UNIVERSITY OF CAMBRIDGE

ENGINEERING TRIPOS PART IIB

Friday 30 April 2004 9 to 10.30

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

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 A perfect gas with specific gas constant R is contained in a vessel of volume V. The gas is at equilibrium at pressure p and temperature T and the molecular velocity distribution f is Maxwellian:

$$f(C_x, C_y, C_z) = (2\pi RT)^{-3/2} \exp\left(-\frac{C_x^2 + C_y^2 + C_z^2}{2RT}\right) .$$

There is a small hole of cross-sectional area A in the wall of the vessel through which the gas effuses into an evacuated space. The diameter of the hole is much smaller than the mean free path of the gas molecules in the vessel and the vessel wall may be assumed to be infinitesimally thin. The x-direction is normal to the cross-sectional plane of the hole and $\psi(u_x)\, du_x$ is defined as the fraction of molecules leaving the vessel having an x-component of velocity u_x in the range $u_x \to u_x + du_x$.

(a) Sketch $\psi(u_x)$ as a function of u_x in the range $-\infty < u_x < \infty$. [10%]

(b) Stating your reasoning, derive an expression for $\psi(u_x)$ as a function of u_x. Depending on your approach, you may require the integral

$$\int_0^\infty \exp(-ax^2)\, dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2} .$$ [15%]

(c) Show that $\bar{u}_x$ (the mean value of u_x for the effusing molecules) is given by

$$\bar{u}_x = \left(\frac{2RT}{\pi}\right)^{1/2} .$$ [20%]

(d) State the definition of 'kinetic temperature'. Find an expression for the mean value of u_x^2 and deduce that the temperature of the effusing molecules is the same as the temperature of the gas in the vessel. [20%]

(e) Using the results derived above (and not otherwise) derive an expression for the mass rate of effusion in terms of R, T, p and A. [15%]

(f) Assuming the temperature in the vessel to remain constant, derive an expression for the variation of gas pressure p with time t in terms of R, T, A, V and p_0, where p_0 is the pressure at $t = 0$. [20%]

2 (a) Using a 'mean free path' kinetic theory model, show that the thermal conductivity k of a monatomic perfect gas can be approximated by

$$k = A \rho \overline{C} \lambda c_v ,$$

where A is a constant, ρ is the gas density, $\overline{C}$ is the mean molecular speed, λ is the mean free path, and c_v is the constant volume specific heat capacity. Obtain a value for the constant A and comment on its likely accuracy. State, giving reasons, how you would expect k to vary with temperature and pressure.

It may be assumed without proof that the one-sided molecular mass flux to a surface is given by $\rho \overline{C}/4$. [40%]

(b) Two parallel plates, 1 and 2, of infinite extent are placed a distance L apart and are maintained at different temperatures T_1 and T_2 respectively ($T_1 > T_2$). The space between the plates contains a monatomic perfect gas in which there are no convection currents. If the gas pressure is such that $L >> \lambda$ derive an expression for q_0 the conduction heat transfer rate per unit area between the plates. [10%]

(c) The gas pressure is now lowered to such an extent that $L << \lambda$, the heat transfer rate per unit area for the same plate temperature difference being denoted q_∞. Collisions between molecules can now be neglected and it may be assumed that all molecules incident on a plate are reflected diffusely. Using kinetic theory, show that the ratio q_0 / q_∞ is given by

$$\frac{q_0}{q_\infty} = \left(\frac{1}{\alpha_1} + \frac{1}{\alpha_2} - 1 \right) B\,Kn \quad ,$$

where B is a constant, $Kn = \lambda/L$ is the Knudsen number, and α_1 and α_2 are the temperature accommodation coefficients on plates 1 and 2 respectively. Obtain a value for the constant B.

Note that the temperature accommodation coefficient is defined in terms of the temperatures of the incident and reflected molecular streams by the expression

$$\alpha = \frac{T_{reflected} - T_{incident}}{T_{plate} - T_{incident}} \quad .$$ [50%]

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3 (a) The Boltzmann distribution is given by

$$\frac{N_j^*}{N} = \frac{1}{Z} C_j e^{-\varepsilon_j / kT} ,$$

where Z is the partition function

$$Z = \sum_j C_j e^{-\varepsilon_j / kT} .$$

Explain the meaning of each of the quantities in the expression for the Boltzmann distribution. Explain also under what conditions the Boltzmann distribution is valid and why it applies to both bosons and fermions. [20%]

(b) The molecules of a particular diatomic ideal gas may possess translational, rotational and vibrational energy. Show that the partition function for such a gas may be written in the form

$$Z = Z_{tr} Z_{int} \approx Z_{tr} Z_{rot} Z_{vib} ,$$

where the subscripts *tr*, *int*, *rot* and *vib* refer to translational, internal-structure, rotational and vibrational energy modes respectively. Explain clearly why the approximately equals sign is appropriate for the right-hand side of this expression. [30%]

(c) Show that, for a system obeying the Boltzmann distribution, the thermodynamic internal energy U is given by

$$U = NkT^2 \left[\frac{\partial}{\partial T} \ln(Z) \right]_V .$$

Hence show that the constant volume specific heat capacity for the gas of part (b) may be expressed as

$$c_v = c_{v,tr} + c_{v,int} \approx c_{v,tr} + c_{v,rot} + c_{v,vib} .$$ [50%]

4 (a) 0.1 kg of helium gas is maintained at 1 bar in a cubic container of volume $V = 0.75\ \mathrm{m}^3$. The quantum energy states for translational kinetic energy of the molecules are given by

$$\varepsilon = \frac{h^2}{8mV^{2/3}}(n_1^2 + n_2^2 + n_3^2) \quad ,$$

where m is the molecular mass, h is Planck's constant (6.626×10^{-34} Js) and n_1, n_2 and n_3 are the quantum numbers.

Calculate the number of energy states available to molecules which have speeds in the ranges:

(i) between zero and the RMS molecular speed,

(ii) between one and two times the RMS molecular speed.

Calculate the total number of molecules in the container and comment on this number in comparison with your answers to (i) and (ii). [40%]

(b) The quantum energy states of a simple harmonic oscillator are given by

$$\varepsilon = (n + \tfrac{1}{2})\, h\nu \quad ,$$

where ν is the frequency of oscillation and n is a non-negative integer. A system is composed of three such oscillators, all with frequency ν. The total energy of the system is $E = (M + \tfrac{1}{2})\, h\nu$, where M is a positive integer.

(i) Draw up a table of the possible microstates when $M = 4$.

(ii) Find an expression for the total number of microstates of the system for the general case when M can take any value.

(iii) Hence, find an expression for the system entropy (in the general case) in terms of h, E, ν and k, where k is Boltzmann's constant. [60%]

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