

# King's College London

UNIVERSITY OF LONDON

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**B.Sc. EXAMINATION**

**CP/2470 Principles of Thermal Physics**

**January 2004**

**Time allowed: THREE Hours**

**Candidates should answer ALL parts of SECTION A,  
and no more than TWO questions from SECTION B.  
No credit will be given for answering further questions.**

**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  
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## Physical Constants

Permittivity of free space	$\epsilon_0 = 8.854 \times 10^{-12}$	$\text{F m}^{-1}$
Permeability of free space	$\mu_0 = 4\pi \times 10^{-7}$	$\text{H m}^{-1}$
Speed of light in free space	$c = 2.998 \times 10^8$	$\text{m s}^{-1}$
Gravitational constant	$G = 6.673 \times 10^{-11}$	$\text{N m}^2 \text{kg}^{-2}$
Elementary charge	$e = 1.602 \times 10^{-19}$	$\text{C}$
Electron rest mass	$m_e = 9.109 \times 10^{-31}$	$\text{kg}$
Unified atomic mass unit	$m_u = 1.661 \times 10^{-27}$	$\text{kg}$
Proton rest mass	$m_p = 1.673 \times 10^{-27}$	$\text{kg}$
Neutron rest mass	$m_n = 1.675 \times 10^{-27}$	$\text{kg}$
Planck constant	$h = 6.626 \times 10^{-34}$	$\text{J s}$
Boltzmann constant	$k_B = 1.381 \times 10^{-23}$	$\text{J K}^{-1}$
Stefan-Boltzmann constant	$\sigma = 5.670 \times 10^{-8}$	$\text{W m}^{-2} \text{K}^{-4}$
Gas constant	$R = 8.314$	$\text{J mol}^{-1} \text{K}^{-1}$
Avogadro constant	$N_A = 6.022 \times 10^{23}$	$\text{mol}^{-1}$
Molar volume of ideal gas at STP	$= 2.241 \times 10^{-2}$	$\text{m}^3$
One standard atmosphere	$P_0 = 1.013 \times 10^5$	$\text{N m}^{-2}$

Throughout this paper,  $T$  denotes the temperature,  $V$  the volume and  $P$  the pressure.  $C_P$  and  $C_V$  respectively denote the heat capacity at constant pressure and the heat capacity at constant volume.  $n$  is the number of moles.

## SECTION A – Answer ALL parts of this section

- 1.1) A mass of 10 kg, which is released from a height of 10 m, falls freely under gravity and hits a piece of iron of mass 1 kg, coming to rest. The heat capacity of iron is  $0.5 \text{ J.g}^{-1}.\text{K}^{-1}$  and it can be assumed that the temperature of the falling mass does not change. If the acceleration due to gravity is  $g \simeq 10 \text{ m.s}^{-2}$ , what is the increase in temperature of the iron?

[7 marks]

- 1.2) A system goes from a state  $A$  to a state  $B$  in an adiabatic process. Explain why the work exchanged with the surroundings is independent of the thermodynamic path of the adiabatic process.

[7 marks]

- 1.3) The internal energy of  $n$  moles of a diatomic ideal gas is  $U = (5/2)nRT$ . Using the Mayer relation for the difference of heat capacities, compute the ratio  $\gamma = C_P/C_V$  of the heat capacities for this gas.

[7 marks]

- 1.4) The Gibbs free energy of a gas is given by

$$G(P, T) = C_P T + nRT \ln \left( \frac{P}{P_0} \right) + nRT \frac{C_P}{C_V - C_P} \ln \left( \frac{T}{T_0} \right),$$

where  $P_0, T_0$  are constants and  $C_P, C_V$  are the heat capacities at constant pressure and constant volume respectively. Given that  $dG = VdP - SdT$  and by considering the partial derivatives of  $G$  with respect to its variables, derive an equation of state of the gas.

[7 marks]

- 1.5) Using the Carnot-Clausius inequality and the First Law applied to cyclic transformations, show that a thermal engine cannot operate with one heat reservoir only. (This is the Kelvin statement of the Second Law)

[7 marks]

- 1.6) The infinitesimal change in internal energy for one mole of a Van der Waals gas is

$$dU = C_V dT + \frac{a}{V^2} dV,$$

where  $a$  is a constant and  $C_V$  could be a function of  $T$  and  $V$ . Using the appropriate Maxwell relation, show that  $C_V$  actually depends on the temperature only.

[7 marks]

- 1.7)  $G(P, T, n)$  is the Gibbs free energy of  $n$  moles of a substance at temperature  $T$  and pressure  $P$ . Explain why  $G = n\mu(P, T)$ , where  $\mu$  is the chemical potential.

[7 marks]

- 1.8)  $A$  and  $B$  are two systems which can exchange heat only and are isolated from the rest of the Universe. Their temperatures are such that  $T_A > T_B$ . From the relation  $(\partial S/\partial U)_V = 1/T$ , where  $S$  is the entropy and  $U$  the internal energy, use the Second Law to show that when  $A$  and  $B$  are in contact, the heat goes from  $A$  to  $B$ .

[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 (from state  $A$  to state  $B$ ) is an isobaric compression with  $P = P_A$ . The second step (from state  $B$  to state  $C$ ) is an adiabatic compression until the pressure reaches the value  $P_C$ . The third step (from state  $C$  to state  $D$ ) is an isobaric expansion with  $P = P_C$  and the last step (from state  $D$  back to state  $A$ ) is an adiabatic expansion where the pressure goes back to its initial value  $P_A$ .
- a) Draw the cycle in a Clapeyron diagram ( $P, V$ ) and give the signs of  $Q_{AB}$  and  $Q_{CD}$ , the heat transfers into the gas during the two isobar processes. [8 marks]
- b)  $C_P$  is the heat capacity at constant pressure of the gas. Express  $Q_{AB}$  and  $Q_{CD}$  in terms of  $C_P$  and the temperatures  $T_A, T_B, T_C$  and  $T_D$ . [4 marks]
- c) From the general definition of the efficiency  $\eta$  and the First Law, show that

$$\eta = 1 + \frac{T_B - T_A}{T_D - T_C}.$$

[5 marks]

- d) A characteristic quantity for this engine is  $a = P_C/P_A$ . Using the equation of state of the gas, derive an expression for  $\eta$  as a function of  $a$  and the volumes  $V_A, V_B, V_C$  and  $V_D$ . [5 marks]
- e) Use the equations of the two adiabatic curves to show that

$$\eta = 1 - a^{\frac{1}{\gamma}-1},$$

where  $\gamma$  is the ratio  $C_P/C_V$ .

[8 marks]

3) A cylinder with adiabatic walls is closed by a piston (mass  $m$ , area  $A$ ) which can move up and down without friction. The cylinder contains an ideal gas. At equilibrium (no motion of the piston) the pressure inside the cylinder is  $P_1$  and the piston is at the height  $h$ . The pressure outside the cylinder is  $P_0$  and  $g$  is the acceleration due to gravity.

a) Show that  $P_1 - P_0 = mg/A$ .

[6 marks]

b) When the piston moves in a reversible way from its equilibrium position with displacement  $z$ , the pressure inside the cylinder becomes  $P$ . Show that

$$P = P_1 \left( \frac{h}{h+z} \right)^\gamma,$$

where  $\gamma$  is the ratio  $C_P/C_V$ .

[8 marks]

c) The deviation from the equilibrium is small ( $z \ll h$ ), such that

$$\left( \frac{h}{h+z} \right)^\gamma \simeq 1 - \gamma \frac{z}{h}.$$

Write the equation of motion for the piston and show that this motion is a harmonic oscillation with angular frequency

$$\omega = \sqrt{\gamma \frac{P_1 A}{mh}}.$$

[10 marks]

d) Show that the dependence on temperature is such that  $\omega$  is proportional to  $1/\sqrt{T}$ .

[6 marks]

- 4) The vapour and liquid states of a pure substance are in equilibrium at temperature  $T$ . The mass fraction of the substance which is vapour is  $x$ . The heat capacities per unit mass are  $c_v$  and  $c_l$  for the vapour and the liquid phases, respectively, and the volumes per unit mass are  $u_v$  and  $u_l$ .  $L$  is the latent heat (defined per unit mass) at temperature  $T$ . The processes which occur in this system are reversible.  $q$  and  $s$  are the heat and entropy per unit mass, respectively.
- a) Show that, when the temperature changes by  $dT$ , the heat per unit mass exchanged with the surroundings is

$$\delta q = xc_v dT + (1-x)c_l dT + Ldx.$$

[8 marks]

- b) Write down, in terms of  $dT$  and  $dx$ , the associated change of entropy per unit mass  $ds$ , and show that the corresponding Maxwell relation gives

$$c_v - c_l = \frac{dL}{dT} - \frac{L}{T}.$$

[8 marks]

- c) Using the previous equality, show that

$$ds = d\left(\frac{xL}{T}\right) + c_l \frac{dT}{T}.$$

[8 marks]

- d) Hence show that the equation corresponding to the adiabatic processes occurring in this system is ( $c_l$  is considered constant):

$$\frac{xL}{T} + c_l \ln\left(\frac{T}{T_0}\right) = \frac{xL_0}{T_0},$$

where  $L_0$  is the latent heat at a given temperature  $T_0$ .

[6 marks]

- 5) A drop of liquid has surface area  $A$  and surface tension  $\psi$  in the air, i.e. the work necessary to increase the area by  $dA$  is  $\delta W = \psi dA$ .
- a) Show that the differential of the internal energy of the drop is  $dU = TdS + \psi dA$ , where  $S$  is the entropy of the drop.

[4 marks]

- b) Considering the Helmholtz free energy  $F = U - TS$ , show that

$$\left(\frac{\partial S}{\partial A}\right)_T = -\left(\frac{\partial \psi}{\partial T}\right)_A.$$

[5 marks]

- c) The heat capacity at constant area  $C_A$  is defined by  $dU = C_A dT + (f + \psi)dA$ , where  $f$  is a function which can depend on  $T$  and  $A$ . Comparing the above expression for  $dU$  and that given in part a), show that

$$f = -T \left(\frac{\partial \psi}{\partial T}\right)_A.$$

[8 marks]

- d) The surface tension is given by  $\psi = aT + b$ , where  $a$  and  $b$  are constants. Determine a corresponding expression for  $f$ .

[4 marks]

- e) Using the Maxwell relation corresponding to the expression  $dU$  given in question c), show that the heat capacity  $C_A$  is independent of area  $A$ .

[4 marks]

- f) The drop is spherical and  $b > 0$ . Determine the sign of the change in internal energy if we split the drop into two identical spherical drops at constant temperature. Is the drop likely to split itself spontaneously?

[5 marks]