PRINT NEATLY *** **USE A BLACK PEN** *** **DO NOT STAPLE**

Course 565/665 Lecture Number ______ Date 2/24/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

LAST TIME - Extensive vs. Intensive Properties

- Extensive Properties - Depend on the size of the system. Examples include, energy, entropy, volume, and the number of molecules.

- Intensive Properties - Does not depend on the size of the system. Examples include pressure, temperature, concentration, and chemical potential.

If a system has reached equilibrium, then the extensive properties will have definite values. If this system is partitioned

$$\frac{S}{kN} = -\sum_i p_i \ln p_i \qquad \text{If there are 2 states.}$$

$$= -(p_A \ln p_A + p_B \ln p_B) = -(\ln p_A^{p_A} + \ln p_B^{p_B})$$

$$\frac{S}{k} = -(n_A \ln p_A + n_B \ln p_B) = -(\ln p_A^{n_A} + \ln p_B^{n_B})$$

$$\frac{S}{k} = \ln(p_A^{n_A} + p_B^{n_B}) \qquad \text{More Tomorrow.}$$

But I will say that $\frac{S}{kN} = -\sum_i p_i \ln p_i = \frac{1}{N} \ln W$. This should still be an extensive property.

PRINT NEATLY *** **USE A BLACK PEN** *** **DO NOT STAPLE**

Course 565/665 Lecture Number ____ Date 2/24/03

Lecturer Cavagnero Note Taker Fulmer

More tomorrow . . .

Extensive Properties of fundamental Importance in Thermodynamics

- Internal Energy (U) $\quad U = U(S, V, N)$
- Entropy (S) $\quad S = S(U, V, N)$

These two quantities are important because they depend only on extensive quantities. Further-more, the familiar intensive quantities temp., pressure, and chemical potential can be defined as the change in U with respect to the extensive properties. Finally, $U = U(S, V, N)$ means that U is a function of entropy, volume, and number of molecules, much the same as $f(x)$ where f is a function of x.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} dN_i$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} dN_i$$

Let us define the following intensive quantities:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

T - temperature

p - pressure

μ - chemical potential

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

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{p}{T}\right) dV - \sum_i \left(\frac{\mu_i}{T}\right) dN_i$$

Implying:

$$\left(\frac{1}{T}\right) = \left(\frac{\partial S}{\partial U}\right)_{V,N} \qquad \left(\frac{p}{T}\right) = \left(\frac{\partial S}{\partial V}\right)_{U,N} \qquad -\left(\frac{\mu_i}{T}\right) = \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}}$$

PRINT NEATLY *** USE A BLACK PEN *** DO NOT STAPLE

Course 565/665 Lecture Number ____ Date 2/24/03

Lecturer Cavagnero Note Taker Fulmer

First Order Homogeneous Functions

Given $F(x, y, z)$, it is 1st Order Homogeneous if

$$F(\lambda x, \lambda y, \lambda z) = \lambda F(x, y, z)$$

Physically speaking, $U = U(S, V, N)$ is a first order homogeneous function. It is an extensive property, and it is a function of only extensive properties.

If the system is increased or decreased by some factor of λ, then its independent variables will change by this same factor λ.

If 1st Order Homogeneous,

$$F = \sum_{i=1}^{M} x_i \left(\frac{\partial F}{\partial x_i}\right)$$

See page 111 for a complete proof.

Augmenting U by λ makes $\lambda U = U(\lambda S, \lambda V, \lambda N)$

Increasing independent variables:

$$dS \rightarrow d\lambda S = \lambda\, dS$$
$$dV \rightarrow d\lambda V = \lambda\, dV$$
$$dN \rightarrow d\lambda N = \lambda\, dN$$

$$\lambda dU = T \lambda dS - P \lambda dV + \sum_{i=1}^{m} \mu_i \lambda dN_i$$

This means that T, P, and μ_i do not change as we vary λ.

$$T = \left(\frac{\partial U}{\partial S}\right) = \frac{\lambda \partial U}{\lambda \partial S} = T$$

T, P, μ are intensive.