SOLUTIONS

PROBLEM SET 1

CHM 3400, Dr. Chatfield

2.7 Ozone molecules in the stratosphere absorb much of the harmful radiation from the sun. Typically, the temperature and partial pressure of ozone in the stratosphere are 250 K and 1.0×10^{-3} atm, respectively. How many ozone molecules are present in 1.0 L of air under these conditions? Assume ideal-gas behavior.

First calculate the number of moles of ozone molecules, from which the number of ozone molecules can be obtained.

$$n = \frac{PV}{RT} = \frac{\left(1.0 \times 10^{-3}\ \text{atm}\right)(1.0\ \text{L})}{\left(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1}\right)(250\ \text{K})} = 4.87 \times 10^{-5}\ \text{mol}$$

$$\text{Number of ozone molecules} = \left(4.87 \times 10^{-5}\ \text{mol}\right)\left(\frac{6.022 \times 10^{23}\ \text{molecules}}{1\ \text{mol}}\right)$$

$$= 3.0 \times 10^{19}\ \text{molecules}$$

2.9 Dissolving 3.00 g of an impure sample of $CaCO_3$ in an excess of HCl acid produced 0.656 L of CO_2 (measured at 20°C and 792 mmHg). Calculate the percent by mass of $CaCO_3$ in the sample.

The relevant reaction is

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Thus, the number of moles of carbonate in the sample is equal to the number of moles of CO_2 evolved, which can be determined from the ideal gas law:

$$n_{CO_2} = \frac{PV}{RT} = \frac{(792\ \text{mmHg})\left(\frac{1\ \text{atm}}{760\ \text{mmHg}}\right)(0.656\ \text{L})}{(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})(20 + 273)\ \text{K}}$$

$$= 2.843 \times 10^{-2}\ \text{mol} = n_{CaCO_3}$$

$$m_{CaCO_3} = \left(2.843 \times 10^{-2}\ \text{mol}\right)\left(100.1\ \text{g mol}^{-1}\right) = 2.846\ \text{g}$$

$$\%CaCO_3 = \frac{m_{CaCO_3}}{\text{mass of sample}} \times 100\% = \frac{2.846\ \text{g}}{3.00\ \text{g}} \times 100\% = 94.9\%$$

2.47 Calculate the molar volume of carbon dioxide at 400 K and 30 atm, given that the second virial coefficient (B) of CO_2 is $-0.0605\ \text{L mol}^{-1}$. Compare your result with that obtained using the ideal-gas equation.

Ignoring higher order terms,

$$Z = \frac{P\overline{V}}{RT} \approx 1 + \frac{B}{\overline{V}} = 1 + B\frac{P}{RT}$$

Thus,

$$Z = 1 + \left(-0.0605\ \text{L mol}^{-1}\right)\frac{30\ \text{atm}}{(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})(400\ \text{K})}$$

$$= 0.9447$$

Then, since $Z = \frac{P\overline{V}}{RT}$,

$$\overline{V} = \frac{ZRT}{P}$$

$$= \frac{0.9447\ (0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (400\ \text{K})}{30\ \text{atm}}$$

$$= 1.03\ \text{L mol}^{-1}$$

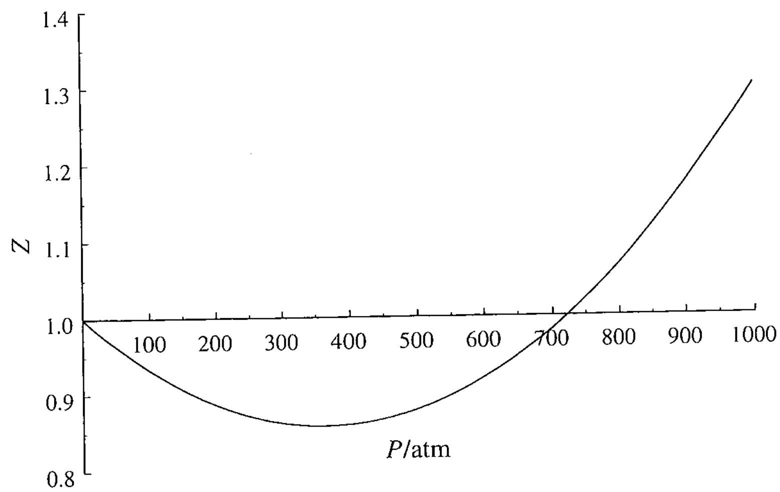
This value for $\overline{V}$ can be compared with the result from the ideal gas law which shows that the real gas is experiencing the effects of attractive intermolecular forces,

$$\overline{V} = \frac{RT}{P}$$

$$= \frac{(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (400\ \text{K})}{30\ \text{atm}}$$

$$= 1.09\ \text{L mol}^{-1}$$

2.48 Consider the virial equation $Z = 1 + B'P + C'P^2$, which describes the behavior of a gas at a certain temperature. From the following plot of Z versus P, deduce the signs of B' and C' (< 0, $= 0$, > 0).



We see that the slope of the Z versus P plot is given by

$$\frac{dZ}{dP} = B' + 2C'P$$

As $P \rightarrow 0$, $\frac{dZ}{dP} \rightarrow B'$.

Additionally, the curvature of the graph is given by

$$\frac{d^2Z}{dP^2} = 2C'$$

Near $P = 0$ the graph has a negative slope, starting at $Z = 1$ and dipping below 1. It does display positive curvature, with the graph turning around to rise above 1. Thus $B' < 0$ and $C' > 0$.

2.54 Calculate the average translational kinetic energy for a N_2 molecule and for 1 mole of N_2 at 20°C.

For one molecule, $\overline{E}_{\text{trans}} = \frac{3}{2}k_B T$.

For one mole of molecules, $\overline{E}_{\text{trans}} = \frac{3}{2}RT$.

Therefore, for a N_2 molecule,

$$\overline{E}_{\text{trans}} = \frac{3}{2}\left(1.381 \times 10^{-23}\ \text{J K}^{-1}\right)(273 + 20)\ \text{K} = 6.07 \times 10^{-21}\ \text{J}$$

whereas for a mole of N_2 molecules,

$$\overline{E}_{\text{trans}} = \frac{3}{2}\left(8.314\ \text{J K}^{-1}\,\text{mol}^{-1}\right)(273 + 20)\ \text{K} = 3.65 \times 10^{3}\ \text{J mol}^{-1}$$

2.63 The speeds of 12 particles (in cm s^{-1}) are 0.5, 1.5, 1.8, 1.8, 1.8, 1.8, 2.0, 2.5, 2.5, 3.0, 3.5, and 4.0. Find **(a)** the average speed, **(b)** the root-mean-square speed, and **(c)** the most probable speed of these particles. Explain your results.

(a) The average speed for the particles is

$$\bar{c} = \frac{\sum_{i=1}^{12} c_i}{N}$$

$$= \frac{(0.5 + 1.5 + 1.8 + 1.8 + 1.8 + 1.8 + 2.0 + 2.5 + 2.5 + 3.0 + 3.5 + 4.0)\ \text{cm s}^{-1}}{12}$$

$$= 2.2\ \text{cm s}^{-1}$$

(b) The mean-square speed for the particles is

$$\overline{c^2} = \frac{\sum_{i=1}^{12} c_i^2}{N}$$

$$= \frac{\left(0.5^2 + 1.5^2 + 1.8^2 + 1.8^2 + 1.8^2 + 1.8^2 + 2.0^2 + 2.5^2 + 2.5^2 + 3.0^2 + 3.5^2 + 4.0^2\right)\ \text{cm}^2\,\text{s}^{-2}}{12}$$

$$= 5.77\ \text{cm}^2\,\text{s}^{-2}$$

The root-mean-square speed for the particles is

$$c_{\text{rms}} = \sqrt{\overline{c^2}} = 2.4\ \text{cm s}^{-1}$$

(c) $c_{\text{mp}} = 1.8\ \text{cm s}^{-1}$, as this is the speed that appears most frequently.

As expected, $c_{\text{rms}} > \bar{c}$. However, because 12 particles do not constitute a macroscopic system, c_{mp} can be greater or smaller than c_{rms} or $\bar{c}$.

2.75 Compare the collision number and the mean free path for air molecules at **(a)** sea level (T = 300 K and density = 1.2 g L^{-1}) and **(b)** in the stratosphere (T = 250 K and density = 5.0×10^{-3} g L^{-1}). The molar mass of air may be taken as 29.0 g, and the collision diameter is 3.72 Å.

Finding the collision number,

$$Z_{11} = \frac{\sqrt{2}}{2}\pi d^2 \bar{c}\left(\frac{N}{V}\right)^2$$

and the mean free path,

$$\lambda = \frac{1}{\sqrt{2}\pi d^2\left(\frac{N}{V}\right)}$$

require knowledge of the average speed, $\bar{c}$ and density, $\frac{N}{V}$.

Sea level:

$$\begin{aligned}\bar{c} &= \sqrt{\frac{8RT}{\pi \mathcal{M}}}\\ &= \sqrt{\frac{8(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(300\ \mathrm{K})}{\pi(29.0 \times 10^{-3}\ \mathrm{kg\,mol^{-1}})}}\\ &= 4.680 \times 10^2\ \mathrm{m\,s^{-1}}\end{aligned}$$

and

$$\begin{aligned}\frac{N}{V} &= \frac{1.2\ \mathrm{g\,L^{-1}}}{29.0\ \mathrm{g\,mol^{-1}}}\left(\frac{1000\ \mathrm{L}}{1\ \mathrm{m^3}}\right)\left(\frac{6.022 \times 10^{23}\ \text{molecules}}{1\ \mathrm{mol}}\right)\\ &= 2.49 \times 10^{25}\ \text{molecules m}^{-3}\end{aligned}$$

Thus,

$$\begin{aligned}Z_{11} &= \frac{\sqrt{2}}{2}\pi d^2 \bar{c}\left(\frac{N}{V}\right)^2\\ &= \frac{\sqrt{2}}{2}\pi(3.72 \times 10^{-10}\ \mathrm{m})^2(4.680 \times 10^2\ \mathrm{m\,s^{-1}})(2.49 \times 10^{25}\ \text{molecules m}^{-3})^2\\ &= 8.9 \times 10^{34}\ \text{collisions m}^{-3}\,\mathrm{s}^{-1}\end{aligned}$$

and

$$\begin{aligned}\lambda &= \frac{1}{\sqrt{2}\pi d^2\left(\frac{N}{V}\right)}\\ &= \frac{1}{\sqrt{2}\pi(3.72 \times 10^{-10}\ \mathrm{m})^2(2.49 \times 10^{25}\ \text{molecules m}^{-3})}\\ &= 6.5 \times 10^{-8}\ \mathrm{m}\end{aligned}$$

Stratosphere:

$$\bar{c} = \sqrt{\frac{8RT}{\pi \mathcal{M}}}$$

$$= \sqrt{\frac{8(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(250 \text{ K})}{\pi(29.0 \times 10^{-3} \text{ kg mol}^{-1})}}$$

$$= 4.272 \times 10^{2} \text{ m s}^{-1}$$

and

$$\frac{N}{V} = \frac{5.0 \times 10^{-3} \text{ g L}^{-1}}{29.0 \text{ g mol}^{-1}} \left(\frac{1000 \text{ L}}{1 \text{ m}^3}\right)\left(\frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}}\right)$$

$$= 1.04 \times 10^{23} \text{ molecules m}^{-3}$$

Thus,

$$Z_{11} = \frac{\sqrt{2}}{2}\pi d^2 \bar{c}\left(\frac{N}{V}\right)^2$$

$$= \frac{\sqrt{2}}{2}\pi(3.72 \times 10^{-10} \text{ m})^2(4.272 \times 10^{2} \text{ m s}^{-1})(1.04 \times 10^{23} \text{ molecules m}^{-3})^2$$

$$= 1.4 \times 10^{30} \text{ collisions m}^{-3} \text{ s}^{-1}$$

and

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \left(\frac{N}{V}\right)}$$

$$= \frac{1}{\sqrt{2}\pi(3.72 \times 10^{-10} \text{ m})^2(1.04 \times 10^{23} \text{ molecules m}^{-3})}$$

$$= 1.6 \times 10^{-5} \text{ m}$$

2.91 Express the van der Waals equation in the form of Equation 2.14. Derive relationships between the van der Waals constants (a and b) and the virial coefficients (B, C, and D), given that

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots \quad |x| < 1$$

The van der Waals equation can be rearranged to give

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

Substitute this expression into $Z = \frac{P\overline{V}}{RT}$:

$$\begin{aligned} Z &= \left(\frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}\right)\frac{\overline{V}}{RT} \\ &= \frac{\overline{V}}{\overline{V} - b} - \frac{a}{\overline{V}RT} \\ &= \frac{1}{1 - \frac{b}{\overline{V}}} - \frac{a}{\overline{V}RT} \end{aligned}$$

Because $b < \overline{V}$, $\frac{b}{\overline{V}} < 1$, the following expression applies:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots$$

to approximate $\frac{1}{1-\frac{b}{\overline{V}}}$ in the expression for Z:

$$\begin{aligned} Z &= 1 + \frac{b}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \frac{b^3}{\overline{V}^3} + \cdots - \frac{a}{\overline{V}RT} \\ &= 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \frac{b^3}{\overline{V}^3} + \cdots \end{aligned}$$

In terms of the virial coefficients, Z can be written as

$$Z = 1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \frac{D}{\overline{V}^3} + \cdots$$

The following expressions are obtained when the coefficients for $\frac{1}{\overline{V}}$, $\frac{1}{\overline{V}^2}$, and $\frac{1}{\overline{V}^3}$ are compared in these expressions for Z.

$$\begin{aligned} B &= b - \frac{a}{RT} \\ C &= b^2 \\ D &= b^3 \end{aligned}$$