King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP 2470 Principles of Thermal Physics

January 2006

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

Physical Constants

Permittivity of free space	ϵ_0	=	8.854×10^{-12}	$\mathrm{F\,m^{-1}}$
Permeability of free space	μ_0	=	$4\pi \times 10^{-7}$	$\mathrm{H\,m^{-1}}$
Speed of light in free space	c	=	2.998×10^{8}	$\mathrm{m\,s^{-1}}$
Gravitational constant	G	=	6.673×10^{-11}	$\mathrm{N\,m^{2}\,kg^{-2}}$
Elementary charge	e	=	1.602×10^{-19}	C
Electron rest mass	m_{e}	=	9.109×10^{-31}	kg
Unified atomic mass unit	m_{u}	=	1.661×10^{-27}	kg
Proton rest mass	m_{p}	=	1.673×10^{-27}	kg
Neutron rest mass	m_{n}	=	1.675×10^{-27}	kg
Planck constant	h	=	6.626×10^{-34}	$\mathrm{J\,s}$
Boltzmann constant	k_{B}	=	1.381×10^{-23}	$\mathrm{J\,K^{-1}}$
Stefan-Boltzmann constant	σ	=	5.670×10^{-8}	$\mathrm{W\,m^{-2}\,K^{-4}}$
Gas constant	R	=	8.314	$\mathrm{J\,mol^{-1}\,K^{-1}}$
Avogadro constant	N_{A}	=	6.022×10^{23}	$\mathrm{mol^{-1}}$
Molar volume of ideal gas at STP		=	2.241×10^{-2}	$\mathrm{m^{3}}$
One standard atmosphere	P_0	=	1.013×10^{5}	$\mathrm{N\,m^{-2}}$

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. $\gamma = C_P/C_V$ and n is the number of moles.

SECTION A – Answer ALL parts of this section

1.1) Give a statement of the First Law of Thermodynamics, discussing the path dependence for the different quantities which appear in this law.

[5 marks]

1.2) Sketch on a Clapeyron diagram (P, V) the isothermal curves of a pure substance of critical temperature T_c in the three cases: $T > T_c$, $T = T_c$ and $T < T_c$. Explain the presence of a plateau in one of these curves.

[6 marks]

1.3) One kilogram of ice-cold water is put in 4 kilograms of boiling water at atmospheric pressure. Explain how to obtain the equilibrium temperature and derive its value in degrees Celsius.

[6 marks]

1.4) The energy equation reads

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

where U is the internal energy of a system that could depend on T and V. Define the enthalpy and explain why it depends on the temperature only for an ideal gas.

[7 marks]

1.5) A system Z with initial temperature T_1 and heat capacity C (independent of T) is put in contact with a heat source at temperature T_0 until the total isolated system (source + Z) reaches equilibrium. Both systems exchange heat only. Derive an expression for the total change in entropy ΔS during the process and check that $\Delta S > 0$.

[8 marks]

1.6) The latent heat of vaporization of a fluid L and the saturated vapour pressure P_s are related by the Clausius-Clapeyron equation

$$L = T(v - u)\frac{\mathrm{d}P_s}{\mathrm{d}T},$$

where v is the volume per unit mole of the vapour phase and u is the volume per unit mole of the liquid phase. If $v >> u$ and the vapour is supposed ideal, derive an expression for the function $P_s(T)$ in the case where L is constant. Sketch $P_s(T)$ and indicate the triple point and the critical point of the fluid.

[8 marks]

SECTION B – Answer TWO questions

2) An ideal gas operates in cycles, decomposed into three steps. The first step (A to B) is an adiabatic compression from the the volume V_A to V_B. The second step (from B to C) is an isobaric expansion and the third step, isochoric, leads back to A.

a) Sketch such a cycle on a Clapeyron diagram (P, V) and indicate the heat transfers, justifying their signs.

[7 marks]

b) Define the efficiency of the cycle and show that it is given by

$$\eta = 1 + \frac{Q_2}{Q_1},$$

where Q_1 is the heat intake and Q_2 is given to the surroundings.

[5 marks]

c) Give an expression for Q_1, Q_2 in terms of the temperatures T_A, T_B, T_C and show that

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

where $p = P_A/P_B$ and $a = V_B/V_A$.

[8 marks]

d) Using an appropriate relation characterizing the adiabatic process, give an expression for the efficiency which depends on γ and a only.

[5 marks]

e) Using the Mayer relation, evaluate γ for a monoatomic ideal gas with internal energy $U = (3/2)nRT$ and hence evaluate η if $a = 0.1$.

[5 marks]

3) A paramagnetic sample with entropy S and total magnetic moment M has an internal energy U such that, in an infinitesimal change, $dU = TdS + BdM$, where B is an external magnetic field applied to the sample.

a) Using analogies with a gas, explain why the enthalpy H and the Gibbs free energy G of the paramagnetic sample are $H = U - BM$ and $G = U - BM - TS$.

[4 marks]

b) The heat capacity at constant field is defined by

$$C_B = \left(\frac{\partial H}{\partial T}\right)_B .$$

Give an expression for dH and show that

$$C_B = T\left(\frac{\partial S}{\partial T}\right)_B .$$

[8 marks]

c) Give an expression for dG and explain why

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

[4 marks]

d) Show that

$$\left(\frac{\partial C_B}{\partial B}\right)_T = T\left(\frac{\partial^2 M}{\partial T^2}\right)_B .$$

[6 marks]

e) The susceptibility of the sample is defined as $\chi = M/(VB)$, where V is the volume of the sample, and experiments show that $\chi = \chi_0/T$, where χ_0 is a constant. Also, in the limit of vanishing field $B \to 0$, $C_B \to aV/T^2$ where a is a constant. Using the previous results, show that

$$C_B = \frac{a + \chi_0 B^2}{T^2} V.$$

[8 marks]

4) Two identical thermally isolated containers of volume V_0 are linked by a valve. Initially one container holds one mole of a gas at pressure P_0, while the other container is empty.

a) The valve is opened. Explain why the internal energy of the gas does not change.

[5 marks]

b) If the gas is ideal, what is the final pressure? Explain your answer.

[5 marks]

c) Suppose that instead the gas satisfies the Van der Waals equation

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

where a, b are constants. An infinitesimal change in the internal energy is

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

where C_V could be a function of T and V. Show that

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

[5 marks]

d) Using the commutativity of partial derivatives of U, and the expression for dU given in question c), show that C_V does not depend on the volume.

[5 marks]

e) The heat capacity C_V is supposed independent of T. Show that, at the end of the expansion, the change in temperature is

$$\Delta T = -\frac{a}{2C_V V_0}.$$

[5 marks]

f) Calculate ΔT, by assuming an ideal gas behaviour as an approximation, for: $a = 0.36$ J m^3 mol^{-2}, $C_V = 28.5$ J K^{-1}, $P_0 = 1$ atm and the initial temperature is $T_0 = 20^0$C.

[5 marks]