOR CONSERVATION OF ENERGY

FIND: $dG = -S\,dT + V\,dp + \sum_i \mu_i\, dN_i$

$$\Longrightarrow \boxed{G = G(T, p, \vec{N})}$$

$$\Longrightarrow \boxed{\begin{aligned} \frac{\partial G(T,p,\vec{N})}{\partial T} &= -S \\ \frac{\partial G(T,p,\vec{N})}{\partial p} &= V \\ \frac{\partial G(T,p,\vec{N})}{\partial N_i} &= \mu_i \end{aligned}}$$

$\leftarrow$ 3 EQUATIONS OF STATE

3. ENTHALPY H

$$\boxed{H := E + pV}$$

SAME TRICK: COMPUTE dH USING CONSERVATION OF ENERGY TO SUBSTITUTE FOR dE

$$\Longrightarrow \quad dH = T\,dS + V\,dp + \sum_i \mu_i\, dN_i$$

$$\Longrightarrow \quad \boxed{H = H(S, p, \vec{N})}$$

APPLY THE DEFINITION OF THE DIFFERENTIAL

$$\boxed{\begin{aligned} \frac{\partial H(S,p,\vec{N})}{\partial S} &= T \\ \frac{\partial H(S,p,\vec{N})}{\partial p} &= V \\ \frac{\partial H(S,p,\vec{N})}{\partial N_i} &= \mu_i \end{aligned}}$$

$\leftarrow$ 3 EQUATIONS OF STATE

COMMENT:

$$\left.\begin{aligned} F &= E - TS \\ G &= E - TS + pV \\ H &= E + pV \end{aligned}\right\}$$

LEGENDRE TRANSFORMS

("TRICK" TO CHANGE VARIABLES)