

Module 4A9
MOLECULAR THERMODYNAMICS
2019 SOLUTIONS
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- 1 (a) (i) For $Q = m$, I is the mass density. Thus (data from tables),

$$I = nm = \rho = \frac{p}{RT} = \frac{10^5}{208 \times 400} = \underline{\underline{1.202 \text{ kg m}^{-3}}}$$

(ii) For $Q = mC_2^2$, I is the normal flux of momentum in the x_2 direction. Since the gas is in equilibrium (i.e., no viscous stresses) this is also equal to the pressure. Thus, $I = p = \underline{\underline{1 \text{ bar}}}$.

(iii) For $Q = \frac{1}{2}mC^2C_3$, I is the net flux of KE in the x_3 direction. Noting that the integrand w.r.t. C_3 is an odd function (or from an equilibrium argument), $\underline{\underline{I = 0}}$.

(iv) For $Q = mC_1C_2$, I is the negative of the shear stress $\tau_{12} = \tau_{21}$ – i.e., it is the flux of x_2 momentum through a plane normal to the x_1 direction (or *vice versa*). Since the gas is at equilibrium, C_1 and C_2 are uncorrelated, hence $\underline{\underline{I = 0}}$. [6]

- (b) The speed and velocity distributions are related by $g(C)dC = f(C)dV_c$. Thus,

$$g(C) = f(C)4\pi C^2 = \frac{4\pi n C^2}{(2\pi RT)^{3/2}} \exp\left\{-\frac{C^2}{2RT}\right\}$$

The average molecular speed is given by

$$\bar{C} = \frac{1}{n} \int_0^\infty C g(C) dC$$

Making the substitution $x = C/\beta$ where $\beta = (2RT)^{1/2}$ gives,

$$\bar{C} = \frac{4\beta}{\pi^{1/2}} \int_0^\infty x^3 \exp(-x^2) dx = \frac{2\beta}{\pi^{1/2}} = \sqrt{\frac{8RT}{\pi}} = \sqrt{\frac{8 \times 208 \times 400}{\pi}} = \underline{\underline{460.3 \text{ ms}^{-1}}}$$

[5]

- (c) (i) Kinetic temperature is defined such that $3kT/2 = mC^2/2$. Thus, $C = \sqrt{3RT} = \sqrt{3 \times 208 \times 400} = \underline{\underline{499.6 \text{ ms}^{-1}}}$. The group velocities (to the nearest ms^{-1}) are thus

$$(600, 50, -100); (100, 550, -100); (100, 50, 400) \text{ ms}^{-1}$$

$$(-400, 50, -100); (100, -450, -100); (100, 50, -600) \text{ ms}^{-1}$$

[3]

(ii) The flux is given by

$$\begin{aligned}
 F_E = \frac{nmA}{6} \frac{1}{2} & \{ (u_1 + C)\{(u_1 + C)^2 + u_2^2 + u_3^2\} \\
 & + (u_1 - C)\{(u_1 - C)^2 + u_2^2 + u_3^2\} \\
 & + u_1\{u_1^2 + (u_2 + C)^2 + u_3^2\} \\
 & + u_1\{u_1^2 + (u_2 - C)^2 + u_3^2\} \\
 & + u_1\{u_1^2 + u_2^2 + (u_3 + C)^2\} \\
 & + u_1\{u_1^2 + u_2^2 + (u_3 - C)^2\} \}
 \end{aligned}$$

Straightforward simplification then gives

$$\begin{aligned}
 F_E &= \frac{\rho A}{6} \frac{1}{2} \{ 6u_1(u_1^2 + u_2^2 + u_3^2 + C^2) + 4Cu_1C \} \\
 &= \rho u_1 A \left\{ \frac{1}{2}(u_1^2 + u_2^2 + u_3^2 + C^2) + \frac{1}{2} \frac{2}{3} C^2 \right\}
 \end{aligned}$$

Substituting $C^2 = 3RT$ gives

$$F_E = \rho u_1 A \left\{ \frac{1}{2}(u_1^2 + u_2^2 + u_3^2) + \frac{5}{2}RT \right\}$$

whence $b = 5$. From a macroscopic thermodynamic perspective, this reflects the fact that F_E is the flux of stagnation *enthalpy* – i.e., $h = c_p T = (3R/2 + R)T$. [6]

Examiner's comment: *Most parts reasonably well answered, but some candidates unnecessarily attempted to undertake lengthy integrals and got lost. A pleasing number gave the correct physical interpretation for the flux of energy in the final section.*

2 (a) The target cross-section of the test molecule is $A = \pi d^2$ (see figure), so the average volume swept out between collisions is $V = \lambda A = \lambda \pi d^2$. By the definition of λ , this must contain precisely one other molecule, and thus

$$\lambda \pi d^2 n = 1$$

giving

$$\lambda = \frac{1}{\pi n d^2}$$

The average time interval between collisions for the test molecule is

$$\tau = \frac{\lambda}{\bar{C}} = \frac{1}{\pi n d^2 \bar{C}}$$

The collision frequency for the test molecule is $z = 1/\tau$, and since there are n molecules per unit volume, the total collision rate per unit volume is

$$Z = \frac{nz}{2} = \frac{n^2 \pi d^2 \bar{C}}{2}$$

[5]

(b) (i) Consider molecules of CO crossing the plane at $x_2 = x_{20}$, as shown in the figure. Assume that molecules crossing the plane in the downward direction make their last collision at $x_2 = x_{20} + \lambda$, at which the concentration of CO is

$$n_{\text{CO}}^+ = n_{\text{CO}}(x_{20}) + \lambda \frac{dn_{\text{CO}}}{dx_2}$$

The downward molecular flux is thus

$$J^- = \frac{n_{\text{CO}}^+ \bar{C}}{4} = \frac{\bar{C}}{4} \left(n_{\text{CO}}(x_{20}) + \lambda \frac{dn_{\text{CO}}}{dx_2} \right)$$

Likewise the upward flux from below the plane is

$$J^+ = \frac{n_{\text{CO}}^- \bar{C}}{4} = \frac{\bar{C}}{4} \left(n_{\text{CO}}(x_{20}) - \lambda \frac{dn_{\text{CO}}}{dx_2} \right)$$

The net upward flux is thus

$$J_{\text{CO}} = J^+ - J^- = -\frac{\lambda \bar{C}}{2} \frac{dn_{\text{CO}}}{dx_2}$$

from which the diffusion coefficient is $D = -\lambda \bar{C}/2$. Note that the analysis is reasonable for N_2 and CO because the molecules have the same mass and (it may be assumed) similar sizes.

[6]

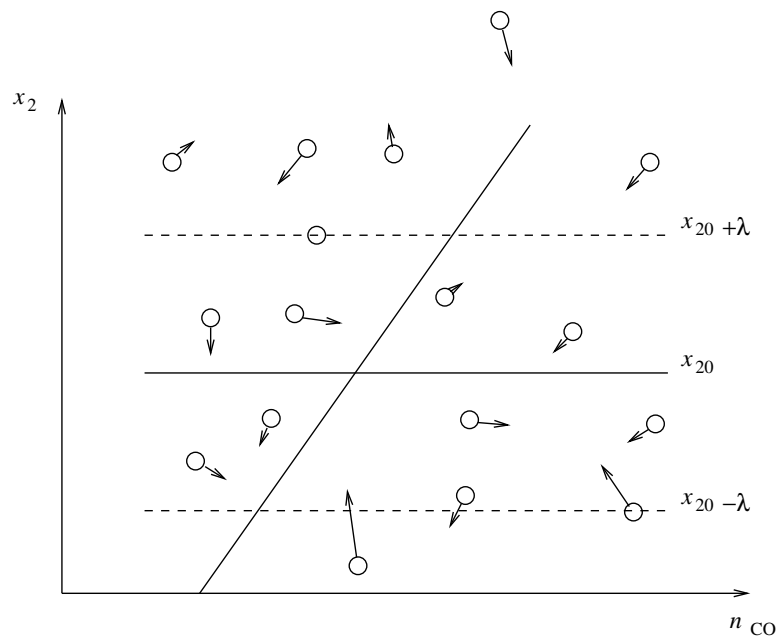
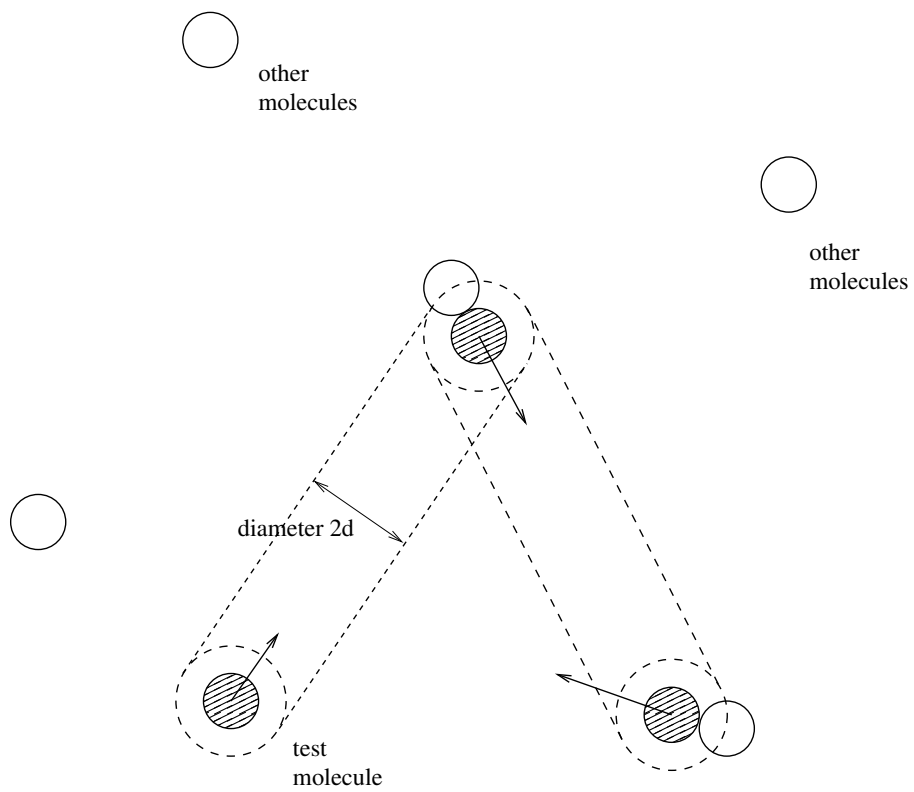


Fig. 1

(ii) From a simple dimensional argument, the time scale associated with the diffusion process is

$$\tau \sim \frac{a^2}{D}$$

so estimating this timescale requires an estimate for D , which in turn comes from an estimate for μ at the correct pressure and temperature.

The dynamic viscosity expression gives

$$\mu = \frac{\rho \bar{C} \lambda}{2} = \frac{nm\bar{C}}{2} \frac{1}{n\pi d^2}$$

From this it can be noted that μ is independent of pressure, but varies with \sqrt{T} (because $\bar{C} \propto \sqrt{T}$). The viscosity of N_2 at 1 bar and 400 K is thus

$$\mu \simeq \sqrt{400/300} \times 16.5 \times 10^{-6} = \underline{\underline{19.1 \times 10^{-6}}}$$

An estimate of D is obtained by dividing this value by the gas density, but the correct value of density to use is that of the gas mixture at 1 bar and 400 K. This is because the relevant mean free path (which does depend on density) in the calculation of D is the mean free path of CO molecules considering collisions with any other molecule (N_2 or CO). Thus,

$$\rho = \frac{p}{RT} = \frac{10^5}{297 \times 400} = 0.842 \text{ kg m}^{-3}$$

and hence $D = \underline{\underline{19.1 \times 10^{-6} / 0.842 = 22.7 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}}}$.

Finally, therefore $\tau \sim a^2/D = \underline{\underline{440 \text{ s}}}$. [7]

(iii) For dissimilar molecules, such as helium and nitrogen, the analysis is very much more complicated because account must be taken of the different sizes in evaluating the mean free paths, and account must be taken of the different average molecular speeds in calculating the molecular fluxes. [2]

Examiner's comment: *Most candidates could correctly derive the mean free path expression and use the mean free path model to obtain an expression for the diffusion coefficient. Most errors occurred in trying to estimate the value of the diffusion coefficient, given the viscosity at a different pressure and temperature.*

3 (a) The symbols have the following meanings :-

ε is the total energy of the particle.

ε_p is the potential energy of the particle.

ψ is the wave function, defined such that $\psi\psi^*dV$ is the probability of finding the particle within the elemental volume dV [2]

(b) For a field-free box, $\varepsilon_p = 0$ and $\varepsilon = \frac{1}{2}mC^2 = \frac{1}{2}(p_1^2 + p_2^2 + p_3^2)/m$ where p_i is the momentum in the x_i direction. Substituting along with $\psi = \psi_1\psi_2\psi_3$ gives

$$\psi_2\psi_3\frac{d^2\psi_1}{dx_1^2} + \psi_1\psi_3\frac{d^2\psi_2}{dx_2^2} + \psi_1\psi_2\frac{d^2\psi_3}{dx_3^2} + \left(\frac{2\pi}{h}\right)^2(p_1^2 + p_2^2 + p_3^2)\psi_1\psi_2\psi_3 = 0$$

which implies

$$\frac{1}{\psi_i}\frac{d^2\psi_i}{dx_i^2} + \left(\frac{2\pi p_i}{h}\right)^2 = 0 \quad \text{for } i = 1, 2, 3$$

The general solution is

$$\psi_i = A_i \sin(2\pi p_i x_i / h) + B_i \cos(2\pi p_i x_i / h) \quad \text{for } i = 1, 2, 3$$

The boundary conditions are that $\psi_i = 0$ on $x_i = 0, a$ for each $i = 1, 2, 3$, giving

$$B_i = 0 \quad ; \quad 2\pi p_i a / h = n_i \pi \quad \text{or} \quad p_i = (n_i h / 2a) \quad \text{where } n_i = 1, 2, \dots$$

The momenta p_i are thus quantised and n_i is the number of half DeBroglie wavelengths that fit inside the box in the x_i direction. The complete solution is

$$\psi = A \sin\left(\frac{n_1 \pi x_1}{a}\right) \sin\left(\frac{n_2 \pi x_2}{a}\right) \sin\left(\frac{n_3 \pi x_3}{a}\right)$$

where $A = A_1 A_2 A_3$. The energy is given by

$$\varepsilon = \frac{p_1^2 + p_2^2 + p_3^2}{2m} = \frac{h^2}{8ma^2} (n_1^2 + n_2^2 + n_3^2)$$

whence $B = h^2 / (8ma^2)$. [11]

(c) Each energy state occupies unit volume in quantum state space (n_1, n_2, n_3) . The number of energy states with energy less than ε is thus one-eighth the volume of a sphere of radius $n = (\varepsilon/B)^{1/2}$ – i.e.,

$$\Gamma(\varepsilon) = \frac{1}{8} \times \frac{4\pi}{3} n^3 = \frac{4\pi a^3}{3h^3} (2m\varepsilon)^{3/2}$$

At twice the RMS molecular speed $\varepsilon = 6kT$, thus

$$\begin{aligned}\Gamma(\varepsilon) &= \frac{4\pi V}{3h^3} (6WkT/N_A)^{3/2} \\ &= \frac{4\pi \times 0.001}{3 \times (6.626 \times 10^{-34})^3} \times \left(\frac{12 \times 40 \times 1.38 \times 10^{-23} \times 400}{6.023 \times 10^{26}} \right)^{3/2} \\ &= \underline{\underline{4.20 \times 10^{30} \text{ states}}}\end{aligned}$$

The number of molecules is

$$N = \frac{pV}{kT} = \frac{10^5 \times 10^{-3}}{1.38 \times 10^{-23} \times 400} = \underline{\underline{1.812 \times 10^{22} \text{ molecules}}}$$

There are roughly 2×10^8 states per molecule and so most states will be empty. [7]

Examiner's comment: *This question was well answered by most candidates. Most had little difficulty in solving the separable differential equation and applying the boundary conditions. Most were also able to apply the results to a sample of gas in a container.*

- 4 (a) (i) False. The microstates are equally probable for an *isolated* system at equilibrium.
- (ii) False. The system could be undergoing a compression, after which the volume is less but the temperature the same. The entropy (and hence the number of microstates) would therefore decrease.
- (iii) True. At temperatures much greater than ε/k , electronic excitation contributes almost nothing to the heat capacity. With three degrees of freedom, $c_v = 3R/2$ and thus $c_p = 5R/2$. [6]

- (b) (i) With $B \gg N$ the probability of finding two or more molecules in each box is very small. The number of arrangements is thus the number of ways of distributing N balls amongst B boxes. For distinguishable balls this is

$$\Omega_{\text{dist.}} = B \times (B-1) \times (B-2) \dots \times (B-N+1) = \frac{B!}{(B-N)!}$$

Taking into account the indistinguishability of the balls (molecules) gives

$$\Omega \simeq \frac{B!}{(B-N)!N!}$$

The “ \simeq ” sign comes from the neglect of the rare cases when there *are* two or more molecules in the same box. [4]

- (ii) Using Stirling’s approximation

$$\begin{aligned} \ln \Omega &= \ln B! - \ln N! - \ln(B-N)! \\ &= B \ln B - B - N \ln N + N - (B-N) \ln(B-N) + (B-N) \\ &= B \ln B - N \ln N - (B-N) \ln(B-N) \\ &= B \ln \left(\frac{B}{B-N} \right) + N \ln \left(\frac{B-N}{N} \right) \end{aligned}$$

The entropy ($S = k \ln \Omega$) is thus

$$S \simeq Nk \ln \left(\frac{B}{N} - 1 \right) - Bk \ln \left(1 - \frac{N}{B} \right)$$

[4]

- (iii) Since $B \gg N$, the above expression can be simplified to

$$S \simeq k(N \ln B - N \ln N + N)$$

but the number of boxes B will be proportional to the volume. Thus,

$$S \simeq Nk \ln V + \text{const.} = MR \ln V + \text{const.}$$

where the constant depends on temperature and use has been made of $R = k/m$. Finally, for an adiabatic, unrestrained expansion of helium (assumed to be an ideal gas), the temperature remains constant (because the First Law gives $U = \text{const.}$) and thus

$$\Delta S = MR \ln(V_2/V_1) = 0.001 \times 2080 \times \ln 2 = \underline{\underline{1.442 \text{ JK}^{-1}}}$$

[6]

Examiner's comment: *This question revealed some uncertainty amongst some candidates about the molecular basis for entropy. Nevertheless, the proofs involving the number of microstates and Stirling's formula were well reproduced. Application to an unresisted expansion caused greater difficulty.*

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