ENGINEERING TRIPOS   PART IIB   2003
MODULE 4A9 – MOLECULAR THERMODYNAMICS
ANSWERS TO TRIPOS QUESTIONS

1.   (b)   (i) $\dfrac{dY_i}{dx} = -N\dfrac{a^2}{d^2}\dfrac{G_i}{G}$

2.   (a) $\beta = 0.5$ (c) $A = \dfrac{\rho \overline{C} \lambda}{2}\,\overline{u}_1(0)$

3.   (a)   (ii) $Z_{rot} = \displaystyle\sum_{m=0}^{\infty} \dfrac{1}{\sigma}(2m+1)\exp\left[-\dfrac{m(m+1)h^2}{8\pi^2 I kT}\right]$

         (iii) $\theta_r = \dfrac{h^2}{8\pi^2 I k}$

4.   (b)   (i) 1.9×10^{-36} m   (ii) 1.7×10^{-34} m   (iii) 8.0×10^{-10} m

       (c)   (i)   1/3, 1/2, 1/6   (iii)   2/3, 1/3

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1.(a)   One-sided mass flux is given by :

$$\text{Flux} = \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty mn\, C_3 (2\pi RT)^{-3/2} \exp\left[- \frac{c_1^2 + c_2^2 + c_3^2}{2RT}\right] dc_1\, dc_2\, dc_3$$

$$= \frac{mn}{(2\pi RT)^{3/2}} \int_0^\infty C_3\, e^{-c_3^2/2RT}\, dc_3 \int_{-\infty}^\infty e^{-c_2^2/2RT}\, dc_2 \int_{-\infty}^\infty e^{-c_1^2/2RT}\, dc_1$$

Now

$$\int_{-\infty}^\infty e^{-c_1^2/2RT}\, dc_1 = (2\pi RT)^{1/2} \quad (\text{from given integral})$$

$$\int_{-\infty}^\infty e^{-c_2^2/2RT}\, dc_2 = (2\pi RT)^{1/2} \quad (\text{from given integral})$$

$$\int_0^\infty C_3\, e^{-c_3^2/2RT}\, dc_3 = \left. -RT\, e^{-c_3^2/2RT} \right|_0^\infty = RT$$
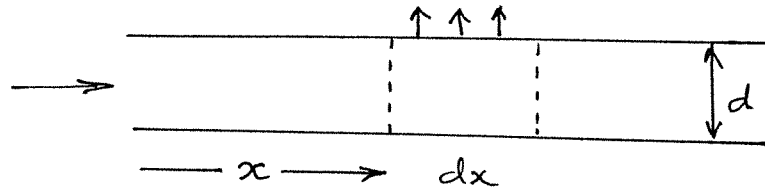
Hence,

$$\text{Mass flux} = \frac{mn}{(2\pi RT)^{3/2}} (2\pi RT)^{1/2} (2\pi RT)^{1/2} RT$$

$$= mn \left(\frac{RT}{2\pi}\right)^{1/2} = \rho \left(\frac{RT}{2\pi}\right)^{1/2} \qquad [8]$$

$$\left[\text{Note that this is the same as } \frac{mn}{4}\left(\frac{8RT}{\pi}\right)^{1/2} = \frac{\rho \bar{c}}{4} \right]$$

(b) (i)

Flow of gas i along tube into CV $= \frac{\pi d^2}{4} Y_i G$

Flow of gas i along tube out of CV $= \frac{\pi d^2}{4} Y_i G + \frac{d}{dx}\left[\frac{\pi d^2}{4} Y_i G\right] dx$

Flow of gas i out of CV through pores $= N \frac{\pi a^2}{4} G_i \, dx$

Conservation of gas i gives:

$$\frac{d}{dx}\left[\frac{\pi d^2}{4} Y_i G\right] = -N \frac{\pi a^2}{4} G_i$$

Assuming G is constant (this is true if the leaking gases are only present in trace amounts):

$$\frac{dY_i}{dx} = -N \frac{a^2}{d^2} \frac{G_i}{G} \qquad\qquad [6]$$

(ii) If a is much smaller than the mean free path of a gas molecule, then the flow through the pores is by effusion. From part (a),

$$G_i = m_i n_i \left(\frac{R_i T}{2\pi}\right)^{\frac{1}{2}} = \rho_i \left(\frac{\bar{R} T}{2\pi M_i}\right)^{1/2}$$

where $\bar{R}$ is the universal gas constant and $\rho_i = Y_i \rho$ with ρ being the density of nitrogen.

$$\therefore \quad \frac{dY_i}{dx} = -N \frac{a^2}{d^2} \left(\frac{\bar{R} T}{2\pi}\right)^{1/2} \frac{\rho}{G} \frac{Y_i}{(M_i)^{1/2}} = -K \frac{Y_i}{M_i^{1/2}}$$
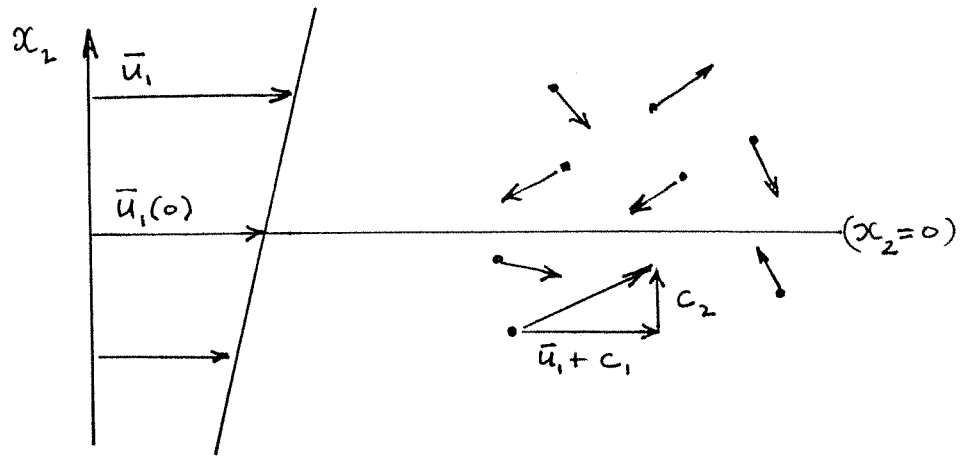
where K is a constant. Integrating subject to $Y_i = Y_{i,0}$ at $x=0$:

$$M_i^{1/2} \ln\left(\frac{Y_i}{Y_{i,0}}\right) = -Kx$$

Hence, at any value of x:

$$\sqrt{M_1} \ln\left(\frac{Y_1}{Y_{1,0}}\right) = \sqrt{M_2} \ln\left(\frac{Y_2}{Y_{2,0}}\right) \qquad\qquad [6]$$

2. (a)

Assume molecules make their last collision before crossing the plane $x_2 = 0$ a distance λ (one mean free path) above or below the plane. Also assume the molecules acquire the local mean x_1 velocity component at this collision.

Mass flux of molecules onto a surface from one side $= \rho\dfrac{\bar{C}}{4}$

Transport of x_1 momentum across plane from below $= \rho\dfrac{\bar{C}}{4}\left[\bar{u}_1(0) - \lambda\dfrac{d\bar{u}_1}{dx_2}\right]$

Transport of x_1 momentum across plane from above $= \rho\dfrac{\bar{C}}{4}\left[\bar{u}_1(0) + \lambda\dfrac{d\bar{u}_1}{dx_2}\right]$

$\therefore$ Net flux of x_1 momentum from above to below $= \rho\dfrac{\bar{C}\lambda}{2}\dfrac{d\bar{u}_1}{dx_2}$

Macroscopically this is interpreted as a shear stress. Hence,

$$\tau_{12} = \beta(\rho\bar{C}\lambda)\dfrac{d\bar{u}_1}{dx_2} \qquad \text{with } \beta = \dfrac{1}{2} \qquad\qquad [7]$$

(b) From the above equation, $\mu = \rho\dfrac{\bar{C}\lambda}{2} = \dfrac{(p/RT)\bar{C}\lambda}{2}$

$\bar{C}$ only depends on temperature but λ is inversely proportional to the molecular number density (i.e., the pressure)

Hence, μ is independent of pressure. $\qquad\qquad [3]$

3(a) (i) ε_m^{rot} : an energy level associated with rotation of a diatomic molecule.

   h Planck's constant

   I Moment of inertia of the molecule

   m Quantum number of rotation (= 0, 1, 2, ...)

   g_m Degeneracy of energy level m

   σ Symmetry factor: takes value 2 for homonuclear molecule

                    1 for heteronuclear molecules   [5]

(ii) The rotational contribution to the partition function is given by,

$$Z_{rot} = \sum_m g_m \exp\left[-\frac{\varepsilon_m}{kT}\right]$$

i.e.,

$$Z_{rot} = \sum_{m=0}^{\infty} \frac{1}{\sigma}(2m+1)\exp\left[-\frac{m(m+1)h^2}{8\pi^2 I kT}\right]$$

[3]

(iii) The characteristic temperature of rotation is,

$$\theta_r = \frac{h^2}{8\pi^2 Ik}$$

[2]

(b) The internal energy is,

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

and the partition function is,

$$Z = Z_{tr}Z_{rot}$$

Thus,

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

or, simply,

$$U = U_{tr} + U_{rot}$$

The translational contribution is,

$$U_{tr} = \frac{3}{2}NkT$$

and, from,

$$Z_{rot} = \frac{T}{\sigma\theta_r}$$

the rotational contribution is,

$$U_{rot} = NkT$$

Thus, with $R = k/m$, the specific internal energy becomes,

$$u = \frac{U}{Nm} = \frac{3}{2}RT + RT = \frac{5}{2}RT$$

The specific heat capacity at constant volume is,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{5}{2}R$$

The specific heat capacity at constant pressure is,

$$c_p = c_v + R = \frac{7}{2}R$$

And, finally,

$$\gamma = \frac{c_p}{c_v} = \frac{7}{5} = 1.4$$

[7]

(c)   A general outline of the following is required:
The vibrational energy levels are given by,

$$\varepsilon_{vib}^{n} = (n + \frac{1}{2})h\nu$$

for $n = 0, 1, 2 \ldots$, with degeneracy $g_n = 1$.
The vibrational contribution to the partition function is,

$$Z_{vib} = \frac{1}{1 - \exp(-\theta_v/T)}$$

with characteristic temperature,

$$\theta_v = \frac{h\nu}{k}$$

Vibrational modes are not excited at room temperature because, for common gases, $\theta >> T$.
For example, for nitrogen, $\theta = 3390$ K.

[3]

4. (a) Einstein and Planck:

$$E = mc^2 = h\nu = \frac{hc}{\lambda}$$

With De Broglie:

$$p = mc = \frac{h\nu}{c} = \frac{h}{\lambda}$$

[3]

(b) (i) Student, estimated mass 70 kg, velocity 5 m/s, $\lambda = \text{l}p = h/mv = \underline{1.89 \times 10^{-36}}\,\text{m}$.

(ii) Tennis ball, estimated mass 0.1 kg, velocity 40 m/s, $\lambda = \underline{1.66\,10^{-34}}\,\text{m}$.

(iii) Hydrogen atom, mass $W/A = 1/6.022 \times 10^6\,\text{kg}$, velocity 500 m/s, $\lambda = \underline{7.98 \times 10^{-10}}\,\text{m}$.

[6]

For both the student and the tennis ball, the wavelength is much less than the length scale.
For the hydrogen atom the wavelength and the length scale (e.g., the diameter) are comparable.

[1]

c) Tabulate:

Microstate	$\varepsilon = 0$	$\varepsilon = 2$	$\varepsilon = 2$	$\varepsilon = 4$	$\varepsilon = 6$
1	x	x			x
2	x		x		x
3		x	x	x	
4		xx		x	
5			xx	x	
6	x			xx	

i) For bosons, any number of particles are allowed in each state, *i.e.*, 6 possible microstates as shown. Macrostates are (1 and 2), (3, 4 and 5), and (6)., *i.e.*, 3 macrostates with thermodynamics probability 1/3, 1/2 and 1/6 respectively.

[7]

(ii) For fermions, only one particle is allowed in each state *i.e.*, 3 possible microstates 1, 2 and 3. Macrostates are (1 and 2), and (3), *i.e.*, 2 macrostates with thermodynamic probability 2/3 and 1/3 respectively.

[3]

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