# King's College London

UNIVERSITY OF LONDON



B.Sc. EXAMINATION

CP/2470 PRINCIPLES OF THERMAL PHYSICS

Summer 2001

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 | $R$ | $= 8.31\ \mathrm{JK^{-1}mol^{-1}}$ |
| Boltzmann constant | $k_{\mathrm{B}}$ | $= 1.38 \times 10^{-23}\ \mathrm{JK^{-1}}$ |
| Triple point of water | $T_{\mathrm{TP}}$ | $= 273.16\ \mathrm{K}$ |

**Throughout this paper, $P$ denotes pressure, $T$ thermodynamic temperature, $V$ volume and $v$ 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 temperature on the mercury-in-glass scale (correct to 2 decimal places) when the length of the mercury column is 80.0 mm?

[7 marks]

1.2) Estimate how much work is done by 1.12 kg of nitrogen gas, $N_2$, at 20 °C when its volume trebles in an isobaric, reversible expansion. State any assumptions that you make. (The atomic mass number of nitrogen is 14.)

[7 marks]

1.3) What is a free expansion? Explain whether it can be used to cool an ideal gas.

[7 marks]

1.4) A reversible Carnot refrigerator operates between reservoirs at 293 K and 273 K. Calculate the coefficient of performance of the refrigerator. During an integral number of complete cycles, the refrigerator absorbs 1911 J of heat from the cooler reservoir. How much work is done on the refrigerator and how much heat is rejected to the reservoir at 293 K?

[7 marks]

1.5) Calculate the change in entropy when 0.5 kg of water at 20 °C is heated at atmospheric pressure and converted into steam at 100 °C . The specific heat capacity $c_P$ of water at constant pressure is 4.18 $\mathrm{kJ\,kg^{-1}K^{-1}}$ and the latent heat of vaporisation of water is 2256 $\mathrm{kJ\,kg^{-1}}$.

[7 marks]

1.6) Starting from the differential form of the First Law, namely

$$\mathrm{d}U = đQ + đW\,,$$

derive the *central equation of thermodynamics*. For which processes is the latter equation valid?

[7 marks]

1.7) Say whether the following statements are **true** or **false**, giving your reasons.

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

(b) Cooling a specimen reduces its entropy and hence the Principle of Increasing Entropy is violated.

[7 marks]

1.8) The Gibbs function $G$ is defined by $G = H - TS$, where $S$ is the entropy and $H$ is the enthalpy. Derive an expression for $\mathrm{d}G$ in terms of the differentials of the natural variables $P$ and $T$. Hence, prove the Maxwell relation

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

[7 marks]

## SECTION B – Answer TWO questions

2) Explain the significance of the constants $a$ and $b$ in Van der Waals' equation of state for one mole of gas

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

[4 marks]

Show that the critical volume of a fluid obeying this equation of state is $3b$.

[13 marks]

The thermal pressure coefficient $(\partial P/\partial T)_V$ of 1 mole of a certain gas at its critical volume is $1.38 \times 10^5$ N m$^{-2}$ K$^{-1}$. Calculate the diameter of the molecules of this gas, assuming it obeys Van der Waals' equation of state. You may assume that

$$b = 4 \times \text{total volume of molecules in 1 mole}\,.$$

[13 marks]

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

[7 marks]

A piece of copper of mass 25 g at 100 °C is placed in a copper calorimeter of mass 200 g and containing 75 g of water at 20 °C. The average specific heat capacity of copper is $c_P = 385\,\mathrm{J\,K^{-1}\,kg^{-1}}$ and of water $c_P = 4200\,\mathrm{J\,K^{-1}\,kg^{-1}}$. Assuming that the heat lost by the piece of copper is equal to the heat gained by the water and the calorimeter, show that the final temperature of the combined system is $T = 21.92\,^\circ$C.

[7 marks]

Calculate the change in the entropy of (i) the piece of copper and (ii) the water plus calorimeter. Comment on the fact that these entropy changes are *not* equal in magnitude and opposite in sign.

[16 marks]

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 $Q_1 > 0$ is supplied to the engine. BC is an isothermal path, temperature $T_0$, at the end of which the volume has increased to $V_2$. Along the isobaric path CA, an amount of heat $Q_2 > 0$ is rejected by the engine. Sketch the cycle on an indicator diagram.

[5 marks]

How much heat $Q_3(> 0)$ is exchanged along the path BC? Is the heat supplied to, or rejected by, the engine?

[5 marks]

Show that the efficiency of the engine can be written in terms of the $\{Q_i;\ i = 1, 2, 3\}$ as

$$\eta = 1 - \frac{Q_2}{Q_1 + Q_3}\,.$$

[5 marks]

Hence show that

$$\eta = 1 - \gamma\frac{\lambda - 1}{(\lambda - 1) + \frac{2}{3}\lambda\,\ell\mathrm{n}\lambda}\,,$$

where $\lambda = V_2/V_1$ and $\gamma$ is the ratio of the principal heat capacities. You may assume that the molar heat capacity at constant volume is $\frac{3}{2}R$.

[10 marks]

5) Define the enthalpy $H$ of a thermodynamic system in equilibrium.

[3 marks]

Explain what is meant by '$H$ is a state function'.

[4 marks]

Derive relations which enable the temperature and volume of the system to be derived, if $H$ is given in terms of its natural variables, entropy $S$ and pressure $P$.

[6 marks]

The molar enthalpy $h(s, P)$ of a system is given by

$$\ell\mathrm{n}\, h(s, P) = \frac{2}{7}(s/R) + \frac{2}{7}\ell\mathrm{n}\, P + \ell\mathrm{n}\, h_0 \,,$$

where $s$ is the molar entropy and $h_0$ is a constant. Derive expressions for the temperature, volume and internal energy of the system.

[12 marks]

Identify the type of system. What can be deduced about the molecules that constitute the system?

[5 marks]