Physics 408 – Final Exam   Name___Solution___

You are graded on your work (with partial credit where it is deserved) so please do not just write down answers with no explanation!

Please give clear, well-organized, understandable solutions.

$h = 6.63 \times 10^{-34}$ J s   [Planck's constant] $k = 1.38 \times 10^{-23}$ J/K   [Boltzmann constant]

$c = 3.00 \times 10^{8}$ m/s   [speed of light] $m_e = 9.11 \times 10^{-31}$ kg   [mass of electron]

$1 \text{ eV} = 1.60 \times 10^{-19}$ J   and $\dfrac{1 \text{ eV}}{k} = 11,600$ K

The variables have their usual meanings: E = energy, S = entropy, V = volume, N = number of particles, T = temperature, P = pressure, μ = chemical potential, B = applied magnetic field, C_V = heat capacity at constant volume, F = Helmholtz free energy, k = Boltzmann constant. Also, $\langle \cdots \rangle$ represents an average.

In case you have a Rick Perry moment at this early hour, let us remind you that $dE = TdS - PdV + \mu dN$!

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1. The enthalpy $H(S,P,N)$ is defined by $H = E + PV$.

(a) (4) Starting with the standard expression for dE in terms of dS, dV, and dN (see above), obtain the expression for dH in terms of dS, dP, and dN.

$$dH = (TdS - PdV + \mu dN) + (PdV + VdP) = \boxed{TdS + VdP + \mu dN}$$

(b) (4) Express 3 physical quantities as derivatives of H with respect to its natural variables.

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \qquad V = \left(\frac{\partial H}{\partial P}\right)_{S,N} \qquad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$$

(c) (4) For a quasiequilibrium process, the infinitesimal heat added to a system is TdS and the change in temperature is dT. Obtain the heat capacity at constant P (and N) as a derivative of the enthalpy.

$$C_P = \frac{TdS}{dT} \quad \text{at constant } P \& N \qquad \text{with} \quad dH = TdS$$

$$\Rightarrow \boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_{P,N}}$$

2. Consider a paramagnetic system of distinguishable noninteracting atoms in a magnetic field $\vec{B}$. Each atom has a magnetic dipole moment whose component parallel to $\vec{B}$ is $\pm m_B$. Its energy is then $\mp m_B B$.

(a) (4) Obtain the partition function z for a single atom. Then obtain the partition function Z for the system of N atoms.

$$\boxed{z = } e^{-(-m_B B)/kT} + e^{-m_B B/kT} = \boxed{e^{m_B B/kT} + e^{-m_B B/kT}}$$

$$\boxed{Z = z^N}$$

(b) (4) If M is the magnetic dipole moment for the system (in the direction of the applied field $\vec{B}$), show that

$$\langle M \rangle = kT \left(\frac{\partial \ln Z}{\partial B} \right)_T$$

(with N implicitly fixed).

$$\boxed{\langle M \rangle = \sum_j M_j} \frac{e^{-(-M_j B/kT)}}{Z} \underbrace{\qquad}_{= P_j} = \boxed{\frac{1}{Z} \sum_j M_j e^{M_j B/kT}}$$

$$Z = \sum_j e^{M_j B/kT} \implies \boxed{\frac{\partial \ln Z}{\partial B} = \frac{1}{Z} \sum_j \frac{M_j}{kT} e^{M_j B/kT}}$$

$$\therefore \quad \langle M \rangle = kT \left(\frac{\partial \ln Z}{\partial B} \right)_T$$

(c) (4) Using the fact that $F \equiv E - TS$, where $F(T,V,N)$ is the Helmholtz free energy, obtain the expression for dF in terms of dT, dV, and dN.

$$\boxed{dF = -SdT - PdV + \mu dN} \quad \text{as in} \quad \text{Problem } 1(a)$$

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(d) (4) Recalling that $F = -kT \ln Z$, obtain the Maxwell relation relating $\left(\dfrac{\partial \langle M \rangle}{\partial T}\right)_B$ to $\left(\dfrac{\partial S}{\partial B}\right)_T$ (with N and V implicitly fixed).

$$\text{From } (\beta), \quad \langle M \rangle = -\frac{\partial F}{\partial B} \quad, \quad \text{From } (c), \quad S = -\frac{\partial F}{\partial T}\ .$$

$$\text{Then } \left(\frac{\partial \langle M \rangle}{\partial T}\right)_B = -\frac{\partial^2 F}{\partial T \partial B} = -\frac{\partial^2 F}{\partial B \partial T} = \left(\frac{\partial S}{\partial B}\right)_T\ .$$

(e) (4) Using your answer to Part (d), give a **CLEAR** explanation of how $\left(\dfrac{\partial \langle M \rangle}{\partial T}\right)_B$ behaves as $T \to 0$, and why.

$$3\text{rd law} \Rightarrow \left(\frac{\partial S}{\partial X}\right)_T \to 0 \quad \text{as} \quad T \to 0 \quad \text{for any } X.$$

$$\left[\frac{\Delta S}{\Delta X} = \frac{S_f - S_i}{\Delta X} \quad \text{with } S_f \to 0 \text{ and } S_i \to 0 \text{ as } T \to 0\right]$$

$$\text{Then } \left(\frac{\partial \langle M \rangle}{\partial T}\right)_B = \left(\frac{\partial S}{\partial B}\right)_T \to 0 \quad \text{as} \quad T \to 0$$

(f) (4) Give a **CONVINCING PHYSICAL** explanation of why $\langle M \rangle$ shows this behavior in a paramagnetic system.

For any fixed B, as $T \to 0$ all the dipole moments line up maximally with B. Then $\langle M \rangle$ approaches a constant as $T \to 0$ and $\dfrac{\partial \langle M \rangle}{\partial T} \to 0$.

3. (a) (4) For a general system, obtain dS in terms of dE, dV, and dN.

$$dE = TdS - PdV + \mu dN \implies \boxed{dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN}$$

(b) (4) Two systems 1 and 2 have different temperatures T_1 and T_2. They are separated by a wall which is fixed and impermeable, so that particles cannot flow from one system to the other. However, energy can flow through the wall. Let E_1 and E_2 be the separate energies of the systems, with

$$E_1 + E_2 = E_{total} = \text{constant}.$$

Also, let S_1 and S_2 be the separate entropies of the systems, with

$$S_1 + S_2 = S_{total}.$$
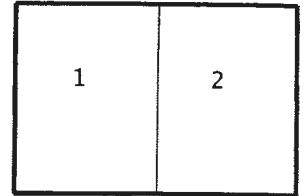
What does the second law of thermodynamics tell you about the rate of change $\dfrac{dS}{dt}$ of the total entropy with respect to time?

$$\frac{dS_{total}}{dt} \geq 0$$

(c) (4) Use the chain rule for derivatives to write $\dfrac{dS}{dt}$ in terms of T_1, T_2, and $\dfrac{dE_1}{dt}$.

$$\boxed{\frac{dS_{total}}{dt} = \frac{\partial S_1}{\partial E_1}\frac{dE_1}{dt} + \frac{\partial S_2}{\partial E_2}\left(-\frac{dE_1}{dt}\right) = \boxed{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt}}}$$

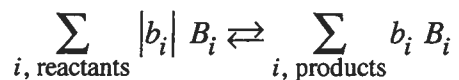(d) (4) If $T_2 > T_1$, what can you conclude about $\dfrac{dE_1}{dt}$? (As always, please **show your work and be clear**.)

$$T_2 > T_1 \implies \frac{1}{T_1} - \frac{1}{T_2} > 0$$

Then $\dfrac{dS_{total}}{dt} \geq 0 \implies \dfrac{dE_1}{dt} \geq 0$.

[For nonzero conductivity of wall, of course,

$$\frac{dE_1}{dt} > 0$$

& heat flows from hot to cold.]

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4. Consider a chemical reaction of the form

$$\sum_{i,\,\text{reactants}} |b_i|\,B_i \rightleftarrows \sum_{i,\,\text{products}} b_i\,B_i$$

with the convention that the stoichiometic coefficients b_i are taken to be positive for products, on the right-hand side, and negative for reactants, on the left-hand side. (An example is $H_2 + Cl_2 \rightleftarrows 2HCl$, with $b_{H_2} = -1$, $b_{Cl_2} = -1$, $b_{HCl} = +2$.) The criterion for chemical equilibrium is that the Helmholtz free energy F be minimized, so that $\dfrac{\partial F}{\partial X} = 0$ or $\dfrac{\Delta F}{\Delta X} = 0$ or $\Delta F = 0$ when some unconstrained variable X is varied by an amount ΔX. Here we subtract $|b_i|\,\Delta N$ particles of each reactant species i, and add $b_i \Delta N$ particles of each product species i.

(a) (4) Referring back to Part (c) of Problem 2, and generalizing to the case where there are several species with different particle numbers N_i and chemical potentials μ_i, write down the expression for dF in terms of the μ_i and dN_i. Then replace dF by ΔF and each dN_i by ΔN_i, to write ΔF in terms of the μ_i and ΔN_i.

$$\boxed{dF = -S\,dT - P\,dV + \sum_i \mu_i\,dN_i}$$

$$\boxed{\Delta F = \sum_i \mu_i\,\Delta N_i}\quad \text{for}\quad T\ \&\ V\ \text{fixed}$$

(b) (4) Recalling the sign convention on the ΔN_i, obtain a fundamental equation involving $\sum_i \mu_i b_i$, where the summation is now over both reactants and products.

$$\Delta N_i = b_i\,\Delta N$$

so $\quad \Delta F = \sum_i \mu_i b_i\,\Delta N$

and $\quad \Delta F = 0 \Rightarrow \boxed{\sum_i \mu_i b_i = 0}$

(c) (6) Now assume that each chemical potential has the form

$$\mu_i = kT \ln\left(n_i f_i(T)\right)$$

where $f(T)$ is a function of T (generalizing the result for an ideal gas). Using your result in Part (b), obtain the law of mass action

$$\prod_i [i]^{b_i} = K(T)$$

where $[i] \equiv n_i$ and $K(T)$ is the equilibrium constant.

$$\sum_i kT \ln\left(n_i f_i(T)\right) b_i = 0$$

$$\Rightarrow \sum_i b_i \ln n_i = -\sum_i b_i \ln f_i(T)$$

$$\Rightarrow \ln \prod_i n_i^{b_i} = -\ln \prod_i f_i(T)^{b_i}$$

$$\Rightarrow \prod_i n_i^{b_i} = \prod_i f_i(T)^{-b_i} \equiv K(T)$$

$$\text{or} \quad \prod_i [i]^{b_i} = K(T)$$

(d) (10) In thermal equilibrium, the reaction $\gamma + \gamma \rightleftarrows e^- + e^+$ produces a steady-state concentration of positrons. Calculate the concentration of positrons, $\left[e^+\right] \equiv n_{e^+} \equiv \dfrac{N_{e^+}}{V}$, in a typical white dwarf. For this estimate, take the chemical potential for electrons to be

$$\mu_{e^-} = m_e c^2 + \varepsilon_F$$

with $\varepsilon_F \sim 50$ keV being typical, $m_e c^2 = 511$ keV, and 1 keV $= 10^3$ eV. For the dilute positrons, the chemical potential can be taken to be

$$\mu_{e^+} = m_e c^2 + kT \ln\left(\frac{\lambda_{th}^3 n_{e^+}}{2}\right) \quad , \quad \lambda_{th} = \frac{h}{(2\pi m_e kT)^{1/2}}$$

with $T \sim 10^7$ K being typical for a white dwarf.

$$\sum_i \mu_i b_i = 0 \qquad \text{and} \quad \mu_\gamma = 0 \qquad [\mu = 0 \ \text{for photons}]$$

$$\Rightarrow \quad \mu_{e^+} + \mu_{e^-} = 0$$

$$\Rightarrow \quad m_e c^2 + kT \ln\left(\frac{\lambda_{th}^3 n_{e^+}}{2}\right) + m_e c^2 + \varepsilon_F = 0$$

$$\Rightarrow \quad -\frac{2 m_e c^2 + \varepsilon_F}{kT} = \ln\left(\frac{\lambda_{th}^3 n_{e^+}}{2}\right)$$

$$\Rightarrow \quad \frac{\lambda_{th}^3 n_{e^+}}{2} = e^{-\frac{1072 \, keV}{kT}} = e^{-\left(\frac{1.072 \times 10^6 \, eV}{k}\right) \cdot \frac{1}{T}}$$

$$\boxed{\text{from first page}}$$

$$= e^{-(1.072 \times 10^6)(11,666 \, k)/10^7 \, K}$$

$$= e^{-1244}$$

$$= 10^{-540} \qquad \text{since} \quad \ln 10 = 2.303$$

$$\lambda_{th} = \frac{6.63 \times 10^{-34}}{((2\pi)(9.11 \times 10^{-31})(1.38 \times 10^{-23})(10^7))^{1/2}} = 2.36 \times 10^{-11} \, m$$

$$\text{Then} \quad n_{e^+} = \frac{2}{(2.36 \times 10^{-11} \, m)^3} \, 10^{-540}$$

$$\sim 10^{-508} m^{-3} \approx 0$$

[The precise number is not important here, of course.]

5. (18) The Planck distribution of radiation energy density in n dimensions has the form
$$u_{\text{Planck},n} = A\frac{v^n}{e^{hv/kT}-1} \; .$$
Show that the frequency v_{peak} at which $u_{\text{Planck},n}$ reaches its maximum value is given by
$$hv_{\text{peak}} = \text{constant} \times kT$$
while at the same time obtaining this constant to one significant figure.

$$\frac{\partial u_{\text{Planck},n}}{\partial v} = 0$$

$$\Rightarrow 0 = \frac{n\, v^{n-1}}{e^{hv/kT}-1} - \frac{v^n}{(e^{hv/kT}-1)^2}\, e^{hv/kT}\left(\frac{h}{kT}\right)$$

$$\Rightarrow 0 = n - \frac{hv/kT}{e^{hv/kT}-1}\, e^{hv/kT}$$

$$= n - \frac{x}{1-e^{-x}} \quad , \quad x \equiv \frac{hv}{kT}$$

$$\Rightarrow \boxed{n(1-e^{-x}) = x}$$

guess : $\boxed{x \approx n}$

better : $\boxed{x \approx n(1-e^{-n})}$

$\left[\text{E.g., for } n=3 \text{ the second version gives}\right.$

$\left. x \approx 3(1-e^{-3}) = 2.85, \text{ compared to the more exact } 2.82 .\right]$

(b) (6) Now let us specialize to our own real world with $n=3$. Sirius, the brightest star in the sky, has a surface temperature of 10,500 K. For Sirius, use your result from Part (a) to approximately calculate v_{peak}, and then the wavelength that corresponds to this frequency. Using the crudest approximation,

$$\frac{hv_{\text{peak}}}{kT} \approx 3 \Rightarrow \boxed{v_{\text{peak}} = }\frac{(3)(1.38\times10^{-23}\ \text{J/k})(11,500\ \text{k})}{6.63\times10^{-34}\ \text{J.s}} = \boxed{7.18\times10^{14}\ \text{Hz}}$$

$$\boxed{\lambda = }\frac{c}{v_{\text{peak}}} = \frac{3.00\times10^8\ \text{m/s}}{7.18\times10^{14}\ \text{Hz}} = 4.18\times10^{-7}\ \text{m} = \boxed{418\ \text{nm}}$$

[very blue]

6. (5 points extra credit) Below discuss 3 substantial things that you learned from the talks last Tuesday. Please be clear and informative! (But an extremely long answer is not necessary.)

(i)

(ii)

(iii)

Happy Holidays, Merry Christmas, and have a fun New Year!