King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/2470 PRINCIPLES OF THERMAL PHYSICS

Summer 1999

Time allowed: THREE Hours

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

Separate answer books must be used for each Section of the paper.

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	$= 8.31\ \mathrm{JK^{-1}mol^{-1}}$
Triple point of water	T_{TP}	$= 273.16\ \mathrm{K}$

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

SECTION A – Answer SIX parts of this section

1.1) The resistance of a wire is given by

$$\mathrm{R} = \mathrm{R}_0(1 + \alpha t)\,,$$

where t is the temperature in degrees Celsius measured on the ideal gas scale. What is the physical significance of the constant R_0? If $\alpha = 4.0 \times 10^{-3}\mathrm{K}^{-1}$, calculate (correct to two decimal places) the temperature on the resistance scale at a temperature of 100 °C on the ideal gas scale.

[7 marks]

1.2) Estimate how much work has to be done on 4 kg of helium at a temperature of 22 °C to compress it quasistatically and isothermally until its initial pressure is trebled. (The atomic mass number of He is 4.)

[7 marks]

1.3) A reversible Carnot engine operates between reservoirs at 600 K and 400 K. During one complete cycle, the engine performs 200 J of work. How much heat is supplied by the hotter reservoir and how much heat is rejected to the colder reservoir?

[7 marks]

1.4) According to the kinetic theory of gases, the pressure P of an ideal monatomic gas is given by

$$P = \frac{1}{3}\rho\,\overline{\mathrm{v}^2}\,,$$

where ρ is the mass density and $\overline{\mathrm{v}^2}$ is the mean square speed of an atom. Using this result derive an expression for the molar specific heat at constant volume.

[7 marks]

1.5) Explain what is meant by an *equation of state*. Discuss the role of the constants a and b in the van der Waals' equation of state

$$(P + \frac{a}{v^2})(V - nb) = nRT\,.$$

[7 marks]

1.6) Explain why the following statements are **incorrect**:

(a) heat must flow into a system for there to be an increase in its entropy;

(b) the relation $\mathrm{d}H = đQ_P$ for an isobaric, reversible process can be integrated to show that the enthalpy change ΔH in an isobaric chemical reaction equals the heat Q generated in the reaction.

[7 marks]

1.7) The *central equation of thermodynamics* is

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V\,.$$

What do the symbols represent, which of them are *state functions* and which have the additional name of *state variable*? For which processes does the equation apply?

[7 marks]

1.8) Write down the four Maxwell thermodynamic relations and prove any one of them.

[7 marks]

SECTION B – Answer TWO questions

2) Give the Kelvin-Planck statement of the Second Law of Thermodynamics.

[5 marks]

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 is supplied to the engine. The path BC is the isochore $V = V_2 > V_1$, where heat Q_2 is rejected. CA is an adiabatic path. Sketch the cycle on an indicator diagram.

[5 marks]

Show that the efficiency of the engine is

$$\eta = 1 - \frac{1}{\gamma}\left(\frac{1-\lambda^\gamma}{1-\lambda}\right)$$

where $\lambda = V_1/V_2$ and γ is the ratio of the principal heat capacities.

[15 marks]

Along which path is the most work done?

[5 marks]

3) State the First Law of Thermodynamics.

[2 marks]

One mole of an ideal gas is to be changed from the state A (P_1, V_1) to the state B (P_2, V_2), where $V_2 < V_1$ and $P_1 V_1 = P_2 V_2$. The change may take place by one of the following methods:

(a) compress the gas quasistatically and isothermally from A to B;

(b) first take the gas quasistatically and isobarically from state A to an intermediate state C (P_1, V_2), and then from C to B at constant volume.

(i) Show the states A,B,C and the paths followed in the methods (a) and (b) on an indicator diagram.

[4 marks]

(ii) Derive an expression for the work done on the gas in method (a).

[5 marks]

(iii) What is the change in the internal energy of the gas during method (a) and during method (b)? Justify your answers.

[4 marks]

(iv) Derive an expression for the total work done in method (b).

[5 marks]

(v) If $V_1 = 5V_2$, determine which of the methods (a) or (b) involves a lower **input** of energy. You may assume that the molar heat capacity at constant volume is $\frac{3}{2}R$.

[10 marks]

4) Give a thermodynamic definition of the exact differential $\mathrm{d}S$, where S is the entropy of the system. Explain why, strictly speaking, thermodynamics allows only entropy *differences* to be defined.

[5 marks]

Calculate the total change of entropy when 10 kg of H_2O at 125 °C are transformed reversibly at constant pressure to ice at 0 °C. You may assume that the specific heat capacity at constant pressure of steam is given by

$$c_P = (1.9 + 3.5 \times 10^{-5}\, T)\,\mathrm{kJ\,kg^{-1}\,K^{-1}},$$

while for liquid water $c_P = 4.18\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$. The latent heat of vaporisation of water is $2256\,\mathrm{kJ\,kg^{-1}}$ and the latent heat of fusion of ice is $333\,\mathrm{kJ\,kg^{-1}}$.

[20 marks]

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

[5 marks]

5) A certain gas is described by Van der Waals' equation of state

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

The molar volume and temperature are changed reversibly from v_1 to v_2 and from T_1 to T_2, respectively. By using the expression $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$, or otherwise, show that the change in the molar internal energy is given by

$$\Delta u \equiv u_2 - u_1 = c_v(T_2 - T_1) + a\left(\frac{1}{v_1} - \frac{1}{v_2}\right)\,,$$

where the molar heat capacity, c_v, may be assumed constant.

[16 marks]

A quantity of oxygen is contained in a vessel with adiabatic walls. It then undergoes a free expansion into a similar vessel, which is initially evacuated. Assuming that oxygen is described by Van der Waals' equation, show that the change in temperature of the gas is given by

$$\Delta T = \frac{a}{c_v}\left(\frac{1}{v_2} - \frac{1}{v_1}\right)\,.$$

[8 marks]

Before expansion the density of the oxygen is $245\,\mathrm{mol\,m^{-3}}$ and after expansion it is $45\,\mathrm{mol\,m^{-3}}$. Calculate the change in temperature of the gas. You may assume that, for oxygen, $c_v = 20.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and the Van der Waals' constant $a = 0.138\,\mathrm{N\,m^4\,mol^{-2}}$.

[6 marks]