Physics 119A Midterm Nov. 22, 2010

NAME: Solutions PERM:

Instructions: The last 2 pages of the exam contain some useful information. Please verify that your exam contains 9 pages (7 of exam and 2 of information; 2 pages are intentionally left blank for additional work space). Show all work and box your final answers to receive full credit.

Question I, 24 points (6 points each): True or False: Provide a brief justification or no credit.

a) **What is $\ln(10^6!)$ to two significant figures?**

$$\sim 10^6 \ln(10^6) - 10^6 = 1.3\times 10^7$$

b) **The total differential of enthalpy may be written dH= TdS + VdP +μdN. Three Maxwell relations follow from this expression. What are they?**

$$\left.\frac{\partial T}{\partial P}\right|_{S,N} = \left.\frac{\partial V}{\partial S}\right|_{P,N} \qquad \left.\frac{\partial T}{\partial N}\right|_{S,P} = \left.\frac{\partial \mu}{\partial S}\right|_{P,N}$$

$$\left.\frac{\partial V}{\partial N}\right|_{P,S} = \left.\frac{\partial \mu}{\partial P}\right|_{S,N}$$

c) **Suppose that you wanted to define a new thermodynamic potential that was a natural function of the variables (S,P, μ) and you call the potential Π(S,P, μ). Write down an expression for this potential and for the total derivative of this potential in terms of variations in its natural variables.**

$$\Pi = U + PV - \mu N \quad \text{-or-} \quad \Pi = TS$$

$$d\Pi = TdS + VdP - Nd\mu$$

d) **The function f(x,y,z) is homogeneous of order one and the function g(x,y) is homogeneous of order zero. If we know that f(1,5,3) = 6 and that g(1,5)=3, what are the following:**

f(3,15,9) = 18

g(1/2,5/2)= 3

Question II, 20 points: You throw a 1 kilogram hot (400K) block of solid lead (Pb) into a swimming pool. The water in the pool starts out at 300 K. Assume the swimming pool is so large that the lead is unable to change the temperature of the water and assume that the swimming pool (including both the lead and the water) is thermally isolated from the rest of the universe and is held at a constant pressure of 1 atm. Calculate ΔS_{Pb}, ΔS_{water}, $\Delta S_{universe}$. What is the final temperature of the lead and how do you know that the change to this final state will actually happen?

The specific heat capacity of lead is 0.150 J g^{-1} K^{-1}
The specific heat capacity of water is 4.184 J g^{-1} K^{-1}

$$q_{Pb} = C_{Pb}\Delta T = 0.150\,\frac{J}{gK} \times 1000\,g \times (300-400)K = -15000\,J$$

$$= -15\,kJ$$

$$q_{H_2O} = -q_{Pb} = +15\,kJ$$

$$\Delta S_{H_2O} = \frac{q_{H_2O}}{T_{H_2O}} = \frac{15\,000\,J}{300\,k} = \boxed{50\,J/k = \Delta S_{H_2O}}$$

$$\Delta S_{Pb} = \int_{400k}^{300k} \frac{C_{Pb}\,dT}{T} = C_{Pb}\ln\left(300/400\right) = 0.150\,J/gk \times 1000\,g \times \ln(.75)$$

$$\boxed{\Delta S_{Pb} = -43.2\,J/k}$$

$$\Delta S_{Pb} + \Delta S_{H_2O} = \boxed{\Delta S_{univ} = +6.8\,J/k}$$

Final temp of Pb is 300 K.

The change will happen since $\Delta S_{univ} > 0$

and the process is spontaneous.

Question III, 20 points: I suggest you read all parts of this problem before beginning.

In class, we started our discussion about the statistical basis of entropy with the system of an ideal gas. We first guessed that the number of microstates for the gas had the following form:

$$\Omega(N,V,U)=\left(\frac{V}{V_0}\right)^N$$

where $V_0=\left[\frac{3h^2}{4em\pi}\frac{N}{U}\right]^{\frac{3}{2}}$ **is predicted by quantum mechanics. (*h* is Planck's constant, *e* is Euler's number and *m* is the mass of a single gas molecule.)**

a) **(5 pts.) This expression must be flawed from a thermodynamic perspective since it yields a ridiculous prediction about the entropy of an ideal gas. What is the incorrect prediction? (You have to explain in words what the problem is. <u>Do not</u> simply write down an expression for S here.)**

Predicts a non-extensive entropy.

b) **(5 pts.) What is the correct expression for $\Omega(N,V,U)$ that fixes this flaw and what is the physical basis for the correction.**

$$\Omega_{correct}=\frac{1}{N!}\left(\frac{V}{V_0}\right)^N$$

The factor $\frac{1}{N!}$ makes the gas particles indistinguishable.

c) **(10 pts.) Show explicitly how the expression from part b leads to reasonable behavior for the entropy, whereas the incorrect expression provided to you leads to the problem discussed in part a.**

$$\ln\left(\frac{1}{N!}\right) = -N\ln N + N = -N\ln N + N\ln e$$

$$S_{correct} = k_B\ln\Omega_{correct} = k_B\left[-N\ln N + N\ln e + N\ln(V/V_0)\right]$$

$$S_{correct} = Nk_B\ln\left(\frac{Ve}{NV_0}\right)$$

is extensive since term in ( ) is intensive.

$$S_{wrong} = k_B\ln\Omega_{wrong} = k_B N\ln(V/V_0)$$

← this is super-extensive it behaves like $N\ln N$

Question IV, 36 points (12 points each): These are derivations. Show your work or no credit.

a) **Starting from the definition** $C_V \equiv \left.\frac{\partial U}{\partial T}\right|_{V,N}$**, derive the equivalent alternate expression** $C_V \equiv T\left.\frac{\partial S}{\partial T}\right|_{V,N}$.

$$C_V = \left.\frac{\partial U}{\partial T}\right|_{V,N} = \left.\frac{\partial U}{\partial S}\right|_{V,N}\left.\frac{\partial S}{\partial T}\right|_{V,N} = T\left.\frac{\partial S}{\partial T}\right|_{V,N}$$

Chain rule

$\left.\frac{\partial U}{\partial S}\right|_{V,N} = T$ from

$dU = TdS - pdV + \mu dN$

b) **Express** $C_P - C_V$ **in terms of the thermodynamic quantities** β, κ, T, V

N is also held constant everywhere.

$$\left.\frac{\partial S}{\partial T}\right|_p = \left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial S}{\partial V}\right|_T\left.\frac{\partial V}{\partial T}\right|_p$$

← "no name" or "ClintEastwood"

$$\left.\frac{\partial S}{\partial T}\right|_p - \left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial p}{\partial T}\right|_V\left.\frac{\partial V}{\partial T}\right|_p$$

← Maxwell relation $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V$

$$= V\beta\left.\frac{\partial p}{\partial T}\right|_V$$

← $V\beta \equiv \left.\frac{\partial V}{\partial T}\right|_p$

$$= -V\beta\left.\frac{\partial V}{\partial T}\right|_p\left.\frac{\partial p}{\partial V}\right|_T$$

← cyclic rule

$$= V\beta\,\frac{\beta V}{\kappa V}$$

← $\kappa V \equiv -\left.\frac{\partial V}{\partial p}\right|_T$ &

$$= \frac{\beta^2 V}{\kappa}$$

Part c on next page...

$$\Downarrow$$

$$\boxed{C_p - C_V = T\left(\left.\frac{\partial S}{\partial T}\right|_p - \left.\frac{\partial S}{\partial T}\right|_V\right) = \frac{T\beta^2 V}{\kappa}}$$

c) The multiplicity of a large Einstein solid with N oscillators and q units of energy is given by $\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!}$. Show that this result implies that the entropy of an Einstein solid is $S(N,q) = k_B N \ln\left(\frac{qe}{N}\right)$ when both N and q are very large and, additionally, that $q >> N$. (e is Euler's number)

$$\Omega \approx \frac{(q+N)!}{q!\,N!}$$

q, N "very large" so can ignore 1's

$S = k_B \ln \Omega$ ↓ Stirling

$$S \approx k_B\left[(q+N)\ln(q+N) - (q+N) - q\ln q + q - N\ln N + N\right]$$

$$= k_B\left[q\ln\left(\frac{q+N}{q}\right) + N\ln\left(\frac{q+N}{N}\right)\right]$$

↓ $\ln(1+x) = x + \dots$ ↓ $q >> N$

$$\approx k_B\left[q\left(\frac{N}{q}\right) + N\ln(q/N)\right]$$

$$= k_B\left[N\ln e + N\ln(q/N)\right]$$

$$\boxed{S \approx k_B N \ln(qe/N)}$$