SYSTEMS WITH VARIABLE PARTICLE NUMBER

- 1^{ST} LAW: $\quad dE = đQ + đW$

- ANOTHER WAY TO CHANGE THE ENERGY OF THE SYSTEM IS TO CHANGE THE No° OF PARTICLES

[FOR EXAMPLE, RECALL THE EQUIPARTITION THEOREM: $\frac{1}{2}k_BT$ PER PARTICLE PER DoF]

ie CHANGE THE No° N_i OF VARIOUS CHEMICAL SPECIES.

- IN THIS CASE, CONSERVATION OF ENERGY TAKES THE FORM

$$dE = đQ + đW + \sum_i \underbrace{\mu_i dN_i}_{\text{CHANGE OF ENERGY DUE TO CHANGE } dN_i \text{ OF No° OF PARTICLES OF SPECIES } i}$$

[FOR A SYSTEM WITH A SINGLE CHEMICAL SPECIES:

$$dE = đQ + đW + \mu dN \quad .$$
]

THE COEFFICIENT μ_i IS CALLED THE

CHEMICAL POTENTIAL OF SPECIES i.

CRUDELY: μ_i IS THE RATE OF ENERGY CHANGE OF THE SYSTEM AS WE VARY N_i.

EQUATIONS OF STATE

1^{ST} LAW: $dE = đQ + đW + \sum_i \mu_i dN_i$

FOR QUASISTATIC PROCESSES:

$$\left.\begin{aligned} đQ &= T dS \\ đW &= -p dV \end{aligned}\right\}$$ UNIVERSAL & APPLY TO ALL SYSTEMS

SO, FOR A QUASISTATIC PROCESS, THE 1^{ST} LAW IS:

$$dE = T dS - p dV + \sum_i \mu_i dN_i$$

$$\Rightarrow \boxed{dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum_i \frac{\mu_i}{T} dN_i} \quad (1)$$

THIS SHOWS: THE CHANGE IN ENTROPY S IS COMPLETELY DETERMINED BY THE CHANGES IN E, V AND N_i. (THIS IS TRUE IN GENERAL, ALL WE HAVE USED IS CONSERVATION OF ENERGY)

IN OTHER WORDS: ENTROPY S IS "NATURALLY" A FUNCTION OF E, V, N_i

$$\boxed{S = S(E, V, \vec{N})}$$

$\vec{N} = (N_1, N_2, \dots)$

- USING THE DEFINITION OF THE DIFFERENTIAL d WE SEE THAT

$$\boxed{dS(E, V, \vec{N}) = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV + \sum_i \frac{\partial S}{\partial N_i} dN_i} \quad (2)$$

COMPARING (1) & (2):

$$\boxed{\begin{aligned} \frac{\partial S(E,V,\vec{N})}{\partial E} &= \frac{1}{T} \\ \frac{\partial S(E,V,\vec{N})}{\partial V} &= \frac{P}{T} \\ \frac{\partial S(E,V,\vec{N})}{\partial N_i} &= -\frac{\mu_i}{T} \end{aligned}}$$

— EQUATIONS OF STATE

— (3)

- LATER WE WILL SEE HOW TO COMPUTE S.
- THE EQUATIONS OF STATE (3) DETERMINE T, P, μ_i IN TERMS OF $S(E,V,\vec{N})$
- $S(E,V,\vec{N})$ – DEPENDS ON THE PARTICULAR SYSTEM, & CAN BE DERIVED USING QUANTUM MECHANICS AND

$$S = k_B \ln \Omega$$