College of Science and Engineering
School of Physics

Thermodynamics & Statistical Mechanics

SCQF Level 9, U03272, PHY-3-ThermStat

Thursday 24th April, 2008

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

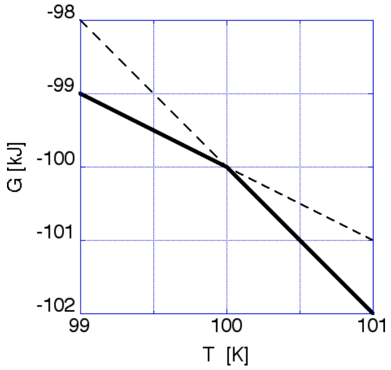
A.1 a) What are the units of entropy? [2]

b) What is the entropy change of a working substance taken around (i) a completely reversible closed cycle and (ii) a closed cycle containing irreversible steps? Explain your reasoning. [3]

A.2 The expression $dU = TdS + \mathbb{F}d\ell$ relates changes of the internal energy of an elastic spring to changes of entropy S and length ℓ, with $\mathbb{F}$ the tension in the spring. From this derive the following Maxwell relation explaining your reasoning: [5]

$$\left(\frac{\partial T}{\partial \ell}\right)_S = \left(\frac{\partial \mathbb{F}}{\partial S}\right)_\ell \quad .$$

A.3



The solid line in the figure shows the temperature dependence of the Gibbs free energy at constant pressure for one Kg of a substance crossing a first order transition at 100 K. Estimate the latent heat for the transition. [5]

A.4 Consider a collection of $N = 3$ weakly interacting dipoles in an external magnetic field H. Each dipole can either be in the $\uparrow$ state of energy $\epsilon_\uparrow = -mH$ or in the $\downarrow$ state of energy $\epsilon_\downarrow = +mH$. Write down all the possible macrostates of the system labelled by the total energy E and the microstates corresponding to each macrostate. [5]

A.5 An atom can be in 4 possible states of energies $\epsilon_0 < \epsilon_1 < \epsilon_2 < \epsilon_3$. Let p_i denote the probability that the atom is in state of energy ϵ_i. At a temperature $T = 300K$, it is found that $p_0 = 0.80$, $p_1 = 0.10$, $p_2 = 0.07$. Calculate the energy difference $\epsilon_1 - \epsilon_0$. [5]

A.6 (a) Write down the Bose-Einstein distribution. Explain the meaning of all the symbols you write down. [**3**]

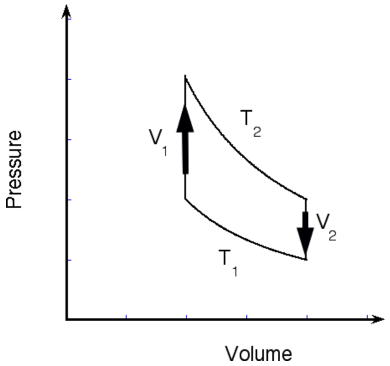
(b) What happens at and below the Bose-Einstein temperature? [**2**]

Section B: Answer THREE questions from this Section

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

B1.1 This question covers the second law and a cyclic process.

a) The Kelvin statement of the second law is that no process is possible which 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 Clausius statement is not true then neither is the Kelvin statement. **[6]**



In a simplified Stirling engine, gas is displaced between hot and cold reservoirs with a plunger. The gas heats or cools rapidly at constant volume when brought into contact with each reservoir. It then expands or contracts at constant temperature doing or requiring the performance of useful work. The cycle is shown in the indicator diagram above.

Consider the working substance to be a **monatomic ideal gas** in the following.

b) Show that the heat absorbed Q and work done W_{done} by the gas going from V_1 to V_2 at constant T are given by: **[5]**

$$W_{\text{done}} = Q = RT\,\ln\left(\frac{V_2}{V_1}\right)$$

per mole of gas.

c) For the isometric (constant volume) changes the gas is brought directly from contact with one reservoir into contact with the other. Determine the heat absorbed **and** the work done by the gas for the process $T_1 \rightarrow T_2$ at volume V_1. [You can assume without proof that the molar heat capacity of a monatomic ideal gas is $c_V = \frac{3}{2}R$.] **[3]**

d) Hence derive an expression for the efficiency of the cycle working between two heat baths at T_1 and T_2 with volumes in the ratio V_2/V_1. **[3]**

e) Explain briefly what ‘regeneration’ is and how this can be used to improve the efficiency. **[3]**

B1.2 This question concerns the adiabatic free expansion (Joule expansion) of a Van der Waals gas.

a) What is the physical significance of coefficients a and b in the Van der Waals equation of state,

$$(p + \frac{a}{v^2})(v - b) = RT \quad ,$$

where v is the molar volume? **[4]**

b) The temperature change for an adiabatic free expansion (Joule expansion) from molar volume v_1 to molar volume v_2 is given by:

$$\Delta T = \int_{v_1}^{v_2} dv\ \mu_J \qquad \text{with} \qquad \mu_J = \left(\frac{\partial T}{\partial v}\right)_U \quad .$$

Outline the derivation of the above expression, explaining carefully why an integral of a differential quantity can be used to calculate the change in temperature for a free expansion, which is not an equilibrium process. **[4]**

c) Show that (for any fluid): **[6]**

$$\mu_J = \frac{1}{c_V}\left(P - T\left(\frac{\partial P}{\partial T}\right)_V\right)$$

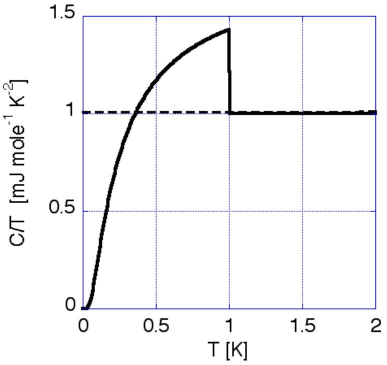
with c_V the constant volume molar heat capacity.

d) Hence show that for a Van der Waals gas: **[3]**

$$\mu_J = -\frac{a}{c_V}\left(\frac{1}{v}\right)^2 \quad .$$

e) In the light of the above, comment on the expected sign of the temperature change in a free expansion. **[3]**

B1.3



This question concerns heat capacity and a continuous (2$^{\text{nd}}$ order) phase transition. The figure shows the heat capacity divided by temperature for a material in zero magnetic field (solid line). Superconductivity occurs below a phase transition at $T = 1$K. Also shown is the heat capacity in an applied field H_{app} sufficient to suppress superconductivity (dashed line); the latter line is indistinguishable from the solid line for $T > 1$ K.

a) The internal energy for a substance in an applied magnetic field H_{app} is given by $dU = TdS + \mu_0 V H_{\text{app}} dM$ with M the sample magnetisation (you can assume changes of volume are zero in this question). Starting from this derive the Maxwell relation: **[7]**

$$\frac{1}{\mu_0 V}\left(\frac{\partial S}{\partial H_{\text{app}}}\right)_T = \left(\frac{\partial M}{\partial T}\right)_{H_{\text{app}}} \quad .$$

b) For $T > 1$K the magnetisation is observed to be independent of temperature. Show that for $T > 1$K this implies that $S(H_{\text{app}}, T) = S(0, T)$. **[3]**

c) Give a statement of the 3$^{\text{rd}}$ law of thermodynamics. From this explain why the entropies of the superconducting state and non-superconducting state must be equal at zero temperature. **[4]**

d) Starting from the definition of heat capacity derive the following expression for the entropy at temperature T. **[3]**

$$S(T) = \int_0^T \frac{C_{H_{\text{app}}}}{T} dT \quad .$$

e) Hence deduce a relationship between the areas enclosed under the solid and dashed lines between 0K and 1K. **[3]**

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

B2.1 Consider a collection of N atoms at temperature T. Each atom can be in either of two states: state 0 with energy ϵ_0 and state 1 of energy ϵ_1, with $\epsilon_0 < \epsilon_1$. Assume there are n_0 atoms in state 0 and $n_1 = N - n_0$ atoms in state 1.

(a) What is the total energy of the system? **[3]**

(b) Calculate the entropy of the system using Boltzmann's law. You may assume that $N \gg 1$, $n_0 \gg 1$ and $n_1 \gg 1$. Give all the steps of the derivation. **[7]**

(c) By minimising the Helmholtz free energy F with respect to $x \equiv n_0/N$, show that in thermal equilibrium

$$\frac{n_1}{n_0} = \exp\left(-\frac{\epsilon_1 - \epsilon_0}{kT}\right) \quad .$$

[10]

B2.2 Consider a semi-classical gas of N relativistic spin $\frac{1}{2}$ particles of mass m with an energy ϵ_k versus wavevector k relation

$$\epsilon_k = \sqrt{\hbar^2 c^2 k^2 + m^2 c^4}$$

where c is the speed of light. The particles are confined to a 2-dimensional square box of side L.

(a) Show that the density of states in k space $\Gamma(k)$ is given by $\Gamma(k) = L^2 k/\pi$. **[5]**

(b) Hence show that the density of states $g(\epsilon)$ is given by

$$g(\epsilon) = \begin{cases} 0 & \text{if } \epsilon \le mc^2 \\ (L^2\epsilon)\,/\,(c^2\hbar^2\pi) & \text{otherwise} \end{cases} \quad .$$

[7]

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

(d) Calculate the partition function Z for the gas and its free energy F in terms of $Z(1)$. **[3]**

B2.3 Consider a quantum gas of weakly interacting electrons with energy versus wavevector relation

$$\epsilon_k = \frac{\hbar^2 k^2}{2m},$$

where k is the wavevector and m the mass of the electron. The electrons are constrained to move in one dimension, along a line of length L. The density of states $g(\epsilon)$ can be shown to be equal to

$$g(\epsilon) = \frac{L}{\pi}\sqrt{\frac{2m}{\hbar^2}}\frac{1}{\sqrt{\epsilon}} \quad .$$

(a) If the total number of electrons is N, calculate the Fermi energy ϵ_F and the Fermi temperature T_F. **[6]**

(b) At zero temperature, calculate the total energy of the gas in terms of the density N/L. **[6]**

(c) What would the corresponding zero temperature ground state energy be if the electrons were assumed to behave as a classical gas of weakly interacting constituents? **[2]**

(d) How do you expect the energy to vary with temperature T for non-zero but low temperature, i.e $T \ll T_F$? **[6]**