Discussion 7

Name and section: ____________________

1. Derive an expression for S as was done in class for U.

Solution: Because of the properties of linear homogenous functions derived in class:

$$S = \frac{U}{T} + \frac{pV}{T} - \sum_i \frac{\mu_i N_i}{T}$$

2. Consider a system in two parts A and B separated by a permeable barrier that contains one type of molecule.

   (a) What equalities will be satisfied at equilibrium?

Solution:

$$\begin{aligned} \mathrm{d}S = 0 = & \left(\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}\right)\mathrm{d}U_A \\ & + \left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}\right)\mathrm{d}V_A \\ & + \left(\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right)\mathrm{d}N_A \end{aligned}$$

$$\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0 \implies T_A = T_B$$
$$\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0 \implies p_A = p_B$$
$$\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B} = 0 \implies \mu_A = \mu_B$$

   (b) Derive expressions for the tendencies of matter and energy to exchange. That is, under what conditions will molecules move from A to B?

Solution:

$$\begin{aligned} 0 \leq \mathrm{d}S = &\left(\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}\right)\mathrm{d}U_A \\ &+ \left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}\right)\mathrm{d}V_A \\ &+ \left(\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right)\mathrm{d}N_A \end{aligned}$$

$$\left(\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}\right)\mathrm{d}U_A \geq 0 \implies T_A \geq T_B \text{ if } \mathrm{d}U_A \leq 0$$

$$\left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}\right)\mathrm{d}V_A \geq 0 \implies p_A \geq p_B \text{ if } \mathrm{d}V_A \geq 0$$

$$\left(\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right)\mathrm{d}N_A \geq 0 \implies \mu_A \geq \mu_B \text{ if } \mathrm{d}N_A \leq 0$$

3. With N ideal gas molecules at p_1, V_0, T_1, reversibly heat the system at constant volume.
   (a) How much work is done on the system in this *isochoric* process?

Solution:

$$w = 0 \tag{1}$$

   (b) If the final system is at p_2, V_0, T_2, find an expression for how much heat was added in terms of C_V, T_1, T_2 and C_V, N, V_0, p_1, p_2. Use the equation:

$$\Delta U = C_V(T_2 - T_1). \tag{2}$$

Solution:

$$dU = \delta q + \delta w = \delta q$$

$$q = \Delta U = C_V(T_2 - T_1) = \frac{C_V}{Nk_B}V_0(p_2 - p_1)$$

   (c) Find an expression for the entropy change ΔS in this process.

Solution:

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) \tag{3}$$

4. Consider a two level system on a lattice of size N with energies ϵ_1 and ϵ_2.

(a) What is the general partition function for one site?

Solution:

$$Q_s = p_1 + p_2$$

(b) What is the general partition function for all sites? Give an expression for distinguishable and indistinguishable sites.

Solution:

$$Q_d = (p_1 + p_2)^N$$
$$Q_i = \frac{(p_1 + p_2)^N}{N!}$$

(c) What is the partition function for one site with Boltzmann weighted probabilities?

Solution:

$$Q_s = \mathrm{e}^{-\epsilon_1 \beta} + \mathrm{e}^{-\epsilon_2 \beta}$$

(d) What is the partition function for all sites with Boltzmann weighted probabilities?

Solution:

$$Q_d = \left(\mathrm{e}^{-\epsilon_1 \beta} + \mathrm{e}^{-\epsilon_2 \beta}\right)^N$$
$$Q_i = \frac{\left(\mathrm{e}^{-\epsilon_1 \beta} + \mathrm{e}^{-\epsilon_2 \beta}\right)^N}{N!}$$

5. Consider a constant-pressure process: With N molecules of an ideal gas in a cylinder with a movable piston at $p_0 = p_{\mathrm{ext}}, V_1, T_1$, transfer and amount of heat q to increase the gas volume and temperature to V_2, T_2.

(a) What is the work done in this *isobaric* process?

Solution:

$$\begin{aligned} w &= -\int_{V_1}^{V_2} p \, \mathrm{d}V \\ &= -p_0(V_2 - V_1) \end{aligned}$$

(b) Using the ideal gas law and eq. (2), find expressions for ΔU, the change in internal energy.

Solution:

$$\begin{aligned}\Delta U &= C_V(T_2 - T_1) \\ &= \frac{C_V}{Nk_B} p_0(V_2 - V_1)\end{aligned}$$

(c) Find an expression for q, the heat applied to the system.

Solution:

$$\begin{aligned}q &= \Delta U - w \\ &= \left(\frac{C_V}{Nk_B} - 1\right) p_0(V_2 - V_1)\end{aligned}$$

(d) Find an expression for the entropy change ΔS in this process.

Solution:

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) \tag{4}$$