

Solutions to homework due 4/15/03
Assignment 7

6.13. (a) We start by calculating the kinetic energy associated with the z -component of the motion of the effused molecules. Proceeding as on page 139 of the text, we get [see eqn. (6.4.11)]

$$\begin{aligned} \left\langle \frac{1}{2} m u_z^2 \right\rangle &= \frac{1}{2} m \langle u^2 \cos^2 \theta \rangle = \frac{1}{2} m \frac{\int_0^{\pi/2} \int_0^{\infty} (u^3 \cos^3 \theta) f(\mathbf{u}) u^2 \sin \theta \, du \, d\theta}{\int_0^{\pi/2} \int_0^{\infty} (u \cos \theta) f(\mathbf{u}) u^2 \sin \theta \, du \, d\theta} \\ &= \frac{1}{4} m \frac{\langle u^3 \rangle}{\langle u \rangle}; \end{aligned}$$

note that the averages on the right-hand side are taken over the gas *inside* the vessel. It is not difficult to show, see the corresponding calculation in Problem 6.6 and the formulae (B.13b), that

$$\frac{\langle u^3 \rangle}{\langle u \rangle} = \frac{I_5}{I_3} = \frac{4}{\beta m},$$

so that $\left\langle \frac{1}{2} m u_z^2 \right\rangle$, for the effused molecules, $= 1/\beta = kT$. The kinetic energy associated with the x - and y -components of the molecular motion will be the same as inside the vessel, viz. $\frac{1}{2} kT$ each. It follows that the mean energy \mathcal{E} of an effused molecule is $2kT$.

(b) Assuming quasi-static equilibrium, the relations $E = (3/2)NkT$ and $P = NkT/V$ will continue to hold for the gas inside the vessel. However, in view of the result obtained in part (a), we shall also have

$$\frac{dE}{dt} \equiv \frac{d}{dt} \left(\frac{3}{2} NkT \right) = 2kT \frac{dN}{dt}.$$

It follows that

$$\frac{dT}{T} = \frac{1}{3} \frac{dN}{N} \quad \text{and hence} \quad T \propto N^{1/3};$$

it further follows that $P \propto N^{4/3}$.

As for explicit variations with t , we make use of eqn. (6.4.13) and write

$$\frac{dN}{dt} = -\frac{1}{4} a n \langle u \rangle = -\frac{1}{4} \frac{aN}{V} \left(\frac{8kT}{\pi m} \right)^{1/2}.$$

Combining the last two results, we get

$$\frac{dT}{T} = -\frac{1}{3} \frac{a}{V} \left(\frac{kT}{2\pi m} \right)^{1/2} dt,$$

so that $T = T_0(1+ct)^{-2}$, where $c = (a/6V)(kT_0/2\pi m)^{1/2}$. The variations of N and P with t follow straightforwardly.

6.15. The rate of effusion of molecules from side A to side B, through a hole of cross-section S, is given by the expression

$$R_{A \rightarrow B} = \frac{1}{4} n_A \sqrt{\frac{8kT_A}{\pi m_A}} S = \frac{P_A}{\sqrt{2\pi m_A k T_A}} S;$$

the same from side B to side A is given by

$$R_{B \rightarrow A} = \frac{1}{4} n_B \sqrt{\frac{8kT_B}{\pi m_B}} S = \frac{P_B}{\sqrt{2\pi m_B k T_B}} S.$$

In the stationary state, these two expressions will be equal — which leads to the condition of dynamic equilibrium

$$P_A / P_B = (m_A T_A / m_B T_B)^{1/2}.$$

If the two gases are samples of the same gas, the condition simplifies to

$$P_A / P_B = (T_A / T_B)^{1/2}.$$

6.20. We extend the treatment of Problem 3.14 to the reaction $AB + CD \leftrightarrow AD + CB$ and obtain, in equilibrium,

$$\frac{n_{AD} n_{CB}}{n_{AB} n_{CD}} = \frac{f_{AD} f_{CB}}{f_{AB} f_{CD}} = K(T).$$

For the given reaction,

$$K(T) = \frac{f_{HD}^2}{f_{HH} f_{DD}},$$

where each f is a product of three factors — the translational, the rotational and the vibrational.

Now, for a *heteronuclear* molecule like HD we have, at high temperatures,

$$f_{HD} \approx V \left(\frac{m_{HD} kT}{2\pi \hbar^2} \right)^{3/2} \cdot \frac{2I_{HD} kT}{\hbar^2} \cdot \frac{kT}{\hbar \omega_{HD}},$$

while for a *homonuclear* molecule like HH we have instead

6.28. The various contributions to the molar specific heat of the gas at 300 K are:

(i) translational — the amount being $(3/2)R$.

(ii) rotational — since the characteristic values of the parameter Θ , in this case are of the order of 10 K, these degrees of freedom may be treated classically, which yields a contribution of $(3/2)R$; see eqn. (6.5.42).

(iii) vibrational — here, the parameters Θ_v are such that the various contributions have to be calculated quantum-mechanically, using formula (6.5.44). We find that

$$\frac{\Theta_{1,2}}{T} \approx 16.00, \quad \frac{\Theta_{3,4}}{T} \approx 4.56, \quad \frac{\Theta_5}{T} \approx 16.37, \quad \frac{\Theta_6}{T} \approx 7.80,$$

with the result that only modes 3 and 4 make appreciable contributions to the specific heat of the gas; it turns out that each of these contributions is about $0.22R$. The contribution from mode 6 is about $0.02R$, while those from modes 1, 2 and 5 are entirely negligible.

The net result is: $3.46R$.