King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/2470 PRINCIPLES OF THERMAL PHYSICS

Summer 2002

Time allowed: THREE Hours

**Candidates should answer SIX parts of SECTION A,
and TWO questions from SECTION B.**

The approximate mark for each part of a question is indicated in square brackets.

**You must not use your own calculator for this paper.
Where necessary, a College calculator will have been supplied.**

TURN OVER WHEN INSTRUCTED

Values of physical constants

Universal gas constant $R = 8.31\ \mathrm{JK^{-1}mol^{-1}}$

Throughout this paper, P denotes pressure, T thermodynamic temperature, V volume and v molar volume.

SECTION A – Answer SIX parts of this section

1.1) The following equation arises when setting up a scale of temperature,

$$T_X = 273.16\left(\frac{X}{X_{\mathrm{TP}}}\right).$$

What do the symbols and the constant represent? Explain the reason for the particular choice of constant.

[7 marks]

1.2) Estimate how much work is done by 2 kg of hydrogen gas at a temperature of 300 K as it expands reversibly and isothermally until its initial volume is doubled. State any assumptions that you make.

[7 marks]

1.3) Explain what is meant by an **equation of state**. Explain why terms such as Q (quantity of heat) and W (work) do not appear in an equation of state. Give a reason for your answer.

[7 marks]

1.4) Show that, for an ideal gas, the adiabatic curve through a point on the $P-V$ indicator diagram is γ times steeper than the isotherm through that point. Here, γ is the ratio of heat capacities C_P/C_V.

[7 marks]

1.5) A reversible Carnot refrigerator operates between reservoirs at 300 K and 270 K. Calculate the coefficient of performance of the refrigerator. During one complete cycle, 10^4 J of work is done on the refrigerator. How much heat is absorbed from the colder reservoir and how much is rejected to the hotter reservoir?

[7 marks]

1.6) Say whether the following statements are **true** or **false**, giving your reasons.

(a) When a gas expands adiabatically there is no exchange of heat (Q) with the surroundings. Since $\mathrm{d}S = \frac{đQ}{T}$, there cannot be any change in the entropy S of the gas.

(b) When an ideal gas expands isothermally and reversibly, it does an amount of work W. Since the expansion is isothermal and the internal energy $U = U(T)$ only, it follows that $\Delta U = 0$. The First Law of Thermodynamics then predicts that the gas must take in an amount of heat Q equal to W. Thus heat is being converted completely into work which violates the Second Law of Thermodynamics.

[7 marks]

1.7) Define the Helmholtz function F and use the fact that $\mathrm{d}F$ is an exact differential to prove the Maxwell relation

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

[7 marks]

1.8) The equation of state of a real gas can be written as a virial expansion,

$$\frac{P}{RT} = \frac{1}{v} + \frac{B_2}{v^2} + \frac{B_3}{v^3} + \ldots,$$

where B_n is the n^{th} virial coefficient and is a function of temperature only. The Boyle temperature, T_{B}, is defined as the temperature at which B_2 is zero.

Derive an expression, in terms of a, b and R, for the Boyle temperature of a gas obeying Dieterici's equation of state,

$$P(v-b) = RT\exp(-a/RTv)\,. \qquad (a \text{ and } b \text{ are constants})$$

Explain the physical significance of T_{B} and b.

[7 marks]

SECTION B – Answer TWO questions

2) A hypothetical engine, with an ideal gas as the working substance, operates in a reversible cycle ABCA. At A, the pressure and volume are P_1 and V_1, respectively. Along the isobaric path AB, an amount of heat $Q_1 > 0$ is supplied to the engine. The path BC is the isochore $V = V_2 > V_1$ along which an amount of heat $Q_2 > 0$ is rejected by the engine. CA is an isothermal path, temperature T_0, at the end of which the volume has decreased to V_1. Sketch the cycle on an indicator diagram.

[6 marks]

How much heat $Q_3 (> 0)$ is exchanged along the path CA? Is the heat supplied to, or rejected by, the engine?

[6 marks]

Show that the efficiency of the engine can be written in terms of the $\{Q_i;\ i = 1, 2, 3\}$ as

$$\eta = 1 - \frac{(Q_2 + Q_3)}{Q_1}.$$

[6 marks]

Hence show that

$$\eta = 1 - \frac{(\lambda - 1) + \frac{2}{3}\ell n\lambda}{\gamma(\lambda - 1)},$$

where $\lambda = V_2/V_1$ and γ is the ratio of the principal heat capacities. You may assume that the molar heat capacity at constant volume is $\frac{3}{2}R$.

[12 marks]

3) Give a thermodynamic definition for the change in entropy of a system.

[5 marks]

One mole of oxygen gas, O_2, is heated reversibly from 1000 K to 2000 K at constant pressure. (The atomic mass number of oxygen is 16.) Calculate the change in entropy of the gas if the specific heat capacity is given by

$$c_P = A + BT - CT^{-2},$$

where $A = 1.08 \times 10^3\,\mathrm{J\,kg^{-1}\,K^{-1}}$, $B = 3.38 \times 10^{-2}\,\mathrm{J\,kg^{-1}\,K^{-2}}$ and $C = 2.45 \times 10^7\,\mathrm{J\,kg^{-1}\,K}$.

[10 marks]

Now calculate the entropy change assuming that the heat capacity of O_2 at constant pressure is the same as that of an ideal gas of rigid diatomic molecules. Any formula you use must be derived, but you may assume that the molar internal energy per degree of freedom is $\frac{1}{2}RT$ and that the difference in the principal molar heat capacities is R.

[10 marks]

What would be the entropy change if the above process occurred irreversibly, and why?

[5 marks]

4) What is meant by the statement 'U is a state function'?

[4 marks]

Explain why the natural variables of U are the entropy S and volume V.

[4 marks]

Derive relations which enable the temperature and pressure to be derived if U is given in terms of its natural variables.

[4 marks]

The molar internal energy $u(s, v)$ of a system is given by

$$\ell\mathrm{n}\, u(s,v) = \frac{2}{3}(s/R) - \frac{2}{3}\ell\mathrm{n}\, v + \ell\mathrm{n}\, u_0\,,$$

where s is the molar entropy, v is the molar volume and u_0 is a constant. Calculate the temperature and pressure of the system.

[8 marks]

Show that the system is an ideal monatomic gas.

[4 marks]

How would the expression for $\ell\mathrm{n}\, u(s,v)$ be modified for the case of an ideal gas of rigid diatomic molecules.

[6 marks]

5) The *energy equation* for any system with the state variables P, V and T is

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

where U is the internal energy. Using this equation, show that the energy density $u\,(= U/V)$ of cavity radiation is given by

$$u = A\,T^4\,,$$

where A is a constant. State any assumptions that you make concerning u and its relationship to the radiation pressure.

[10 marks]

Use the *central equation of thermodynamics* to prove that the entropy associated with cavity radiation is given by

$$S = \frac{4}{3}AT^3V + S_0\,,$$

where S_0 is a constant.

[15 marks]

Explain how the Third Law of Thermodynamics suggests a numerical value for S_0.

[5 marks]