

EGT3
ENGINEERING TRIPOS PART IIB

Monday 29 April 2019 9.30 to 11.10

Module 4A9

MOLECULAR THERMODYNAMICS

*Answer not more than **three** questions.*

All questions carry the same number of marks.

*The **approximate** percentage of marks allocated to each part of a question is indicated in the right margin.*

*Write your candidate number **not** your name on the cover sheet.*

STATIONERY REQUIREMENTS

Single-sided script paper

SPECIAL REQUIREMENTS TO BE SUPPLIED FOR THIS EXAM

CUED approved calculator allowed

Engineering Data Book

10 minutes reading time is allowed for this paper at the start of the exam.

You may not start to read the questions printed on the subsequent pages of this question paper until instructed to do so.

1 Information relevant to this question can be found on the next page. Throughout this question argon may be treated as a perfect gas.

(a) Argon gas at 1 bar and 400 K is in a stationary, equilibrium state such that its molecular velocity distribution f is Maxwellian. The Cartesian components of molecular peculiar velocity are C_1 , C_2 and C_3 , and the corresponding molecular speed is C . Consider the integral

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Qf \, dC_1 \, dC_2 \, dC_3$$

for the cases where

- (i) $Q = m$, the molecular mass
- (ii) $Q = mC_2^2$
- (iii) $Q = \frac{1}{2}mC^2C_3$
- (iv) $Q = mC_1C_2$

For each case, give a physical interpretation of the quantity I , and calculate its value for argon gas at the above conditions. [30%]

(b) Write down an expression for the molecular speed distribution $g(C)$ for a stationary gas at equilibrium. Hence determine the mean molecular speed \bar{C} for argon at 1 bar and 400 K. [25%]

(c) Argon gas at 1 bar and 400 K flows with a bulk velocity of

$$(u_1, u_2, u_3) = (100, 50, -100) \text{ m s}^{-1}$$

The molecular velocity distribution is to be modelled approximately by dividing the molecules into six groups. Each group contains the same number of molecules and each molecule within a group moves with the same velocity. All molecules have the same random thermal speed C , with one sixth moving in the positive x_1 direction, one sixth in the negative x_1 direction, one sixth in the positive x_2 direction and so on.

- (i) Determine the absolute velocity components for the six groups. [15%]
- (ii) Show that the net flux of energy crossing a plane of area A normal to the x_1 direction may be written as

$$F_E = \rho A u_1 \left\{ b \frac{RT}{2} + \frac{1}{2}(u_1^2 + u_2^2 + u_3^2) \right\}$$

and give the value of the integer b . Explain from a macroscopic thermodynamic perspective why b takes this value. [30%]

Information for Question 1

The Maxwellian velocity distribution for a stationary gas at temperature T and with specific gas constant R is given by

$$f(C_1, C_2, C_3) = \frac{n}{(2\pi RT)^{3/2}} \exp \left\{ -\frac{(C_1^2 + C_2^2 + C_3^2)}{2RT} \right\}$$

where n is the number density of molecules.

Some definite integrals:

$$I(n) = \int_0^{\infty} x^n \exp(-x^2) dx$$

n	$I(n)$
0	$\frac{\sqrt{\pi}}{2}$
1	$\frac{1}{2}$
2	$\frac{\sqrt{\pi}}{4}$
3	$\frac{1}{2}$

2 (a) Consider a gas composed of molecules with number density n per unit volume, each of diameter d . By considering a ‘test molecule’ moving at the mean molecular speed \bar{C} (and assuming all other molecules are at rest), derive approximate expressions for the molecular mean free path λ and for the total rate of intermolecular collisions Z per unit volume. [25%]

(b) A cubic vessel of side $a = 10$ cm contains a mixture of nitrogen and carbon monoxide at uniform pressure and temperature of 1 bar and 400 K. The molecular number densities of carbon monoxide n_{CO} and nitrogen n_{N_2} vary only in the x_2 direction, which is normal to one face of the vessel.

(i) Using a ‘mean free path’ analysis and stating your assumptions, show that the net diffusive flux of carbon monoxide molecules (per unit area and per unit time) in the positive x_2 direction is given by

$$J_{\text{CO}} = -D \frac{dn_{\text{CO}}}{dx_2}$$

where D is the diffusion coefficient. Determine an expression for D in terms of appropriate quantities. You may assume that for a gas with molecular density n and mean molecular speed \bar{C} , the molecular flux (per unit area and per unit time) on one side of a surface is given by $n\bar{C}/4$. [30%]

(ii) Given that the dynamic viscosity of nitrogen at 2 bar and 300 K is approximately $16.5 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$, estimate a time scale for initial non-uniformities within the vessel to disperse. You may use without proof the following approximate expression for viscosity

$$\mu = \frac{\rho \bar{C} \lambda}{2}$$

where ρ is the density. [35%]

(iii) Describe briefly how the analysis would differ for the diffusion of helium in nitrogen (detailed analysis is not required). [10%]

3 (a) For a particle of mass m , the time-independent form of the Schrödinger wave equation may be written as

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (\epsilon - \epsilon_p) \psi = 0$$

where h is Planck's constant. Explain what each of ψ , ϵ and ϵ_p represent, giving a quantitative definition for ψ . [10%]

(b) By writing $\psi = \psi_1(x_1)\psi_2(x_2)\psi_3(x_3)$ find the general solution to the above equation for a particle that possesses only translational kinetic energy and that is confined to a field-free cubic box of side a . Hence show that ϵ is quantised such that

$$\epsilon = B \left(n_1^2 + n_2^2 + n_3^2 \right)$$

and find an expression for the constant B in terms of quantities defined above. What is the physical significance of the quantum numbers n_1 , n_2 and n_3 ? [55%]

(c) 1 litre of argon gas is contained within a cubic container at 1 bar and 400 K. Calculate the number of energy states available to molecules that have speeds in the range zero to twice the RMS molecular speed. Calculate also the total number of molecules in the container and comment on the comparison between the two results. [35%]

4 (a) State whether each of the following statements is true or false, giving a brief but full explanation for each of your answers.

(i) The microstates of a closed system at equilibrium are equally probable.

(ii) A system undergoes an irreversible, isothermal process. At the end of the process, the number of microstates of the system must have increased.

(iii) The molecules of a certain monatomic, ideal gas have a single electronic excitation state, which has energy ε . At temperatures much greater than ε/k (where k is Boltzmann's constant), a reasonable estimate for the isobaric specific heat capacity of the gas is $c_p = 5R/2$, where R is the specific gas constant. [30%]

(b) A simple model for the volume dependence of the entropy of an ideal gas at constant temperature involves dividing the volume occupied by the gas into a number of identical boxes. The number of boxes B may be chosen such that $B \gg N$, where N is the number of molecules.

(i) Stating your assumptions and explaining your reasoning, show that the number of distinct arrangements of the N molecules amongst the B boxes may be estimated as

$$\Omega \approx \frac{B!}{N!(B-N)!} \quad [20\%]$$

(ii) Stirling's approximation states that $\ln(n!) \approx n \ln(n) - n$ for large n . Use this to show that the dependence of entropy on B and N is given by

$$S \approx Nk \ln \left(\frac{B}{N} - 1 \right) - Bk \ln \left(1 - \frac{N}{B} \right) \quad [20\%]$$

(iii) 1 gram of helium gas at 300 K is confined to one half of a rigid, insulated vessel by means of a diaphragm, as shown in Fig. 1. The diaphragm is burst such that the gas undergoes an unrestrained expansion, doubling its volume. Using the above model, determine the change in entropy of the helium as a result of this process. [30%]

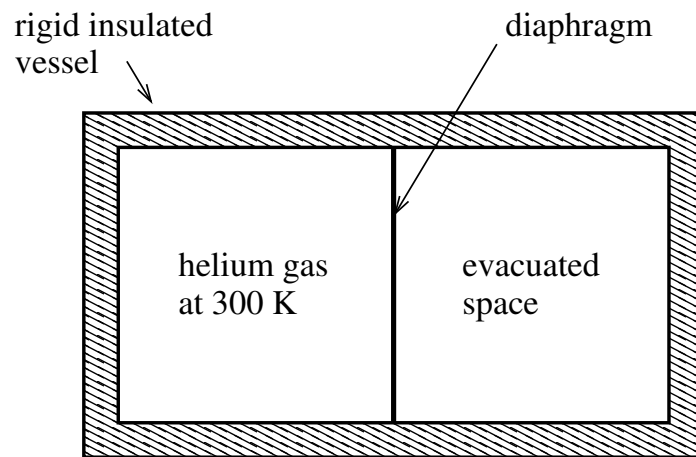


Fig. 1

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Answers

1. (a) (i) 1.20 kg m^{-3} (ii) 1 bar (iii) 0 (iv) 0
(b) 440 m s^{-1}
(c) (i) $(100 \pm 500, 50, -100)$; $(100, 50 \pm 500, -100)$; $(100, 50, -100 \pm 500)$
(ii) $b = 5$
2. (b) (ii) $\sim 440 \text{ s}$
3. (c) 4.2×10^{30} states 1.81×10^{22} molecules
4. (b) (iii) 1.44 J K^{-1}