Course 565/665 Lecture Number ____ Date 2/25/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

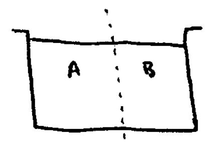
Last Time

Problem 6.10 - There is a problem/typo. The alpha that is mentioned should just be $\langle \varepsilon \rangle$. Make this substitution.

Entropy per mole:

$S \rightarrow$ Extensive

$\frac{S}{kN} \longrightarrow$ Intensive



$V_A = V_B$
$N_A = N_B$
$S_A = S_B$

$$\frac{S}{kN} = \frac{S_A + S_B}{k(N_A + N_B)} = \frac{2S_A}{2kN_A} = \frac{2S_B}{2kN_B}$$

If this quantity were intensive or extensive,

Intensive: $\frac{S}{kN} = \frac{S_A}{kN_A} = \frac{S_B}{kN_B}$

Extensive: $\frac{S}{kN} = \frac{S_A}{kN_A} + \frac{S_B}{kN_B}$

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

T reflects the response of a system from entropy changes. Heat generally flows from hot to cold bodies.

At equilibrium S is maximized:

$S_{TOTAL} = S_A + S_B =$ constant at equilibrium.

As equilibrium is reached, S_{TOTAL} increases until S_{MAX} is reached.

$U_{TOTAL} = U_1 + U_2 =$ CONSTANT.

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At constant N,

$$dS = \left(\frac{\partial S_A}{\partial U_A}\right)_V dU_A + \left(\frac{\partial S_B}{\partial U_B}\right)_V dU_B + \left(\frac{\partial S_A}{\partial V_A}\right)_U dV_A$$

$$+ \left(\frac{\partial S_B}{\partial V_B}\right)_U dV_B = 0$$

Constraint:

$$U_{TOTAL} = dU_A + dU_B = 0$$

$$dU_A = -dU_B$$

At constant V as well,

$$dS = 0 = \left(\frac{\partial S_A}{\partial U_A}\right)_V dU_A + \left(\frac{\partial S_B}{\partial U_B}\right)_V dU_B$$

$$0 = \frac{1}{T_A} dU_A - \frac{1}{T_B} dU_A$$

$$0 = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A$$

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Thus, at equilibrium,

$$\boxed{T_A = T_B}$$

At equilibrium, temperatures in all parts of an isolated system are the same.

We can measure T, but we are <u>not</u> able to directly measure entropy (S).

As equilibrium is being reached,

$$dS \geq 0 \,.$$

[Entropy is a nondecreasing function of energy.]

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A \geq 0$$

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Both terms in the above relationship must have the same sign. Thus, if $T_A > T_B$, $\left(\frac{1}{T_A} - \frac{1}{T_B}\right) < 0$. To ensure $dS \geq 0$, dU_A must also be less than zero. The opposite is also true. Thus, if (A) is hotter than (B), heat flows from (A) to (B). This maximizes the entropy for the system.

<u>P describes the tendency to change V.</u>

Constraint: $V_{TOT} = V_A + V_B = \text{constant}$.

$$dV_{TOT} = dV_A + dV_B = 0$$

$$dV_A = -dV_B$$

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At equilibrium:

$$dS = \left(\frac{\partial S_A}{\partial V_A}\right) dV_A + \left(\frac{\partial S_B}{\partial V_B}\right) dV_B + \left(\frac{\partial S_A}{\partial U_A}\right) dU_A + \left(\frac{\partial S_B}{\partial U_B}\right) dU_B$$

Additional constraints:

(1) $U_{TOTAL} = U_A + U_B = \text{constant}$

$$dU_A = -dU_B$$

$$dS = \left[\left(\frac{\partial S_A}{\partial V_A}\right) - \left(\frac{\partial S_B}{\partial V_B}\right)\right] dV_A + \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A = 0$$

At equilibrium, $T_A = T_B$ (2nd term $\longrightarrow 0$)

$$\left(\frac{\partial S_A}{\partial V_A}\right) = \left(\frac{\partial S_B}{\partial V_B}\right) \Rightarrow \frac{P_A}{T_A} = \frac{P_B}{T_B}$$

The pressures will equalize at equilibrium.