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You may assume the following:

elementary charge	e	$=$	1.6×10^{-19} C
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mass of the electron	m_e	$=$	9.11×10^{-31} kg
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$$\int_{-\infty}^{\infty} \exp(-\alpha x^2) dx = (\pi/\alpha)^{1/2}$$

$$\int_{-\infty}^{\infty} x^2 \exp(-\alpha x^2) dx = \frac{1}{2\alpha}(\pi/\alpha)^{1/2}$$

$$\int_{-\infty}^{\infty} x^4 \exp(-\alpha x^2) dx = \frac{3}{4\alpha^2}(\pi/\alpha)^{1/2}$$

SECTION A

[Part marks]

1. (a) Explain what is meant by a heat bath and a particle bath. [1]

   (b) Describe the meaning of microcanonical, canonical and grand canonical ensembles. [3]

   (c) Provide an example of a physical system that can be treated by each ensemble. [3]

2. (a) Briefly explain what is meant by a microstate and a macrostate of a system. [3]

   (b) Define what is meant by an *intensive* and *extensive* state function and give an example of each. [3]

3. (a) Write down an integral for the classical canonical partition function for an ideal monatomic gas. [3]

   (b) Show that the mean energy per particle of an ideal monatomic gas is $3kT/2$, where k is Boltzmann's constant and T is the temperature. (You may need to use the integrals in the rubric). [5]

4. From energy conservation, it may be shown that a column of air in the earth's atmosphere satisfies the following condition:

$$T\frac{dp}{p} = -\frac{mg}{k}dh$$

where T is temperature, p is the pressure, m is the molecular mass, g is the acceleration due to gravity, k is Boltzmann's constant and h is the height. Assume that the atmosphere is a well mixed ideal monatomic gas, and that parcels of atmospheric air obey the law of adiabatic expansion pV^{γ}=constant, where $\gamma = 5/3$, as they rise and fall.

   (a) What is the law of adiabatic expansion in terms of temperature and pressure? [2]

   (b) Show that

$$(1-\gamma)\frac{dp}{p} + \gamma\frac{dT}{T} = 0$$

   [2]

   (c) Hence derive an expression for temperature as a function of height. [2]

5. (a) Write down the Clausius-Clapeyron equation and define all the quantities involved. [3]

   (b) From the equation obtain an approximate expression for the saturated vapour pressure of a liquid as a function of temperature. [4]

6. The Fermi energy of electrons in copper is 1.1×10^{-18} J.

   (a) Calculate the Fermi temperature. [1]

   (b) If the electrons in copper were replaced by muons, with mass roughly 200 times the electron mass, calculate the Fermi temperature of muons in copper. (You may assume that the Fermi temperature is inversely proportional to particle mass). [2]

   (c) Can Maxwell-Boltzmann statistics be used to describe electrons in copper at room temperature? Can they be used to describe muons in copper, also at room temperature? Justify your answers. [3]

SECTION B

7. (a) Describe the meaning of the Second Law of Thermodynamics within classical thermodynamics. You should include a discussion of reversible and irreversible processes, and illustrate your understanding with examples. [9]

(b) Write down the fundamental relation of thermodynamics for a system defined by functions of state E, S, T, p, V, and with fixed number of particles N. [2]

(c) Employing the Helmholtz free energy $F = E - TS$, derive the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

[3]

(d) The heat capacity at constant volume (C_V), isothermal compressibility (κ_T) and thermal expansion coefficient at constant pressure (α) of the system are given by

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Show that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

[3]

You may use the identities

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

and

$$\left(\frac{\partial x}{\partial y}\right)_z = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]^{-1}$$

(e) Furthermore, show that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T\alpha}{C_V \kappa_T}$$

[3]

8. (a) Define what is meant by the microstate multiplicity, or statistical weight, $\Omega(E, \alpha)$ of a system described by an energy E and internal unconstrained parameter α. [4]

(b) Discuss the principle of equal *a priori* microstate probabilities. [3]

(c) Discuss Boltzmann's interpretation of the entropy of a system, and explain why an isolated system evolves, after a constraint on the parameter α is removed, in such a way as to maximise its entropy. [5]

(d) Consider a system in weak thermal contact with a reservoir. The total energy is E_{tot}. The probability that the system has an energy E is

$$p(E) \propto \Omega(E)\Omega_r(E_{tot} - E)$$

where the microstate multiplicities (statistical weights) of system and reservoir are $\Omega(E)$ and $\Omega_r(E_{tot} - E)$ respectively. Show that for an infinite reservoir,

$$p(E) = \frac{1}{Z}\Omega(E)\exp(-\beta E)$$

and discuss the meaning of the parameter β. By what name is the normalising factor Z usually known? [4]

(e) Sketch the typical shape of the probability distribution $p(E)$ for a finite system. What shape might it tend towards for a very large system? [4]

9. The magnetic moment of an atom may take two orientations with respect to an external magnetic field B: aligned with the field, with energy $-\alpha B$, or against the field with energy $+\alpha B$. The partition function of an array of N atoms in a heat bath at temperature T is given by

$$Z = \left(2\cosh\left(\frac{\alpha B}{kT}\right)\right)^N$$

(a) Show that the mean energy of the array is given by

$$\langle E \rangle = -N\alpha B \tanh\left(\frac{\alpha B}{kT}\right)$$

[4]

(b) Use the definition of the Helmholtz free energy to show that the entropy of the array is given by

$$S = -\frac{N\alpha B}{T}\tanh\left(\frac{\alpha B}{kT}\right) + Nk\ln\left(2\cosh\left(\frac{\alpha B}{kT}\right)\right)$$

[3]

(c) Evaluate and comment on the entropy of the array for $B = 0$ and $B \to \infty$. [6]

(d) The standard deviation of the energy is given by $\sigma = \left(\langle E^2 \rangle - \langle E \rangle^2\right)^{1/2}$. Show that

$$\sigma = \frac{\alpha B N^{1/2}}{\cosh(\alpha B/(kT))}$$

[7]

10. (a) Explain briefly what is meant by black-body radiation and why it can be characterised by a single temperature. [6]

(b) What is the relationship between radiative energy flux and temperature? [2]

(c) You may assume that the mean number of photons occupying a state at energy $\epsilon = \hbar\omega$ when the radiation has a temperature T is

$$\langle N \rangle = \frac{1}{\exp(\epsilon/kT) - 1}$$

You may also assume that the number of available states in the angular frequency range ω to $\omega + d\omega$, in a cavity of volume V, is given by

$$g(\omega)d\omega = \frac{V\omega^2}{c^3\pi^2}d\omega$$

where c is the speed of light.

Show that the average number of photons per unit volume in the cavity for a temperature T is given by

$$n = \frac{I}{\pi^2}\left(\frac{kT}{c\hbar}\right)^3$$

where $I = \int_0^\infty dx\, x^2(\exp(x) - 1)^{-1} = 2.404$. [7]

(d) Contrast the result in part (c) with the behaviour of the density of an ideal molecular gas in a cavity of fixed volume as the temperature increases, and explain the difference. Above what temperature, approximately, would the photon density exceed the molecular density of air in a typical exam hall, which is about 2×10^{25} m^{-3}? [5]

11. (a) An analysis of the quantum mechanics of a single particle in a system defines a set of single particle states. Consider a gas of non-interacting particles placed in the system. How do fermions and bosons differ in the way they are allowed to occupy the single particle states? Briefly explain why. [5]

(b) The grand partition function of a state at single particle energy ϵ, when the gas has chemical potential μ and temperature T, is

$$Z_G(\mu, T) = \sum_N \exp(-(E - N\mu)/kT)$$

where $E = N\epsilon$ is the energy when there are N particles occupying the state.

i. Show that the mean number of particles occupying the state is given by

$$\langle N \rangle = kT \left(\frac{\partial \ln Z_G}{\partial \mu} \right)_T$$

[3]

ii. If the particles are fermions, show that

$$Z_G = 1 + \exp(-(\epsilon - \mu)/kT)$$

and hence that

$$\langle N \rangle = \frac{1}{\exp((\epsilon - \mu)/kT) + 1}$$

[5]

(c) For electrons, the density of single particle states is given by

$$g(\epsilon) \propto \epsilon^{1/2}$$

Show that at $T = 0$ the mean energy per particle in the electron gas is $3\mu/5$. [7]

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SECTION A

[Part marks]

1. (a) State the Second Law of thermodynamics. [2]

   (b) An ideal gas undergoes free expansion into a larger volume. After equilibrium is reestablished, has its entropy gone up, down or stayed the same? Explain your answer. [2]

   (c) The temperature of an ideal gas is rapidly reduced at constant volume. After equilibrium is reestablished, has its entropy gone up, down, or stayed the same? Explain your answer. [2]

2. (a) State the fundamental relation of thermodynamics, naming all quantities involved. [3]

   (b) Define the Helmholtz free energy, and describe the circumstances where it might be used to determine an equilibrium state of a system. [3]

3. (a) What physical property determines whether a particle is a fermion or a boson? What values of this property are distinctive for bosons? [2]

   (b) State an important symmetry property that must be satisfied by the wavefunction of a system of many bosons. What is the corresponding property that must be possessed by the wavefunction of a system of many fermions? [2]

   (c) What distinctive phenomenon does a gas of bosons exhibit at low temperatures? Name a physical effect that is thought to be due to this phenomenon. [2]

4. (a) State the relationship between microstate multiplicity and Boltzmann entropy. [2]

   (b) State the relationship between equilibrium microstate probabilities and Gibbs entropy. [2]

   (c) Define the canonical partition function of a system and state how it is related to a particular thermodynamic potential. [2]

5. (a) Explain what is meant by a heat and particle bath at temperature T and chemical potential μ. [2]

   (b) Write down the probability $P(E, N)$ that a system in contact with such a heat and particle bath, and with a grand canonical partition function Z_G, might be found in a macrostate with particle number N, energy E and microstate multiplicity $\Omega(N, E)$. For a large system, sketch the form of $P(E, N)$ you would expect it to take as a function of N for constant E. [3]

   (c) A system can take two phases, liquid or solid. Above the melting temperature, which phase has the lower chemical potential, and why? At which temperature do both phases have the same chemical potential? [3]

6. A classical ideal monatomic gas has a heat capacity at constant volume equal to $3k/2$ per particle. The electrons in a metal at room temperature form a gas, at least to a first approximation, but have a heat capacity per particle much less than this value.

   (a) How might you describe the condition of this electron gas? [1]

   (b) Sketch the Fermi-Dirac distribution $f_{FD}(E)$ for such an electron gas and indicate the position of the chemical potential of the gas on the energy axis. [2]

   (c) Explain what f_{FD} represents. [1]

   (d) Define what is meant by the Fermi energy. [1]

   (e) Compare the Fermi temperature of this gas with room temperature. [1]

   (f) Why is the heat capacity of the electron gas suppressed? [2]

SECTION B

7. (a) Describe what is meant by a reversible thermodynamic process. [2]

   (b) State the relationship between the entropy change of a system and the heat transferred to it from a heat bath at temperature T, for a reversible, and for an irreversible process. [2]

   (c) Show that for a reversible isothermal compression, the work done on a system is equal to the change in Helmholtz free energy of the system. [2]

   (d) Establish whether the work done on a system during an irreversible isothermal compression is greater than, less than, or equal to the change in Helmholtz free energy of the system. [2]

   (e) An evacuated container with volume V and at a temperature T contains black body radiation with an energy density equal to $4\sigma T^4/c$.

      i. Determine the heat capacity, at constant volume, of the radiation. [2]

      ii. Hence show that the entropy of the radiation is given by

$$S(T,V) = \frac{16\sigma V T^3}{3c}$$

[3]

      iii. The container is placed in thermal contact with a heat bath at temperature T_r. If the heat capacity of the cavity material itself is negligible, show that the overall change in entropy of the universe after the system and heat bath have reached thermal equilibrium is

$$\Delta S_{\text{tot}} = \frac{4\sigma V T_r^3}{3c}\left(1 - t^3\,(4 - 3t)\right)$$

where $t = T/T_r$. [5]

      iv. Comment on the sign of ΔS_{tot} as a function of t. [2]

8. (a) The classical canonical partition function of a one-dimensional harmonic oscillator of mass m and spring constant κ may be written

$$Z = \frac{1}{h_0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\, dp \exp\left(-\frac{p^2}{2mkT}\right)\exp\left(-\frac{\kappa x^2}{2kT}\right)$$

where h_0 is a constant.

i. Evaluate Z and hence determine the mean energy $\langle E\rangle$ of the oscillator when in equilibrium with a heat bath at temperature T. [4]

ii. Using the general formula $S = \frac{1}{T}\langle E\rangle + k\ln Z$, show that the entropy of such an oscillator is given by

$$S = k\left(1 + \ln\left(\frac{2\pi kT}{h_0\omega}\right)\right)$$

where $\omega = (\kappa/m)^{1/2}$ is the natural angular frequency of the oscillator. [2]

iii. What is the Third Law of thermodynamics? Demonstrate that the expression given above for the oscillator entropy does not satisfy this Law and explain physically why this is so. [3]

(b) The quantum canonical partition function of a 1-d harmonic oscillator is

$$Z = \frac{1}{2\sinh(x/2)}$$

where $x = \hbar\omega/kT$.

i. Evaluate the mean energy of the quantum oscillator when in equilibrium with a heat bath at temperature T. [3]

ii. By considering the limiting form of the quantum partition function for large T, and comparing it with the expression found in part a(i), identify the constant h_0 employed in the classical treatment. [You may assume that $\sinh z \approx z$ for small z]. [2]

(c) The spring constant is very slowly changed from κ to 2κ whilst the oscillator remains in thermal equilibrium with the heat bath.

i. Using the classical results derived in part (a), calculate the change in entropy of the oscillator. [2]

ii. Deduce the heat delivered to the heat bath during the process. [2]

iii. What is the work done on the oscillator during the process? [2]

9. (a) What is a microcanonical statistical ensemble? [2]

(b) What is the principle of equal *a priori* probabilities? [2]

(c) Consider a set of atoms in a system. Under what circumstances might the atoms be distinguishable and when might they be indistinguishable? Why does this matter in statistical thermodynamics? [4]

(d) A system consists of N identical atoms, each one trapped in its own spatially separated harmonic potential. Neglecting zero point energy, the oscillatory energy of each atom is an integer number (including zero) of quanta of energy $\hbar\omega$, where ω is the common classical angular frequency of oscillation.

Show that the microstate multiplicity, when the total energy of the system is $E = Q\hbar\omega$, is given by

$$\Omega(N, Q) = \frac{(N - 1 + Q)!}{(N - 1)!Q!}$$

[7]

(e) Now consider N atoms placed in a single harmonic potential. If $N = 2$ and $Q = 4$, identify the available microstates, and determine the factor by which the multiplicity given in part (d) has to be corrected. [5]

10. (a) The grand partition function $Z_G(\mu, T)$ of a system in equilibrium with a heat and particle bath, or reservoir, at temperature T and chemical potential μ, is given by

$$Z_G(\mu, T) = \sum_N \sum_i \exp\left(-\frac{(E_i - \mu N)}{kT}\right)$$

where E_i is the energy of microstate i. Show that the mean number of particles in the system is given by

$$\langle N \rangle = kT \left(\frac{\partial \ln Z_G}{\partial \mu}\right)_T$$

[4]

(b) The grand partition function of a gas of non-interacting bosons in equilibrium with such a reservoir may be written

$$\ln Z_G = \int_0^\infty g(E) \ln Z_G^E dE$$

where the grand partition function Z_G^E of a single particle state at energy E is given by

$$Z_G^E = (1 - \exp((\mu - E)/kT))^{-1}$$

and where, according to a certain model, the density of single particle states in energy is given by

$$g(E) = \frac{(2s+1)V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

where s is the spin and m the mass of the boson, and V is the size of the box containing the gas.

i. Evaluate the mean number of particles $\langle N \rangle_E$ in a single particle state at energy $E \geq 0$ and thereby demonstrate that the chemical potential of the reservoir, and hence of the gas, cannot be positive. [5]

ii. Derive an expression for the mean number of particles in the entire gas, in terms of an integral over energy. [3]

iii. Provide an argument that the density of the gas cannot, according to this model, exceed a certain multiple (which need not be determined) of the quantum concentration defined by

$$n_q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

[5]

iv. What aspect of the model must be corrected in order to accommodate gas densities above this apparent limit? [3]

11. According to the non-relativistic quantum mechanics of a particle of mass m in a cubic box of volume $V = L^3$, the single particle energy levels are given by

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

where k is the magnitude of the wavevector $\mathbf{k} = (k_x, k_y, k_z)$, and where the components of $\mathbf{k}$ are quantised as $k_x = \pi n_x / L$ etc, with $n_x = 0, 1, 2, \ldots$

(a) Show that the density in k-space of the single particle states that are available to electrons is given by

$$\rho(k) = \frac{V k^2}{\pi^2}$$

[6]

(b) Hence show that the total kinetic energy of a non-relativistic gas of N electrons at $T = 0$ is

$$E = \frac{V}{5\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} E_F^{5/2}$$

where E_F is the Fermi energy. [5]

(c) Furthermore, show that E_F is given by

$$E_F = \frac{\hbar^2}{2m_e} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

[3]

(d) Show that the electron density $n = N/V$ at which the mean kinetic energy of an electron in the gas is equal to its rest mass energy, is given by

$$n = \frac{1}{3\pi^2} \left(\frac{10}{3} \right)^{3/2} \left(\frac{m_e c}{\hbar} \right)^3$$

What is the significance of this density with regard to the stability of white dwarf stars? [6]

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mass of the electron	m_e	$=$	9.11×10^{-31} kg
mass of the neutron	m_n	$=$	1.67×10^{-27} kg
Gravitational constant	G	$=$	6.67×10^{-11} m^{3}kg^{-1}s^{-1}
Mass of the sun		$=$	2×10^{30} kg

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}$$

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

SECTION A

[Part marks]

1. (a) State the four laws of thermodynamics. [4]

   (b) Which of the following is not an increment in a thermodynamic state variable?

   $$dT, dQ, dE, dp, d\mu$$

   Define what this increment actually represents. [2]

2. (a) Define what is meant by a microstate and a macrostate, and the meaning of the microstate multiplicity. [3]

   (b) Explain what is meant by the principle of equal *a priori* probabilities. [2]

   (c) Explain, according to Boltzmann's ideas, and using the concept of microstate multiplicity, why the entropy of a gas increases during free expansion from volume V into a larger volume V'. [3]

3. (a) Write down an expression for the canonical partition function Z and define its relationship to the Helmholtz free energy. [3]

   (b) Derive the following expression for the mean energy of a system in the canonical ensemble:
$$\langle E\rangle = -\frac{\partial \ln Z(\beta)}{\partial \beta}$$
   where $\beta = 1/(kT)$ [3]

4. (a) Write down expressions for the mean occupation number of a quantum state at energy E when in equilibrium with a heat and particle bath at temperature T and chemical potential μ, according to (i) Fermi-Dirac and (ii) Bose-Einstein statistics. [2]

   (b) Sketch each mean occupation number as a function of $E - \mu$. [4]

   (c) Which expression is appropriate for occupation of the state by electrons, and why? [1]

5. The energy of photons of black body radiation, per unit range in angular frequency ω, at temperature T in a volume V, may be written
$$\frac{V\hbar}{c^3\pi^2}\frac{\omega^3}{(\exp(\hbar\omega/kT) - 1)}$$

   (a) Show that the total energy of the entire spectrum of black body radiation, per unit volume, is given by
$$\frac{4\sigma}{c}T^4$$
   and deduce an expression for the Stefan-Boltzmann constant σ in terms of elementary constants. [4]

   (b) What role does chemical potential play with regard to thermodynamic systems able to exchange particles? [2]

   (c) Why is the chemical potential of black body radiation equal to zero? [1]

6. (a) Write down an integral representation of the canonical partition function, valid for a classical one-particle system at temperature T, and characterised by the Hamiltonian $H(p, q)$, where p is the particle momentum and q is its position. [3]

   (b) The classical canonical partition function for N ideal gas particles takes the form
$$Z_N = \frac{1}{N!}Z_1^N$$
   where Z_1 is the partition function for a single particle. Why is the factor of $1/N!$ present? [3]

SECTION B

7. (a) The fundamental relation of thermodynamics, for a system with constant number of particles, may be written

$$dS = \frac{1}{T}dE + \frac{p}{T}dV$$

Show that this can be recast in the form

$$dS = \left(\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{p}{T}\right)dV + \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT$$

and derive expressions for

$$\left(\frac{\partial S}{\partial V}\right)_T \qquad \text{and} \qquad \left(\frac{\partial S}{\partial T}\right)_V$$

[4]

(b) Hence show that

$$\left(\frac{\partial E}{\partial V}\right)_T = T^2\left(\frac{\partial(p/T)}{\partial T}\right)_V$$

[6]

(c) Use this relationship to demonstrate that the energy of an ideal classical gas does not change when it is expanded or compressed at constant temperature. [2]

(d) The Van der Waals equation of state, with positive parameters a and b, is

$$\left(p + a\left(\frac{N}{V}\right)^2\right)\left(V - b\frac{N}{V}\right) = NkT$$

Use the above result for $(\partial E/\partial V)_T$ to show that the energy of a Van der Waals gas does change upon isothermal expansion. Does it increase or decrease? Argue physically in support of the direction of change that you deduce. [6]

(e) Calculate $(\partial S/\partial V)_T$ for the Van der Waals gas. [2]

8. (a) Describe the meaning of the equation

$$dS = \frac{dQ}{T_r} + dS_i$$

What are the properties of dS_i and under what circumstances might it be equal to zero? [5]

(b) The energy of a monatomic ideal classical gas is $E = 3NkT/2$ and its entropy is given by

$$S(T, V, N) = Nk \ln \left(\frac{(kT)^{3/2}}{\hat{c}N/V} \right)$$

where $\hat{c}$ is a constant. Use these expressions to demonstrate, graphically if possible, that the entropy change of the universe, associated with a non-quasistatic heat transfer process between the gas and a heat bath at a fixed temperature T_r, cannot be negative, irrespective of the initial temperature T_0 of the gas. [9]

(c) The relevant part of the availability A of a monatomic ideal classical gas coupled to a heat and volume bath at temperature T_r and pressure p_r is given by $E - T_r S + p_r V$.

i. Show that

$$A = \frac{3}{2}Nk \left(T - T_r \ln \left(\frac{kT}{(\hat{c}N/V)^{2/3}} \right) \right) + p_r V$$

[2]

ii. A vessel of initial volume V_0 holds N particles of a monatomic ideal classical gas with initial pressure p_0 and temperature T_0. Thermal contact is established between the vessel and a heat and volume bath at temperature T_r and pressure p_r. By an analysis of the dependence of the availability on the unconstrained system volume V, show that the final equilibrium volume of the gas is given by NkT_r/p_r. [4]

9. (a) Consider a system of three indistinguishable bosons occupying a system where there are three energy levels: zero, ϵ and 2ϵ. Identify all 10 microstates of the system in terms of the population in each level. Evaluate the number of microstates with energies zero, ϵ, 2ϵ, 3ϵ, 4ϵ, 5ϵ, and 6ϵ. [5]

(b) Calculate the canonical partition function of the system at temperature T in terms of $x = \exp(-\epsilon/kT)$. [2]

(c) Derive an expression for the mean energy of the system when in thermal contact with a heat bath at a temperature T. What is the mean energy at $T = 0$, $T = \epsilon/k$ and as $T \to \infty$? [6]

(d) The system is given an energy 2ϵ and then thermally isolated. Determine the mean and standard deviation of the boson population in the ground state. [4]

(e) State the relationship between temperature and a derivative of entropy. [1]

(f) If the system were given an energy greater than 3ϵ and again isolated, what can be said about the temperature of the system? [2]

10. A molecule consists of two atoms bound together by a harmonic potential such that the allowed vibrational energy states are given by

$$E_v(n) = \left(n + \frac{1}{2}\right)\hbar\omega$$

where n is a non-negative integer and ω is the fundamental vibrational angular frequency.

(a) Considering just the vibrational contributions to its energy, show that the canonical partition function of the molecule in a heat bath at temperature T is given by

$$Z = \frac{1}{2\sinh(\hbar\omega/(2kT))}$$

[3]

(b) Calculate the mean vibrational energy of the molecule. [4]

(c) Show that the vibrations make a contribution to the heat capacity of the molecule in the form

$$C_v = \frac{\hbar^2\omega^2}{4kT^2\sinh^2(\hbar\omega/2kT)}$$

[5]

(d) The rotational energy of the molecule is quantised according to

$$E_r(\ell) = \ell(\ell+1)\Theta$$

where Θ is a constant, and with $\ell = 0, 1, 2$ etc. The number of rotational quantum states at a given value of ℓ is $2\ell + 1$.

i. Write down the rotational canonical partition function of the molecule as a sum over ℓ. [2]

ii. Write down the probability that the molecule might be found with a particular value of ℓ. [2]

iii. At high temperatures it is possible to regard the general term in the sum as a function of a continuous variable ℓ. Show that the most probable value of ℓ in these circumstances is

$$\ell_{\text{mode}} = \frac{1}{2}\left(\left(\frac{2kT}{\Theta}\right)^{1/2} - 1\right)$$

[4]

11. (a) A fermion gas well below its Fermi temperature is degenerate. Define the meaning of *fermion*, *Fermi temperature* (and the related *Fermi energy*) and *degenerate*. [6]

(b) The pressure of a non-relativistic degenerate fermion gas is given by

$$p = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2E_F^{5/2}}{5}$$

where the Fermi energy is given by

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

and where m is the mass of the fermion and n is the fermion density in particles per unit volume.

i. Describe how a star, near the end of its life and short of material suitable for nuclear fusion, can stabilise itself against gravitational collapse. You should discuss at least two long-term stabilised modes, and the nature of the core of the star in each case. [9]

ii. An astronomical object is discovered with an apparent radius of 2.5 km. Assuming it is a stabilised, partially collapsed star with a mass of that of the sun, and that the gravity-induced pressure at the centre of a sphere of mass M and radius r is approximately $3GM^2/(4\pi r^4)$, deduce the approximate mass of the fermions within the star, and their likely nature, assuming there is only one species present. [5]

 END OF PAPER

Answer ALL SIX questions in Section A and THREE questions from Section B.

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question.

You may assume the following:

elementary charge	e	$=$	1.6×10^{-19} C
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mass of the electron	m_e	$=$	9.11×10^{-31} kg
mass of the neutron	m_n	$=$	1.67×10^{-27} kg
Gravitational constant	G	$=$	6.67×10^{-11} m^{3}kg^{-1}s^{-2}
Mass of the sun		$=$	2×10^{30} kg

SECTION A

[Part marks]

1. (a) Write down the Clausius and Kelvin statements of the Second Law of thermodynamics. [4]

   (b) Write down Boltzmann's expression for thermodynamic entropy. [1]

   (c) Explain how Boltzmann's expression accounts for an increase in the entropy of an isolated system when a constraint upon it is released. [2]

2. (a) Write down an expression for the Gibbs entropy of a system. [2]

   (b) Write down the probability associated with a microstate in a microcanonical ensemble of Ω microstates. [1]

   (c) Calculate the Gibbs entropy of a system described by such a microcanonical ensemble. [3]

3. (a) What is meant by the thermodynamic limit? What statistical property of a system exposed to a heat bath is expected to vanish in this limit? [3]

   (b) Give an example of a thermodynamic potential and describe the specific circumstances under which it might be used to identify an equilibrium state of a system. [3]

4. (a) Briefly describe what is meant by a degenerate Fermi gas. [3]

   (b) Briefly describe what is meant by a Bose-Einstein condensate. [3]

   (c) Would you expect to observe these states of matter when the particle density lies above, below or precisely at the quantum concentration? [1]

5. (a) Write down the general form of a Boltzmann factor. [2]

   (b) Specify the statistical ensemble where it is employed and the physical circumstances that the ensemble is designed to represent. [2]

   (c) Write down the form of the Maxwell-Boltzmann distribution of particle speed v in a three dimensional gas of atoms each of mass m, disregarding the normalisation constant. [2]

6. (a) Write down the fundamental relation of thermodynamics. [2]

   (b) Show that [3]

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$$

   (c) Using the Helmholtz free energy derive the Maxwell relation [3]

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

SECTION B

7. (a) Assuming that the relevant density of states is

$$g(E) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{1/2}$$

show that the Fermi energy of a gas of N electrons confined to a volume V at zero temperature is given by

$$E_F = \frac{\hbar^2}{2m_e}\left(3\pi^2 N/V\right)^{2/3}$$

and that the mean energy per electron in such conditions is $3E_F/5$. [6]

(b) The relationship between the mean energy E and the entropy S of a low temperature electron gas is

$$E = \frac{3}{5}NE_F\left(1 + \frac{5}{3}\left(\frac{S}{\pi N k}\right)^2\right)$$

i. Show that the relationship between temperature and entropy for this system is given by [2]

$$T = \frac{2E_F S}{(\pi k)^2 N}$$

ii. State the third law of thermodynamics and determine whether the gas violates it. [2]

iii. Express E and S in terms of T to show that the Helmholtz free energy is given by [4]

$$F = \frac{3}{5}NE_F - \frac{N(\pi k T)^2}{4E_F}$$

iv. Hence show that the pressure of the gas is

$$p = \frac{2NkT_F}{5V}\left(1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right)$$

where the Fermi temperature is given by $T_F = E_F/k$. [4]

(c) In a particular metal the Fermi temperature is 57000 K. Calculate the entropy per electron at $T = 300$ K. [2]

8. The chemical potential of a classical monatomic ideal gas of N particles occupying a volume V is given by

$$\mu = kT \ln\left(\frac{N}{V}\lambda_{th}^3\right)$$

where the thermal de Broglie wavelength λ_{th} of the gas is a function of temperature T.

(a) Consider two classical monatomic ideal gases, one coloured red and one coloured green. A container is divided in half by a partition that is permeable to red gas particles only. Initially, the right hand subvolume of the container holds red gas at a certain pressure, whilst the left hand subvolume holds red and green gas in equal proportions such that the total pressure on each side of the partition is the same. The container is in thermal contact with a heat bath at temperature T.

i. Determine the chemical potential of red gas in the two subvolumes and deduce, giving your reasons, whether the partition, if it is free to move, is likely to slide to the left, to the right, or remain in place. [6]

ii. A colour-blind professor observes the system and believes a law of thermodynamics is being violated: which one and why? [4]

(b) Show that an increment in the Gibbs free energy $G = E - TS + pV$ satisfies the relation [2]

$$dG = -SdT + Vdp + \mu dN$$

(c) Assuming G may also be written as μN, derive the Gibbs-Duhem relation

$$d\mu = -sdT + vdp$$

where $s = S/N$ and $v = V/N$. [3]

(d) Explaining your reasoning, deduce the Clausius-Clapeyron equation for the slope of a coexistence curve on a p-T phase diagram. [5]

9. A system consists of two levels with energies 0 and ϵ, respectively.

(a) Calculate the canonical partition function Z_1 of the system when it accommodates one particle and is in contact with a heat bath at temperature T. Express your result in terms of the parameter $y = \exp(-\epsilon/kT)$. [2]

(b) Calculate the mean energy of the particle. [3]

(c) The Helmholtz free energy of the particle is given by $F = -kT\ln(1+y)$. The energy difference ϵ depends on an externally controlled field x according to $\epsilon = \epsilon_0 + \alpha x$ where ϵ_0 and α are positive constants. Derive the coefficient X that appears in the expression [3]

$$dF = -SdT + Xdx$$

(d) Derive the entropy of the system and deduce its limiting value as $x \to \infty$. [6]

(e) Calculate the canonical partition function Z_2 when the system accommodates two indistinguishable fermions, if each level can occupy one particle at most. [2]

(f) The system is exposed to an environment that is a source of indistinguishable fermions at a chemical potential μ, and heat at a temperature T. The grand canonical partition function is given by a sum

$$Z_G(\mu, T) = \sum_N \exp(\mu N/kT) Z_N$$

over an appropriate range of the number of particles in the system, N.

Determine the mean number of particles in the system $\langle N \rangle$, in terms of y and $w = \exp(\mu/kT)$. [4]

10. The microstate multiplicity of a macrostate of N quantum harmonic oscillators, labelled by the set of populations $\{n_k\}\equiv\{n_0, n_1, \cdots, n_Q\}$ where n_k is the number of oscillators that possess k quanta, is given by

$$\Omega(N, Q, \{n_k\}) = \frac{N!}{n_0! \cdots n_Q!}$$

such that

$$\sum_{k=0}^{Q} n_k = N \quad \text{and} \quad \sum_{k=0}^{Q} k n_k = Q.$$

where Q is the fixed total number of quanta in the system.

(a) For the case $N = 3$ and $Q = 4$, identify the four macrostates and their microstate multiplicities. [6]

(b) A measurement is made of the 'spikiness' of the oscillator system, defined as the difference in number of quanta possessed by the highest occupied and lowest occupied oscillator at a given instant of time.

i. Show that the four population macrostates labelled by the $\{n_k\}$ are each characterised by a unique spikiness value, and list those values. [4]

ii. Determine the probability distribution of the system over the macrostates, assuming that the statistics are governed by the principle of equal a priori probabilities. [2]

(c) For a system where N and the n_k are very large, show that [3]

$$\ln \Omega \approx - \sum_{k=0}^{Q} n_k \ln(n_k/N)$$

(You may assume that $\ln n! \approx n \ln n - n$ for large n.)

(d) Hence show that the maximum entropy macrostate of this system is characterised by the populations [5]

$$n_k^* = \frac{N \exp(-k\beta)}{\sum_{m=0}^{Q} \exp(-m\beta)}$$

where β is a constant.

11. The eigenstates of a one dimensional quantum harmonic oscillator are characterised by energies $(n + 1/2)\hbar\omega$, where ω is the natural angular frequency of the oscillator and n is a non-negative integer. Disregarding the zero point energy $\hbar\omega/2$, the mean energy of the oscillator when in equilibrium with a heat bath at temperature T is

$$\langle E \rangle = \frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1}$$

(a) Standing electromagnetic wave modes inside a cavity of volume V are quantised as a cubic array in three dimensional wavevector space with separation between modes $\Delta k = \pi/L$ in each dimension, where $L = V^{1/3}$.

i. Using an appropriate dispersion relation, show that the density, in the space of angular frequency ω, of electromagnetic wave modes is given by

$$g(\omega) = \frac{\alpha V \omega^2}{2c^3\pi^2}$$

and explain why the factor α is equal to two. [7]

ii. Regarding each electromagnetic wave mode as a 1-d quantum harmonic oscillator, but ignoring the zero point energy, calculate the mean energy of the radiation in the frequency range $\omega \to \omega + d\omega$. [2]

iii. Demonstrate the mathematical difficulty that would emerge if we were to attempt to calculate the total mean energy in the cavity, including the zero point energy of the electromagnetic field. [2]

(b) In the Einstein model of the vibrational energy of a solid, every atom is imagined to oscillate in three dimensions about its equilibrium position at a common angular frequency ω_E known as the Einstein frequency.

i. Calculate the constant volume heat capacity C_v of a solid consisting of N atoms according to this model. [4]

ii. Determine its value as $T \to \infty$ and show that at low temperatures it may be represented as

$$C_v \approx 3Nkx^2 \exp(-x)$$

where $x = \hbar\omega_E/kT$. [5]

END OF PAPER

UNIVERSITY COLLEGE LONDON

EXAMINATION FOR INTERNAL STUDENTS

MODULE CODE	:	**PHAS2228**
ASSESSMENT PATTERN	:	**PHAS2228A**
MODULE NAME	:	**Statistical Thermodynamics**
DATE	:	**14-May-13**
TIME	:	**10:00**
TIME ALLOWED	:	**2 Hours 30 Minutes**

2012/13-PHAS2228A-001-EXAM-163

TURN OVER

Answer ALL SIX questions in Section A and THREE questions from Section B.

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question.

You may assume the following:

elementary charge	e	=	1.6×10^{-19} C
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$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}$$

$$\sum_{n=0}^{\infty} nr^n = \frac{r}{(1-r)^2}$$

SECTION A

[Part marks]

1. (a) Define the meaning of the terms microstate and macrostate. [2]

   (b) Describe what is meant by the following concepts:
   (i) the principle of equal *a priori* probabilities and (ii) thermal equilibrium. [4]

2. (a) Write down an expression for the Gibbs free energy G in terms of V, E, S, p and T. [1]

   (b) Define the meaning of extensivity and identify which state variable(s) listed in part (a) are extensive. [3]

   (c) Show that
   $$dG = -SdT + Vdp + \mu dN,$$
   and hence that $G = \mu N$. [4]

3. (a) Define what is meant by a canonical ensemble. Include in your answer a specification of a canonical probability in its usual form, and a definition of the canonical partition function. [4]

   (b) A paramagnetic atom has two microstates with energies $\pm\mu_B B$ where μ_B is the Bohr magneton and B is the external magnetic field. Determine the canonical partition function of the atom. [2]

4. (a) Define what is meant by a particle bath. [2]

   (b) Show that the mean particle population for a system described by a grand canonical ensemble is
$$\langle N \rangle = kT \left(\frac{\partial \ln Z_G}{\partial \mu} \right)_T ,$$
   where Z_G is the grand partition function. [4]

5. (a) With reference to the statistics of occupation of single particle states and the concept of the Fermi energy, describe what is meant by a degenerate fermion gas. [2]

   (b) Give an example of a physical property of a degenerate fermion gas that differs from classical expectation. [2]

   (c) What name is given to the temperature above which a degenerate fermion gas of a given density begins to behave as a classical gas? [1]

   (d) Apart from raising its temperature, how might a degenerate gas otherwise be made to behave classically? [1]

6. (a) Determine the microstate multiplicity if three indistinguishable objects are shared between three distinguishable boxes. [3]

   (b) If the boxes are indistinguishable, determine the microstate multiplicity. [2]

   (c) Explain the importance of taking into account particle indistinguishability when modelling the statistical thermodynamic properties of a system. [3]

SECTION B

7. (a) Derive the grand partition function Z_G for a system consisting of a single particle state at energy ϵ exposed to a heat and particle bath at temperature T and chemical potential μ, assuming the available particles are fermions. [3]

(b) Using the result

$$\langle N \rangle = kT \left(\frac{\partial \ln Z_G}{\partial \mu} \right)_T ,$$

proved in question 4(b), derive the Fermi-Dirac expression $\langle N \rangle$ for the mean number of particles occupying the system. [2]

(c) Given that the Gibbs entropy of the system can be written in the form

$$S_G = k \ln Z_G + \frac{(\epsilon - \mu)}{T} \langle N \rangle,$$

show that S_G may be expressed as [5]

$$S_G = -k\langle N \rangle \ln\langle N \rangle - k\,(1 - \langle N \rangle) \ln (1 - \langle N \rangle)\,.$$

(d) $\langle N \rangle$ can take a certain range of values.

i. Evaluate the Gibbs entropy of the system when $\langle N \rangle$ takes its minimum and maximum values, respectively. [5]

ii. Determine the value of $\langle N \rangle$ when S_G is at a maximum and evaluate this maximum. [3]

iii. Interpret the variation of S_G with $\langle N \rangle$ in terms of the uncertainty surrounding the microstate adopted by the system. [2]

You may find it useful to know that l'Hôpital's rule states that if

$$\lim_{x \to x_0} g(x) = \lim_{x \to x_0} f(x) = 0 \text{ or } \pm\infty \text{ then } \lim_{x \to x_0} (g(x)/f(x)) = \lim_{x \to x_0} (g'(x)/f'(x))$$

where the primes indicate differentiation with respect to x.

8. (a) Write down an expression for the Gibbs entropy S_G in terms of probabilities of microstate occupation P_i. [2]

(b) Show that [2]

$$dS_G = -k\sum_i \ln P_i dP_i.$$

(c) Assume that the probabilities are of the form $P_i = Z^{-1}\exp(-E_i/kT)$, and the microstate energies E_i depend on the system volume V. Show that a change in mean energy $\langle E\rangle = \sum_i P_i E_i$ is given by [3]

$$d\langle E\rangle = TdS_G - pdV,$$

and demonstrate that the pressure p in this expression is given by [2]

$$p = -\sum_i \frac{dE_i}{dV}P_i.$$

(d) Derive the Maxwell relation that involves the derivative [3]

$$\left(\frac{\partial p}{\partial T}\right)_V.$$

(e) According to a recent model of the gluon plasma (a phase of matter predicted to exist at very high temperature and density) the mean energy and pressure are given by the expressions

$$\langle E\rangle = V(\hat{\sigma}T^4 + B) \quad \text{and} \quad p = \frac{1}{3}\hat{\sigma}T^4 - B - AT.$$

for system volume V and temperature T, where $\hat{\sigma}$, A and B are constants.

i. Calculate the heat capacity of the gluon plasma at constant volume. [2]

ii. Show that the entropy of the gluon plasma is given by $(4\hat{\sigma}/3)VT^3$. [3]

iii. Use the Maxwell relation derived in part (d) to show that the proposed model is thermodynamically inconsistent if $A \neq 0$. [3]

9. (a) A one dimensional quantum oscillator with natural frequency ω and energy spectrum $E_n = (n + \frac{1}{2})\hbar\omega$ is in thermal equilibrium with a heat bath at a temperature T.

i. Determine the canonical partition function of the oscillator, expressing your answer in terms of $y = \exp(-\hbar\omega/(2kT))$. [2]

ii. What is the probability that the oscillator might be found in a state with an even value of the quantum number n? Determine also the probability that the quantum number is found to be odd. [5]

iii. The oscillator is examined with an experimental device that gives a signal of $x = 1$ if the quantum number is even and $x = -1$ if the quantum number is odd. Determine the mean of x in terms of y. [2]

(b) The DNA molecule can be roughly represented as pair of strands held together by regularly spaced links, rather like a ladder. The links can break with an associated increase in system energy of ϵ per link, but only if the link is at the very end of the molecule, or is adjacent to a broken link. In other words, the molecule can unzip from the ends. We ignore all other contributions to the energy of the molecule.

i. Assuming for the moment that the DNA molecule can unzip only from one end (i.e. links at the other end are unbreakable), calculate the microstate multiplicity when there are m broken links. [2]

ii. Taking DNA to be very long, such that it can contain many links, determine the canonical partition function Z_1 of the molecule at a temperature T in terms of $w = \exp(-\epsilon/(kT))$. [2]

iii. Show that the average number of broken links is given by [2]

$$\langle m \rangle = \frac{w}{1-w}.$$

iv. If the DNA molecule can unzip from **both** ends, calculate the microstate multiplicity when there are m broken links and show that the canonical partition function is now given by [5]

$$Z_2 = \frac{1}{(1-w)^2}.$$

10. A forgetful professor finds a scrap of paper in his pocket on which he seems to have written

$$E(N, V, S) = f(N, V)S^{4/3}\exp(S/(3Nk)).$$

He imagines that the symbols take their usual meaning and reckons that $f(N, V)$ is an unspecified function. Help him work out what physical system he was attempting to model:

(a) Derive an expression for the temperature of the system T in terms of E, S and N. [2]

(b) Using an expression for the temperature as a function of N, V and S, show that $T \to 0$ as $S \to 0$ at constant N and V. What law of thermodynamics is this? [3]

(c) In a low temperature regime, for which $S \ll 3Nk$, simplify the expressions for the system temperature obtained in (a) and (b) to obtain an approximate expression for E in terms of T and f. [3]

(d) Show that the heat capacity of the system at constant volume is proportional to T^3 in this low temperature regime. [2]

(e) In a high temperature regime, for which $S \gg 3Nk$, write down an approximate expression for E in terms of T and N and show that the heat capacity at constant volume is equal to $3Nk$. [2]

(f) State what system you think the professor was trying to model, explaining your reasons. [2]

In his other pocket he finds another scrap of paper bearing what looks like an expression for a grand partition function for a gas of particles:

$$\ln Z_G(\mu, T) = -\int_0^\infty g(\epsilon)\ln(1 - \exp((\mu - \epsilon)/kT))d\epsilon,$$

in which he reckons $g(\epsilon)$ is a density of states in single particle energy ϵ.

(g) Determine the mean population of particles in the system at temperature T and chemical potential μ, using the expression

$$\langle N\rangle = kT\left(\frac{\partial \ln Z_G}{\partial \mu}\right)_T,$$

derived in question 4(b). [3]

(h) Deduce the mean population of particles in a state with energy ϵ, and carefully explaining your reasons, tell the forgetful professor whether he had been considering fermions or bosons. [3]

11. (a) The change in system entropy brought about by a thermodynamic process can be written in the form

$$\Delta S = \int_{t_i}^{t_f} \frac{J}{T_r} dt + \Delta S_i,$$

where T_r is the temperature of a heat reservoir from which heat is drawn at a rate J. Explain what is meant by the term ΔS_i. [2]

(b) A neglected mug of tea cools down from an initial temperature 90°C to a final temperature equal to the ambient 20°C. The entropy of the tea may be represented by the expression $C_V \ln(bT)$ where b is a constant and the constant volume heat capacity C_V of the tea is 1000 JK^{-1}, for the temperature range of interest. Calculate ΔS_i for this cooling down process. [4]

(c) The mug is placed in a microwave oven for sufficient time to heat the tea back to its initial temperature. The injection of energy from such a device may be classed as work and not heat transfer. Calculate the ΔS_i associated with the reheating of the tea. [2]

(d) The entropy of an ideal classical gas of N particles occupying a volume V and at temperature T is given by

$$S(T, V, N) = Nk \ln\left(\frac{(kT)^{3/2}}{\hat{c}N/V}\right).$$

Write down the entropy of a system consisting of a mixture of two ideal gases in a volume V, in thermal equilibrium with a reservoir at temperature T_r, when there are N_A particles of gas A and N_B particles of gas B. [2]

(e) A student devises a machine involving pistons and semipermeable membranes to separate the gases inside the volume V, such that after its operation pure gas A occupies volume V_A and pure gas B occupies volume $V_B = V - V_A$, both in thermal equilibrium with the reservoir, and in mechanical equilibrium with each other. Determine the entropy of the final equilibrium system of separated gases and show that it is lower than the entropy of the initial gas mixture by an amount

$$\Delta S_m = -(N_A + N_B)k(x_A \ln x_A + x_B \ln x_B).$$

where $x_A = N_A/(N_A + N_B)$ and $x_B = N_B/(N_A + N_B)$ are the proportions of particles of type A and B in the original mixture. Interpret this reduction in entropy in terms of uncertainty in system microstate. [4]

(f) She operates the separation machine quasistatically while maintaining the gases in thermal contact with the reservoir. What is the entropy change of the reservoir? What work is required to perform the separation? [3]

(g) On a second run she operates the machine rapidly. Is the work required greater than, less than or the same as the work required in part (f)? Why? [3]

END OF PAPER