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PHYSICS 214A Midterm Exam February 10, 2009

- 1. Do not open the exam until instructed to do so.
- 2. Write your answers in the spaces provided for each part of each problem. Place answers in the boxes if provided. Show your calculations in the available space or the blank facing page. Please write clearly. If we can't read your writing, you won't get credit.

R = 8.314 J/K-mol	$k_B = 1.38054 \times 10^{-16} \text{ ergs/K}$
$1 \text{ atm} = 1.013 \times 10^6 \text{ dynes/cm}^2$	273 K = 0° C

DO NOT WRITE BELOW THIS LINE

А	MAX POINTS	SCORE	INITIALS
Problem 1	20		
Problem 2	20		
Problem 3	20		
Problem 4	20		
Problem 5	20		
Problem 6	20		
Total	100		

(a) (5 points) If a three dimensional system has 10⁶ particles, how many dimensions does its phase space have? You may neglect internal degrees of freedom of the particles.

Answer: Number of dimensions of phase space $= 6N = 6 \times 10^6$

(b) (5 points) What is the most important fundamental assumption of statistical mechanics?

Answer: An isolated system in equilibrium is equally likely to be in any of its accessible microstates.

(c) (5 points) Is anything wrong with the plot of entropy S versus energy E? If so, explain.



Answer: Yes, something is wrong. At high temperatures the temperature is negative because

$$\frac{1}{T} = \frac{\partial S}{\partial E} < 0 \tag{1}$$

 $\partial S/\partial E$ is the slope of the curve. Also note that $\partial S/\partial E = 0$ which implies the temperature is infinity at the maximum. Then T < 0 for $E < E_{max}$ which implies that the temperature T is discontinuous.

(d) (5 points) Is anything wrong with the plot of entropy S versus temperature T? If so, explain.



Answer: Yes, something is wrong. The specific heat at constant volume

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V \tag{2}$$

The region with negative slope $(\partial S/\partial T < 0)$ has a negative specific heat which is unphysical.

2. (20 points) Use the Legendre transformation to derive the Gibbs free energy G(T, p) from the Helmholtz free energy F(T, V). In other words, derive the relation between G and F. Also derive the associated Maxwell relation.

Answer:

$$dF = -SdT - pdV \tag{3}$$

Use a Legendre transformation to change the independent variable from p to V.

$$d(pV) = pdV + Vdp$$

$$pdV = d(pV) - Vdp$$

$$dF = -SdT - [d(pV) - Vdp]$$

$$= -SdT - d(pV) + Vdp$$

$$d(F + pV) = -SdT + Vdp$$

Since the Gibbs free energy is defined as G = F + pV, we have

$$dG = -SdT + Vdp \tag{4}$$

From this we see that

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p}$$
$$V = \left(\frac{\partial G}{\partial p}\right)_{T}$$

Using

$$\frac{\partial G}{\partial p \partial T} = \frac{\partial G}{\partial T \partial p} \tag{5}$$

we have the Maxwell relation

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \tag{6}$$

3. (20 points) An ideal monatomic gas at 300K expands adiabatically and reversibly to twice its volume. What is its final temperature?

Answer: For an adiabatic process $pV^{\gamma} = \text{const}$ where $\gamma = c_P/c_V = 5/3$. Method I:

$$p_i V_i^{\gamma} = p_f V_f^{\gamma}$$

$$V_f = 2V_i$$

$$p_i V_i^{\gamma} = p_f (2V_i^{\gamma})$$

$$p_i = 2^{\gamma} p_f$$

$$p_f = 2^{-\gamma} p_i$$

$$p_f V_f = nRT_f$$

$$p_f V_f = (2^{-\gamma} p_i) (2V_i) = nRT_f$$

$$2^{1-\gamma} p_i V_i = nRT_f$$

$$p_i V_i = nRT_f$$

$$2^{1-\gamma} (nRT_i) = nRT_f$$

$$T_f = 2^{1-\gamma}T_i \quad T_i = 300 \text{ K}$$

$$= 2^{1-\frac{5}{3}} (300 \text{ K})$$

$$= 189 \text{ K}$$

Method II:

$$V^{\gamma-1}T = \text{const}$$

$$V_i^{\gamma-1}T_i = V_f^{\gamma-1}T_f$$

$$V_f = 2V_i$$

$$V_i^{\gamma-1}T_i = (2V_i)^{\gamma-1}T_f$$

$$T_i = 2^{\gamma-1}T_f$$

$$T_f = \frac{T_i}{2^{\gamma-1}}$$

$$= \frac{(300 \text{ K})}{2^{\frac{5}{3}-1}}$$

$$= 189 \text{ K}$$

$$T_{\rm final} = 189 \ {\rm K}$$

4. (20 points) Two "identical" bodies, each with constant heat capacity C_p , originally at temperatures T_1 and T_2 , respectively, are used as heat reservoirs for a Carnot engine operating with infinitesimal reversible cycles. If the bodies remain at constant pressure and undergo no phase changes, the engine will eventually come to rest with both bodies at a final temperature T_f . Find T_f in terms of T_1 and T_2 .



Answer: A Carnot engine has $\Delta S = 0$.

$$\Delta S = \int \frac{dQ}{T}$$

= $\int_{T_1}^{T_f} \frac{C_p dT}{T} + \int_{T_2}^{T_f} \frac{C_p dT}{T}$
= $C_p \ln\left(\frac{T_f}{T_1}\right) + C_p \ln\left(\frac{T_f}{T_2}\right)$
= $C_p \ln\left(\frac{T_f^2}{T_1 T_2}\right)$
= 0

This implies that

$$\frac{T_f^2}{T_1 T_2} = 1 T_f^2 = T_1 T_2 T_f = \sqrt{T_1 T_2}$$

$$T_f = \sqrt{T_1 T_2}$$

5. (20 points) Two volumes of gas are separated by a partition. The system as whole is thermally isolated. In volume V_1 there is 1 mole of helium gas. In volume V_2 there are 2 moles of argon. $V_2 = 2V_1$. At time t = 0 the partition is removed. After a while equilibrium is established. What is the change in entropy $\Delta S = S_f - S_i$ between the initial and final states? (You may treat the gases as ideal gases.)



Answer: The change in entropy is due to the increase in the number of configurations of the gas particles when the partition is removed.

Method I:

Let Ω be the number of states.

$$S = k_B \ln \Omega \qquad V_2 = 2V_1 \qquad N_2 = 2N_1$$

$$\Omega_i \propto V_1^{N_1} V_2^{N_2} = V_1^{N_1} (2V_1)^{2N_1} = 2^{2N_1} V_1^{3N_1}$$

$$\Omega_f \propto (3V_1)^{N_1 + N_2} = (3V_1)^{N_1 + N_2} = (3V_1)^{3N_1} = 3^{3N_1} V_1^{3N_1}$$

$$\Delta S = k_B \ln \Omega_f - k_B \ln \Omega_i$$

$$= k_B \ln \left(\frac{\Omega_f}{\Omega_i}\right)$$

$$= k_B \ln \left(\frac{3^{3N_1}}{2^{2N_1}}\right)$$

$$= N_1 k_B \left[\ln \left(\frac{3^3}{2^2}\right)\right] \qquad \text{where } N_1 = 1 \text{ mole}$$

$$= R \ln \left(\frac{27}{4}\right)$$

$$= (8.3 \frac{J}{K - \text{mole}}) \left(\ln \left(\frac{27}{4}\right)\right)$$

$$= 15.8 \text{ J/K}$$

Method II: The energy is constant. For systems with interacting particles, the temperature is not well defined. However, for an ideal gas, the particles are noninteracting, so the energy and temperature do not change when the volume changes as long as the system is thermally isolated.

$$d\overline{E} = 0$$

$$dQ = TdS = d\overline{E} + dW = dW = pdV$$

$$dS = \frac{pdV}{T}$$

$$p = \frac{nRT}{V}$$

$$dS = nR\frac{dV}{V}$$

$$\Delta S = nR\int \frac{dV}{V} = nR\ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S_{\text{He}} = n_1R\ln(3)$$

$$\Delta S_{\text{Ar}} = n_2R\ln\left(\frac{3}{2}\right)$$

$$\Delta S = \Delta S_{\text{He}} + \Delta S_{\text{Ar}}$$

$$= R\ln(3^{n_1}) + R\ln\left(\left(\frac{3}{2}\right)^{n_2}\right)$$

$$= R\left[\ln\left(\frac{3^{n_1+n_2}}{2^{n_2}}\right)\right]$$

$$= R\left[\ln\left(\frac{3^3}{2^2}\right)\right]$$

$$= R\ln\left(\frac{27}{4}\right)$$

$$= 15.8 \text{ J/K}$$

 \mathbf{Method} III: Start with the Maxwell relation:

$$\begin{pmatrix} \frac{\partial S}{\partial V} \end{pmatrix}_{T} = \left(\frac{\partial p}{\partial T} \right)_{V} \\ dS = \int \left(\frac{\partial p}{\partial T} \right)_{V} dV \\ p = \frac{nRT}{V} \\ \left(\frac{\partial p}{\partial T} \right)_{V} = \frac{nR}{V} \\ dS = nR \frac{dV}{V} \\ \Delta S = nR \int \frac{dV}{V} = nR \ln \left(\frac{V_{f}}{V_{i}} \right) \\ \Delta S_{\text{He}} = n_{1}R \ln(3) \\ \Delta S_{\text{Ar}} = n_{2}R \ln \left(\frac{3}{2} \right) \\ \Delta S = \Delta S_{\text{He}} + \Delta S_{\text{Ar}} \end{cases}$$

$$= R \ln (3^{n_1}) + R \ln \left(\left(\frac{3}{2}\right)^{n_2} \right)$$
$$= R \left[\ln \left(\frac{3^{n_1+n_2}}{2^{n_2}}\right) \right]$$
$$= R \left[\ln \left(\frac{3^3}{2^2}\right) \right]$$
$$= R \ln \left(\frac{27}{4}\right)$$
$$= 15.8 \text{ J/K}$$