King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/2470 PRINCIPLES OF THERMAL PHYSICS

Summer 2000

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	$= 8.31\ \mathrm{JK^{-1}mol^{-1}}$
Atmospheric pressure	1 atmosphere	$= 1.01 \times 10^5\ \mathrm{Nm^{-2}}$
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) State the law of thermodynamics that provides the scientific basis for our concept of temperature.

When the bulb of a mercury-in-glass thermometer is immersed in water at its triple point, the length of the mercury column is 50.0 mm. What is the length of the mercury column (correct to the nearest mm) when the temperature on the mercury-in-glass scale is 400° C?

[7 marks]

1.2) Estimate how much work is done by 10 kg of oxygen gas, O_2, at 15° C when its volume doubles in an isobaric, reversible expansion. State any assumptions that you make. (The atomic mass number of oxygen is 16.)

[7 marks]

1.3) Prove that the heat capacity at constant pressure, C_P, is given by

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

where H is the enthalpy.

[7 marks]

1.4) A reversible Carnot engine operates between reservoirs at 500 K and 200 K. During one complete cycle, the hotter reservoir supplies 900 J of heat. How much heat is rejected to the colder reservoir and how much work is performed by the engine?

[7 marks]

1.5) Use the *central equation of thermodynamics* to derive the Maxwell relation

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

[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) In a refrigerator, heat is transferred from a point at a low temperature to the surroundings at a higher temperature. Hence, the second law of thermodynamics is violated.

[7 marks]

1.7) Calculate the change of entropy when 5 kg of water at 15° C is converted into ice at 0° C.

(Assume that the specific heat capacity of water is 4.18 $\mathrm{kJ\,kg^{-1}K^{-1}}$ and the latent heat of fusion is 333 $\mathrm{kJ\,kg^{-1}}$.)

[7 marks]

1.8) The following well-known result relates some apparently unconnected quantities:

$$C_P = C_V + T\beta^2 KV.$$

What do the symbols represent and which of them are state variables?

[7 marks]

SECTION B – Answer TWO questions

2) State the *principle of equipartition of energy.* Hence derive an expression for the molar internal energy of an ideal gas of rigid diatomic molecules.

[8 marks]

Fifty moles of an ideal gas of rigid diatomic molecules, occupying a volume of $3\,\mathrm{m}^3$ at 300 K, are compressed to $1\,\mathrm{m}^3$ at (i) constant pressure, or (ii) constant temperature.

(a) Show the two processes on a (V, T) diagram.

[4 marks]

(b) Calculate the change in internal energy in each case.

[8 marks]

(c) How much work is done in case (ii), and how much heat is exchanged with the surroundings?

[10 marks]

3) 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 the second virial coefficient is zero.

Assuming that hydrogen obeys Berthelot's equation of state,

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

calculate the Boyle temperature and explain its physical significance.

[8 marks]

At the critical point,

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0\,.$$

Prove that the critical values of P, T and v for a gas obeying Berthelot's equation are

$$P_c = \frac{1}{12b}\left(\frac{2aR}{3b}\right)^{\frac{1}{2}}, \qquad T_c = \left(\frac{8}{27}\frac{a}{bR}\right)^{\frac{1}{2}}, \qquad v_c = 3b\,.$$

[14 marks]

Given that for hydrogen, $P_c = 12.8\,\text{atm}$ and $v_c = 65.5\,\text{cm}^3\text{mol}^{-1}$, calculate numerical values for T_{B} and T_c according to Berthelot's equation of state.

[8 marks]

Hint: You may assume that for $| x | < 1$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots\,.$$

4) 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. The path AB is the isochore $V = V_1$ along which an amount of heat Q_1 is supplied to the engine. BC is an adiabatic path at the end of which the volume has increased to V_2. Along the isobaric path CA, an amount of heat Q_2 is rejected by the engine. Sketch the cycle on an indicator diagram.

[5 marks]

Along which path is the most work done?

[5 marks]

Show that the efficiency of the engine is

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

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

[15 marks]

5) Define the Gibbs function G of a thermodynamic system in equilibrium.

[3 marks]

Explain what is meant by 'G is a state function'.

[4 marks]

Derive relations which enable the volume and entropy of the system to be derived from G.

[6 marks]

The molar Gibbs function of a system is given by

$$g(P,T) = RT\ell\mathrm{n}P - \frac{5}{2}RT\ell\mathrm{n}T + \frac{5}{2}RT - c_0RT\,,$$

where c_0 is a constant. Derive expressions for the volume, entropy, enthalpy and internal energy of the system.

[12 marks]

Identify the type of system.

[5 marks]