Chapter 2

Solutions to problems

1. Assuming the form of the Maxwell distribution allowing for motion in three directions to be

$$f(v) = Nv^2 e^{-\frac{mv^2}{2k_B T}}$$

derive the correct expression for N such that the distribution is normalized. Hint: a table of definite integrals indicates

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\frac{\sqrt{\pi}}{a^{3/2}}$$

Let's let

$$a = \frac{m}{2k_b T}$$

So

$$\int_0^\infty f(v)dv = \int_0^\infty Nv^2 e^{-av^2} dv$$

We can pull the constant N from the integral and substitute using the result from the table of integrals.

$$N\int_0^\infty v^2 e^{-av^2} dv = N\left[\frac{1}{4}\frac{\sqrt{\pi}}{a^{3/2}}\right] = 1$$

Solving for N:

$$N = \left[\frac{4a^{3/2}}{\sqrt{\pi}}\right] = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_B T}\right)^{\frac{3}{2}}$$

This simplifies to

$$N = \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_B T}\right)^{\frac{3}{2}} = 4\pi\sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}$$

2. Dry ice (solid CO_2) has a density of 1.6 g/cm^3. Assuming spherical molecules, estimate the collisional cross section for CO_2. How does it compare to the value listed in the text?

We can use the density to get the volume per molecule.

$$\frac{cm^3}{1.6\ g} \cdot \frac{44.01\ g}{mol} \cdot \frac{mol}{6.022 \cdot 10^{23} molec} = 4.568 \cdot 10^{-23} \frac{cm^3}{molec}$$

Now, assuming a spherical molecule, the radius of the sphere van be calculated from the expression for the volume:

$$V = \frac{4}{3}\pi r^3 = 4.568 \cdot 10^{-23} cm^3$$

This yields a radius of $2.218 \cdot 10^{-8}$ cm (or 0.2218 nm.) The collisional cross section is then given by

$$\sigma = \pi(2r)^2 = \pi(2 \cdot 0.2218\ nm)^2 = 0.62\ nm^2$$

3. Calculate the pressure exerted by 1.00 mol of Ar, N_2, and CO_2 as an ideal gas, a van der Waals gas, and a Redlich-Kwong gas, at 25 ^oC and 24.4 L.

4. The compression factor Z for CO_2 at 0 ^oC and 100 atm is 0.2007. Calculate the volume of a 2.50 mole sample of CO_2 at 0 ^oC and 100 atm.

5.

	Ar	**N_2**	**CO_2**
ideal			
van der Waals			
Redlich-Kwong			

6. What is the maximum pressure that will afford a N_2 molecule a mean-free-path of at least 1.00 m at 25 ^oC?

The formula for mean free path is given by

$$\lambda = \frac{k_B T}{\sqrt{2}\,\sigma\, p}$$

In this case, we know the mean-free-path we want to insure, and need to solve for the pressure. Or,

$$p = \frac{k_B T}{\sqrt{2}\,\sigma\,\lambda}$$

Plugging in the value and keeping everything in MKS units yields

$$p = \frac{\left(1.38 \cdot 10^{-23}\frac{J}{K}\right)(298\ K)}{\sqrt{2}(0.43 \cdot 10^{-18} m^2)(1.00\ m)} = 0.00676\,\frac{J}{m^3} = 0.00676\ Pa$$

7. In a Knudsen cell, the effusion orifice is measured to be 0.50 mm^2. If a sample of naphthalene is allowed to effuse for 1.0 hr at a temperature of 40.3 ^oC, the cell loses 0.0236 g. From this data, calculate the vapor pressure of naphthalene at this temperature.

The formula for finding the vapor pressure of a volatile substance using the Knudsen Cell experiment is

$$p = \frac{g}{A\,\Delta t}\left(\frac{2\pi RT}{MW}\right)^{1/2}$$

For simplicity, I want to keep everything in MKS units, so the pressure will come out in units of Pa. So,

$$p = \frac{0.0236 \cdot 10^{-3} kg}{(0.50 \cdot 10^{-6} m^2)(3600\ s)}\left(\frac{2\pi\left(8.314\,\frac{J}{mol\ K}\right)(314.45\ K)}{128.174 \cdot 10^{-3}\,\frac{kg}{mol}}\right)^{1/2}$$
$$= 4.686\ Pa$$

8. The vapor pressure of scandium was determined using a Knudsen cell [Kirkorian, *J. Phys. Chem.*, **67**, 1586 (1963)]. The data from the experiment are given below.

Vapor Pressure of Scandium	
Temperature	1555.4 K
Time	110.5 min
Mass loss	9.57 mg
Diameter of orifice	0.2965 cm

From this data, find the vapor pressure of scandium at 1555.4 K.

9. A thermalized sample of gas is one that has a distribution of molecular speeds given by the Maxwell-Boltzmann distribution. Considering a sample of N_2 at 25 ^cC what fraction of the molecules have a speed less than
   a. the most probably speed
   b. the average speed
   c. the RMS speed?

d. The RMS speed of helium atoms under the same conditions?

10. Assume that a person has a body surface area of 2.0 m^2. Calculate the number of collisions per second with the total surface area of this person at 25 ^{o}C and 1.00 atm. (For convenience, assume air is 100% N_2)

11. Two identical balloons are inflated to a volume of 1.00 L with a particular gas. After 12 hours, the volume of one balloon has decreased by 0.200 L. In the same time, the volume of the other balloon has decreased by 0.0603 L. If the lighter of the two gases was helium, what is the molar mass of the heavier gas?

12. Assuming it is a van der Waals gas, calculate the critical temperature, pressure and volume for CO_2.

13. Find an expression in terms of van der Waals coefficients for the Boyle temperature. (*Hint*: use the viral expansion of the van der Waals equation to find an expression for the second viral coefficient!)

14. Consider a gas that follows the equation of state

$$p = \frac{RT}{V_m - b}$$

Using a virial expansion, find an expression for the second virial coefficient.

15. Consider a gas that obeys the equation of state

$$p = \frac{nRT}{V - nb} - \frac{an}{V}$$

where a and b are non-zero constants. Does this gas exhibit critical behavior? If so, find expressions for p_c, V_c, and T_c in terms of the constants a, b, and R.

16. Consider a gas that obeys the equation of state

$$pV = nRT + anpT + nbp$$

a. Find an expression for the Boyle temperature in terms of the constant a, b, and R.
b. Does this gas exhibit critical behavior? If so, find expressions for p_c, V_c, and T_c in terms of the constants a, b, and R.