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Fourth Edition

Physical Chemistry

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$$\times \exp\left(-\frac{(44.010 \times 10^{-3} \text{ kg mol}^{-1})(402.5 \text{ m s}^{-1})^2}{2(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(400 \text{ K})}\right) \times (405 - 400) \text{ m s}^{-1}$$

$$= 0.0107, \text{ just over 1\%}$$

1B.4(b) The most probable, mean, and mean relative speeds are, respectively

$$v_{mp} = \left(\frac{2RT}{M}\right)^{1/2} \quad [1B.9] \quad v_{rms} = \left(\frac{3RT}{M}\right)^{1/2} \quad [1B.8] \quad v_{rel} = \left(\frac{8RT}{\pi M}\right)^{1/2} \quad [1B.10b]$$

The temperature is $T = (20 + 273) \text{ K} = 293 \text{ K}$.

$$\text{so } v_{mp} = \left(\frac{2(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{2 \times 1.008 \times 10^{-3} \text{ kg mol}^{-1}}\right)^{1/2} = 1.55 \times 10^3 \text{ m s}^{-1}$$

$$\text{and } v_{rms} = \left(\frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{\pi(2 \times 1.008 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = 1.75 \times 10^3 \text{ m s}^{-1}$$

For many purposes, air can be considered as a gas with an average molar mass of 29.0 g mol^{-1} . In that case, the reduced molar mass [1B.10b] is

$$\mu = \frac{M_a M_b}{M_a + M_b} = \frac{(29.0 \text{ g mol}^{-1})(2 \times 1.008 \text{ g mol}^{-1})}{(29.0 + 2 \times 1.008) \text{ g mol}^{-1}} = 1.88 \text{ g mol}^{-1}$$

$$\text{and } v_{rel} = \left(\frac{8(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{\pi(1.88 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = 1.81 \times 10^3 \text{ m s}^{-1}$$

Comment. One computes the average molar mass of air just as one computes the average molar mass of an isotopically mixed element, namely by taking an average of the species that have different masses weighted by their abundances.

Comment. Note that v_{rel} and v_{rms} are very nearly equal. This is because the reduced mass between two very dissimilar species is nearly equal to the mass of the lighter species (in this case, H_2).

$$1B.5(b) \quad (i) \quad v_{rms} = \left(\frac{3RT}{M}\right)^{1/2} \quad [1B.8] = \left(\frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{\pi(2 \times 14.007 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = 475 \text{ m s}^{-1}$$

(ii) The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p} = \frac{kT}{\pi d^2 p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{\pi(395 \times 10^{-12} \text{ m})^2(1 \times 10^{-7} \text{ Torr})} \times \frac{1 \text{ Torr}}{133.3 \text{ Pa}}$$

$$= 6.3 \times 10^7 \text{ m} = 63 \text{ km}$$

The mean free path is much larger than the dimensions of the pumping apparatus used to generate the very low pressure.

(iii) The collision frequency is related to the mean free path and relative mean speed by [1B.12]

$$\lambda = \frac{v_{rel}}{z} \quad \text{so} \quad z = \frac{v_{rel}}{\lambda} = \frac{2^{1/2} v_{rms}}{\lambda} \quad [1B.10a]$$

$$z = \frac{2^{1/2}(475 \text{ m s}^{-1})}{6.3 \times 10^7 \text{ m}} = 1.7 \times 10^{-5} \text{ s}^{-1}$$

1B.6(b) The collision diameter is related to the collision cross section by

$$\sigma = \pi d^2 \quad \text{so} \quad d = (\sigma/\pi)^{1/2} = (0.36 \text{ nm}^2/\pi)^{1/2} = 0.34 \text{ nm}$$

The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p}$$

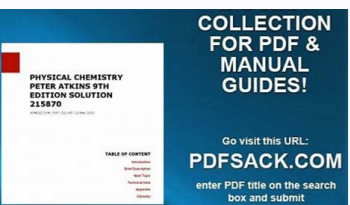
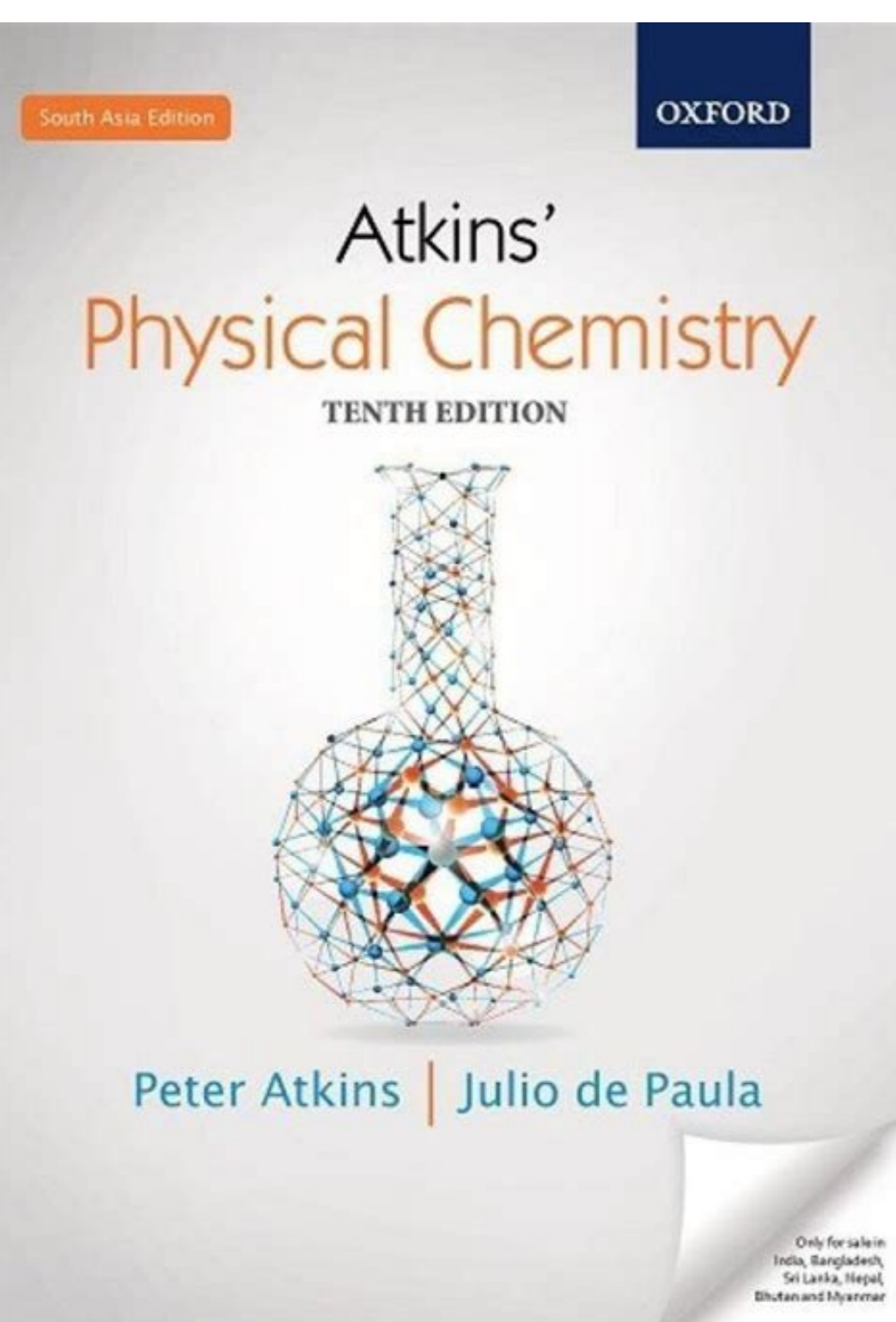
Solve this expression for the pressure and set λ equal to $10d$:



Student Solutions Manual to Accompany Atkins' Physical Chemistry

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