King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/2470 Principles of Thermal Physics

January 2003

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

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

SECTION A – Answer SIX parts of this section

1.1) Write down the expression for the vertical pressure gradient in a liquid of constant density ρ that is subject to a constant gravitational acceleration g. Use this to derive the pressure at the bottom of a lake of depth 10 m (take $\rho = 10^3$ kg m^{-3}, $g = 10$ m s^{-2} and the atmospheric pressure $P_0 = 10^5$ Pa).

[7 marks]

1.2) Two systems A and B exchange heat at constant pressure. The initial temperatures are T_A and T_B, and the heat capacities C_A and C_B respectively. Derive an expression for the temperature of the system once the equilibrium has been reached.

[7 marks]

1.3) Two identical thermally isolated containers of volume V_0 are linked by a valve. Initially one container holds an ideal gas at pressure P_0, while the other container is empty. The valve is then opened. What is the change in internal energy of the gas and what is the final pressure of the gas in the combined system?

[7 marks]

1.4) The first law of thermodynamics may be stated as $dU = \delta W + \delta Q$. Explain the significance of the different notations dU, δW and δQ. What is the physical origin of this difference?

[7 marks]

1.5) When two systems A and B at initial temperatures T_A and T_B exchange heat, the total change in entropy is $\Delta S = C\epsilon^2$+higher orders in ϵ, where C is a positive constant and $T_B = T_A(1+\epsilon)$, with $|\epsilon| << 1$. What physical consequences follow from this expression for the change in entropy?

[7 marks]

1.6) Consider the Gibbs free energy G. Derive an expression for the differential dG in terms of T, P, S and V and hence deduce the associated Maxwell relation.

[7 marks]

1.7) The Van der Waals equation of state for one mole of gas is

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

where a, b and R are constants. Derive the corresponding equation of state for n moles, taking into account the extensive or intensive properties of the different state parameters.

[7 marks]

1.8) During a change of phase between liquid and vapour at a given pressure, the differential of the Gibbs free energy is $dG = \mu_l dn_l + \mu_v dn_v$ where μ_l, μ_v are the chemical potentials of the liquid and the vapour, and n_l, n_v their number of moles respectively. Explain why, for the system to reach equilibrium, matter transforms from the phase with the larger chemical potential to the phase with the smaller chemical potential.

[7 marks]

SECTION B – Answer TWO questions

2) A heat engine operates cyclically, using an ideal gas as the working fluid. Each cycle may be split into 4 steps. The first step is an adiabatic compression from state A to state B. The second is an isochoric process from B to C. The third step is an adiabatic expansion from C to D and the last step an isochoric process from D back to A.

a) Draw the cycle on a Clapeyron diagram (P, V) and give the signs of the heat transfers Q_{BC} and Q_{DA} during the two isochoric processes.

[7 marks]

b) Express Q_{BC} and Q_{DA} in terms of the temperatures T_A, T_B, T_C, T_D and C_V, where C_V is the heat capacity at constant volume of the gas.

[5 marks]

c) Given the general definition of the efficiency $\eta = -W/Q_2$, where W is the work done and Q_2 the heat intake, express the efficiency of the engine as a function of T_A, T_B, T_C and T_D.

[5 marks]

d) Use the equation of state of the gas to express η as a function of P_A, P_B, P_C, P_D and the ratio $a = V_A/V_B$.

[5 marks]

e) Use the equations for the two adiabatic curves to express η as a function of a and the ratio $\gamma = C_P/C_V$, where C_P is the heat capacity at constant pressure.

[8 marks]

3) A closed cylinder is of cross section A. It contains n_0 moles of vapour and $N - n_0$ moles of liquid of the same substance. The phases are in equilibrium at an initial temperature T_0 and the vapour phase can be treated as if it was an ideal gas. Assume that the volume of the liquid phase is negligible compared to the volume of the vapour phase and that the saturated vapour pressure at temperature T is given by the function $P_s(T)$.

a) Heat is supplied to the system so that the temperature is increased from T_0 to T_1. Derive an expression for the number of moles n_1 in the vapour phase, assuming that some liquid is still present.

[5 marks]

b) The density ρ of the liquid phase is constant and M is its molar mass. What is the decrease Δh in the depth of liquid when the temperature goes from T_0 to T_1?

[7 marks]

c) On further increasing the temperature to $T = T_2$, the last drop of liquid disappears. Show that

$$\frac{P_s(T_2)}{T_2} = \frac{N}{n_0} \frac{P_s(T_0)}{T_0}.$$

[5 marks]

d) How does the pressure vary with T for $T \geq T_2$? Sketch the curve $P_S(T)$ for values of T from 0 to beyond T_2.

[5 marks]

e) Derive an expression for the function $P_s(T)$, assuming that the latent heat L is a constant and that the Clausius-Clapeyron equation can be written

$$L = vT \frac{dP_s}{dT},$$

where v is the volume per unit mole of the vapour (neglect the volume per unit mole of the liquid).

[8 marks]

4) A vertical cylinder is closed by a piston (of area A and mass m_0) and contains n moles of an ideal gas. The piston is initially at the height h_0 from the bottom of the cylinder. The internal pressure is balanced by the weight of the piston and the external pressure is negligible.

a) What is the expression for the initial temperature T_0 in terms of the quantities mentioned above?

[5 marks]

b) A mass m is added on the piston, quickly compressing the gas in an adiabatic process. Show that the work done to compress the gas from the state (P_0, V_0) to the state (P_1, V_1) is given by

$$W = \frac{P_1 V_1 - P_0 V_0}{\gamma - 1}$$

where γ is the ratio of the heat capacities of the gas. State why this expression is independent of the path between the initial and final states.

[5 marks]

c) The work is actually done by gravity and is $W = (m + m_0) g \Delta h$, where Δh is the change in height of the piston. Show that Δh is given by the expression

$$\Delta h = \frac{h_0}{\gamma} \frac{m}{m_0 + m}.$$

[7 marks]

d) What is the expression for the final temperature T_1 corresponding to the change Δh?

[3 marks]

e) The gas is instead compressed in a *reversible* way, by adding progressively small masses δm until the total additional mass is m. Since the system is isolated, the process remains adiabatic. Show that the corresponding change of height $\Delta h'$ is now given by the expression

$$\Delta h' = h_0 \left[1 - \left(\frac{m_0}{m_0 + m} \right)^{1/\gamma} \right].$$

[7 marks]

f) What is the expression for the final temperature T_1' corresponding to the change $\Delta h'$?

[3 marks]

5) A metallic wire increases in length by an amount x which is a function of the external force f and the temperature T. The work δW necessary to generate an increase dx is $\delta W = +f dx$.

a) By considering the Helmholtz free energy F, which has natural variables T and x, derive dF and deduce the corresponding Maxwell relation:

$$\left(\frac{\partial S}{\partial x}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_x .$$

[8 marks]

b) If the internal energy is a function of T and x, an infinitesimal change in U can be written as $dU = C_x dT + (k+f)dx$, where C_x is the heat capacity at constant length and k is a parameter. Both C_x and k could depend on x and T. Use the First Law of Thermodynamics to show that

$$k = T\left(\frac{\partial S}{\partial x}\right)_T .$$

[5 marks]

c) The equation of state of the wire is

$$x = \frac{f + \alpha(T - T_0)}{\mu_0[1 + \beta(T - T_0)]},$$

where α, β, μ_0 and T_0 are constants. Use the Maxwell equation found in part a) to show that

$$k = (\alpha - x\mu_0\beta)T.$$

[5 marks]

d) State the Maxwell relation corresponding to dU given in part b) and show that

$$\left(\frac{\partial C_x}{\partial x}\right)_T = 0.$$

What is the physical significance of this result?

[5 marks]

e) The wire is stretched quickly enough for the process to be adiabatic. T_0 is the initial temperature and T is the temperature corresponding to the length increase x. Give an expression for T, assuming that C_x is a constant.

[7 marks]