College of Science and Engineering
School of Physics

Thermodynamics

SCQF Level 9, U01359, PHY-3-Thermo

Wednesday 26th April, 2006
9.30 – 11.30 a.m.

Chairman of Examiners
Professor D M Campbell

External Examiner
Professor P Main

Answer **ALL** of the questions in **Section I**
and **TWO** questions from **Section II**

**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.

1. Explain why the differential of a *state function* must be an exact differential. Give a thermodynamic example of an inexact differential, and illustrate why the stated differential is inexact by describing a suitable process. [5]

2. As a crystal of ammonium bromide is cooled from room temperature, it undergoes a continuous phase transition at $T_c = 234.5$K at which the ammonium groups order. Its constant pressure molar heat capacity as a function of temperature, $c_p(T)$ is known. Explain how this information can be used to obtain a measure of the entropy change as we cool one mole of ammonium bromide from T_c to very low temperatures $(T \to 0)$. This molar entropy change is found to be $\Delta s = -5.76 \, \text{JK}^{-1}\text{mol}^{-1}$. Recalling the statistical meaning of entropy (per mole), viz., $s = R \ln W$, where W is the number of microstates, suggest a brief interpretation of the Δs value for ammonium bromide. [5]

3. A rubber band of unstretched length L_0 is put under tension f. As the rubber band is stretched, its volume remains constant. Show that the First Law of Thermodynamics for the rubber band now takes the form

$$dU = TdS + fdL \, ,$$

explaining carefully why the pressure does not feature in this result. [5]

4. The equation of state for a non-ideal gas can be written in the form of a virial expansion:

$$P = RT \left(\frac{1}{v} + \frac{B_2}{v^2} + \frac{B_3}{v^3} + \dots \right) \, ,$$

where $\{B_i\}$ are the (temperature dependent) virial coefficients and v is the molar volume. For the van der Waals equation of state

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT \, ,$$

it can be shown that the second virial coefficient is given by

$$B_2(T) = \left(b - \frac{a}{RT} \right) \, .$$

Using this result, explain in terms of molecular properties (i) why B_2 should be positive at high temperatures and negative at low temperatures, and (ii) the effect of the sign of B_2 on the pressure of the gas. [5]

Section II
Answer **TWO** of the questions from this **Section**

5. A quantity of interest in meteorology and oceanography is the rate at which the temperature of a volume V of air or water changes with pressure at constant entropy, $(\partial T/\partial P)_S$. This question is about relating this quantity to other material properties.

(a) Confusingly, the quantity $(\partial T/\partial P)_S$ is usually known as the 'adiabatic lapse rate', even though it is an 'isentropic', or constant entropy, thermodynamic derivative. Explain briefly why a process involving zero heat exchange (adiabatic) is, in general, *not* necessarily a constant-entropy (isentropic) process. [3]

(b) Define the heat capacity at constant pressure. By appealing to the differential of the enthalpy, $H = U + PV$, or otherwise, show that

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P .$$

[5]

(c) By considering the differential of the appropriate thermodynamic potential, prove the following Maxwell's relation:

$$\left(\frac{\partial P}{\partial S} \right)_T = - \left(\frac{\partial T}{\partial V} \right)_P .$$

[5]

(d) Show that the 'adiabatic lapse rate' is given by

$$\left(\frac{\partial T}{\partial P} \right)_S = \frac{T}{C_P} V \beta_P .$$

where β_P is the constant-pressure thermal expansivity. [4]

(e) Explain why the adiabatic lapse rate for (liquid) water can be both positive and negative. [3]

6. This question is concerned with various aspects of the Second Law.

(a) The Kelvin-Planck statement of the Second Law of Thermodynamics is: It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work. Write down the alternative statement of the Second Law, due to Clausius. **[3]**

(b) By considering a composite device comprising one appropriate engine and one refrigerator, show that if the Kelvin-Planck statement is false so is that due to Clausius. **[5]**

(c) A cyclic device C operates between a high temperature reservoir at T_1 and a low temperature reservoir at T_2. The device operates in turn as (i) an engine, (ii) a refrigerator and (iii) a heat pump. In *each case*, define the efficiency, and give an expression for the *maximum* possible efficiency. **[6]**

(d) A metal block at temperature T is placed in thermal contact with a reservoir at temperature $T_0 < T$. The heat capacity at constant pressure of the block is C_P. After sufficient time has elapsed, the metal block reaches the temperature of the reservoir.

  (i) Given an expression for the entropy change of the reservoir, ΔS_0.

  (ii) Why is the entropy change of the block *not* given by $-\Delta S_0$?

  (iii) Give an expression for the entropy change of the block. **[6]**

7. This is a question about phase diagrams and phase transitions.

(a) Sketch the PT phase diagram of a typical simple substance. Label all relevant regions and features. Sketch into this diagram the process of condensation. [7]

(b) Show that the molar Gibbs' function, g, satisfies the following differential relationship:
$$dg = vdP - sdT ,$$
where v and s are the molar volume and entropy respectively. [4]

(c) By considering the molar Gibbs' function at two neighbouring points on a coexistence boundary on a PT phase diagram, show that the volume and entropy change at a first order phase transition is related to the slope of the phase boundary by the Clausius-Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} .$$
[5]

(d) Consider the PT phase diagram you sketched under (a) above. Explain what feature of this diagram will change qualitatively if it now refers to water. Use the Clausius-Clapeyron relation to explain the physical significance of this change. [4]