1 (a)   All effusing molecules have $u_x > 0$ and have come from the vessel where the velocity distribution is Maxwellian. Hence the distribution $\psi(u_x)$ must have the form:
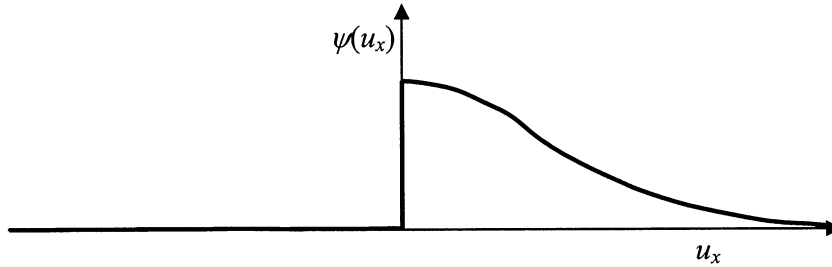


[10%]

(b)   The mathematical form of the distribution is therefore:

For $-\infty < u_x < 0,$ $\qquad \psi(u_x) = 0$

For $0 \le u_x < \infty,$ $\qquad \psi(u_x) = A\exp\left(-\dfrac{u_x^2}{2RT}\right)$

The constant $A$ can be found from the normalisation condition using the given integral:

$$\int_{-\infty}^{\infty}\psi(u_x)\,du_x = \int_{0}^{\infty}A\exp\left(-\frac{u_x^2}{2RT}\right)du_x = A\frac{1}{2}(2\pi RT)^{1/2} = 1 \quad \Rightarrow \quad A = \left(\frac{2}{\pi RT}\right)^{1/2}$$

[15%]

This can also be deduced from the Maxwellian distribution by noting that, within the vessel,

$$\psi(C_x) = \left(\frac{1}{2\pi RT}\right)^{1/2}\exp\left(-\frac{C_x^2}{2RT}\right)$$

but that this includes molecules with negative as well as positive $C_x$. If the negative contribution is removed, then $\psi$ must be doubled in the positive region to maintain the correct normalisation.

(c)   The mean value of $u_x$ is given by:

$$\bar{u}_x = \int_{-\infty}^{\infty}u_x\psi(u_x)\,du_x = \int_{0}^{\infty}\left(\frac{2}{\pi RT}\right)^{1/2}u_x\exp\left(-\frac{u_x^2}{2RT}\right)du_x$$

$$= \left(\frac{2RT}{\pi}\right)^{1/2}\left[-\exp\left(-\frac{u_x^2}{2RT}\right)\right]_{0}^{\infty} = \left(\frac{2RT}{\pi}\right)^{1/2}$$

[20%]

1

(d) Kinetic temperature is defined by 'mean translational KE per unit mass = $3RT/2$'.

The mean value of $u_x^2$ is given by:

$$\overline{u_x^2} = \int_{-\infty}^{\infty} u_x^2\, \psi(u_x)\, du_x = \int_0^{\infty} \left(\frac{2}{\pi RT}\right)^{1/2} u_x^2 \exp\left(-\frac{u_x^2}{2RT}\right) du_x$$

$$= \left[ u_x \left(\frac{2}{\pi RT}\right)^{1/2} (-RT) \exp\left(-\frac{u_x^2}{2RT}\right) \right]_0^{\infty} - \int_0^{\infty} \left(\frac{2}{\pi RT}\right)^{1/2} (-RT) \exp\left(-\frac{u_x^2}{2RT}\right) du_x$$

$$= \left(\frac{2RT}{\pi}\right)^{1/2} \frac{(2\pi RT)^{1/2}}{2} \qquad \text{(using the given integral)}$$

$$= RT$$

We also have $\dfrac{\overline{u_y^2}}{2} = \dfrac{\overline{u_z^2}}{2} = \dfrac{RT}{2}$ because the distribution of molecular velocities in the $y$- and $z$-directions is obviously the same as in the vessel. Hence,

$$\frac{\overline{u^2}}{2} = \frac{\overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}}{2} = \frac{3RT}{2}$$

and so the temperature of the effusing molecules is $T$, the temperature of the gas in the vessel.  [20%]

(e) The number density of effusing molecules is half that in the vessel because only molecules with $u_x > 0$ can get out. Hence,

$$\dot{m} = \frac{1}{2}\rho \bar{u}_x A = \frac{1}{2}\frac{p}{RT}\left(\frac{2RT}{\pi}\right)^{1/2} A = \frac{pA}{(2\pi RT)^{1/2}} \qquad \text{[15%]}$$

(f) If $V$ is the volume of the vessel, then,

$$V\frac{d\rho}{dt} = \frac{V}{RT}\frac{dp}{dt} = -\frac{pA}{(2\pi RT)^{1/2}}$$

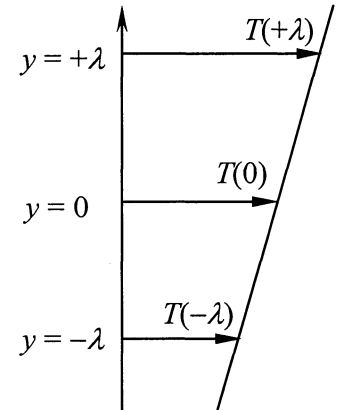$$\frac{dp}{p} = -\frac{A}{V}\left(\frac{RT}{2\pi}\right)^{1/2} dt$$

$$\frac{p}{p_0} = \exp\left(-\frac{t}{\tau}\right) \qquad \text{where} \qquad \tau = \frac{V}{A}\left(\frac{2\pi}{RT}\right)^{1/2} \qquad \text{[20%]}$$

2 (a)

Assume molecules make their last collision one mean free path above or below the plane $y = 0$.

Flux of KE from below $= \dfrac{\rho \overline{C}}{4}\left[ c_v T(0) - c_v \lambda \dfrac{dT}{dy} \right]$

Flux of KE from above $= \dfrac{\rho \overline{C}}{4}\left[ c_v T(0) + c_v \lambda \dfrac{dT}{dy} \right]$

Net flux of KE (in positive $y$-direction) $= q = - \dfrac{\rho \overline{C} \lambda c_v}{2} \dfrac{dT}{dy}$

Macroscopically thermal conductivity is defined by $q = -k\dfrac{dT}{dy}$ and hence, $k = \dfrac{\rho \overline{C} \lambda c_v}{2}$.

Thus $A = \dfrac{1}{2}$. [25%]

More exact kinetic theories give a value of $A$ about 2.5 times larger. This is because the simple theory neglects the correlation between molecular velocity and distance travelled (molecules with high KE crossing the plane $y = 0$ tend to come from further away). [5%]

The mean molecular speed $\overline{C}$ varies with $T^{1/2}$ and the mean free path $\lambda$ varies with $\rho^{-1}$. Hence, the thermal conductivity $k$ varies approximately with $T^{1/2}$ and is almost independent of pressure. [10%]

(b)　　If $L \gg \lambda$, the gas may be treated as a continuum so that $q_0 = -k\dfrac{dT}{dy}$ with boundary conditions $T = T_1$ at $y = 0$, and $T = T_2$ at $y = L$. Hence,

$$q_0 = \frac{k(T_1 - T_2)}{L}$$

Using the result of the simple theory,

$$q_0 = \frac{\rho \overline{C} \lambda c_v}{2L} (T_1 - T_2)$$

[10%]

3

(c)  If $L \ll \lambda$, collisions between molecules may be neglected in favour of collisions with the plates. This is the regime of free-molecule heat transfer.

Let the temperature of molecules reflected from Plates 1 and 2 be $T_{R1}$ and $T_{R2}$ respectively.

Energy flux incident on Plate 1  $= \dfrac{\rho \overline{C}}{4} c_v T_{R2}$

Energy flux incident on Plate 2  $= \dfrac{\rho \overline{C}}{4} c_v T_{R1}$

Hence, net heat transfer rate from Plate 1 to Plate 2  $= q_\infty = \dfrac{\rho \overline{C}}{4} c_v (T_{R1} - T_{R2})$

From the definition of the accomodation coefficient for Plate 1,  $T_1 - T_{R2} = \dfrac{T_{R1} - T_{R2}}{\alpha_1}$

From the definition of the accomodation coefficient for Plate 2,  $T_2 - T_{R1} = \dfrac{T_{R2} - T_{R1}}{\alpha_2}$

Hence:  $\qquad (T_1 - T_2) + (T_{R1} - T_{R2}) = (T_{R1} - T_{R2})\left( \dfrac{1}{\alpha_1} + \dfrac{1}{\alpha_2} \right)$

That is:  $\qquad (T_1 - T_2) = (T_{R1} - T_{R2})\left( \dfrac{1}{\alpha_1} + \dfrac{1}{\alpha_2} - 1 \right)$

Thus:  $\qquad q_\infty = \dfrac{\rho \overline{C} c_v}{4} \left( \dfrac{1}{\alpha_1} + \dfrac{1}{\alpha_2} - 1 \right)^{-1} (T_1 - T_2)$

The ratio of the continuum to free-molecule heat flux is therefore given by,

$$\frac{q_0}{q_\infty} = \frac{\rho \overline{C} \lambda c_v}{2L} \frac{4}{\rho \overline{C} c_v} \left( \frac{1}{\alpha_1} + \frac{1}{\alpha_2} - 1 \right) = \left( \frac{1}{\alpha_1} + \frac{1}{\alpha_2} - 1 \right) \frac{2\lambda}{L} = \left( \frac{1}{\alpha_1} + \frac{1}{\alpha_2} - 1 \right) 2Kn$$

where $Kn = \lambda /L$ is the Knudsen number and the simple theory for $k$ has been used giving $B = 2$.  [50%]

4

3 (a) $N_j^*$    –   The number of particles in energy group (or level) $j$, corresponding to the most probable macrostate.

$C_j$    –   The number of energy states within group $j$.

$N$    –   The total number of particles.

$\varepsilon_j$    –   (Average) energy of $j$-th group energy states.  [10%]

The Boltzmann distribution is valid in the so-called 'Boltzmann limit' – at elevated temperatures. The energy states are then very closely spaced and are sparsely populated by the particles. The chances of two particles existing in the same energy state are so small that there is no difference between B-E and F-D statistics.  [10%]

(b)
$$Z = \sum_j C_j e^{-\varepsilon_j / kT} = \sum_i e^{-\varepsilon_i / kT}$$

where the second summation is over all energy states (for which $C_i = 1$). The energy of each state can be written as $\varepsilon_{kl} = \varepsilon_{k,tr} + \varepsilon_{l,int}$. Thus,

$$Z = \sum_{k,l} e^{-\left(\varepsilon_{k,tr} + \varepsilon_{l,int}\right)/ kT} = \sum_k e^{-\varepsilon_{k,tr} / kT} \sum_l e^{-\varepsilon_{l,tr} / kT} = Z_{tr} Z_{int}.$$  [20%]

This is possible because the translational and internal energy modes are independent. A similar analysis gives $Z_{int} \approx Z_{rot} Z_{vib}$, but this is approximate since the rotational and vibrational modes are not truly independent: vibration affects the moment of inertia of the molecules, and the centrifugal field affects the vibration.  [10%]

(c)
$$Z = \sum_j C_j e^{-\varepsilon_j / kT}$$

$\therefore$
$$\left(\frac{\partial Z}{\partial T}\right)_V = \frac{1}{kT^2} \sum_j \varepsilon_j C_j e^{-\varepsilon_j / kT}$$

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

$\therefore$
$$\left(\frac{\partial Z}{\partial T}\right)_V = \frac{Z}{NkT^2} \sum_j \varepsilon_j N_j^* = \frac{UZ}{NkT^2}$$

$\therefore$
$$U = NkT^2 \left[\frac{\partial}{\partial T} \ln(z)\right]_V$$  [30%]

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

$$U = NkT^2 \left[ \frac{\partial}{\partial T} \ln(Z_{tr}) \right]_V + NkT^2 \left[ \frac{\partial}{\partial T} \ln(Z_{int}) \right]_V$$

$$= U_{tr} + U_{int} \left( \approx U_{tr} + U_{rot} + U_{vib} \right)$$

from whence it follows that,

$$c_v = \left( \frac{\partial U}{\partial T} \right)_V = c_{v,tr} + c_{v,int} \approx c_{v,tr} + c_{v,rot} + c_{v,vib}$$

[20%]

6

4 (a)    The number of energy states with energy less than $\varepsilon$ is given by the volume of one eighth of the sphere of radius $n$, where $n^2 = n_1^2 + n_2^2 + n_3^2$. Thus,

$$\Gamma(\varepsilon) = \frac{1}{8} \times \frac{4\pi}{3} \left( 2\frac{V^{1/3}}{h} (2m\varepsilon)^{1/2} \right)^3 = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}$$    [15%]

At the RMS speed, $\varepsilon = 3kT/2$, and at twice the RMS speed $\varepsilon = 6kT$.

$$T = \frac{p}{\rho R} = \frac{10^5}{(0.1/0.75) \times (8315/4.0)} = 360.8K$$    [10%]

Substitution into the expression for $\Gamma$ (with $m = W/N_0$) gives,

[5%]

(i)    Number of states between 0 & RMS speed $= 1.07 \times 10^{31}$    [5%]

(ii)   Number of states between 1 & 2×RMS speed $= 7 \times 1.07 \times 10^{31} = 7.48 \times 10^{31}$    [5%]

The total number of particles $= (0.1/4.0) \times N_0 = 1.506 \times 10^{24}$, hence the majority of energy states are empty.    [5%]

(b)   The total energy is given by,
$$E = \left(M + \frac{1}{2}\right)h\nu = \left(n_1 + \frac{1}{2} + n_2 + \frac{1}{2} + n_3 + \frac{1}{2}\right)h\nu$$
$$\therefore \qquad n_1 + n_2 + n_3 = M - 1$$

(i)    For $M = 4$, $n_1 + n_2 + n_3 = 3$ and the possible microstates are:

| $n_1$ | $n_2$ | $n_3$ |
|---|---|---|
| 0 | 0 | 3 |
| 0 | 1 | 2 |
| 0 | 2 | 1 |
| 0 | 3 | 0 |
| 1 | 0 | 2 |
| 1 | 1 | 1 |
| 1 | 2 | 0 |
| 2 | 0 | 1 |
| 2 | 1 | 0 |
| 3 | 0 | 0 |

[25%]

(ii) For $M = 4$, the total number of microstates is, $\Omega = 4 + 3 + 2 + 1$

Extending this to the general case when $M$ can take any value:

$$\Omega = M + (M-1) + (M-2) + \dots + 1$$

This is an arithmetic series and hence,

$$\Omega = \frac{M}{2}(M+1) \qquad \text{[20\%]}$$

(iii) In terms of the total energy $E$,

$$M = \frac{E}{h\nu} - \frac{1}{2}$$

Hence, the system entropy is given by,

$$S = k\ln(\Omega) = k\ln\left[\frac{1}{2}\left(\frac{E^2}{h^2\nu^2} - \frac{1}{4}\right)\right] \qquad \text{[15\%]}$$