College of Science and Engineering
School of Physics

Degree Examination

Paper T
Thermodynamics
Monday, 2nd June 2003
2.00pm - 4.00pm

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.

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Thermodynamics

Section A

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

1. It can be shown that the heat capacities at constant pressure and volume are related by

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P .$$

Show, using this result, that $C_P - C_V = R$ for 1 mole of ideal (or perfect) gas. **[5]**

2. 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.

(a) Give an expression for the entropy change of the reservoir, ΔS_0.

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

(c) Give an expression for the entropy change of the block. **[5]**

3. A volume V of an ideal (or perfect) gas, initially at temperature T, is compressed adiabatically and reversibly to a volume $V/3$. If the ratio of the heat capacities of the gas is $\gamma = C_P/C_V = 1.4$, what is the final temperature of the gas? **[5]**

4. The van der Waals equation of state for one mole of a non-ideal gas is

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

Explain carefully the physical significance of the quantities a and b, paying particular attention to the *signs* of the terms in which they make their appearance. **[5]**

Section B

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 an adiabatic process is, in general, *not* necessarily an 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 is a question about the Second Law and reversible cyclic heat engines.

(a) Sketch the Carnot cycle for an ideal gas on a pressure-volume diagram and identify its main features. Explain carefully how it can operate as (i) an engine and (ii) a refrigerator. In each case, explain the significance of the *area* enclosed by the cycle on your sketch. **[6]**

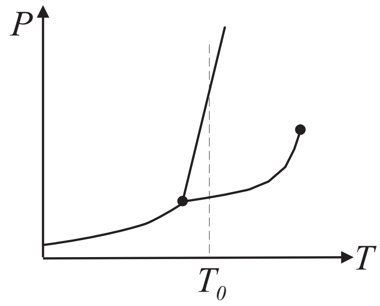
(b) Kelvin's statement of the second law of thermodynamics is that no process is possible whose sole result is the complete conversion of heat into work. Give the statement of the second law due to Clausius. **[4]**

(c) By considering a 'composite' heat engine, comprising two separate engines, show that if Kelvin's statement is false so is that due to Clausius. **[6]**

(d) A scientist applies to a venture capital company for money to develop a new heat pump which is claimed to deliver 1500 J to a room at 280 K by consuming 50 J of work per cycle pumping heat from the surroundings at 270 K. Would you advise the company to back the scientist? Give your reasons. **[4]**

7. This is a question about phase diagrams and phase transitions. *Please read through Parts (a) and (b) first before attempting to answer Part (a).*

(a) The PT phase diagram of a simple substance is given below. Copy this into your script book. Label all relevant regions and features. Sketch into this diagram the processes of sublimation. **[5]**



(b) To the left of your PT phase diagram, sketch the corresponding Pv phase diagram, with the respective P axes parallel and *to the same scale*. Again label all relevant features. Sketch as accurately as possible the isotherm at temperature T_0. **[5]**

(c) 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]**

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

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

[6]