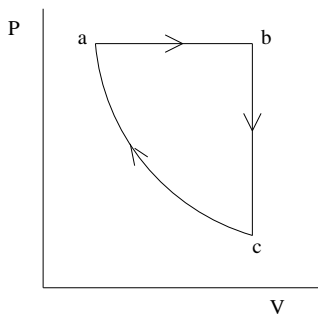


## SECTION A:

Answer ALL questions in Section A.

- A1 State the Zeroth Law of Thermodynamics. [2]
- A2 Explain briefly how an *empirical temperature scale* is conventionally defined using an electrical resistance as the thermometric property. [2]
- A3 Explain briefly how the *ideal gas temperature scale* is defined. [2]
- A4 Molecules of  $CO_2$  (molecular weight 44 amu) in the Martian atmosphere have a mean kinetic energy of 0.0285 eV. Assuming the atmosphere to be in thermal equilibrium, estimate its ideal gas temperature. Calculate the root mean squared speed of the  $CO_2$  molecules. What is the root mean squared speed of the nitrogen molecules in this atmosphere ( $N_2$ , molecular weight 28 amu)? [5]
- A5 State the First Law of Thermodynamics for a system undergoing an infinitesimal change. Explain clearly any notations or conventions used. [5]
- A6 How is work done on a gas during a reversible process related to an area in a  $P - V$  diagram? [2]
- A7 State the equation of state for an ideal gas. What is the change in internal energy of an ideal gas during an *isothermal* process? [2]
- A8 Define what is meant respectively by an *isobaric* process, an *isochoric* process and an *adiabatic* process. [3]
- A9 A system consists of gas contained in a cylinder fitted with a frictionless piston. The gas is taken between states  $a$ ,  $b$ ,  $c$  as shown on the  $P - V$  diagram below where the process  $c \rightarrow a$  is an adiabatic process.



During the process  $a \rightarrow b$ , 150 J of heat flow into the gas which does 60 J of work on its surroundings. What is the internal energy change of the gas during  $a \rightarrow b$ ? [3]

- A10 During the process  $b \rightarrow c$ , the gas loses 108 J of heat to its surroundings. What is the internal energy change of the gas during  $b \rightarrow c$ ? [3]
- A11 What is the work done on the gas during the adiabatic process  $c \rightarrow a$ ? [4]
- A12 For a particular ideal diatomic gas the internal energy is given by  $U = \frac{7}{2}PV$ . Using the infinitesimal form of the First Law, or otherwise, show that during an adiabatic change the gas will obey a relation of the form

$$PV^\gamma = \text{constant} \quad ,$$

and derive the value of the constant  $\gamma$ . [5]

- A13 How is the adiabatic constant  $\gamma$  related to the heat capacities of the gas? [2]

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## SECTION B:

Answer **TWO** questions only from this Section.

B1 (a)

i) State the Second Law of Thermodynamics in the form due to Clausius. [3]

ii) A heat pump takes in work  $W$ , removes heat  $Q_2$  from a cold source and delivers heat  $Q_1$  to a higher temperature reservoir. Give the definition of the figure of merit for the heat pump and express it entirely in terms of the heat flows  $Q_1$  and  $Q_2$ . [3]

iii) An ideal heat pump has a figure of merit  $\eta_{HP} = 10$ . It removes heat from a low temperature source at the rate of 9 kW. What is the rate of work required to drive the heat pump and what is the rate at which heat is delivered to the high temperature output reservoir? [4]

(b) An engine is constructed with one mole of an ideal diatomic gas as the working substance for which the internal energy is  $U = \frac{5}{2}PV$  and the adiabatic constant  $\gamma$  has the value  $\gamma = \frac{7}{5}$ . It operates reversibly in a cycle  $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ . The process  $1 \rightarrow 2$  is an *isochoric* process at volume  $V_1$  during which the pressure increases from  $P_1$  to  $P_2$  and heat  $Q_1$  is absorbed. The process  $2 \rightarrow 3$  is an *adiabatic* expansion back to the initial pressure  $P_1$  and volume  $V_3$ . The process  $3 \rightarrow 1$  is an *isobaric* compression during which heat  $Q_2$  is ejected and the working substance returns to its initial state.

i) Sketch the engine cycle in a  $P - V$  diagram. [3]

ii) By applying the First Law to the processes  $1 \rightarrow 2$  and  $3 \rightarrow 1$ , obtain expressions for the heat flows  $Q_1$  and  $Q_2$  in terms of the pressures  $P_1$  and  $P_2$  and the volumes  $V_1, V_3$  corresponding respectively to the states 1, 2, 3. [4]

iii) Show that the efficiency of this engine can be expressed solely in terms of the pressure ratio  $p = P_2/P_1$  as

$$\eta_E = 1 - \frac{7}{5} \frac{p^{5/7} - 1}{p - 1} .$$

[5]

(c) The engine in (b) is designed so that  $V_1 = 0.0001 \text{ m}^3$ ,  $V_3 = 0.001 \text{ m}^3$ , and  $P_1 = 1 \text{ atm}$ .

i) Calculate the pressure ratio  $p$ . [2]

ii) Calculate the engine efficiency  $\eta_E$ . [2]

iii) Calculate the work produced by this engine in one cycle. [4]

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- B2 (a)**
- i) State the entropy form of the Second law of Thermodynamics for thermally isolated systems. [3]
  - ii) Describe briefly Boltzmann's microscopic interpretation of the entropy. [3]
- (b) A bucket containing 3 kg of water at a temperature of 15 °C is placed outside in winter on a cold day when the ambient temperature is −5 °C.
- i) Ignoring evaporation, describe the final equilibrium state. [1]
  - ii) Using information from the data sheet and neglecting evaporation, calculate the entropy change of the water between its initial state and its final equilibrium state. [6]
  - iii) Calculate the entropy change of the surrounding environment. [3]
  - iv) Stating appropriate criteria, show whether or not the Second Law of Thermodynamics is obeyed in the processes above. [2]
- (c) The thermodynamic identity for a fluid system has the form  $dU = TdS - PdV$ .
- i) A diatomic ideal gas has internal energy  $U = \frac{5}{2}PV$  and obeys the equation of state  $PV = Nk_B T$ . It undergoes a process taking it from initial equilibrium state  $T_1, V_1$  to a final equilibrium state  $T_2, V_2$ . Use the thermodynamic identity to show that the entropy change of the gas may be expressed as [5]

$$\Delta S = S_2 - S_1 = \frac{5}{2}Nk_B \ln\left(\frac{T_2}{T_1}\right) + Nk_B \ln\left(\frac{V_2}{V_1}\right) \quad .$$

- ii) Describe briefly the Joule free expansion experiment. What function of state is constant during such a process? [3]
- iii) The ideal gas in i) undergoes a Joule free expansion with final volume  $V_2 = 3V_1$ . What is the entropy change of the gas? Explain how this entropy change is consistent with Boltzmann's interpretation in (a)(ii) above. [4]

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**B3 (a)** For a simple fluid, the thermodynamic identity has the form  $dU = TdS - PdV$ .

- i) The Helmholtz free energy  $F$  and the Gibbs function  $G$  for this system are defined by  $F = U - TS$  and  $G = U - TS + PV$ . Using the thermodynamic identity to evaluate the infinitesimal changes  $dF$  and  $dG$ , derive the following Maxwell relations [6]

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

- ii) Use the thermodynamic identity to show that the heat capacity at constant volume of the system,  $C_V$ , can be expressed as [2]

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad .$$

- iii) Use the thermodynamic identity and an appropriate Maxwell relation to show that [3]

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

- iv) For  $n$  moles of a monatomic van der Waals gas the heat capacity  $C_V$  is the same as for an ideal gas

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR \quad ,$$

while the equation of state is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad ,$$

where  $a$  and  $b$  are constants. Derive an expression for the internal energy  $U(T, V)$  of the van der Waals gas. [7]

- (b) Simple substances can exist in three phases. Sketch the phase diagram of such a material in a  $P - T$  plot, labelling the vapour, liquid and solid phase regions. Explain briefly what are the critical point and the triple point and label them on your diagram. [6]

- (c) The Clausius-Clapeyron equation for the slope of the liquid-vapour co-existence curve may be written as

$$\frac{dP}{dT} = \frac{\ell^{LV}}{T(v^V - v^L)} \quad ,$$

where the superscripts  $L$  and  $V$  refer to liquid and vapour phases respectively,  $v$  denotes the volume per mole of material and  $\ell^{LV}$  is the latent heat of vaporisation per mole.

- i) Treating the vapour as an ideal gas, assuming that  $\ell^{LV}$  is constant and that  $v^V \gg v^L$ , show that for two points  $P_0, T_0$  and  $P_1, T_1$  on the co-existence curve [6]

$$\ln\left(\frac{P_1}{P_0}\right) = -\frac{\ell^{LV}}{R} \left(\frac{1}{T_1} - \frac{1}{T_0}\right) \quad .$$

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B4 (a)

Explain briefly what is meant by *cavity radiation*. What determines its temperature? [2]

Cavity radiation can be regarded as a photon gas, a  $P - V - T$  system whose internal energy is related to its pressure and volume by  $U = 3PV$ . Moreover, the energy density,  $u = U/V$ , depends only on the temperature of the gas as

$$u(T) = \frac{4\sigma}{c}T^4 \quad ,$$

where  $\sigma$  and  $c$  are universal constants, given on the data sheet.

- i) Calculate the pressure of the cosmic background radiation whose temperature is about 2.7 K. [3]
  - ii) Calculate the temperature of a photon gas whose pressure is 1 atm. [3]
- (b) Using the thermodynamic identity,  $dU = TdS - PdV$ , and the information in (a), prove that the entropy of cavity radiation has the form [8]

$$S = \frac{16\sigma}{3c}T^3V + \text{constant} \quad .$$

A photon gas at temperature  $T_1$  and volume  $V_1$  is expanded reversibly and adiabatically to volume  $V_2 = 64 V_1$  and final temperature  $T_2$ . What is the final temperature  $T_2$ ? [2]

- (c) Define the mean free path  $\lambda$  of a molecule in a gas. [1]
- i) The mean free path may be estimated approximately by the expression

$$\lambda \approx \frac{1}{n\sigma} \quad .$$

Explain what  $n$  and  $\sigma$  are. [2]

- ii) Explain what is meant by *effusion* of a gas through a small aperture. [2]
- iii) A gas in equilibrium at temperature  $T$  consists of 10% helium atoms (atomic weight 4 amu) and 90% argon atoms (atomic weight 40 amu). The mixture is held in a container with a porous wall surrounded by an evacuated chamber. Assuming that effusion occurs through the porous wall, estimate the percentage of helium atoms in the escaped gas mixture in the outside chamber. [7]

[ You may use the following without proof.

In a gas in equilibrium the number of molecules per second striking unit area of a bounding wall is given by  $\frac{1}{4}n\bar{v}$ . The mean speed  $\bar{v}$  is given as  $\bar{v} = \sqrt{8k_B T/\pi m}$ . ]

**END OF EXAM - R. B. JONES**

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## DATA SHEET

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$N_A = \textit{Avogadro number} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$c = \textit{Speed of light in vacuum} = 3.00 \times 10^8 \text{ m s}^{-1}$$

$$k_B = \textit{Boltzmann constant} = 1.38 \times 10^{-23} \text{ J K}^{-1} = 8.63 \times 10^{-5} \text{ eV K}^{-1}$$

$$R = \textit{Gas constant} = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T_s = \textit{Ice point of water} = 273.15 \text{ K}$$

$$P_s = \textit{Atmospheric pressure} = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$$

$$\sigma = \textit{Stefan - Boltzmann constant} = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$$

$$c_P = \textit{Specific heat of water at constant pressure}$$

$$= 4.2 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$c_P^{ice} = \textit{Specific heat of ice at constant pressure} = 2.1 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\ell^{SL} = \textit{Latent heat of melting ice} = 3.33 \times 10^5 \text{ J kg}^{-1}$$

$$\ell^{LV} = \textit{Latent heat of evaporating water} = 2.26 \times 10^6 \text{ J kg}^{-1}$$