College of Science and Engineering
School of Physics

Degree Examination

Paper T
Thermodynamics
Monday, 31st May 2004
2.30 – 4.30 p.m.

Chairman of Examiners
Professor M Cates

External Examiner
Professor P Main

Answer **ALL** of the questions in **Section A**
and **TWO** questions from **Section B**

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.

Printed: August 5, 2004

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Section A

Answer **ALL** the questions from this **Section**

1. Give an expression for the differential of the internal energy, dU, for a simple fluid incorporating the First and Second Laws of Thermodynamics. Using this result, show that the internal energy of a simple fluid satisfies

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P\,.$$

Give all the steps in your derivation, indicating clearly where you may have quoted results without proof. **[5]**

2. Define the heat capacities at constant pressure and constant volume, C_P and C_V. Give expressions for these quantities in terms of relevant derivatives of the entropy. Explain qualitatively why you expect $C_P > C_V$. **[5]**

3. 'One mole of an ideal gas expands adiabatically and doubles its volume. The entropy change of the gas is $R\ln 2$.' A student claims that this statement cannot be true, reasoning that since no heat entered the system the entropy change had to be zero. Explain carefully what is wrong with this student's reasoning. **[5]**

4. The Clausius-Clapeyron equation states that

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}\,.$$

With the aid of a suitable sketch, explain carefully the context in which this equation appears, and what it means. **[5]**

Section B

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

5. A rubber band of unstretched length L_0 is put under tension f. It satisfies Hooke's law, i.e., its length L at constant temperature is related to the tension by

$$L - L_0 = \lambda f \ ,$$

where λ is the spring constant. As the rubber band is stretched, its volume remains constant.

(a) Show that the First Law of Thermodynamics for the rubber band now takes the form

$$dU = TdS + fdL \ .$$ **[4]**

(b) Define the Helmholtz function for any thermodynamic system. Give an expression for the differential of the Helmholtz function for the rubber band. Hence prove the following Maxwell relation:

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L \ .$$ **[7]**

(c) Hence, by appealing to the appropriate rule for the manipulation of partial derivatives, show that

$$\left(\frac{\partial L}{\partial T}\right)_f = \lambda \left(\frac{\partial S}{\partial L}\right)_T \ .$$ **[5]**

(d) Experimentally it is observed that a rubber band under constant tension shrinks when it is heated. Explain briefly why this should lead us to conclude that the constituent molecules of the rubber band order when the rubber band is being stretched. **[4]**

6. (a) The Clausius statement of the Second Law of Thermodynamics states that no cyclic process is possible whose sole effect is the transfer of heat from a cold to a hot source. State the Kelvin statement of the Second Law. **[4]**

(b) By considering a suitable 'composite heat engine', show that the falsity of the Clausius statement implies the falsity of the Kelvin statement. **[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 body of mass m and isobaric specific heat capacity c_p cools from temperature T_i to T_f. Show that its entropy changes by

$$\Delta S = mc_p \ln\left(\frac{T_f}{T_i}\right) ,$$

explaining carefully your reasoning in deriving this result. **[5]**

7. (a) Explain what is meant by the 'equation of state' of a simple substance. **[3]**

(b) Define the Gibbs function, G, and give an expression for dG for a simple substance. **[5]**

(c) The Gibbs function for one mole of a certain gas (molar volume v) is given by

$$g = RT \ln P + A + BP + \frac{1}{2}CP^2 + \frac{1}{3}DP^3 ,$$

where A, B, C and D are constants. Find the equation of state for this gas. Comment on the behaviour of this equation of state in the low pressure regime. **[6]**

(d) Sketch the Gibbs function of the vapour and liquid states of a simple substance as functions of temperature in the vicinity of the boiling point, and relate features on your sketch to the change in entropy of the substance at boiling, and hence to the latent heat of vaporization. **[6]**