8

Gases

Answers to worked examples

W.E. 8.1   **Using Boyle's law (on p. 348 in *Chemistry*³)**

An inflated balloon has a volume of 1 dm³ at 1 atm pressure. At what pressure will it occupy a volume of 1.5 dm³?

Strategy

Use Boyle's law (Equation 8.1), which tells us that the pressure of a gas is inversely proportional to its volume

$$p \propto 1/V$$

Solution

The volume of the balloon increases from V_1 = 1 dm³ to V_2 = 1.5 dm³, which is a factor of 1.5. The pressure of gas within the balloon therefore decreases by a factor of 1.5. The initial pressure is 1 atm, so that, according to Boyle's law, the final pressure is

$$1 \text{ atm} \times \frac{V_1}{V_2} = 1 \text{ atm} \times \frac{1 \text{ dm}^3}{1.5 \text{ dm}^3} = 0.67 \text{ atm}$$

W.E. 8.2   **Using columns of liquid to measure pressures (on p. 351 in *Chemistry*³)**

The pressure at the top of a high mountain is 0.4 atm. Calculate the height of the mercury column in a barometer at the top of the mountain.

Strategy

Rearrange Equation 8.6 and use it to calculate the height of the column of mercury, remembering to use SI units throughout.

Solution

From Table 8.1 we know that

$$1 \text{ atm} = 101325 \text{ Pa}$$

and therefore that a pressure of 0.4 atm corresponds to

$$p = 0.4 \text{ atm} \times 101325 \text{ Pa atm}^{-1} = 40530 \text{ Pa}$$

Since 1 g = 1 × 10⁻³ kg, to convert from units of g to kg, we must multiply by a conversion factor of

$$\frac{1 \times 10^{-3} \text{kg}}{1 \text{ g}}$$

and because 1 cm³ = 1 × 10⁻⁶ m³, then to convert from cm³ to m³ we must multiply by

$$\frac{1 \times 10^{-6} \text{m}^3}{1 \text{ cm}^3}$$

The density of mercury is thus

$$\rho = 13.6 \text{ g cm}^{-3} \times \frac{1 \times 10^{-3} \text{kg}}{1 \text{ g}} \times \frac{1 \times 10^{-6} \text{m}^3}{1 \text{ cm}^3} = 13600 \text{ kg m}^{-3}$$

Rearranging Equation 8.6 and substituting the appropriate values for the density, pressure and acceleration due to gravity

$$h = \frac{p}{\rho g} = \frac{40530 \text{ Pa}}{13600 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2}} = \frac{40530 \text{ kg m}^{-1} \text{ s}^{-2}}{13600 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2}} 0.30 \text{ m}$$

W.E. 8.3 **Using the ideal gas equation to calculate the amount of gas (on p. 352 in *Chemistry³*)**

A gas cylinder contains 10 kg of oxygen at a pressure of 20 bar at 25°C. Calculate the volume of the cylinder, in m^3.

Strategy

Use the molar mass of oxygen to find the amount of substance, i.e. the number of moles, of gas present. Rearrange the ideal gas equation to give an expression for the volume and substitute the values, once converted to SI units, for the pressure, temperature and amount of substance.

Solution

The molar mass of oxygen, O_2, is

$$M = (16.02 \times 2)\text{g mol}^{-1} = 32.04 \times 10^{-3}\text{kg}$$

Thus, 10 kg of oxygen must correspond to an amount

$$n = m/M = 10\text{ kg}/32.04\text{ kg mol}^{-1} = 312\text{ mol}$$

The temperature should be expressed in units of kelvin, where

$$T/\text{K} = \theta/°\text{C} + 273.15 = 25 + 273.15 = 298$$

if the temperature on the Celsius scale is θ. The equation has been written in this way to ensure that the units are consistent. Table 8.1 gives the conversion factors for the various units of pressure, so that, because 1 bar ≡ 10^5 Pa,

$$p = 20\text{ bar} \times (10^5\text{Pa bar}^{-1}) = 20 \times 10^5\text{ Pa} = 20 \times 10^5\text{J m}^{-3}$$

The ideal gas equation, Equation 8.5, may be rearranged to give an expression for the volume of the cylinder, and the appropriate values, expressed in SI units, substituted

$$V = nRT/p$$
$$= 312\text{ mol} \times 8.3145\text{ J K}^{-1}\text{mol}^{-1} \times 298\text{ K}/20 \times 10^5\text{J m}^{-3}$$

$$= 0.387 \; m^3$$

It is helpful to express the units of pressure as $J \; m^{-3}$ rather than Pa, in order to help us to confirm that the units of the result are indeed the SI units of volume, m^3.

W.E. 8.4   **The effect of changing conditions (on p. 352 in *Chemistry*[3])**

A container fitted with a piston contains gas at 1 atm and 25°C. Calculate the pressure if the piston is moved so as to halve the pressure. (Assume the temperature is constant.)

Strategy

Use the ideal gas equation, written in the form of Equation 8.7, remembering to express the pressure in SI units.

Solution

We may simplify Equation 8.7 because we can assume that the temperature remains constant

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$p_1 V_1 = p_2 V_2$$

and rearrange it to give an expression for the final pressure

$$p_2 = p_1 V_1 / V_2$$

Because the volume halves,

$$V_1 / V_2 = 2$$

so that

$$p_2 = 2 p_1 = 2 \times 1 \; atm = 2 \; atm$$

Thus, halving the volume results in a doubling of the pressure, providing the amount of substance and temperature remain constant.

We may use the conversion factor in Table 8.1 to express this pressure in SI units

$$p_2 = 2 \text{ atm} \times 101325 \text{ Pa atm}^{-1} = 202650 \text{ Pa}$$

although because the initial pressure was quoted to only one significant figure, it is probably inappropriate to quote the pressure in pascals to this level of precision.

W.E. 8.5   The molar volume of an ideal gas (on p. 354 in *Chemistry*³)

Calculate the molar volume (in m^3) of an ideal gas at 1.00 atm and exactly 0°C.

<u>Strategy</u>

Use the ideal gas equation, Equation 8.5, remembering to express all values in SI units.

<u>Solution</u>

Use of the conversion factors in Table 8.1 shows that a pressure of 1.00 atm corresponds to

$$p = 1.00 \text{ atm} \times 101325 \text{ Pa atm}^{-1} = 101325 \text{ Pa} = 101325 \text{ J m}^{-3}$$

A temperature of exactly 0°C corresponds to 273.15 K. Rearranging Equation 8.5, gives

$$V = nRT/p$$

which, if n = 1 mol, becomes

$$
\begin{aligned}
V_m &= RT/p \\
&= 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 273.15 \text{ K} / 101325 \text{ J m}^{-3} \\
&= 22.4 \times 10^{-3}\text{m}^3
\end{aligned}
$$

Because 1 $dm^3 \equiv 10^{-3}$ m^3, this is equivalent to 22.4 dm^3.

W.E. 8.6   Partial pressures of gases (on p. 357 in *Chemistry³*)

Calculate the partial pressure of ethane in the gas at the same total pressure. Give your answer in atm.

<u>Strategy</u>

Use Dalton's law, Equation 8.10, to calculate the partial pressure of ethane from its mole fraction and the total pressure.

<u>Solution</u>

If the mole fraction of ethane is 6%, then 6 out of every 100 molecules in the gas are ethane. This is equivalent to a mole fraction of ethane of 0.06. We may use Dalton's law in the form of Equation 8.10 directly

$$p_{C_2H_6} = x_{C_2H_6} p_{total} = 0.06 \times 5 \text{ atm} = 0.3 \text{ atm}$$

W.E. 8.7   How fast do molecules move? (on p. 362 in *Chemistry³*)

Calculate the root mean square speeds of helium molecules and carbon dioxide molecules at 15°C.

<u>Strategy</u>

Use Equation 8.19, remembering to express the molar mass of the molecules in units of kilogramme and the temperature in units of kelvin.

<u>Solution</u>

The molar mass of helium is

$$M_{He} = 4.00 \text{ g mol}^{-1} = 4.00 \times 10^{-3} \text{ kg mol}^{-1}$$

and of carbon dioxide is

$$M_{CO_2} = [12.01 + (2 \times 16.00)] \text{ g mol}^{-1} = 44.01 \times 10^{-3} \text{ kg mol}^{-1}$$

A temperature of 15°C is equivalent to

$$T/\text{K} = \theta/°\text{C} + 273.15 = 25 + 273.15 = 298$$

Applying Equation 8.19 then gives the speeds of helium atoms and carbon dioxide molecules as

$$c_{\text{He}} = \left(\frac{3RT}{M_{\text{He}}}\right)^{1/2} = \left(\frac{3 \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{4.00 \times 10^{-3} \text{ kg mol}^{-1}}\right)^{1/2} = 1363 \text{ m s}^{-1}$$

and

$$c_{\text{CO}_2} = \left(\frac{3RT}{M_{\text{CO}_2}}\right)^{1/2} = \left(\frac{3 \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{44.01 \times 10^{-3} \text{ kg mol}^{-1}}\right)^{1/2} = 411 \text{ m s}^{-1}$$

W.E. 8.8   Relative rates of effusion (on p. 366 in *Chemistry*³)

Calculate the relative rates of effusion of oxygen, carbon dioxide, and nitrogen through a porous film at a fixed temperature.

<u>Strategy</u>

Use Equation 8.21, which shows how the relative rates of effusion depend upon the molar mass of the molecules.

<u>Solution</u>

We may apply Equation 8.21 directly, to express the rate of effusion of oxygen and carbon dioxide relative to that of nitrogen. The molar masses of the species are

$$M_{\text{O}_2} = (2 \times 16.00) \text{ g mol}^{-1} = 32.00 \text{ g mol}^{-1}$$

$$M_{\text{CO}_2} = [12.01 + (2 \times 16.00)] \text{ g mol}^{-1} = 44.01 \text{ g mol}^{-1}$$

$$M_{\text{N}_2} = (2 \times 14.00) \text{ g mol}^{-1} = 28.00 \text{ g mol}^{-1}$$

so that the relative rates of effusion are

$$\frac{\text{Rate of effusion of O}_2}{\text{Rate of effusion of N}_2} = \left(\frac{M_{\text{N}_2}}{M_{\text{O}_2}}\right)^{1/2} = \left(\frac{28.00 \text{ g mol}^{-1}}{32.00 \text{ g mol}^{-1}}\right)^{1/2} = 0.935$$

and

$$\frac{\text{Rate of effusion of CO}_2}{\text{Rate of effusion of N}_2} = \left(\frac{M_{N_2}}{M_{CO_2}}\right)^{1/2} = \left(\frac{28.00 \text{ g mol}^{-1}}{44.01 \text{ g mol}^{-1}}\right)^{1/2} = 0.798$$

W.E. 8.9   How often do molecules collide? (on p. 370 in *Chemistry*[3])

Calculate the collisional frequency in hydrogen gas at SATP and account for the difference from that for nitrogen. (For H_2, $\sigma = 0.27$ nm^2 and the mean speed, $\bar{c} = 1780$ m s^{-1} at 298 K.)

Strategy

Use Equation 8.22 directly.

Solution

If we note that

$$\sigma_{H_2} = 0.27 \text{ nm}^2 = 0.27 \times 10^{-18} \text{m}^2$$

because 1 nm^2 = 10^{-18} m^2, and that standard ambient temperature and pressure correspond to

$$p = 1 \text{ bar} = 10^5 \text{Pa} = 10^5 \text{J m}^{-3}$$

and

$$T = 298 \text{ K}$$

then we may use Equation 8.22 directly,

$$Z = \sqrt{2}N_A\bar{c}\sigma \times \frac{p}{RT}$$

$$= \sqrt{2} \times 6.022 \times 10^{23}\text{mol}^{-1} \times 1780 \text{ ms}^{-1} \times 0.27 \times 10^{-18}\text{m}^2$$

$$\times \frac{10^5 \text{ J m}^{-3}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}$$

$$= 1.65 \times 10^{10}\text{s}^{-1}$$

The collisional frequency is 2.4× greater than that for nitrogen under the same conditions because, even though the collision cross section of a hydrogen molecule is smaller, the hydrogen molecules are moving much faster because their mass is so small.

W.E.8.10   Molecular collisions at low pressures (on p. 371 in *Chemistry*³)

Calculate the pressure at which the mean free path of N_2 is 10 cm at 298 K.

Strategy

Rearrange Equation 8.23 to obtain an expression for the pressure of a gas in terms of the mean free path, collision cross section and temperature.

Solution

Rearranging Equation 8.23 gives

$$p = \frac{RT}{\sqrt{2}N_A\sigma\lambda}$$

The collision cross section of N_2 is given in Table 8.3 as σ = 0.43 nm², which is equivalent to 0.43×10^{-18} m². The mean free path is λ = 10 cm, which is equivalent to 0.1 m. Thus, substituting gives

$$p = \frac{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{\sqrt{2} \times 6.022 \times 10^{23}\text{mol}^{-1} \times 0.43 \times 10^{-18}\text{m}^2 \times 0.1 \text{ m}}$$
$$= 0.0677 \text{ J m}^{-3}$$
$$= 0.0677 \text{ Pa}$$

W.E. 8.11   Using the van der Waals equation (on p. 376 in *Chemistry*³)

Work out the percentage reduction in *V* due to the term *nb* and compare it to the percentage reduction in *p* due to the term *a(n/V)²*. Which correction factor makes the larger change?

Strategy

Work out the percentage reduction in V due to the term nb and compare it to the percentage reduction in p due to the $a(n/V)^2$ term.

Solution

The term in b increases the volume by a factor of

$$V/(V - nb) = 0.150 \text{ m}^3/(0.150 \text{ m}^3 - 1250 \text{ mol} \times 3.9 \times 10^{-5} \text{m}^3\text{mol}^{-1})$$
$$= 1.48$$

which is equivalent to a change of +48%. The term in a, however, reduces the pressure predicted from the ideal gas equation of 203 bar = 203 × 10⁵ Pa by a factor of

$$\frac{a(n\backslash V)^2}{p} = \frac{0.137 \text{ Pa m}^6\text{mol}^{-2} \times (1250 \text{ mol}/0.150 \text{ m}^3)^2}{203 \times 10^5 \text{ Pa}} = 0.469$$

which is equivalent to a change of –53%. The term in a, which attempts to accommodate the attractive interactions therefore has a larger effect than the term in b, which models the repulsive interactions. However, the magnitudes of the two effects are similar but act in opposing ways.

Answers to boxes

Box 8.1 **Car air bags (on p. 353 in *Chemistry³*)**

An air bag needs 60 dm^3 of gas to inflate it at 298 K. Calculate:

(a) the number of moles of N_2 gas at 298 K required to inflate the air bag to a pressure of 1 atm;

(b) the number of moles of NaN_3 required to produce this amount of gas;

(c) the mass of NaN_3 required.

Strategy

Apply the ideal gas equation, Equation 8.5, to calculate the amount of gas required. Use the stoichiometry of the reaction that produces the N_2 gas that expands the air bag to calculate the amount of NaN_3 required. Then use the molar mass of NaN_3 to determine the mass of solid required.

Solution

(a) In order to apply the ideal gas equation, we must first convert the value given for the pressure to SI units of pascals using the conversion factor listed in Table 8.1

$$p = 1.00 \text{ atm} \times 101325 \text{ Pa atm}^{-1} = 101325 \text{ Pa} = 101325 \text{ J m}^{-3}$$

We must also remember to convert the volume from units of dm^3 to m^3, where 1 $dm^3 \equiv 10^{-3}$ m^3, so that 60 $dm^3 \equiv 60 \times 10^{-3}$ m^3. Rearranging Equation 8.5, and substituting then gives

$$n_{N_2} = \frac{pV}{RT} = \frac{101325 \text{ J m}^{-3} \times 60 \times 10^{-3} \text{m}^3}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} = 2.454 \text{ mol}$$

(b) The stoichiometry of the chemical equation for the production of N_2 gas from solid NaN_3

$$2 \text{ NaN}_3(s) \rightarrow 2 \text{ Na}(s) + 3 \text{ N}_2(g)$$
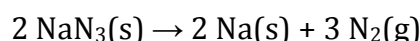
shows that every 1 mol of N_2 that is produced requires 1.5 mol of solid NaN_3. The amount of NaN_3 required is therefore

$$n_{\text{NaN}_3} = 1.5 \times 2.454 \text{ mol} = 9.815 \text{ mol}$$

(c) The molar mass of NaN_3 is

$$M = [22.99 + (3 \times 14.00)] \text{ g mol}^{-1}$$
$$= 64.99 \text{ g mol}^{-1} = 64.99 \times 10^{-3} \text{ kg mol}^{-1}$$

The mass of NaN_3 required is thus

$$m = n \times M = 9.815 \text{ mol} \times 65.00 \times 10^{-3} \text{kg mol}^{-1} = 0.637 \text{ kg}$$

Box 8.3   **Measuring the distribution of speeds in a gas (on p. 364 in *Chemistry³*)**

Why must the apparatus be contained in a sealed vessel at low pressure?

Solution

A sealed vessel ensures that it is only molecules from the sample gas that are reaching the detector, and a low pressure reduces the number of intermolecular collisions between gas molecules, which would otherwise affect their speed.

Box 8.4   **Enriching uranium: a practical application of effusion (on p. 367 in *Chemistry³*)**

Use Graham's law to calculate the relative rates of effusion of $^{239}UF_6$ and $^{235}UF_6$. (There is only one common isotope of fluorine, ^{19}F.)

Strategy

Use Equation 8.21, which is a statement of Graham's law that shows how the relative rate of effusion depends upon the molar mass.

Solution

The molar masses of the two different isotopomers of UF_6 are

$$M_{^{235}\text{UF}_6} = [235.00 + (6 \times 19.00)] \text{ g mol}^{-1} = 349.00 \text{ g mol}^{-1}$$

$$M_{^{239}UF_6} = [239.00 + (6 \times 19.00)] \text{ g mol}^{-1} = 353.00 \text{ g mol}^{-1}.$$

Applying Equation 8.21, the relative rates of effusion are then

$$\frac{\text{Rate of effusion of } ^{239}UF_6}{\text{Rate of effusion of } ^{235}UF_6} = \left(\frac{M_{^{235}UF_6}}{M_{^{239}UF_6}}\right)^{1/2} = \left(\frac{349.00 \text{ g mol}^{-1}}{353.00 \text{ g mol}^{-1}}\right)^{1/2} = 0.994$$

Answers to end-of-chapter questions

1.   3.036 g of a gas occupy a volume of 426 cm³ at 273 K and 1.00 atm pressure. Calculate the molar mass of the gas.

Strategy

Use the ideal gas equation to determine the amount of gas present. Calculate the molar mass from the amount and mass of gas.

Solution

In order to apply the ideal gas equation, all values should be expressed in SI units without prefixes. A volume of 426 cm³ is equivalent to 426 × 10⁻⁶ m³, whilst a pressure of 1.00 atm corresponds to a 101325 Pa ≡ 101325 J m⁻³. Using Equation 8.5,

$$n = \frac{pV}{RT} = \frac{101325 \text{ J m}^{-3} \times 426 \times 10^{-6} \text{m}^3}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 273 \text{ K}} = 0.0190 \text{ mol}$$

The molar mass is then given by

$$M = m/n = 3.036 \text{ g}/0.0190 \text{ mol} = 160 \text{ g mol}^{-1}$$

2.   At 27°C and 1.0 atm pressure, the density of a gaseous hydrocarbon is 1.22 g dm⁻³. What is the hydrocarbon?

Strategy

Combine the definition of density with the ideal gas equation to give an expression for the molar mass of the gas for a given temperature, pressure and density. Substitute the values using appropriate SI units.

Solution

Density is the ratio of mass to volume.

$$\rho = m/V$$

Since mass may be expressed in terms of the amount of substance present and the molar mass as

$$m = n \times M$$

then

$$\rho = n \times M/V$$

and so

$$M = \rho V/n$$

But we know from the ideal gas equation, Equation 8.5, that

$$V/n = RT/p$$

so we can eliminate the amount and volume of gas from our expression

$$M = \rho \times RT/p$$

Before we can use the expression, we must convert the values quoted to appropriate SI units without prefixes. A density of 1.22 g dm^{-3} corresponds to

$$\rho = 1.22 \text{ g dm}^{-3} \times 10^{-3}\text{kg g}^{-1} \times 10^3 \text{dm}^3\text{m}^{-3} = 1.22 \text{ kg m}^{-3}$$

whilst a pressure of 1.0 atm is equivalent to 101325 Pa $\equiv$ 101325 J m^{-3}. A temperature of 27°C corresponds to

$$T/K = \theta/°\text{C} + 273.15 = 27 + 273.15 = 300$$

Substituting gives

$$M = 1.22 \text{ kg m}^{-3} \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 300 \text{ K}/101325 \text{ J m}^{-3}$$
$$= 0.030 \text{ kg mol}^{-1} = 30.0 \text{ g mol}^{-1}$$

This suggests that the gas is ethane, which has a molar mass of

$$M = [(2 \times 12.01) + (6 \times 1.01)] \text{ g mol}^{-1} = 30.08 \text{ g mol}^{-1}$$

3.   A sample of gas has a volume of 346 cm^3 at 25°C when the pressure is 1.00 atm. What volume will it occupy if the conditions are changed to 35°C and 1.25 atm?

<u>Strategy</u>

Rearrange Equation 8.7, which shows how pressure, volume and temperature are related when the conditions change for a fixed amount of gas.

<u>Solution</u>

If, from Equation 8.7,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

then

$$V_2 = V_1 \times \frac{p_1}{p_2} \times \frac{T_2}{T_1}$$

Whilst it is often safest to convert all values to SI units, there is no need to change the pressures given from units of atmospheres to pascals, because the units will cancel anyway. It is, however, necessary to convert the temperatures to kelvins, so that

$$T_1/K = \theta/°C + 273.15 = 25 + 273.15 = 298$$
$$T_2/K = \theta/°C + 273.15 = 35 + 273.15 = 308$$

Thus,

$$V_2 = 346 \ cm^3 \times \frac{1.00 \ atm}{1.25 \ atm} \times \frac{308 \ K}{298 \ K} = 286 \ cm^3$$

4.   The air that we breathe is about 21% oxygen, by volume. Exhaled air contains about 14% oxygen. The absorption of oxygen within the lungs takes place in tiny spherical compartments called alveoli, which have a diameter of the order of 0.1 mm. Estimate the number of oxygen molecules absorbed in one breath in each of the alveoli. (Assume the body temperature is 37°C.)

Strategy

Use the ideal gas equation to determine the amount of air contained in each of the alveoli. Then calculate the amount of oxygen that is absorbed in each breath knowing the proportion of air that is oxygen.

Solution

The volume of each of the spherical alveoli is

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \times (0.1 \times 10^{-3}\,\text{m})^3 = 4.2 \times 10^{-12}\,\text{m}^3$$

The amount of gas contained in this volume at atmospheric pressure of 101325 Pa and a physiological temperature of 37°C ≡ 308 K may then be calculated from the ideal gas equation, Equation 8.5,

$$n = \frac{pV}{RT} = \frac{101325\ \text{Pa} \times 4.2 \times 10^{-12}\,\text{m}^3}{8.3145\ \text{J K}^{-1}\text{mol}^{-1} \times 308\ \text{K}} = 1.57 \times 10^{-5}\ \text{mol}$$

We know that the proportion of this gas that is absorbed is 21% – 14% = 7% and that every mole of gas contains Avogadro's number of molecules. The number of oxygen molecules absorbed in each breath must therefore be

$$N = 7\% \times N_A \times n$$
$$= 0.07 \times 6.022 \times 10^{23}\text{mol}^{-1} \times 1.57 \times 10^{-5}\text{mol}$$
$$= 6.6 \times 10^{17}$$

5.   Incandescent light bulbs, which have only recently gone out of use, were filled with an inert gas to prevent the filament from burning. Find the mass of argon needed to fill a 75 cm³ light bulb to a pressure of 1.05 atm at 25 °C.

<u>Strategy</u>

You can use the ideal gas equation to determine the amount of gas present in the light bulb and then use the atomic mass to find mass of Argon gas.

<u>Solution</u>

Using the ideal gas equation to find the number of moles needed,

$$pV = nRT$$

$$n = \frac{pV}{RT} = \frac{(1.05 \text{ atm} \times 1.013 \times 10^5 \text{ Pa atm}^{-1}) \times (75 \times 10^{-6} \text{ m}^3)}{8.314 \text{ JK}^{-1}\text{mol}^{-1} \times (25 + 273.15)\text{K}}$$

$$= 3.22 \times 10^{-3} \text{ mol}$$

Remember that 1 cm³ = 1 × 10⁻⁶ m⁻³ and 1 atm = 101325 Pa

A_R for argon is 39.95 g mol⁻¹ so

mass = 3.2 × 10⁻³ mol × 39.95 g mol⁻¹ = 0.128 g

6.   A vessel of volume 50.0 dm³ contains 2.50 moles of argon and 1.20 moles of nitrogen at 273.15 K.

(i) Calculate the partial pressure (in bar) of each gas.

(ii) Calculate the total pressure in bar.

(iii)   How many additional moles of nitrogen must be pumped into the vessel in order to raise the pressure to 5 bar?

<u>Strategy</u>

The partial pressure is the pressure that the gas would exert is alone in the container. You can find these using the ideal gas equation. The total pressure will be the sum of the partial pressures. One you know the

pressure of hydrogen that is needed then you can use the ideal gas equation
to find how many moles are needed.

Solution

For an ideal gas, the two gases act independently. Using the ideal gas
equation,

(i)   For argon

$$pV = nRT \quad \left(R = 8.314 \mathrm{JK^{-1}mol^{-1}}\right)$$

$$p = \frac{nRT}{V} = \frac{8.314 \mathrm{JK^{-1}mol^{-1}} \times 273.15 \mathrm{K} \times 2.50 \mathrm{mol}}{(50.0 \times 10^{-3} \mathrm{m^3})} = 1.135 \times 10^5 \mathrm{Pa} = 1.135 \mathrm{bar}$$

For nitrogen

$$p = \frac{nRT}{V} = \frac{8.314 \mathrm{JK^{-1}mol^{-1}} \times 273.15 \mathrm{K} \times 1.20 \mathrm{mol}}{(50.0 \times 10^{-3} \mathrm{m^3})} = 54500 \times 10^4 \mathrm{Pa} = 0.545 \mathrm{bar}$$

(ii)   Total pressure = p(argon) + p(nitrogen) = 1.14 bar + 0.55 bar =
1.69 bar

(iii)   From the ideal gas equation, we can find out how many moles are
needed to generate a pressure of 5 bar and subtract the 3.70 mol of gas that
we already have

$$pV = nRT$$

$$n = \frac{pV}{RT} = \frac{(5.0 \times 10^5 \mathrm{Pa}) \times (50.0 \times 10^{-3} \mathrm{m^3})}{8.314 \mathrm{JK^{-1}mol^{-1}} \times 273.15 \mathrm{K}} \quad \left(1 \mathrm{Pa} = 1 \mathrm{Jm^{-3}}\right)$$

$$= 11.0 \text{ mol}$$

Hence we need (11.0 – 3.70) = 7.3 mol of nitrogen

7.   A mixture of methane and ethane is contained in a 500 cm³ container at
298.15 K. The pressure is 1.25 bar and the mass of gas is 0.530 g. Find the
mass of methane in the mixture.

Strategy

You can use the ideal gas equation to determine the amount of gas present in the container. Knowing the molar masses of the two gases, the mass of each can be found by proportion.

Solution

Using the ideal gas equation can be used to find the number of moles in the container

$$pV = nRT$$

$$n = \frac{pV}{RT} = \frac{(1.25 \text{ bar} \times 1 \times 10^5 \text{Pa bar}^{-1}) \times (500 \times 10^{-6} \text{m}^3)}{8.314 \text{JK}^{-1}\text{mol}^{-1} \times (25 + 273.15)\text{K}}$$

$$= 0.0252 \text{mol}$$

Hence, $n_{CH_4} + n_{C_2H_6} = 0.0252$ mol

M_R for methane is methane is 16.04 g mol⁻¹ and for ethane is 30.07 g mol⁻¹

so

(16.04 g mol⁻¹ × n_{CH_4} mol) + (30.07 g mol⁻¹ × (0.0252 - n_{CH_4}) mol) = 0.530 g

From which n_{CH_4} = 0.016 mol ≡ 0.016 × 16.04 g mol⁻¹ = 0.260 g

8.   Two bulbs A and B, with volumes V_A = 1 dm³ and V_B = 5 dm³, are connected via a tap. The volume of the connecting tubing is negligible.
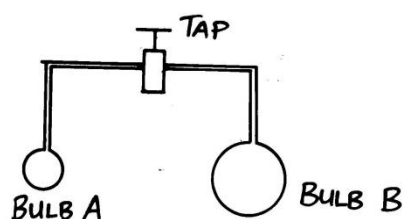
Bulb A contains gas at a pressure of 6 bar while bulb B contains a vacuum.

(i) The temperature of the whole apparatus is maintained at 298 K. If the tap is opened, calculate the pressure of gas in the system after opening the tap.

(ii)   The tap is closed and bulb B is then immersed in an oil bath at a temperature of 423 K while the temperature of bulb A is maintained at 298 K. Calculate the resulting pressures in each bulb.

(iii)   The tap is opened again. What is the final pressure and the number of moles of gas in each bulb?

Strategy

(i)   You can use Boyle's law since the temperature and number of moles are constant. (ii) Now we have constant volume but changing temperature so can use Charles' Law for the hot bulb. (iii) The ideal gas equation can be used to find the total amount of gas present. Knowing the molar masses of the two gases, the mass of each can be found by proportion.

Solution

(i) Applying Boyle's law since the temperature and number of moles are constant

$$p_1 V_1 = p_2 V_2$$
$$\left(6 \text{ bar}\right) \times \left(1 \text{ dm}^3\right) = \left(p_2 \ / \text{ bar}\right) \times \left((1+5) \text{ dm}^3\right)$$
$$p_2 = 1 \text{ bar}$$

(ii)   Since bulb A remains sealed (constant volume) at the same temperature the pressure is unchanged.

For bulb B, the pressure increases due to the higher temperature

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\frac{1\text{ bar}}{298\text{K}} = \frac{p_2 / \text{bar}}{423\text{ K}}$$

$$p_2 = 1.42 \text{ bar}$$

(iii)   Now, when the tap is opened, the pressure will equalise through the system. Say the number of moles in each bulb are n_A and n_B in bulbs A and B respectively. We can work out the number of moles of gas in the system from the data in (i).

$$pV = nRT$$

$$n = \frac{pV}{RT} = \frac{(6\times10^5\,\text{Pa})\times(1\times10^{-3}\,\text{m}^3)}{8.314\text{JK}^{-1}\text{mol}^{-1}\times298\text{K}}$$

$$= 0.24 \text{ mol}$$

So $n_A + n_B = 0.24$ mol   or $n_B = (0.24 - n_A)$ mol

If the tap is opened, the pressure in both bulbs must be equal so $p_A = p_B$. From the ideal gas equation,

$$p_A = p_B$$

$$p = \frac{nRT}{V} \quad \text{so} \quad \frac{n_A RT_A}{V_A} = \frac{n_B RT_B}{V_B} = \frac{(0.24 - n_A)RT_B}{V_B}$$

$$\frac{n_A \times 8.314\text{JK}^{-1}\text{mol}^{-1}\times298\text{K}}{(1\times10^{-3}\,\text{m}^3)} = \frac{(0.24 - n_A)\times8.314\text{JK}^{-1}\text{mol}^{-1}\times423\text{K}}{(5\times10^{-3}\,\text{m}^3)}$$

$$2.5\times10^6\,\text{Jm}^{-3}\times n_A = (0.24 - n_A)\times7.0\times10^5\,\text{Jm}^{-3}$$

$$2.5\times10^6\,\text{Jm}^{-3}\times n_A = (1.69\times10^5\,\text{Jm}^{-3}) - (7.0\times10^5\,\text{Jm}^{-3}\times n_A)$$

$$n_A = 0.05\text{mol}$$

$$n_B = (0.24 - n_A)\text{mol} = (0.24\text{mol} - 0.05\text{mol}) = 0.19\text{mol}$$

We can find the pressure from the values in either bulb (since the pressures must be the same)

$$p_A = p_B = \frac{n_A RT_A}{V_A} = \frac{0.05\text{mol} \times 8.314\text{JK}^{-1}\text{mol}^{-1} \times 298\text{K}}{(1 \times 10^{-3}\text{m}^3)}$$
$$= 1.2 \times 10^5\,\text{Pa} = 1.2\,\text{bar}$$

9. Divers "bends" are caused by the formation of bubbles of nitrogen in blood as the solubility reduces when the diver returns to the surface. The solubility of nitrogen in water at 1 atm pressure is approximately 13.0 mg kg^{-1} at body temperature of 37 °C and increases linearly with pressure. In water, the pressure increases at the rate of 1 atmosphere per 10 m depth.

Estimate the volume of gas that comes out of solution when a diver who has 4.5 kg of blood rapidly ascends from a depth of 50 m of water to the surface. Assume the solubility of nitrogen in blood is the same as in water.

Strategy

From the data, you can calculate the total amount of nitrogen dissolved in the diver's blood at 50 m depth. Comparing this with the amount that dissolves at the surface gives the amount that comes out of the blood which can be converted to a volume using the ideal gas equation.

Solution

50 m depth would correspond to a pressure of 5 atm = 5 × 101325 Pa

= 5.066 ×10^5 Pa.

For 4.5 kg of blood, the total amount dissolved at 1 atm pressure

= 4.5 kg × 13.0 mg kg^{-1} = 58.5 mg

The solubility at 50 m depth or 5 atm pressure would be approx. five times greater than at 1 atm so amount of N₂ dissolved = 5 × 58.5 mg = 292.5 mg kg⁻¹.

When the diver ascends, the amount of N₂ coming out of solution is 292.5 mg − 58.5 mg = 234.0 mg.

To find the number of moles, divide by the relative molar mass

234.0 mg = (234.0 × 10⁻³ g) ÷ 32 g mol⁻¹ = 7.31 × 10⁻³ mol

This can be converted to a gas volume using the ideal gas equation

$$pV = nRT$$
$$V = \frac{nRT}{p} = \frac{(7.31 \times 10^{-3}\,\text{mol}) \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times (37 + 273.15)\text{K}}{(1.013 \times 10^{5}\,\text{Pa})}$$
$$= 1.86 \times 10^{-4}\,\text{m}^3$$
$$= 186\ \text{cm}^3$$

10. A mixture of nitrogen and carbon dioxide contains 38.4% N₂ by mass. What is the mole fraction of nitrogen in the mixture? If the total pressure is 1.2 atm, what is the partial pressure of each gas in Pa?

Strategy

Calculate the molar masses of nitrogen and carbon dioxide and hence determine the mole fraction of each in the gas. Use Dalton's law to deduce the partial pressures.

Solution

The proportion of N₂ by mass is

$$\frac{m_{N_2}}{m_{total}} = \frac{m_{N_2}}{m_{N_2} + m_{CO_2}}$$

$$= \frac{n_{N_2} M_{N_2}}{n_{N_2} M_{N_2} + n_{CO_2} M_{CO_2}}$$

$$= \frac{1}{1 + (n_{CO_2}/n_{N_2})(M_{CO_2}/M_{N_2})} = 0.384$$

Rearranging,

$$1 + (n_{CO_2}/n_{N_2})(M_{CO_2}/M_{N_2}) = 1/0.384 = 2.60$$

Hence,

$$(n_{CO_2}/n_{N_2})(M_{CO_2}/M_{N_2}) = 2.60 - 1 = 1.60$$

and

$$(n_{CO_2}/n_{N_2}) = 1.60/(M_{CO_2}/M_{N_2})$$

But

$$M_{CO_2} = [12.01 + (2 \times 16.00)] \text{g mol}^{-1} = 44.01 \text{ g mol}^{-1}$$
$$M_{N_2} = (2 \times 14.00) \text{g mol}^{-1} = 28.00 \text{ g mol}^{-1}$$

so that

$$(n_{CO_2}/n_{N_2}) = 1.60/(44.01 \text{ g mol}^{-1}/28.00 \text{ g mol}^{-1}) = 1.02$$

The mole fraction of nitrogen is

$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{CO_2}} = \frac{1}{1 + (n_{CO_2}/n_{N_2})}$$

so that substituting for the ration of the amounts of the two species gives

$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{CO_2}} = \frac{1}{1 + (n_{CO_2}/n_{N_2})} = \frac{1}{1 + 1.02} = 0.495$$

The mole fraction of carbon dioxide is

We should then use Equation 8.10,

$$p_{N_2} = x_{N_2}p = 0.495 \times 1.2 \text{ atm} = 0.59 \text{ atm}$$

11. How much faster is the rate of effusion of helium than carbon dioxide, when both gases are at the same temperature?

Strategy

Use Equation 8.21, which shows how the relative rates of effusion depend upon the molar mass of the molecules.

Solution

The molar masses of carbon dioxide and helium are

$$M_{CO_2} = [12.01 + (2 \times 16.00)]\text{g mol}^{-1} = 44.01 \text{ g mol}^{-1}$$
$$M_{He} = 4.00 \text{ g mol}^{-1}$$

Using Equation 8.21,

$$\frac{\text{Rate of effusion of He}}{\text{Rate of effusion of CO}_2} = \left(\frac{M_{CO_2}}{M_{He}}\right)^{1/2} = \left(\frac{44.01 \text{ g mol}^{-1}}{4.00 \text{ g mol}^{-1}}\right)^{1/2} = 3.31$$

Thus, helium effuses at a rate that is over three times faster than carbon dioxide.

12. Two identical flasks contain nitrogen gas at the same pressure. Each has an identical pin-hole. One flask is kept at 25°C while the other is heated to 125°C. Calculate the relative rates of effusion of nitrogen from the two flasks.

Strategy

Consider how temperature affects the rate at which molecules might escape through the pin-hole.

Solution

The rate at which molecules collide with the pin-hole depends upon their speed. The root mean square speed is given by equation 8.19,

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

Thus the rate at which the molecules escape is proportional to the square root of temperature

$$Z \propto T^{1/2}$$

Effusion from the hotter flask, which is at a temperature T_2, therefore occurs at a rate that is $(T_2/T_1)^{1/2}$ times faster than from the colder falsk, which is at T_1. We must remember, however, that in using this expression, the temperatures should be expressed in kelvin, where

$$T_1/K = \theta/°C + 273.15 = 25 + 273.15 = 298$$
$$T_2/K = \theta/°C + 273.15 = 125 + 273.15 = 398$$

Thus

$$\left(\frac{T_2}{T_1}\right)^{1/2} = \left(\frac{398\ K}{298\ K}\right)^{1/2} = 1.16$$

Effusion therefore occurs from the hotter flask at a rate that is 1.16 times faster than from the colder flask.

13. An evacuated flask is filled with dry air and weighed. The same flask is filled at the same temperature to the same pressure with moist air on a humid day. Will it weigh more, less, or the same? Explain your answer.

Strategy

Apply Dalton's law and consider the effect of changing the composition of the gas on the total mass.

Solution

The mass of a mixture of gases is given by the sum of the masses of the components, which depend upon the amount and molar mass of each species. Thus

$$m = n_1 M_1 + n_2 M_2 + \ ...$$

which we may write more succinctly as

$$m = \sum_i n_i M_i$$

We may express this in terms of the mole fraction of each component,

$$m = n_{total} \sum_i x_i M_i$$

because the amount of each component is just

$$n_i = x_i n_{total}$$

The total amount of substance is the same in both the dry and moist air samples. The ideal gas equation, Equation 8.5, shows that if the pressure, volume and temperature of two samples are the same, then they must contain the same amount of substance

$$n = \frac{pV}{RT}$$

Dry air is made up of 78% nitrogen, N_2, and 21% oxygen, O_2, along with some other minor constituents. Thus

$$x_{N_2} = 0.78 \text{ and } x_{O_2} = 0.21$$

Moist air contains water, and so the mole fractions of nitrogen and oxygen are lower. The molar mass of water is less than that of both nitrogen and oxygen. Moist air therefore contains a proportion of lighter molecules than dry air. As a result, the total mass of moist air is lower than that of dry air.

14.   The equation for the complete combustion of methane is

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$
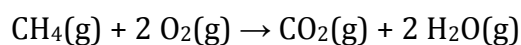
What volume of oxygen at SATP is needed to react exactly with 10 g of methane?

<u>Strategy</u>

Calculate the amount of methane that corresponds to 10 g. Then consider the stoichiometry of the equation to deduce the amount of oxygen that is necessary to react completely. Use the idea gas equation, Equation 8.5, to determine the volume of this amount of gas at SATP.

<u>Solution</u>

The molar mass of methane, CH_4, is

$$M_{CH_4} = [12.01 + (4 \times 1.01)]\text{g mol}^{-1} = 16.05\ \text{g mol}^{-1}$$

Thus, 10 g corresponds to an amount

$$n_{CH_4} = m_{CH_4}/M_{CH_4} = 10\ \text{g}/16.05\ \text{g mol}^{-1} = 0.6231\ \text{mol}$$

The chemical equation shows that the amount of oxygen required for combustion is double the amount of methane, so that

$$n_{O_2} = 2 \times 0.6231\ \text{mol} = 1.246\ \text{mol}$$

Standard ambient temperature and pressure are 298 K and 101325 Pa, so applying the ideal gas equation, 8.5, gives

$$V = \frac{n_{O_2}RT}{p} = \frac{1.246\ \text{mol} \times 8.3145\ \text{J K}^{-1}\text{mol}^{-1} \times 298\ \text{K}}{101325\ \text{J m}^{-3}} = 0.0305\ \text{m}^3$$

which, because $1\ \text{dm}^3 \equiv 10^{-3}\ \text{m}^3$, is equivalent to 30.5 dm^3.

15.   The average (root mean square) speed of an oxygen molecule is 425 m s^{-1} at 0°C. Calculate the average speed at 100°C.

Strategy

Use Equation 8.19, which expresses how the average speed of the molecules in a gas varies with temperature.

Solution

We know from Equation 8.19 that

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

and so

$$c \propto T^{1/2}$$

If we know the average speed c_1, at a temperature T_1, then we may calculate the average speed c_2 at another temperature T_2, since

$$c_2 = c_1 \times (T_2/T_1)^{1/2}$$

The temperatures should be expressed in kelvin, so that for this example

$$T_1/K = \theta/°C + 273.15 = 0 + 273.15 = 273$$
$$T_2/K = \theta/°C + 273.15 = 100 + 273.15 = 373$$

and therefore

$$c_2 = 425 \text{ m s}^{-1} \times (373 \text{ K}/273 \text{ K})^{1/2} = 497 \text{ m s}^{-1}$$

16. A balloon that is porous to both gases is filled with nitrogen and placed in a box containing helium. What will happen?

Strategy

Consider the effects of both effusion and diffusion on the gases.

Solution

Effusion is the escape of molecules through a porous membrane. If the balloon is porous, the helium and the nitrogen molecules will effuse through

the membrane until the composition and pressure both inside the balloon and outside the balloon are equal. The rate of effusion is inversely proportional to the square root of the molar mass of the molecules. Heavy molecules therefore effuse more slowly than light molecules. The probability of an individual helium atom effusing into the balloon is therefore greater than the probability of an individual nitrogen molecule effusing in the opposite direction. The absolute rate of effusion of the two species will, however, depend upon the relative amounts of the two gases present.

The driving force for this process is thermodynamic because entropy favours the mixing of ideal gases. Eventually, the composition of the balloon and the box become equal. Even at equilibrium, however, molecules still effuse across the membrane. The helium molecules effuse more quickly than nitrogen molecules, but the number escaping in each direction is the same. The system is therefore at a dynamic, rather than static equilibrium.

17.   The atmospheric pressure and temperature both fall as the altitude increases. The total pressure at a height of 20 km is about 5% of that of the Earth's surface (that is, at sea level) and the temperature is about –55°C. Estimate the collision frequency and the mean free path of oxygen molecules under these conditions. (for oxygen at this temperature, the mean speed, $\bar{c} = 380$ m s^{-1}.)

Strategy

Use Equation 8.22 to calculate the collisional frequency.

Solution

The collisional frequency is given by Equation 8.22

$$Z = \sqrt{2} N_A \bar{c} \sigma \times \frac{p}{RT}$$

The collision cross section for oxygen is given in Table 8.3 as

$$\sigma = 0.40 \text{ nm}^2 = 0.40 \times 10^{-18} \text{m}^2$$

The ambient pressure at the Earth's surface is 101325 Pa, so that at an altitude of 20 km,

$$p = 0.05 \times 101325 \text{ Pa} = 5067 \text{ Pa} = 5067 \text{ J m}^{-3}$$

A temperature of –55°C is equivalent to

$$T/K = \theta/°C + 273.15 = -55 + 273.15 = 218$$

Substituting into Equation 8.22 then gives

$$Z = \sqrt{2}N_A \bar{c}\sigma \times \frac{p}{RT}$$

$$= \sqrt{2} \times 6.022 \times 10^{23} \text{mol}^{-1} \times 380 \text{ ms}^{-1} \times 0.40 \times 10^{-18} \text{m}^2$$

$$\times \frac{5067 \text{ J m}^{-3}}{8.3145 \text{ J K}^{-1} \text{mol}^{-1} \times 218 \text{ K}}$$

$$= 3.6 \times 10^8 \text{s}^{-1}$$

The mean free path is related to the collisional frequency and mean speed through Equation 8.23. Thus

$$\lambda = \bar{c}/Z = 380 \text{ m s}^{-1}/3.6 \times 10^8 \text{s}^{-1} = 1.1 \times 10^{-6} \text{ m}$$

18. Argon has a collision cross-section of 0.36 nm². At 0°C, what pressure is needed so that its mean free path becomes equal to the diameter of the molecules?

Strategy

Calculate the diameter of an argon atom from the cross-sectional area. Rearrange equation 8.23, using the diameter of the atoms as the value for the mean free path.

Solution

The collision cross section may be considered as the cross-sectional area of the atoms and is therefore related to diameter of the atoms through

$$\sigma = \pi d^2$$

Thus

$$d = \sqrt{\sigma / \pi}$$
$$= \sqrt{0.36 \text{ nm}^2 / \pi}$$
$$= \sqrt{0.36 \times 10^{-18} \text{m}^2 / \pi}$$
$$= 3.4 \times 10^{-10} \text{m}$$

Using a rearranged version of Equation 8.21 gives

$$p = \frac{RT}{\sqrt{2} N_A \sigma \lambda} = \frac{RT}{\sqrt{2} N_A \sigma d}$$
$$= \frac{8.3145 \text{ J K}^{-1} \text{mol}^{-1} \times 273 \text{ K}}{\sqrt{2} \times 6.022 \times 10^{23} \text{mol}^{-1} \times 0.36 \times 10^{-18} \text{m}^2 \times 3.4 \times 10^{-10} \text{m}}$$
$$= 22 \times 10^6 \text{ J m}^{-3} = 22 \text{ MPa}$$

which is equivalent to

$$p = 22 \times 10^6 \text{Pa} / 101325 \text{ Pa atm}^{-1} = 220 \text{ atm}$$

19. Suggest why there is little hydrogen or helium in the atmosphere around the Earth or Mars, although these gases form the major constituent of the atmosphere of huge planets such as Jupiter or Saturn.

Strategy

Consider the effect of gravity on the composition of the atmospheres of the planets.

Solution

The atmospheres of the planets arise because gravitational attraction

prevents the gases from escaping. Atmospheric pressure decreases with altitude because the attractive force becomes weaker with the distance from the surface of the planet.

The attractive force depends upon the mass of the molecules and the mass of the planet. Light molecules such as hydrogen or atoms such as helium are attracted only weakly by small plants such as the Earth or Mars. For heavier planets, the gravitational attraction is much stronger, meaning that light molecules and atoms remain trapped.

20. The atmosphere of a spacecraft with volume 27 m^3 consists of 80% helium and 20% oxygen by volume. The gases continually escape by effusion through small leaks in the walls. The leak amounts to 1000 Pa per day. The temperature inside the spacecraft is 20 °C. What masses of helium and oxygen must be carried to replace the gas that leaks during a 10 day mission?

<u>Strategy</u>

You can find the total pressure of gas that will be lost as well as the relative rates of effusion of the two gases. Then, you can use the ideal gas equation to calculate the number of moles lost.

<u>Solution</u>

The total rate of loss of the gases is 1000 Pa day^{-1} so for a 10 day mission, 10000 Pa could be lost. The relative amounts of He and O$_2$ can be calculated from the relative rates of effusion of the two gases. The relative rates of effusion are inversely proportional to the relative molar/atomic masses.

$$\frac{\text{Rate of effusion of He}}{\text{Rate of effusion of O}_2} = \left(\frac{M_{O_2}}{M_{He}}\right)^{1/2} = \left(\frac{32.0 \text{ g mol}^{-1}}{4.0 \text{ g mol}^{-1}}\right)^{1/2} = 8^{\frac{1}{2}} = 2.83$$

Hence for each 1 mol of O$_2$ that escapes, 2.83 mol of He will escape. The pressures of each gas that escape are therefore 2611 Pa of O$_2$ and 7389 Pa of

He respectively. Using the ideal gas equation to calculate the number of moles lost:

$$pV = nRT \qquad \text{so} \quad n = \frac{pV}{RT}$$

For O_2 $\quad n = \dfrac{pV}{RT} = \dfrac{2611 \text{ Pa} \times 27 \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 293\text{K}} = 28.9 \text{ mol}$

Multiplying by the relative molar mass of 32 g mol^{-1}, 28.9 mol = 926 g

For He $\quad n = \dfrac{pV}{RT} = \dfrac{7389 \text{ Pa} \times 27 \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 293\text{K}} = 81.9 \text{ mol}$

Multiplying by the relative molar mass of 4 g mol^{-1}, 81.9 mol = 328 g

Total mass of gas needed = 1254 g.

21. (a) State (i) the ideal gas equation (ii) the Van der Waal's equation of state. Explain how the additional terms in the Van der Waal's equation account for the actual behaviour of real gases.

(b) Without performing any numerical calculations, show that, in the limit of high temperatures and low pressures, the van der Waals and ideal gas equations are identical.

Strategy

Quote equations 8.5 and 8.25, and compare the additional terms. Consider the effect on the volume of the gas of high temperatures and pressures. Simplify the Van der Waals equation in this limit.

Solution

(a) (i)

$$pV = nRT$$

(ii)

$$\left[p + a\left(\frac{n}{V}\right)^2\right](V - nb)$$

The $a(n/V)^2$ term accounts for the intermolecular attractions in real gases, which reduce the force with which molecules can collide with the wall of the container. This term makes up for the slightly reduced pressure. The nb term corrects for the fact that molecules in a real gas do have a volume, and so there is less volume in which molecules can actually move.

(b) High temperatures and low pressures result in relatively high volumes. We can see this most easily by rearranging the ideal gas equation, Equation 8.5,

$$V = nRT/p$$

so that

$$V \propto T/p$$

The van der Waals equation, Equation 8.26

$$\left(p + a(n^2/V^2)\right)(V - nb) = nRT$$

 includes two additional terms in the volume. In the limit of high volume, the additional term in the first bracket becomes negligible, because as $V \rightarrow \infty$, $1/V^2 \rightarrow \infty$. In the same way, the additional term in the second bracket also becomes insignificant, because as V becomes so much bigger than nb, $(V - nb) \rightarrow V$.

22. Dry air with the following composition is used to fill a SCUBA cylinder for a dive.

Gas	Composition of dry air by volume
N_2	78%
O_2	21%

Ar	1%

(a) At 10 m depth, a diver experiences an external pressure of 2 atm. Write an expression for the total pressure of the air in terms of the partial pressures of N_2, O_2 and Ar.

(b) What is the molar percentage of oxygen in the air inhaled at 2 atm?

(c) What is the partial pressure of O_2 in air inhaled at: (i) 1 atm; (ii) 2 atm.

(d) How does the number of molecules of O_2 inhaled per breath at 10 m depth compare with the number inhaled per breath at sea level? Suggest why some deep-sea divers dive with a gas mixture containing 10% oxygen.

<u>Strategy</u>

Consider how partial pressure depends upon the total pressure.

<u>Solution</u>

(a) Using Dalton's law, the total pressure of the air is given by the sum of the partial pressures of the individual components

$$p = p_{N_2} + p_{O_2} + p_{Ar}$$

(b) The composition of air given may be rewritten in terms of mole fractions as

$$x_{N_2} = 0.78, \quad x_{O_2} = 0.21, \quad x_{Ar} = 0.01$$

The molar percentage of each component absorbed is independent of the total pressure, so that at 2 atm, the air still contains 21% oxygen.

(c) The partial pressure of oxygen is

$$p_{O_2} = x_{O_2}p$$

so that at the surface, when the total pressure is $p = 1$ atm,

$$p_{O_2} = 0.21 \times 1 \text{ atm} = 0.21 \text{ atm}$$

and when the total pressure is $p = 2$ atm,

$$p_{O_2} = 0.21 \times 2 \text{ atm} = 0.42 \text{ atm}$$

(d) The calculations show that the partial pressure of oxygen is greater underwater than at the surface, because of the increase in the total pressure. Filling the SCUBA tank with air with a lower proportion of oxygen would help to correct for this change.

23. A 10 dm³ SCUBA cylinder is filled with air to a pressure of 300 atm at a temperature of 20°C (293 K).

(a) Calculate the amount, in moles of gas in the cylinder, assuming the air behaves as an ideal gas.

(b) When the diver jumps into cold water at 278 K, the pressure gauge shows an alarming drop in pressure. Explain the reason why and calculate the new pressure inside the cylinder.

(c) In fact, the compressed gases do not behave as ideal gases. Explain why. Use the van der Waals equation (for air, a = 0.137 Pa m⁶ mol⁻² and b = 3.7 × 10⁻⁵ m³ mol⁻¹) to show that the amount of air in the cylinder is 115 mol. In view of your answer to part (a) above, what are the implications of this for divers?

Strategy

Use the ideal gas equation, Equation 8.5, to determine the amount of gas in the cylinder, remembering to convert all values to SI units. Repeat the calculation using the van der Waals equation, Equation 8.25.

Solution

(a) We may rearrange the ideal gas equation, Equation 8.5, to give an expression for the amount of gas

$$n = \frac{pV}{RT}$$

We may use the conversion factor given in Table 8.1 to convert the pressure to SI units, so that

$$p = 300 \text{ atm} \times 101325 \text{ Pa atm}^{-1} = 30.4 \times 10^6 \text{ Pa} = 30.4 \text{ MPa}$$

A volume of 10 dm³ is equivalent to

$$V = 10 \times 10^{-3}\,\text{m}^3 = 10^{-2}\,\text{m}^3$$

so that

$$n = \frac{30.4 \times 10^6 \text{ Pa} \times 10^{-2}\,\text{m}^3}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 293 \text{ K}} = 125 \text{ mol}$$

(b) The sudden drop in temperature causes a decrease in the pressure of the gas because the molecules have less thermal energy. We may apply the ideal gas equation, Equation 8.5, to determine the new pressure. If

$$pV = nRT$$

so that

$$p \propto 1/T$$

then for constant amount and volume,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

then

$$p_2 = p_1 \times \frac{T_2}{T_1} = 300 \text{ atm} \times \frac{278 \text{ K}}{293 \text{ K}} = 285 \text{ atm}$$

which is equivalent to 28.8 MPa.

(c) Compressed gases do not behave in an ideal way because, when the molecules are close together, the magnitude of the attractive interactions becomes significant and the volume taken up by the finite size of the molecules becomes an appreciable proportion of the total volume.
The van der Waals equation, Equation 8.25, is actually a cubic equation in *n*. It is thus not possible to rearrange this equation to give an expression for *n*. Instead, it is simpler to assume the revised value for the amount given, *n* = 115 mol, and show that this is consistent with a pressure of 300 atm.

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

$$= \frac{115 \text{ mol} \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 293 \text{ K}}{10^{-2}\text{m}^3 - 115 \text{ mol} \times 3.7 \times 10^{-5}\text{m}^3\text{mol}^{-1}} - 0.137 \text{ Pa m}^6\text{mol}^{-1}\left(\frac{115 \text{ mol}}{10^{-2}\text{m}^3}\right)^2$$

$$= 30.4 \times 10^6 \text{Pa}$$

which we already know is equivalent to a pressure of 300 atm. The cylinder therefore contains less air than might be expected from a simple calculation based on the ideal gas equation.

24. The space between the stars in the universe contains a mixture of gases at very low pressure as well as some dust. The gas is mainly hydrogen with a little helium, but many other molecules have also been detected in tiny amounts (see Chapter 4, p.167). For a helium atom, the collisional cross section σ = 0.21 nm². The conditions in interstellar space are around T = 10 K and p = 1 × 10⁻¹⁸ atm.

(a) Calculate the mean free path, λ, of helium atoms at SATP.

(b) Estimate the value of λ for helium atoms in interstellar space. (For the atoms at 10 K, c = 230 m s⁻¹.)

<u>Strategy</u>

Use Equation 8.23 to determine the mean free path under the conditions given. Calculate the time between collisions as the reciprocal of the collisional frequency.

<u>Solution</u>

A collision cross section of 0.21 nm² is equivalent to 0.21 × 10⁻¹⁸ nm², because 1 nm² ≡ 10⁻¹⁸ m². The mean free path of the molecules within a gas at standard ambient temperature and pressure may therefore be calculated using Equation 8.23

$$\lambda = \frac{RT}{\sqrt{2}N_A\sigma p}$$

$$= \frac{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{\sqrt{2} \times 6.022 \times 10^{23}\text{mol}^{-1} \times 0.21 \times 10^{-18} \text{ nm}^2 \times 101325 \text{ J m}^{-3}}$$

$$= 137 \times 10^{-9} \text{m}$$
$$= 137 \text{ nm}$$

(b) In order to calculate the mean free path under the conditions in the interstellar medium, it is not necessary to repeat the entire calculation . We know that

$$\lambda \propto T/p$$

so, if, in the interstellar medium, the pressure is 10^{-18} atm $/1$ atm $= 10^{-18}$ times less, and the temperature 10 K / 298 K $\approx$ 0.034 times less, then the mean free path may be estimated as

$$\lambda = 137 \times 10^{-9} \text{ m} \times (0.034/ 10^{-18}) = 4.7 \times 10^{9} \text{m}$$

(c) The time between collisions is the reciprocal of the collisional frequency

$$t = 1/Z$$

Mean free path and collisional frequency are related through the mean speed

$$\lambda = \bar{c}/Z$$

Combining these two equations, and substituting gives

$$t = \lambda/\bar{c} = 4.7 \times 10^{9} \text{m}/230 \text{ m s}^{-1} = 20 \times 10^{6} \text{s}$$

25. Sketch graphs to show how the distribution of molecular speeds differs between

(a) helium at 100 K and helium at 300 K

(b) helium at 100 K and xenon at 100 K

Strategy

Consider the effects of temperature and molecular mass on speed, as shown in figures 8.12(b) and 8.12(a).

Solution

(a) <Unnumbered figure 8.1, as in back-of-book answers>

(b) <Unnumbered figure 8.2, as in back-of-book answers>

26.   Using the kinetic theory of gases, it can be shown that $pV = \frac{1}{3}nN_Amc^2$.

(a) Explain each of the terms in this equation.

(b) Show how this equation is equivalent to the ideal gas equation, $pV = nRT$.

(c) Using these equations as examples, explain the difference between an empirical <u>approach and a theoretical approach to modelling a chemical</u> <u>system.</u>

Strategy

Use equation 8.14 to relate the expression given in the question to the ideal gas equation. Think about how both the empirical and theoretical equations are derived.

Solution

(a) p is the pressure of the gas, in Pa, V is the volume in m^3, n is the number of moles of gas, N_A is Avogadro's constant, m is the mass of a molecule and c is the average molecular speed.

(b) The left hand side of both equations equals pV, therefore we can say that the right hand sides equal each other, so that

$$\frac{1}{3}nN_Amc^2 = nRT$$

n appears on both sides, so can be cancelled, leaving

$$\frac{1}{3}N_Amc^2 = RT$$

The kinetic energy of a molecule can be expressed by equation 8.14, which can be rearranged as follows;

$$E_{KE} = \frac{1}{2}mc^2$$

$$2\,E_{KE} = mc^2$$

Substituting this into the theory-derived equation above, we get

$$pV = \frac{1}{3} nN_A \, (2 \, E_{KE})$$

Since kinetic energy is proportional to temperature, and N_A is a constant, this can be simplified to say that

$$pV = \text{constant x } T$$

which is equivalent to the ideal gas equation, with R as the constant.

(c) The ideal gas equation is derived from experimental observations, and introduces R as a proportionality constant.. The theoretical approach starts off by considering the momentum of a single molecule colliding with the wall of a container, and applies physical laws to the behaviour of molecules in an ideal gas to rrive at an expression relating P, V and T.

27. Consider the following gases at SATP:

argon, krypton, nitrogen, methane, hydrogen chloride, chlorine, carbon

dioxide, helium

(a) Which gas would be expected to most closely follow ideal behaviour?

(b) Which gas would <u>deviate most from ideal behaviour?</u>

(c) Which gas would have the highest and lowest root mean square speeds?

(d) Which gas would effuse most slowly?

Strategy

Think about the assumptions made in the ideal gas equation, and what makes a gas 'ideal'. Look at equation 8.19 to see the relationship between molecular mass and the root mean square speed of a gas, and equation 8.20 for the rate of effusion.

Solution

(a) For an ideal gas we assume the molecules have no volume and no intermolecular attractions. Therefore the most ideal gas will have a small

volume, be non-polar and have few electrons to create weak Van der Waals forces. Therefore helium would most closely follow ideal behaviour.

(b) A gas with large volume and strong intermolecular forces deviates from ideal behaviour, so in this case the answer is hydrogen chloride, because its molecules are polar and therefore have the greatest intermolecular forces.

(c) The root mean square speed is inversely proportional to molecular mass, so helium, with the lowest molecular mass, has the highest root mean square speed. Carbon dioxide has the greatest molecular mass, and so the lowest root mean square speed.

(d) The rate of effusion is inversely proportional to the square root of molecular mass, so carbon dioxide will effuse most slowly.

28.   The molecular speeds in a sample of 100 molecules are distributed as follows:

Number of molecules	10	20	40	15	10	5
Speed / m s^{-1}	60	80	100	120	140	160

(a) What is the most probable speed?
(b) Calculate the mean speed of the molecules in the sample
(c) Calculate the r.m.s speed of the molecules in the sample

Strategy

The mean speed is the sum of the molecular speeds divided by the total number of molecules. To find the root mean square speed, use the sum of each molecule's speed squared, divide by the total number of molecules, and take the square root of the answer.

Solution

(a) The most probable speed is that which is measured most often: 100 m s^{-1}.

(b) Sum the speeds of all molecules, and then divide by the total number of molecules.

(10 x 60 m s⁻¹) + (20 x 80 m s⁻¹) + (40 x 100 m s⁻¹) + (15 x 120 m s⁻¹) + (10 x 140 m s⁻¹) + (5 x 160 m s⁻¹) = 10200 m s⁻¹.

10200 m s⁻¹/100 = 102 m s⁻¹

(c) Firstly sum the squares of each molecule's speed.

10 (60 m s⁻¹)² + 20 (80 m s⁻¹)² + 40 (100 m s⁻¹)² + 15 (120 m s⁻¹)² + 10 (140 m s⁻¹)² + 5 (160 m s⁻¹)² = 1104000 m² s⁻⁴

Now divide this by the total number of molecules, and take the square root of the answer.

1104000 m² s⁻⁴/ 100 = 11040 m s⁻¹

(1104 m² s⁻⁴)¹ᐟ² = 105 m s⁻¹

29.   The density of nitrogen gas in a container at 300 K and 1.0 bar pressure is 1.25 g dm⁻³.

(a) Calculate the r.m.s speed of the molecules.

(b) At what temperature will the r.m.s speed be twice as fast?

Strategy

Use equation 8.19 to calculate the root mean square speed, being careful with units. Look at the relationship between the root mean square speed and temperature.

Solution

(a) The molar mass of nitrogen is 28.0 g mol⁻¹, which is equivalent to 0.028 kg mol⁻¹. Substituting into equation 8.19, using T = 300 K, we get

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

= [(3 x 8.314 J mol⁻¹ K⁻¹ x 300 K)/0.028 kg mol⁻¹]¹ᐟ²

= 517 m s⁻¹

(b) Equation 8.19 shows that the root mean square speed is proportional to the square root of temperature. Therefore if c is twice as large, c^2 is four times greater, so the temperature would need to be four times greater, so T = 1200 K.

*30. A sample of gaseous uranium hexafluoride, UF_6, is held at a temperature of 300 K and a pressure of 0.1 mbar. The collision diameter of UF_6 is 0.40 nm.

(a) What is the r.m.s speed of the molecules?

(b) Estimate the collision frequency and mean free path under these conditions.

Strategy

Use equation 8.19 directly to find the r.m.s. speed. Calculate the collision cross sectional area, and then use equation 8.22, converting to standard units first. Use the root mean square speed and the collision frequency to find the mean free path.

Solution

(a) The value of M for UF_6 is 352 g mol⁻¹ = 0.352 kg mol⁻¹. Substituting this into equation 8.19 gives:

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

= [(3 x 8.314 J mol⁻¹ K⁻¹ x 300 K)/ 0.352 kg mol⁻¹)]¹ᐟ²

c = 146 m s⁻¹

(b) The cross sectional area is calculated using

$$\sigma = \pi \, d^2$$

= π x (0.4 x 10⁻⁹ m)²

= 5.03 x 10⁻¹⁹ m²

Substitute this value into the equation for collision frequency. Note that 1 bar = 1 x 10^{5} Pa, and so 0.1 x 10^{-3} bar = 10 Pa

$$Z = \sqrt{2} N_A (\bar{c}\sigma) \times \left(\frac{p}{RT} \right)$$

= √2 (6.02 x 10²³ mol⁻¹) x (146 ms⁻¹) x (5.03 x 10⁻¹⁹ m²) x 10 Pa/(8.314 J mol⁻¹ K⁻¹ x 300 K)

= 250 x 10³ s⁻¹

The mean free path is obtained from the expression

$$\lambda = c / Z$$

= 146 ms⁻¹ / 250 x 10³ s⁻¹

= 5.8 x 10⁻⁴ m

31.   (a) Explain how the fact that gases such as nitrogen or carbon dioxide can be liquefied by applying high pressure shows that the ideal gas equation can only be an approximation.

(b) Why is a lower pressure needed to liquefy CO_2 than for N_2?

Strategy

Consider the intermolecular forces in gases and liquids, and the assumptions made about them in the ideal gas equation. What is required to liquefy a gas?

Solution

(a) The fact that a gas can be liquefied shows that there are intermolecular forces between gas molecules. If this were not the case, as assumed in the ideal gas equation, it would not be possible to liquefy the gas.

(b) CO_2 is a less 'ideal' gas than N_2. It has a larger mass and contains polar bonds, therefore there are greater Van der Waals forces between molecules of CO_2 than between molecules of N_2. If there are more intermolecular attractions, it will be easier to liquefy the gas by compression.

32.   Predict which of the following substances will have (i) the highest and (ii) the lowest values of the van der Waals constants 'a' and 'b'.

N$_2$, He, NO$_2$

<u>Strategy</u>

Consider what each of the terms represents and relate them to the molecular properties of the molecules of the three gases.

<u>Solution</u>

The value of 'a' is related to the strength of intermolecular attractions in the atom/molecules. He and N$_2$ are non-polar and interact only through van der Waals interaction. NO$_2$ has two (slightly) polar bonds due to electronegativity differences and so will also have dipolar interactions. Therefore NO$_2$ would have the largest 'a'. The electrons in He are closer to the nucleus than those in N$_2$ and so He is less polarisable and would have the weakest van der Waals interactions and hence the lowest 'a' value.

The value of 'b' is related to the actual volume occupied by the molecules and hence the molecular size. He is the smallest of the three molecules (so the lowest 'b') while NO$_2$ is the biggest and so has the highest 'b' value.

33.   Calculate the temperature at which 20 mol of helium would exert a pressure of 120 atm in a 10 dm^3 cylinder. a= 0.034 dm^6 atm mol^{-2} b = 0.024 dm^3 mol^{-1} using both the ideal gas equation and the van der Waals equation.

<u>Strategy</u>

You can substitute the data into both the ideal gas equation and van der Waals' equation, remembering to perform any relevant unit conversions to maintain consistency.

Solution

For the ideal gas equation:

$$pV = nRT \quad \text{so} \quad T = \frac{pV}{nR}$$

In this problem, it is more convenient to use the value of R in different units, $R = 0.08206$ dm³ atm K⁻¹ mol⁻¹ (given in the text). Alternatively, the data could be converted to SI units as in the worked examples in the text..

$$T = \frac{pV}{nR} = \frac{120 \text{ atm} \times 10 \text{ dm}^3}{20 \text{ mol} \times 0.08206 \text{ dm}^3 \text{ atm K}^{-1}\text{mol}^{-1}} = 731 \text{ K}$$

For the van der Waals equation:

$$p + a\left(\frac{n}{V}\right)^2 (V - nb) = nRT \quad \text{so} \quad T = \frac{p + a\left(\frac{n}{V}\right)^2 \times (V - nb)}{nR}$$

$$T = \frac{\left[p + a\left(\frac{n}{V}\right)^2\right] \times (V - nb)}{nR}$$

$$T = \frac{\left(120 \text{ atm} + 0.034 \text{dm}^6\text{atm mol}^{-2} \times \left(\frac{20 \text{ mol}}{10 \text{ dm}^3}\right)^2\right) \times \left(10 \text{ dm}^3 - 20 \text{ mol} \times 0.024 \text{ dm}^3\text{mol}^{-1}\right)}{20 \text{ mol} \times 0.08206 \text{ dm}^3 \text{ atm K}^{-1}\text{mol}^{-1}} = 697\text{K}$$