

College of Science and Engineering  
School of Physics



**Thermodynamics & Statistical  
Mechanics**  
SCQF Level 9, U03272, PHY-3-ThermStat  
Thursday 3rd May, 2007  
9.30 a.m. – 12.30 p.m.

**Chairman of Examiners**  
Professor D M Campbell

**External Examiner**  
Professor M Green

Answer ALL of the questions in Section A,  
and THREE questions from Section B with at  
least one question from Section B1 and one  
question from Section B2.

The bracketed numbers give an indication of the value assigned  
to each portion of a question.

Only the supplied Electronic Calculators may be used during this examination.

ANONYMITY OF THE CANDIDATE WILL BE MAINTAINED DURING THE MARKING OF  
THIS EXAMINATION.

**Section A: Answer ALL of the questions in this Section**

- A.1** (a) Give the mathematical definition of constant volume and constant pressure heat capacities ( $C_V$  and  $C_p$ ) in terms of differential quantities. [4]
- (b) Expanding the internal energy,  $U$ , as a function of  $T$  and  $V$ , or otherwise, show that the following relationship is true for ANY fluid: [6]

$$C_p = C_V + \left\{ \left( \frac{\partial U}{\partial V} \right)_T + p \right\} \left( \frac{\partial V}{\partial T} \right)_p .$$

- A.2** The Kelvin statement of the second law is that no process is possible that transforms heat entirely into work. The statement of the second law due to Clausius is that no cyclic process is possible whose only effect is the transfer of heat from a colder to a hotter body. By considering a ‘composite’ engine, comprising two separate engines, show that if the Kelvin statement is not true then neither is the Clausius statement. [10]

- A.3** (a) Derive the Maxwell relation relating  $\left( \frac{\partial S}{\partial P} \right)_T$  to  $\left( \frac{\partial V}{\partial T} \right)_P$  starting from the standard differential form for the Gibbs Free Energy. Explain clearly at what point in the derivation you use the fact that  $G$  is a state function. [5]
- (b) Give a statement of the third law of thermodynamics. Deduce from the third law the limiting form for the linear expansion coefficient,  $\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ , as  $T \rightarrow 0$ , explaining carefully your reasoning. [5]

- A.4** (a) Give the definition of a microstate and that of a macrostate. [6]
- (b) Give the statistical mechanical definition of entropy, i.e Boltzmann’s Law. Explain the symbols you write down. [4]

- A.5** (a) Give the expression for the Fermi-Dirac distribution. Explain the symbols you write down. [6]
- (b) Give the definitions of the Fermi energy  $\epsilon_F$  and of the Fermi temperature  $T_F$ . [4]

**A.6** Consider a quasi-classical ideal gas of indistinguishable particles of mass  $M$  in two dimensions, in a box of area  $A = L^2$  where  $L$  is the length of the box in each dimension. The single particle density of states  $g(\epsilon) = \frac{ML^2}{2\pi\hbar^2}$ .

(a) Calculate the single particle partition function  $Z(1)$ . [5]

(b) Calculate the free energy of the system when there are  $N$  particles. [5]

**Section B: Answer THREE questions from this Section**

**Part B1: Answer AT LEAST ONE question from this Part.**

**B1.1** This question concerns the Joule-Kelvin expansion (throttling) of a fluid.

In a Joule-Kelvin expansion (throttling) a fluid is pushed through an insulating porous plug from an insulated chamber maintained at pressure  $p_1$  to an insulated chamber maintained at pressure  $p_2$ .

(a) Explain why the enthalpy,  $H$ , of the fluid is unchanged in this process. [7]

(b) The change in temperature is given by:

$$\Delta T = \int_{p_1}^{p_2} \mu_{JK} dp$$

where  $\mu_{JK} \equiv \left(\frac{\partial T}{\partial p}\right)_H$ . Although the throttling process is not an equilibrium process, explain why the above expression can be used to calculate the change in temperature of the fluid. [3]

(c) Show that [10]

$$\mu_{JK} = \frac{1}{C_p} \left( T \left( \frac{\partial V}{\partial T} \right)_p - V \right) .$$

**B1.2** This question concerns latent heat, the Clausius Clapeyron equation, and ice skating.

- (a) Starting from the equality of the Gibbs Free Energy along a first order transition line, derive the Clausius-Clapeyron equation that relates the slope of a pressure versus temperature phase boundary to a change in volume,  $\Delta V$ , and latent heat,  $L$ :

[10]

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \quad .$$

- (b) A skate slides easily on ice because a film of water is formed immediately under the skate. Below we consider two models to explain why this film might form, assuming that one skate blade is in contact with the ice at any one time and slides along its length, the dimension of the skate is length $\times$ width =200mm $\times$ 0.5mm and the mass of the skater is 50 kg.

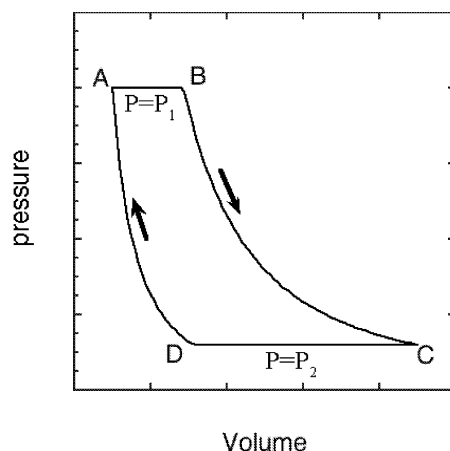
- (i) In the first model the pressure exerted by the skate is claimed to lower the melting point of the ice sufficiently for it to melt. For water the latent heat of melting is 334 J/g and the specific volumes of ice and water at 0° C are 1.09 cm<sup>3</sup>/g and 1.00 cm<sup>3</sup>/g. Estimate the minimum temperature of the ice for which skating would still be possible according to this model given that the pressure exerted by the blade is 50 atmospheres (1 atm  $\approx$  1  $\times$  10<sup>5</sup>Pa).

[5]

- (ii) In the second model the increase in pressure is ignored and the ice is considered to melt due to friction. The frictional force acting on the skate has been measured to be around 2.5 N. Estimate the lowest temperature at which the moving skate would form by friction a film of liquid water of thickness greater than 0.01 mm under the skate blade. Assume that the conduction of heat away from the skate-ice interface can be neglected. (Solid ice has a heat capacity of 1.96 J/K/g).

[5]

- B1.3** This question considers taking a ideal gas round a closed cycle. The cycle is shown in the figure below. The processes AB and CD are at constant pressures  $P_1$  and  $P_2$  respectively. Processes BC and DA are adiabatic and reversible.



- (a) State the general form of the first law. Starting from this and the equation of state for an ideal gas, derive the relation

$$P^{1-\gamma}T^\gamma = \text{constant} \quad ,$$

for an ideal gas undergoing a reversible adiabatic expansion ( $\gamma \equiv C_p/C_V$ ).

[8]

You can assume the molar heat capacities of an ideal gas at constant pressure ( $C_p$ ) and constant volume ( $C_V$ ) are independent of pressure and temperature, and  $C_p - C_V = R$ .

- (b) Suppose heat is absorbed by the ideal gas in process AB by bringing the gas initially at temperature  $T_A$  (corresponding to point A) into direct contact with a reservoir at the temperature corresponding to point B. The heat transferred to the ideal gas is

$$Q_{AB} = C_p \times (T_B - T_A) \quad .$$

What is the entropy change of the ideal gas going from A to B? Explain carefully your reasoning.

[5]

- (c) At pressure  $P_2$ , heat  $Q_{DC} = C_p \times (T_C - T_D)$ , is transferred from the ideal gas initially at temperature  $T_C$  to a second reservoir, maintained at temperature  $T_D$ , by bringing it into contact with this reservoir. Show that the efficiency of a heat engine working between the two reservoirs maintained at  $T_B$  and  $T_D$  for the above cycle is given by:

[7]

$$\eta = 1 - \left( \frac{p_2}{p_1} \right)^{1-1/\gamma} \quad .$$

**Part B2: Answer AT LEAST ONE question from this Part.**

**B2.1** Suppose there are  $N_A$  particles of species  $A$  and  $N_B$  particles of species  $B$  which are assumed to live on a 3-dimensional cubic lattice. We further assume that together the particles always completely fill a lattice of  $N$  sites, with  $N = N_A + N_B$ . Let  $\epsilon_{AA}$ ,  $\epsilon_{BB}$  and  $\epsilon_{AB}$  be the binding energies of  $A - A$ ,  $B - B$  and  $A - B$  bonds respectively. We denote by  $m_{AA}$ ,  $m_{BB}$  and  $m_{AB}$  the number of  $A - A$ ,  $B - B$ ,  $A - B$  bonds respectively. It can be shown that  $6N_A = 2m_{AA} + m_{AB}$  and  $6N_B = 2m_{BB} + m_{AB}$ .

(a) Show that the energy  $E(N_A, N_B)$  of a configuration can be written as

$$E(N_A, N_B) = 3\epsilon_{AA}N_A + 3\epsilon_{BB}N_B + \left[ \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \right] m_{AB} \quad .$$

[8]

(b) In the mean-field approximation, one writes  $m_{AB} = 6N_A N_B / N$ . Using Stirling's approximation for the logarithms, show that the free energy of the system in the mean-field approximation can be written as

$$F(N_A, N_B) = 3\epsilon_{AA}N_A + 3\epsilon_{BB}N_B + kTN \left[ \chi_{AB} \frac{N_A}{N} \frac{N_B}{N} + \frac{N_A}{N} \ln \left( \frac{N_A}{N} \right) + \frac{N_B}{N} \ln \left( \frac{N_B}{N} \right) \right]$$

where  $\chi_{AB} = \frac{6}{kT} \left[ \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \right]$  and  $k$  is Boltzmann's constant.

[8]

(c) In studying the mixing of oil and water, we are actually interested in the free energy of mixing  $\Delta F_{mix}$ , which is the difference in the free energies of the mixed state and the pure  $A$  and  $B$  phases, and is defined as

$$\begin{aligned} \frac{\Delta F_{mix}}{NkT} &\equiv \frac{F(N_A, N_B) - F(N_A, 0) - F(0, N_B)}{NkT} \\ &= \chi_{AB}x(1-x) + x \ln(x) + (1-x) \ln(1-x) \end{aligned}$$

where  $x = \frac{N_A}{N}$ . For hydrocarbon/water interactions at room temperature  $\chi_{AB} \approx 5$ . Take  $\chi_{AB} = 5$  and calculate  $\frac{\Delta F_{mix}}{NkT}$  for a concentration of oil in water  $x = 0.3$ . Is mixing favourable? Repeat the calculation for  $x = 10^{-4}$ . Is mixing favourable? So when can oil and water mix at room temperature according to this model?

[4]

**B2.2** By shining an intense laser beam on a semiconductor, one can create a collection of electrons (charge  $-e$ , and effective mass  $m_e$ ) and holes (charge  $+e$ , and effective mass  $m_h$ ) in the bulk. The oppositely charged particles may pair up (as in a hydrogen atom) to form a gas of *excitons*, or they may dissociate into an electron-hole plasma.

(a) Write down the single particle partition functions  $Z_e(1)$  and  $Z_h(1)$  at temperature  $T$  in a volume  $V$  for electrons and holes respectively. (The thermal wavelength  $\lambda$  for a particle of mass  $m$  is  $\lambda = \frac{h}{\sqrt{2\pi mkT}}$ .) [6]

(b) By pairing into an exciton, the electron-hole pair lowers its energy by  $\epsilon$ . Write down the single particle partition functions  $Z_p(1)$  at temperature  $T$  in a volume  $V$  for excitons of mass  $m_e + m_h$ . [3]

(c) Consider a semi-classical gas of  $N_e \gg 1$  indistinguishable electrons,  $N_h \gg 1$  indistinguishable holes and  $N_p \gg 1$  indistinguishable excitons. Calculate the chemical potentials  $\mu_e$ ,  $\mu_h$ ,  $\mu_p$  of the electron, hole and exciton states, respectively. [9]

(d) Express the equilibrium condition between excitons and electron/holes in terms of their chemical potentials. [2]



**B2.3** Consider a weakly interacting gas of  $N$  identical spin-zero bosons with an energy-momentum relationship given by  $\epsilon_{\mathbf{k}} = Ak^s$ , where  $k$  is the magnitude of the wavevector  $\mathbf{k}$ ,  $k = |\mathbf{k}|$ .  $A$  and  $s$  are some fixed numbers.

The dimensionality of the gas is  $d$  which means that the density of states in  $k$ -space can be written as  $\Gamma(k) = \alpha(d)Vk^{d-1}$ , where  $V$  is the volume of the gas and  $\alpha(d)$  is a number that depends on the dimensionality of space but will not be of interest to us here.

- (a) The density of states  $g(\epsilon)$  is defined such that  $g(\epsilon)d\epsilon$  is the number of states available to a particle in the energy range  $[\epsilon, \epsilon + d\epsilon]$ . Show that in  $d$  dimensions

$$g(\epsilon) = \frac{\alpha(d)V}{sA^{\frac{d}{s}}}\epsilon^{\frac{d}{s}-1} \quad . \quad [8]$$

- (b) Express the total number of particles  $N$  in terms of  $g(\epsilon)$ , the temperature  $T$  and the chemical potential  $\mu$ . [4]

- (c) At the Bose-Einstein temperature  $T_B$ , the chemical potential  $\mu$  goes to zero. From an examination of the expression for  $N$  show that there is a Bose-Einstein transition (i.e  $T_B \neq 0$ ) only if  $s < d$ . (Hint: consider the change of variable  $x = \frac{\epsilon}{kT_B}$ .) [4]

- (d) Show that when there is a Bose-Einstein transition, the number of particles with zero momentum  $N_0$  is given by

$$N_0 = N \left[ 1 - \left( \frac{T}{T_B} \right)^{\frac{d}{s}} \right] \quad . \quad [4]$$