ENGINEERING TRIPOS   PART IIB

Wednesday 24 April 2013   9.30 to 11

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.*

There are no attachments.

STATIONERY REQUIREMENTS
Single-sided script paper

SPECIAL REQUIREMENTS
Engineering Data Book
CUED approved calculator allowed

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

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1 *Information relevant to this question can be found on the next page.*

A monatomic perfect gas flows with free-stream speed V over a flat plate aligned with the flow direction. The viscous boundary layer on the plate is laminar.

(a) Discuss briefly whether the molecular velocity distribution function is Maxwellian and whether the Navier-Stokes equations are valid at :

(i) A point in the free-stream far from the plate ;

(ii) A point in the boundary layer where the flow speed is $0.1V$;

(iii) A point on the surface of the plate, assuming that molecules incident on the plate surface are reflected diffusely. [25%]

(b) In the free-stream the molecular velocity distribution function is given by

$$f(c_1, c_2, c_3) = \frac{n}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(c_1 - V)^2 + c_2^2 + c_3^2}{2RT}\right)\right].$$

where c_1, c_2 and c_3 are the components of the absolute velocity of a molecule, n is the number density of molecules, R is the specific gas constant and T is the temperature.

(i) Write down an integral expression for the flowrate of molecular energy in the x_1 direction per unit cross-sectional area and transform the expression to new variables w_1, w_2 and w_3 defined by

$$w_1 = \frac{(c_1 - V)}{\sqrt{2RT}}, \quad w_2 = \frac{c_2}{\sqrt{2RT}}, \quad w_3 = \frac{c_3}{\sqrt{2RT}}.$$

[15%]

(ii) Show that, if ρ is the gas density, the flowrate of molecular energy in the x_1 direction per unit cross-sectional area is given by

$$\rho V \left(\frac{5RT}{2} + \frac{V^2}{2}\right)$$

[40%]

(iii) Kinetic theory can be used to show that the energy of the gas per unit mass is $(3RT/2 + V^2/2)$. Do not prove this result but explain from a macroscopic viewpoint why the energy flowrate calculated in (ii) is not $\rho V(3RT/2 + V^2/2)$. [20%]

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} x e^{-x^2} dx = 0$$

$$\int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^{\infty} x^3 e^{-x^2} dx = 0$$

The flowrate of a molecular property $Q(c_1, c_2, c_3)$ in the x_i direction per unit cross-sectional area is given by

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} (c_i Q f)\, dc_1 dc_2 dc_3$$

Information for Question 1

2 *Information relevant to this question can be found on the next page.*

Nitrogen of mass density ρ flows steadily with mean velocity V through a tube of diameter D. The nitrogen contains trace amounts of two different gas impurities having molar masses M_i $(i = 1$ or $2)$. The tube wall has a large number of very small circular holes of diameter a, there being N holes per unit length of tube. The gas impurities leak out through the holes so that their mass fractions Y_i decrease with distance x along the length of the tube. It may be assumed that the leakage through a hole occurs under free-molecule conditions. The gas outside the tube is effectively nitrogen with no impurities and is at the same pressure p as inside the tube. The temperature T is uniform everywhere and it may be assumed that at any distance x the Y_i are uniform over the cross-section of the tube. Diffusion of the impurities along the tube in the x-direction may be neglected.

(a) By considering a control volume of length dx, show that

$$\frac{dY_i}{dx} = -A\frac{Y_i}{\sqrt{M_i}}$$

and find an expression for the coefficient A in terms of the quantities defined above. [35%]

(b) Given that $Y_i = Y_{i,0}$ at $x = 0$, find the relationship between Y_1 and Y_2 at any value of x. [25%]

(c) The mean free path λ_i of gas impurity i is defined as the average distance between collisions of an i-molecule of diameter d_i with a nitrogen molecule of diameter d. Stating your assumptions clearly, use a simple hard-sphere kinetic model to derive an expression for λ_i in terms of d, d_i and λ (the molecular mean free path of pure nitrogen). If M is the molar mass and μ is the dynamic viscosity of pure nitrogen, show that the leakage of gas impurity i through a hole will occur under free-molecule conditions if

$$a << B_i\frac{\mu}{p}\left(\frac{8\pi\bar{R}T}{M}\right)^{1/2}$$

and find an expression for the coefficient B_i . [40%]

The mean molecular speed $\overline{C}$ of a perfect gas is given by

$$\overline{C} = \left(\frac{8\overline{R}T}{\pi M}\right)^{1/2}$$

where $\overline{R}$ is the molar gas constant, T is the gas temperature and M is the molar mass.

The dynamic viscosity μ of a perfect gas is given by

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

where ρ is the gas mass density and λ is the molecular mean free path.

The 'one-sided' number flux of molecules incident on unit area per unit time is given by

$$\frac{n\overline{C}}{4}$$

where n is the number density of molecules.

Information for Question 2

3 (a) The vibrational energy levels of a diatomic molecule are non-degenerate and, relative to the ground state, take the values

$$\varepsilon_n = nh\nu \qquad \text{for} \quad n = 0, 1, 2, 3, \ldots$$

where h is Planck's constant and ν is the harmonic oscillator frequency. Show that the vibrational component of the single-molecule partition function at temperature T, may be written

$$Z_{vib} = \frac{1}{1 - e^{-\theta_v/T}}$$

and find an expression for the characteristic temperature of vibration, θ_v. Assume that the molecules do not dissociate. [25%]

(b) The effects of dissociation may be approximated by truncating the energy states at the dissociation energy, ε_d, such that states for which $\varepsilon_n \geq \varepsilon_d$ are inaccessible. Show that with this model

$$Z_{vib} = \frac{1 - e^{-\theta_d/T}}{1 - e^{-\theta_v/T}}$$

and find an expression for the characteristic temperature of dissociation, θ_d. [35%]

(c) For a particular diatomic gas, $\varepsilon_d/(h\nu) = 8$. In the absence of dissociation the vibrational component of the specific heat capacity is

$$c_{v,vib} = R \left(\frac{\theta_v}{T} \right)^2 \frac{e^{\theta_v/T}}{(e^{\theta_v/T} - 1)^2}$$

where R is the specific gas constant. Calculate $c_{v,vib}/R$ at $T = \theta_v$ when dissociation is neglected and find the percentage reduction in $c_{v,vib}$ due to dissociation at this temperature. [40%]

You may use without proof the following expression for the specific internal energy

$$u = RT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \qquad \text{where} \qquad Z = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT}$$

and k is the Boltzmann constant.

4 (a) For a system that has Ω accessible microstates and for which the probability of the i-th microstate is P_i, the statistical analogue of its entropy is given by

$$S = -k \sum_{i=1}^{\Omega} P_i \ln P_i$$

where k is the Boltzmann constant. Derive an expression for S in terms of k and Ω only for an isolated system at equilibrium. Demonstrate that your expression is consistent with the extensive nature of entropy. [20%]

(b) A system comprising 1 gram of neon (molar mass 20 kg kmol^{-1}) occupies a volume $V_0 = 1.25$ litres and is at temperature $T_0 = 300$ K. At this condition, the number of microstates accessible by the system is denoted Ω_0. The system undergoes the following processes:

(i) reversible, adiabatic compression to a volume of 1 litre;

(ii) cooling back to 300 K at constant volume.

Calculate the number of microstates at the end of each process as a multiple of Ω_0. Take $k = 1.38 \times 10^{-23}$ J K^{-1} and the molar gas constant $\overline{R} = 8314$ J kmol^{-1} K^{-1}. [30%]

(c) The system of part (b) is maintained at volume V_0 in a rigid, thermally conducting vessel immersed in a large water bath at temperature T_0. Find an expression for the number of microstates of the neon system when it has uniform temperature T. Hence show that the probability that the system has temperature T may be written in the form

$$P(T) = P(T_0) \left(\frac{T}{T_0} \right)^{\alpha} e^{\alpha(1-T/T_0)}$$

and find the value of the constant α. Sketch a graph of this relationship and discuss briefly the implications for the magnitude of energy fluctuations. [50%]

Note that for a system of fixed volume in thermal equilibrium with an infinite reservoir at temperature T_0, the probability that the system is in its i-th microstate is given by

$$P_i = \frac{e^{-E_i/kT_0}}{Q}$$

where E_i is the energy of the i-th microstate and Q is the system partition function.

END OF PAPER

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