

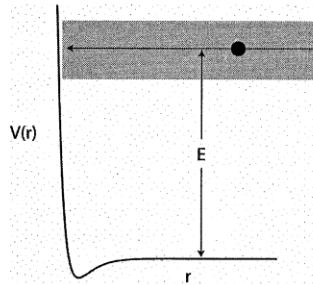
1 Fundamental Concepts of Thermodynamics

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

- Q1.1** Real walls are never totally adiabatic. Use your experience to order the following walls in increasing order with respect to being diathermal: 1-cm-thick concrete, 1-cm-thick vacuum, 1-cm-thick copper, 1-cm-thick cork.
1-cm-thick vacuum < 1-cm-thick cork < 1-cm-thick concrete < 1-cm-thick copper
- Q1.2** The parameter a in the van der Waals equation is greater for H_2O than for He. What does this say about the difference in the form of the potential function in Figure 1.10 for the two gases?
It says that the depth of the attractive potential is greater for H_2O than for He.
- Q1.3** Give an example based on molecule–molecule interactions illustrating how the total pressure upon mixing two real gases could be different from the sum of the partial pressures.
If the two gases interacted by the formation of hydrogen bonds the total pressure would be less than the sum of the partial pressures.
- Q1.4** Can temperature be measured directly? Explain your answer.
Temperature cannot be measured directly. It is measured indirectly by the effect of temperature on a property such as the volume of a liquid, the pressure of a gas, the electrical resistance of a metal, or the voltage across the junction of two dissimilar metals (a thermocouple).
- Q1.5** Explain how the ideal gas law can be deduced from the measurements shown in Figures 1.5 and 1.8.
Figure 1.5 shows that at constant volume, P increases linearly with T , so $P = \alpha f(V)T$.
Figure 1.8 shows that the product PV is a constant at constant T . Therefore $PV = \beta T$, where α and β are constants to be determined from measurements and the units chosen for P , V , and T .
- Q1.6** The location of the boundary between the system and the surroundings is a choice that must be made by the thermodynamicist. Consider a beaker of boiling water in an airtight room. Is the system open or closed if you place the boundary just outside the liquid water? Is the system open or closed if you place the boundary just inside the walls of the room?
If the system boundaries are just outside of the liquid water, the system is open because water can escape from the top surface. The system is closed if the boundary is just inside the walls, because the room is airtight.
- Q1.7** Give an example of two systems that are in equilibrium with respect to only one of two state variables.
The contents of a compressed gas cylinder are in thermal equilibrium with the surroundings, but the pressures are different. A gas enclosed in a thermally insulating piston and cylinder assembly will be in equilibrium with respect to pressure, but not to temperature.

- Q1.8** At sufficiently high temperatures, the van der Waals equation has the form $P \approx \frac{RT}{V_m - b}$. Note that the attractive part of the potential has no influence in this expression. Justify this behavior using the potential energy diagram in Figure 1.10. At high temperatures, the energy of the molecule is large as indicated by the colored rectangular area in the figure below.



In this case, the well depth is a small fraction of the total energy. Therefore, the particle is unaffected by the attractive part of the potential.

- Q1.9** Give an example of two systems separated by a wall that are in thermal but not chemical equilibrium. Hydrogen and oxygen cylinders are stored in a room held at constant temperature.
- Q1.10** Which of the following systems are open? (a) a dog, (b) an incandescent light bulb, (c) a tomato plant, (d) a can of tomatoes. Explain your answers.
An open system can exchange matter with the surroundings. Using this criterion:
- A dog is an open system.
 - The light bulb is a closed system.
 - A tomato plant is an open system.
 - A can of tomatoes is a closed system.
- Q1.11** Which of the following systems are isolated? (a) a bottle of wine, (b) a tightly sealed, perfectly insulated thermos bottle, (c) a tube of toothpaste, (d) our solar system. Explain your answers.
An isolated system cannot exchange matter or energy with the surroundings. Using this criterion:
- The bottle of wine is not an isolated system because it can exchange energy with the surroundings.
 - The thermos bottle is an isolated system.
 - A tube of toothpaste is not an isolated system because it can exchange energy with the surroundings.
 - Our solar system is not an isolated system because it can exchange energy and mass with the rest of the universe.
- Q1.12** Why do the z and y components of the velocity not change in the collision depicted in Figure 1.2?
The z and y components of the velocity do not change in the collision because there is no force acting on the particle in those directions.
- Q1.13** If the wall depicted in Figure 1.2 were a movable piston, under what conditions would it move as a result of the molecular collisions?
It would move if the momentum transferred to it from the two sides was different. This is the case if there is a pressure difference across the wall.

- Q1.14** The mass of an He atom is less than that of an Ar atom. Does that mean that because of its larger mass, Argon exerts a higher pressure on the container walls than He at the same molar density, volume, and temperature? Explain your answer.

The pressure exerted on the wall depends on the momentum transfer, which is proportional to $m\langle v_x^2 \rangle$. Because $\frac{m\langle v_x^2 \rangle}{2} = \frac{kT}{2}$, the momentum transfer depends on the temperature, but not on the mass of the atom striking the wall.

- Q1.15** Explain why attractive interactions between molecules in gas make the pressure less than that predicted by the ideal gas equation of state.

The pressure exerted by a gas on the walls which contain it is determined by the force exerted on the wall by molecular collisions. If the molecules nearest the wall experience an attractive interaction to the molecules near them, this will lessen the force that they exert on the wall. Therefore, the pressure will be less.

Numerical Problems

- PI.1** Approximately how many oxygen molecules arrive each second at the mitochondrion of an active person with a mass of 84 kg? The following data are available: Oxygen consumption is about 40. mL of O_2 per minute per kilogram of body weight, measured at $T = 300. \text{ K}$ and $P = 1.00. \text{ atm}$. In an adult there are about 1.6×10^{10} cells per kg body mass. Each cell contains about 800. mitochondria.

We first calculate the number of moles of O_2 consumed per unit time and convert this quantity into molecules per unit time using the Avogadro number.

$$n_{O_2} = \frac{PV}{RT} = \frac{1 \text{ atm} \times 40. \times 10^{-3} \text{ L min}^{-1} \text{ kg}^{-1}}{8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300. \text{ K}} \times \frac{1 \text{ min}}{60 \text{ s}} \times 84 \text{ kg}$$

$$= 2.27 \times 10^{-3} \text{ mol s}^{-1}$$

$$\text{Molecules } O_2 \text{ per mitochondrion} = \frac{N_A \times n_{O_2}}{\text{number of cells/kg} \times \text{number of mitochondria/cell} \times \text{body weight}}$$

$$= \frac{2.27 \times 10^{-3} \text{ mol s}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{1.6 \times 10^{10} \text{ cells kg}^{-1} \times 800. \text{ cells}^{-1} \times 84 \text{ kg}} = 1.27 \times 10^6 \text{ molecules s}^{-1}$$

- PI.2** A compressed cylinder of gas contains $2.74 \times 10^3 \text{ g}$ of N_2 gas at a pressure of $3.75 \times 10^7 \text{ Pa}$ and a temperature of 18.7°C . What volume of gas has been released into the atmosphere if the final pressure in the cylinder is $1.80 \times 10^5 \text{ Pa}$? Assume ideal behavior and that the gas temperature is unchanged.

Let n_i and n_f be the initial and final number of mols of N_2 in the cylinder.

$$\frac{n_i RT}{P_i} = \frac{n_f RT}{P_f}$$

$$n_f = n_i \frac{P_f}{P_i} = \frac{2.74 \times 10^3 \text{ g}}{28.01 \text{ g mol}^{-1}} \times \frac{1.80 \times 10^5 \text{ Pa}}{3.75 \times 10^7 \text{ Pa}} = 0.470 \text{ mol}$$

$$n_i = \frac{2.74 \times 10^3 \text{ g}}{28.01 \text{ g mol}^{-1}} = 97.8 \text{ mol}$$

The volume of gas released into the atmosphere is given by

$$V = \frac{(n_f - n_i)RT}{P} = \frac{(97.8 - 0.470) \text{ mol} \times 8.2057 \times 10^{-2} \text{ L atm mol}^{-1} \text{K}^{-1} \times (273.15 + 18.7) \text{ K}}{1 \text{ atm}} = 2.33 \times 10^3 \text{ L}$$

- P1.3** Calculate the pressure exerted by Ar for a molar volume of 1.31 L mol^{-1} at 426 K using the van der Waals equation of state. The van der Waals parameters a and b for Ar are $1.355 \text{ bar dm}^6 \text{ mol}^{-2}$ and $0.0320 \text{ dm}^3 \text{ mol}^{-1}$, respectively. Is the attractive or repulsive portion of the potential dominant under these conditions?

$$\begin{aligned} P &= \frac{RT}{V_m - b} - \frac{a}{V_m^2} \\ &= \frac{8.314 \times 10^{-2} \text{ bar dm}^3 \text{ mol}^{-1} \text{K}^{-1} \times 426 \text{ K}}{1.31 \text{ dm}^3 \text{ mol}^{-1} - 0.0320 \text{ dm}^3 \text{ mol}^{-1}} - \frac{1.355 \text{ bar dm}^6 \text{ mol}^{-2}}{(1.31 \text{ dm}^3 \text{ mol}^{-1})^2} = 26.9 \text{ bar} \\ P_{\text{ideal}} &= \frac{RT}{V} = \frac{8.3145 \times 10^{-2} \times \text{L bar mol}^{-1} \text{K}^{-1} \times 426 \text{ K}}{1.31 \text{ L}} = 27.0 \text{ bar} \end{aligned}$$

Because $P < P_{\text{ideal}}$, the attractive part of the potential dominates.

- P1.4** A sample of propane (C_3H_8) is placed in a closed vessel together with an amount of O_2 that is 2.15 times the amount needed to completely oxidize the propane to CO_2 and H_2O at constant temperature. Calculate the mole fraction of each component in the resulting mixture after oxidation, assuming that the H_2O is present as a gas.

The reaction is $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$. If m mol of propane are present initially, there must be $2.15 \times 5m$ mol of O_2 . After the reaction is complete, there are $3m$ mol of CO_2 , $4m$ mol of H_2O , and $(5 \times 2.15 - 5)m$ mol of O_2 .

Given these relationships, we can calculate the mol fractions.

$$\begin{aligned} x_{\text{CO}_2} &= \frac{3m}{3m + 4m + (5 \times 2.15 - 5)m} = 0.235; & x_{\text{H}_2\text{O}} &= \frac{4m}{3m + 4m + (5 \times 2.15 - 5)m} = 0.314; \\ x_{\text{O}_2} &= \frac{(5 \times 2.15 - 5)m}{3m + 4m + (5 \times 2.15 - 5)m} = 0.451 \end{aligned}$$

- P1.5** A gas sample is known to be a mixture of ethane and butane. A bulb having a 230.0 cm^3 capacity is filled with the gas to a pressure of $97.5 \times 10^3 \text{ Pa}$ at 23.1°C . If the mass of the gas in the bulb is 0.3554 g , what is the mole percent of butane in the mixture?

$$\begin{aligned} n_1 &= \text{moles of ethane} & n_2 &= \text{moles of butane} \\ n_1 + n_2 &= \frac{PV}{RT} = \frac{97.5 \times 10^3 \text{ Pa} \times 0.230 \times 10^{-3} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{K}^{-1} \times (273.15 + 23.1) \text{ K}} = 9.10 \times 10^{-3} \text{ mol} \end{aligned}$$

The total mass is $n_1M_1 + n_2M_2 = 0.3554 \text{ g}$.

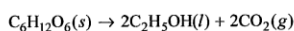
Dividing this equation by $n_1 + n_2$,

$$\begin{aligned} \frac{n_1M_1 + n_2M_2}{n_1 + n_2} &= \frac{0.3554 \text{ g}}{9.10 \times 10^{-3} \text{ mol}} = 39.0 \text{ g mol}^{-1} \\ x_1M_1 + x_2M_2 &= (1 - x_2)M_1 + x_2M_2 = 39.0 \text{ g mol}^{-1} \\ x_2 &= \frac{37.0 \text{ g mol}^{-1} - M_1}{M_2 - M_1} = \frac{39.0 \text{ g mol}^{-1} - 30.069 \text{ g mol}^{-1}}{58.123 \text{ g mol}^{-1} - 30.069 \text{ g mol}^{-1}} = 0.320 \text{ mole \%} = 32.0\% \end{aligned}$$

- P1.6** One liter of fully oxygenated blood can carry 0.18 liters of O_2 measured at $T = 298\text{ K}$ and $P = 1.00\text{ atm}$. Calculate the number of moles of O_2 carried per liter of blood. Hemoglobin, the oxygen transport protein in blood, has four oxygen binding sites. How many hemoglobin molecules are required to transport the O_2 in 1.0 L of fully oxygenated blood?

$$\begin{aligned}n_{O_2} &= \frac{PV}{RT} = \frac{1\text{ atm} \times 0.18\text{ L}}{8.206 \times 10^{-2}\text{ L atm mol}^{-1}\text{ K}^{-1} \times 298\text{ K}} \\&= 7.36 \times 10^{-3}\text{ mol} \\N_{\text{hemoglobin}} &= \frac{n_{O_2} \times N_A}{4} = \frac{7.36 \times 10^{-3}\text{ mol} \times 6.022 \times 10^{23}}{4} \\&= 1.11 \times 10^{21}\text{ molecules}\end{aligned}$$

- P1.7** Yeast and other organisms can convert glucose ($C_6H_{12}O_6$) to ethanol (CH_3CH_2OH) by a process called alcoholic fermentation. The net reaction is



Calculate the mass of glucose required to produce 2.25 L of CO_2 measured at $P = 1.00\text{ atm}$ and $T = 295\text{ K}$.

$$\begin{aligned}m_{\text{glucose}} &= M_{\text{glucose}} \times \frac{PV}{RT} \times \frac{n_{\text{glucose}}}{n_{CO_2}} \\&= 180.16\text{ g mol}^{-1} \times \frac{1.00\text{ atm} \times 2.25\text{ L}}{8.206 \times 10^{-2}\text{ L atm mol}^{-1}\text{ K}^{-1} \times 295\text{ K}} \times 0.5 \\&= 8.37\text{ g}\end{aligned}$$

- P1.8** A vessel contains 1.15 g liq H_2O in equilibrium with water vapor at $30.^\circ\text{C}$. At this temperature, the vapor pressure of H_2O is 31.82 torr. What volume increase is necessary for all the water to evaporate?

We calculate the volume at which the gas pressure is equal to the partial pressure. For smaller volumes, some of the water will remain as a liquid.

$$\begin{aligned}V &= \frac{nRT}{P} = \frac{\frac{1.15\text{ g}}{18.02\text{ g}} \times 8.206 \times 10^{-2}\text{ L atm mol}^{-1}\text{ K}^{-1} \times (273.15 + 30.)\text{K}}{31.82\text{ Torr} \times \frac{1\text{ atm}}{760\text{ Torr}}} \\&= 37.9\text{ L}\end{aligned}$$

- P1.9** Consider a 31.0 L sample of moist air at $60.^\circ\text{C}$ and one atm in which the partial pressure of water vapor is 0.131 atm. Assume that dry air has the composition 78.0 mole percent N_2 , 21.0 mole percent O_2 , and 1.00 mole percent Ar.
- What are the mole percentages of each of the gases in the sample?
 - The percent relative humidity is defined as $\%RH = P_{H_2O} / P_{H_2O}^*$ where P_{H_2O} is the partial pressure of water in the sample and $P_{H_2O}^* = 0.197\text{ atm}$ is the equilibrium vapor pressure of water at $60.^\circ\text{C}$. The gas is compressed at $60.^\circ\text{C}$ until the relative humidity is 100.%. What volume does the mixture contain now?
 - What fraction of the water will be condensed if the total pressure of the mixture is isothermally increased to 81.0 atm?

$$\begin{aligned} \text{(a) mol \% N}_2 &= 100 \times \frac{P_{N_2}}{P_{total}} = 100 \times \frac{0.78 \times 0.869 \text{ atm}}{1 \text{ atm}} = 67.8\% \\ \text{mol \% O}_2 &= 100 \times \frac{P_{O_2}}{P_{total}} = 100 \times \frac{0.21 \times 0.869 \text{ atm}}{1 \text{ atm}} = 18.2\% \\ \text{mol \% Ar} &= 100 \times \frac{P_{Ar}}{P_{total}} = 100 \times \frac{0.01 \times 0.869 \text{ atm}}{1 \text{ atm}} = 0.869\% \\ \text{mol \% H}_2\text{O} &= 100 \times \frac{P_{H_2O}}{P_{total}} = 100 \times \frac{0.131 \text{ atm}}{1 \text{ atm}} = 13.1\% \end{aligned}$$

$$\begin{aligned} \text{(b) } P_{H_2O} &= \frac{n_{H_2O}RT}{V} \\ P'_{H_2O}V' &= P_{H_2O}V \text{ where the primed quantities refer to 100\% RH} \\ V' &= \frac{P_{H_2O}V}{P'_{H_2O}} = \frac{0.131 \text{ atm} \times 31.0 \text{ L}}{0.197 \text{ atm}} = 20.6 \text{ L} \end{aligned}$$

(c) If all the water remained in the gas phase, the partial pressure of water at a total pressure of 81.0 atm would be

$$P_{H_2O} = P_{total} \times \text{mol fraction H}_2\text{O} = 81.0 \text{ atm} \times 0.131 = 10.6 \text{ atm}$$

However, the partial pressure of water cannot be greater than 0.197 atm, and the excess will condense. The fraction that condenses is given by

$$\text{fraction condensed} = \frac{10.6 \text{ atm} - 0.197 \text{ atm}}{10.6 \text{ atm}} = 0.981$$

P1.10 A typical diver inhales 0.450 liters of air per breath and carries a 25 L breathing tank containing air at a pressure of 300. bar. As she dives deeper, the pressure increases by 1 bar for every 10.08 m. How many breaths can the diver take from this tank at a depth of 35 m? Assume that the temperature remains constant.

$$V_{35m} = \frac{V_{surface} P_{surface}}{P_{35m}} = \frac{25 \text{ L} \times 300. \text{ bar}}{1 \text{ bar} + \frac{35 \text{ m}}{10.08 \text{ m}}} = 1.68 \times 10^3 \text{ L}$$

$$\text{number breaths} = \frac{V_{35m}}{V_{breath}} = 3.7 \times 10^3$$

P1.11 Use the ideal gas and van der Waals equations to calculate the pressure when 2.25 mol H₂ are confined to a volume of 1.65 L at 298 K. Is the gas in the repulsive or attractive region of the molecule–molecule potential?

$$\begin{aligned} P &= \frac{nRT}{V_m - nb} - \frac{n^2 a}{V_m^2} \\ &= \frac{(2.25 \text{ mol}) \times 8.314 \times 10^{-2} \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1.65 \text{ dm}^3 \text{ mol}^{-1} - 2.25 \text{ mol} \times 0.0265 \text{ dm}^3 \text{ mol}^{-1}} - \frac{(2.25 \text{ mol})^2 \times 0.2452 \text{ bar dm}^6 \text{ mol}^{-2}}{(1.65 \text{ dm}^3 \text{ mol}^{-1})^2} \\ &= 34.6 \text{ bar} \\ P_{ideal} &= \frac{nRT}{V} = \frac{2.25 \text{ mol} \times 8.3145 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1.65 \text{ L}} = 33.8 \text{ bar} \end{aligned}$$

Because $P > P_{ideal}$, the repulsive part of the potential dominates.

P1.12 A rigid vessel of volume 0.400 m³ containing H₂ at 21.25°C and a pressure of 715 × 10³ Pa is connected to a second rigid vessel of volume 0.750 m³ containing Ar at 30.15°C and a pressure of 203 × 10³ Pa. A valve separating the two vessels is opened and both are cooled to a temperature of 12.2°C. What is the final pressure in the vessels?

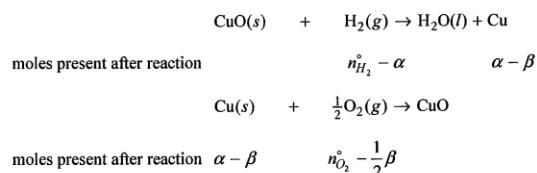
$$n_{H_2} = \frac{PV}{RT} = \frac{715 \times 10^3 \text{ Pa} \times 0.400 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 21.25) \text{ K}} = 116.8 \text{ mol}$$

$$n_{Ar} = \frac{PV}{RT} = \frac{203 \times 10^3 \text{ Pa} \times 0.750 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 30.15) \text{ K}} = 60.38 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{(116.8 + 60.38) \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 12.2) \text{ K}}{(0.400 + 0.750) \text{ m}^3} = 3.66 \times 10^5 \text{ Pa}$$

P1.13 A mixture of oxygen and hydrogen is analyzed by passing it over hot copper oxide and through a drying tube. Hydrogen reduces the CuO according to the reaction $\text{CuO}(s) + \text{H}_2(g) \rightarrow \text{Cu}(s) + \text{H}_2\text{O}(l)$, and oxygen reoxidizes the copper formed according to $\text{Cu}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CuO}(s)$. At 25°C and 750. Torr, 172.0 cm³ of the mixture yields 77.5 cm³ of dry oxygen measured at 25°C and 750. Torr after passage over CuO and the drying agent. What is the original composition of the mixture?

Two consecutive reactions must be considered. In the following reactions alpha (α) represents the number of moles of $\text{H}_2(g)$ that react with $\text{CuO}(s)$ and beta (β) represents the number of moles of Cu that react with $\text{O}_2(g)$.



In the final state, only O_2 is present. Therefore $\alpha = n_{H_2}^\circ$. In an excess of O_2 , all the copper is oxidized. Therefore $\alpha - \beta = 0$ or $\beta = n_{H_2}^\circ$. We conclude that $n_{O_2} = n_{O_2}^\circ - \frac{1}{2}n_{H_2}^\circ$.

Let V_1 and V_2 be the initial and final volumes.

$$V_1 = \left(n_{H_2}^\circ + n_{O_2}^\circ \right) \frac{RT}{P} \qquad V_2 = \left(n_{O_2}^\circ - \frac{1}{2}n_{H_2}^\circ \right) \frac{RT}{P}$$

Dividing the second equation by the first yields

$$\frac{V_2}{V_1} = \frac{n_{O_2}^\circ}{n_{H_2}^\circ + n_{O_2}^\circ} - \frac{1}{2} \frac{n_{H_2}^\circ}{n_{H_2}^\circ + n_{O_2}^\circ} = x_{O_2}^\circ - \frac{1}{2}x_{H_2}^\circ = 1 - x_{H_2}^\circ - \frac{1}{2}x_{H_2}^\circ = 1 - \frac{3}{2}x_{H_2}^\circ$$

$$x_{H_2}^\circ = \frac{2}{3} \left(1 - \frac{V_2}{V_1} \right) = \frac{2}{3} \left(1 - \frac{77.5 \text{ cm}^3}{172 \text{ cm}^3} \right) = 0.366; \qquad x_{O_2}^\circ = 1 - x_{H_2}^\circ = 0.634$$

P1.14 An athlete at high performance inhales ~3.75 L of air at 1.00 atm and 298 K. The inhaled and exhaled air contain 0.50 and 6.2% by volume of water, respectively. For a respiration rate of 32 breaths per minute, how many moles of water per minute are expelled from the body through the lungs?

$$\begin{aligned} V_{H_2O} &= \text{number breaths} \times V_{air} \times (\text{fraction inhaled} - \text{fraction exhaled}) \\ &= 32 \times 3.75 \text{ L} \times (0.062 - 0.0050) = 6.84 \text{ L} \\ \text{mol H}_2\text{O} &= \frac{PV_{H_2O}}{RT} = \frac{1 \text{ atm} \times 6.84 \text{ L}}{8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.280 \text{ mol} \end{aligned}$$

P1.15 Devise a temperature scale, abbreviated G, for which the magnitude of the ideal gas constant is $5.52 \text{ J G}^{-1} \text{ mol}^{-1}$.

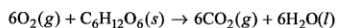
Let T and T' represent the Kelvin and G scales, and R and R' represent the gas constant in each of these scales. Then

$$PV = nRT = nR'T'$$

$$T' = \frac{R}{R'}T = \frac{8.314}{5.52}T = 1.51T$$

The temperature on the G scale is the value in K multiplied by 1.51.

P1.16 Aerobic cells metabolize glucose in the respiratory system. This reaction proceeds according to the overall reaction



Calculate the volume of oxygen required at STP to metabolize 0.025 kg of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). STP refers to standard temperature and pressure, that is, $T = 273 \text{ K}$ and $P = 1.00 \text{ atm}$. Assume oxygen behaves ideally at STP.

From the stoichiometric equation, we see that 6 mol of O_2 are required for each mol of glucose. Therefore

$$V_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{P} = \frac{\frac{6 \times 25 \text{ g}}{180.18 \text{ g mol}^{-1}} \times 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}}{1 \text{ atm}} = 18.6 \text{ L}$$

P1.17 An athlete at high performance inhales $\sim 3.75 \text{ L}$ of air at 1.0 atm and 298 K at a respiration rate of 32 breaths per minute. If the exhaled and inhaled air contain 15.3 and 20.9% by volume of oxygen, respectively, how many moles of oxygen per minute are absorbed by the athlete's body?

$$V_{\text{O}_2} = \text{number breaths} \times V_{\text{air}} \times (\text{fraction inhaled} - \text{fraction exhaled})$$

$$= 32 \times 3.75 \text{ L} \times (0.209 - 0.153) = 6.72 \text{ L}$$

$$\text{mol O}_2 = \frac{PV_{\text{O}_2}}{RT} = \frac{1 \text{ atm} \times 6.72 \text{ L}}{8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.27 \text{ mol}$$

P1.18 A mixture of $2.10 \times 10^{-3} \text{ g}$ of O_2 , $3.88 \times 10^{-3} \text{ mol}$ of N_2 , and 5.25×10^{20} molecules of CO are placed into a vessel of volume 5.25 L at 12.5°C .

- Calculate the total pressure in the vessel.
- Calculate the mole fractions and partial pressures of each gas.

$$(a) \quad n_{\text{O}_2} = \frac{2.10 \times 10^{-3} \text{ g}}{32.0 \text{ g mol}^{-1}} = 6.56 \times 10^{-5} \text{ mol}$$

$$n_{\text{CO}} = \frac{5.25 \times 10^{20} \text{ molecules}}{6.022 \times 10^{23} \text{ molecules mol}^{-1}} = 8.71 \times 10^{-4} \text{ mol}$$

$$n_{\text{total}} = n_{\text{O}_2} + n_{\text{N}_2} + n_{\text{CO}} = 6.56 \times 10^{-5} \text{ mol} + 3.88 \times 10^{-3} \text{ mol} + 8.72 \times 10^{-4} \text{ mol} = 4.82 \times 10^{-3} \text{ mol}$$

$$P_{\text{total}} = \frac{nRT}{V} = \frac{4.82 \times 10^{-3} \text{ mol} \times 8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times (273.15 + 12.5) \text{ K}}{5.25 \text{ L}} = 2.18 \times 10^{-2} \text{ bar}$$

$$(b) \quad x_{\text{O}_2} = \frac{6.56 \times 10^{-5} \text{ mol}}{4.82 \times 10^{-3} \text{ mol}} = 0.0136; \quad x_{\text{N}_2} = \frac{3.88 \times 10^{-3} \text{ mol}}{4.82 \times 10^{-3} \text{ mol}} = 0.805; \quad x_{\text{CO}} = \frac{8.71 \times 10^{-4} \text{ mol}}{4.82 \times 10^{-3} \text{ mol}} = 0.181$$

$$P_{\text{O}_2} = x_{\text{O}_2} P_{\text{total}} = 0.0136 \times 2.18 \times 10^{-2} \text{ bar} = 2.97 \times 10^{-4} \text{ bar}$$

$$P_{\text{N}_2} = x_{\text{N}_2} P_{\text{total}} = 0.805 \times 2.18 \times 10^{-2} \text{ bar} = 1.76 \times 10^{-2} \text{ bar}$$

$$P_{\text{CO}} = x_{\text{CO}} P_{\text{total}} = 0.181 \times 2.18 \times 10^{-2} \text{ bar} = 3.94 \times 10^{-3} \text{ bar}$$

- P1.19** Calculate the pressure exerted by benzene for a molar volume of 2.00 L at 595 K using the Redlich–Kwong equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T} V (V + nb)}$$

The Redlich–Kwong parameters a and b for benzene are $452.0 \text{ bar dm}^6 \text{ mol}^{-2} \text{ K}^{1/2}$ and $0.08271 \text{ dm}^3 \text{ mol}^{-1}$, respectively. Is the attractive or repulsive portion of the potential dominant under these conditions?

$$\begin{aligned} P &= \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)} \\ &= \frac{8.314 \times 10^{-2} \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 595 \text{ K}}{2.00 \text{ dm}^3 \text{ mol}^{-1} - 0.08271 \text{ dm}^3 \text{ mol}^{-1}} - \frac{452.0 \text{ bar dm}^6 \text{ mol}^{-2} \text{ K}^{1/2}}{\sqrt{595 \text{ K}}} \\ &\quad \times \frac{1}{2.00 \text{ dm}^3 \text{ mol}^{-1} \times (2.00 \text{ dm}^3 \text{ mol}^{-1} + 0.08271 \text{ dm}^3 \text{ mol}^{-1})} \\ P &= 21.4 \text{ bar} \\ P_{\text{ideal}} &= \frac{RT}{V} = \frac{8.3145 \times 10^{-2} \times \text{L bar mol}^{-1} \text{ K}^{-1} \times 595 \text{ K}}{2.00 \text{ L}} = 24.7 \text{ bar} \end{aligned}$$

Because $P < P_{\text{ideal}}$, the attractive part of the potential dominates.

- P1.20** In the absence of turbulent mixing, the partial pressure of each constituent of air would fall off with height above sea level in the Earth's atmosphere as $P_i = P_i^0 e^{-M_i g z / RT}$ where P_i is the partial pressure at the height z , P_i^0 is the partial pressure of component i at sea level, g is the acceleration of gravity, R is the gas constant, T is the absolute temperature, and M_i is the molecular mass of the gas. As a result of turbulent mixing, the composition of the Earth's atmosphere is constant below an altitude of 100 km, but the total pressure decreases with altitude as $P = P^0 e^{-M_{\text{ave}} g z / RT}$ where M_{ave} is the mean molecular weight of air. At sea level, $x_{N_2} = 0.78084$, $x_{He} = 0.00000524$, and $T = 300 \text{ K}$.

- Calculate the total pressure at 8.5 km assuming a mean molecular mass of 28.9 g mol^{-1} and that $T = 300 \text{ K}$ throughout this altitude range.
- Calculate the value that x_{N_2} / x_{He} would have at 8.5 km in the absence of turbulent mixing. Compare your answer with the correct value.

$$P_{\text{tot}} = P_{N_2}^0 e^{\frac{M_{\text{ave}} g z}{RT}} = 1.0125 \times 10^5 \text{ Pa} \exp\left(-\frac{28.9 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 8.5 \times 10^3 \text{ m}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}\right) = 3.86 \times 10^4 \text{ Pa}$$

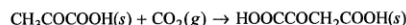
$$P_{N_2} = P_{N_2}^0 e^{\frac{M_{N_2} g z}{RT}} = 0.78084 \times 1.0125 \times 10^5 \text{ Pa} \exp\left(-\frac{28.02 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 8.5 \times 10^3 \text{ m}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}\right) = 3.10 \times 10^4 \text{ Pa}$$

$$P_{He} = P_{He}^0 e^{\frac{M_{He} g z}{RT}} = 5.24 \times 10^{-6} \times 1.0125 \times 10^5 \text{ Pa} \exp\left(-\frac{4.003 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 8.5 \times 10^3 \text{ m}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}\right) = 0.464 \text{ Pa}$$

$$\frac{P_{N_2}}{P_{He}} = 6.68 \times 10^4 \text{ without mixing}$$

$$\frac{P_{N_2}}{P_{He}} = \frac{x_{N_2}}{x_{He}} = \frac{0.78084}{5.24 \times 10^{-6}} = 1.49 \times 10^5 \text{ with mixing}$$

- P1.21** An initial step in the biosynthesis of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ is the carboxylation of pyruvic acid $\text{CH}_3\text{COCO}(\text{OH})$ to form oxaloacetic acid $\text{HOCCOCH}_2\text{COOH}$



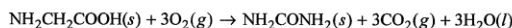
If you knew nothing else about the intervening reactions involved in glucose biosynthesis other than no further carboxylations occur, what volume of CO_2 is required to produce 1.10 g of glucose? Assume $P = 1 \text{ atm}$ and $T = 298. \text{ K}$.

From the stoichiometric equation,

$$n_{\text{CO}_2} = n_{\text{glucose}} = \frac{m_{\text{glucose}}}{M_{\text{glucose}}} = \frac{1.10 \text{ g}}{180.18 \text{ g mol}^{-1}} = 6.10 \times 10^{-3} \text{ mol}$$

$$V_{\text{CO}_2} = \frac{n_{\text{CO}_2} RT}{P} = \frac{6.10 \times 10^{-3} \text{ mol} \times 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ atm}} = 0.149 \text{ L}$$

P1.22 Consider the oxidation of the amino acid glycine $\text{NH}_2\text{CH}_2\text{COOH}$ to produce water, carbon dioxide, and urea NH_2CONH_2 :



Calculate the volume of carbon dioxide evolved at $P = 1.00 \text{ atm}$ and $T = 305. \text{ K}$ from the oxidation of 0.022 g of glycine.

From the stoichiometric equation,

$$n_{\text{CO}_2} = 3n_{\text{glycine}} = 3 \frac{0.022 \text{ g}}{75.07 \text{ g mol}^{-1}} = 8.79 \times 10^{-4} \text{ mol}$$

$$V_{\text{CO}_2} = \frac{n_{\text{CO}_2} RT}{P} = \frac{8.79 \times 10^{-4} \times 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 305 \text{ K}}{1.00 \text{ atm}} = 2.20 \times 10^{-2} \text{ L}$$

P1.23 Assume that air has a mean molar mass of 28.9 g mol^{-1} and that the atmosphere has a uniform temperature of 25.0°C . Calculate the barometric pressure in Pa in Santa Fe, for which $z = 7000. \text{ ft}$. Use the information contained in Problem P1.20.

$$P = P^0 e^{-\frac{M_{\text{air}}gz}{RT}} = 10^5 \text{ Pa} \exp\left(-\frac{28.9 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 7000. \text{ ft} \times 0.3048 \text{ m ft}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}\right) = 7.95 \times 10^4 \text{ Pa}$$

P1.24 When Julius Caesar expired, his last exhalation had a volume of $450. \text{ cm}^3$ and contained 1.00 mole percent argon. Assume that $T = 300. \text{ K}$ and $P = 1.00 \text{ atm}$ at the location of his demise. Assume further that T has the same value throughout the Earth's atmosphere. If all of his exhaled Ar atoms are now uniformly distributed throughout the atmosphere, how many inhalations of $450. \text{ cm}^3$ must we make to inhale one of the Ar atoms exhaled in Caesar's last breath? Assume the radius of the Earth to be $6.37 \times 10^6 \text{ m}$. [Hint: Calculate the number of Ar atoms in the atmosphere in the simplified geometry of a plane of area equal to that of the Earth's surface. See Problem 1.20 for the dependence of the barometric pressure on the height above the Earth's surface.]

The density of Ar atoms in the atmosphere at the surface of the Earth, \tilde{N}_{Ar}^s , is given by

$$\tilde{N}_{\text{Ar}}^s = \frac{N_{\text{Ar}} P_{\text{Ar}}}{RT} = \frac{6.022 \times 10^{23} \times 0.0100 \times 1 \times 10^5 \text{ Pa}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = 2.41 \times 10^{23} \text{ m}^{-3}$$

The total number of Ar atoms in the atmosphere is

$$N_{\text{Ar}} = \int_0^\infty \tilde{N}_{\text{Ar}} A dz = \tilde{N}_{\text{Ar}}^s \int_0^\infty e^{-\frac{M_{\text{ave}}gz}{RT}} A dz = \tilde{N}_{\text{Ar}}^s A \frac{RT}{M_{\text{ave}}g}$$

$$= \frac{2.41 \times 10^{23} \text{ m}^{-3} \times 4\pi \times (6.37 \times 10^6 \text{ m})^2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300. \text{ K}}{28.9 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2}} = 1.08 \times 10^{42}$$

We have used the fact stated in P1.20 that turbulent mixing results in a height independent composition of the atmosphere. The fraction of these atoms that came from Caesar's last breath, f , is given by

$$f = \frac{\bar{N}_{Ar} V}{N_{Ar}} = \frac{2.41 \times 10^{23} \text{ m}^{-3} \times 0.450 \times 10^{-3} \text{ m}^3}{1.08 \times 10^{42}} = 1.00 \times 10^{-22}$$

The number of Ar atoms that we inhale with each breath is

$$N = N_A \frac{PV}{RT} = 6.023 \times 10^{23} \times \frac{10^{-2} \times 1.01325 \times 10^5 \text{ Pa} \times 0.450 \times 10^{-3} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}} = 1.10 \times 10^{20}$$

The number of these that came from Caesar's last breath is fN

$$fN = 1.00 \times 10^{-22} \times 1.10 \times 10^{20} = 1.10 \times 10^{-2}$$

The reciprocal of this result, or 91, is the number of breaths needed to inhale one Ar atom that Caesar exhaled in his last breath.

P1.25 Calculate the number of molecules per m^3 in an ideal gas at the standard temperature and pressure conditions of 0.00°C and 1.00 atm .

$$N = N_A \times \frac{PV}{RT} = 6.022 \times 10^{23} \times \frac{1 \text{ atm} \times 1000. \text{ L}}{8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}} = 2.69 \times 10^{25}$$

P1.26 Consider a gas mixture in a 1.50-dm^3 flask at 22.0°C . For each of the following mixtures, calculate the partial pressure of each gas, the total pressure, and the composition of the mixture in mole percent:

- 3.06 g H_2 and 2.98 g O_2
- 2.30 g N_2 and 1.61 g O_2
- 2.02 g CH_4 and 1.70 g NH_3

$$(a) \quad P_{\text{H}_2} = \frac{n_{\text{H}_2} RT}{V} = \frac{(3.06/2.016) \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 295.15 \text{ K}}{1.50 \times 10^{-3} \text{ m}^3} = 2.48 \times 10^6 \text{ Pa}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{V} = \frac{2.98/32.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 295.15 \text{ K}}{1.50 \times 10^{-3} \text{ m}^3} = 1.52 \times 10^5 \text{ Pa}$$

$$P_{\text{total}} = 2.64 \times 10^6 \text{ Pa}$$

$$\text{mol \% H}_2 = 100 \times \frac{\text{mol H}_2}{\text{mol H}_2 + \text{mol O}_2} = 100 \times \frac{3.06/2.016}{3.06/2.016 + 2.98/32.00} = 94.2\%$$

$$\text{mol \% O}_2 = 100 \times \frac{\text{mol O}_2}{\text{mol H}_2 + \text{mol O}_2} = 100 \times \frac{2.98/32.00}{3.06/2.016 + 2.98/32.00} = 5.78\%$$

$$(b) \quad P_{\text{N}_2} = \frac{n_{\text{N}_2} RT}{V} = \frac{2.30/28.02 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 295.15 \text{ K}}{1.50 \times 10^{-3} \text{ m}^3} = 1.34 \times 10^5 \text{ Pa}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{V} = \frac{1.61/32.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 295.15 \text{ K}}{1.50 \times 10^{-3} \text{ m}^3} = 8.23 \times 10^4 \text{ Pa}$$

$$P_{\text{total}} = 2.17 \times 10^5 \text{ Pa}$$

$$\text{mol \% N}_2 = 100 \times \frac{\text{mol N}_2}{\text{mol N}_2 + \text{mol O}_2} = 100 \times \frac{2.30/28.02}{2.30/28.02 + 1.61/32.00} = 62.0\%$$

$$\text{mol \% O}_2 = 100 \times \frac{\text{mol O}_2}{\text{mol N}_2 + \text{mol O}_2} = 100 \times \frac{1.61/32.00}{2.30/28.02 + 1.61/32.00} = 38.0\%$$

$$(c) \quad P_{\text{NH}_3} = \frac{n_{\text{NH}_3}RT}{V} = \frac{1.70/17.03 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 295.15 \text{ K}}{1.50 \times 10^{-3} \text{ m}^3} = 1.63 \times 10^5 \text{ Pa}$$

$$P_{\text{CH}_4} = \frac{n_{\text{CH}_4}RT}{V} = \frac{2.02/16.04 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 295.15 \text{ K}}{1.50 \times 10^{-3} \text{ m}^3} = 2.06 \times 10^5 \text{ Pa}$$

$$P_{\text{total}} = 3.69 \times 10^5 \text{ Pa}$$

$$\text{mol \% NH}_3 = 100 \times \frac{\text{mol NH}_3}{\text{mol NH}_3 + \text{mol CH}_4} = 100 \times \frac{1.70/17.03}{1.70/17.03 + 2.02/16.04} = 44.2\%$$

$$\text{mol \% CH}_4 = 100 \times \frac{\text{mol CH}_4}{\text{mol NH}_3 + \text{mol CH}_4} = 100 \times \frac{2.02/16.04}{1.70/17.03 + 2.02/16.04} = 55.8\%$$

- P1.27** A mixture of H_2 and NH_3 has a volume of 139.0 cm^3 at 0.00°C and 1 atm. The mixture is cooled to the temperature of liquid nitrogen, at which ammonia freezes out and the remaining gas is removed from the vessel. Upon warming the vessel to 0.00°C and 1 atm, the volume is 77.4 cm^3 . Calculate the mole fraction of NH_3 in the original mixture.

We can calculate the total number of mols of both gases from the information in the first sentence. The number of mols of ammonia can be calculated from the information in the third sentence.

$$n_{\text{total}} = \frac{PV_1}{RT} = \frac{1 \text{ atm} \times 0.1390 \text{ L}}{8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}} = 6.20 \times 10^{-3} \text{ mol}$$

$$n_{\text{NH}_3} = \frac{PV_2}{RT} = \frac{1 \text{ atm} \times 0.0774 \text{ L}}{8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}} = 3.45 \times 10^{-3} \text{ mol}$$

$$x_{\text{NH}_3} = \frac{n_{\text{NH}_3}}{n_{\text{total}}} = \frac{3.45 \times 10^{-3} \text{ mol}}{6.20 \times 10^{-3} \text{ mol}} = 0.557$$

- P1.28** A sealed flask with a capacity of 1.22 dm^3 contains 4.50 g of carbon dioxide. The flask is so weak that it will burst if the pressure exceeds $9.50 \times 10^5 \text{ Pa}$. At what temperature will the pressure of the gas exceed the bursting pressure?

$$T = \frac{PV}{nR} = \frac{9.50 \times 10^5 \text{ Pa} \times 10^{-3} \text{ m}^3}{\frac{4.50 \text{ g}}{44.01 \text{ g mol}^{-1}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} = 1.36 \times 10^3 \text{ K}$$

- P1.29** A balloon filled with 11.50 L of Ar at 18.7°C and one atm rises to a height in the atmosphere where the pressure is 207 Torr and the temperature is -32.4°C . What is the final volume of the balloon? Assume that the pressure inside and outside the balloon have the same value.

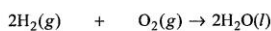
$$V_f = \frac{P_i T_f}{P_f T_i} V_i = \frac{760 \text{ Torr} \times (273.15 - 32.4) \text{ K}}{207 \text{ Torr} \times (273.15 + 18.7) \text{ K}} \times 11.5 \text{ L} = 34.8 \text{ L}$$

- P1.30** Carbon monoxide competes with oxygen for binding sites on the transport protein hemoglobin. CO can be poisonous if inhaled in large quantities. A safe level of CO in air is 50 parts per million (ppm). When the CO level increases to 800 ppm, dizziness, nausea, and unconsciousness occur, followed by death. Assuming the partial pressure of oxygen in air at sea level is 0.20 atm, what proportion of CO to O_2 is fatal?

$$x_{\text{O}_2} = \frac{0.20 \text{ atm}}{1 \text{ atm}} = 2.0 \times 10^5 \text{ ppm}$$

$$\frac{x_{\text{CO}}}{x_{\text{O}_2}} = \frac{800 \text{ ppm}}{2.0 \times 10^5 \text{ ppm}} = 4.0 \times 10^{-3}$$

- P1.31** The total pressure of a mixture of oxygen and hydrogen is 1.65 atm. The mixture is ignited and the water is removed. The remaining gas is pure hydrogen and exerts a pressure of 0.190 atm when measured at the same values of T and V as the original mixture. What was the composition of the original mixture in mole percent?



$$\text{initial moles} \quad n_{\text{H}_2}^{\circ} \quad n_{\text{O}_2}^{\circ} \quad 0$$

$$\text{after reaction} \quad n_{\text{H}_2}^{\circ} - 2\alpha \quad n_{\text{O}_2}^{\circ} - \alpha \quad 2\alpha$$

If the O_2 is completely consumed, $n_{\text{O}_2}^{\circ} - \alpha = 0$ or $\alpha = n_{\text{O}_2}^{\circ}$. The number of moles of H_2 remaining is $n_{\text{H}_2}^{\circ} - 2\alpha = n_{\text{H}_2}^{\circ} - 2n_{\text{O}_2}^{\circ}$.

Let P_1 be the initial total pressure and P_2 be the total pressure after all the O_2 is consumed.

$$P_1 = \left(n_{\text{H}_2}^{\circ} + n_{\text{O}_2}^{\circ} \right) \frac{RT}{V} \quad \text{and} \quad P_2 = \left(n_{\text{H}_2}^{\circ} - 2n_{\text{O}_2}^{\circ} \right) \frac{RT}{V}$$

Dividing the second equation by the first

$$\frac{P_2}{P_1} = \frac{n_{\text{H}_2}^{\circ}}{n_{\text{H}_2}^{\circ} + n_{\text{O}_2}^{\circ}} - 2 \frac{n_{\text{O}_2}^{\circ}}{n_{\text{H}_2}^{\circ} + n_{\text{O}_2}^{\circ}} = x_{\text{H}_2} - 2x_{\text{O}_2} = 1 - x_{\text{O}_2} - 2x_{\text{O}_2} = 1 - 3x_{\text{O}_2}$$

$$x_{\text{O}_2} = \frac{1}{3} \left(1 - \frac{P_2}{P_1} \right) = \frac{1}{3} \left(1 - \frac{0.190 \text{ atm}}{1.65 \text{ atm}_1} \right) = 0.295; \quad x_{\text{H}_2} = 0.705$$

- P1.32** Suppose that you measured the product PV of 1 mol of a dilute gas and found that $PV = 24.35 \text{ L atm}$ at 0.00°C and 33.54 L atm at 100°C . Assume that the ideal gas law is valid, with $T = t(^{\circ}\text{C}) + a$, and that the values of R and a are not known. Determine R and a from the measurements provided.

Expressing the ideal gas law in the form $PV = R'(t + a)$

$$R' = \frac{\Delta PV}{\Delta t} = \frac{(33.54 - 24.35) \text{ L atm mol}^{-1}}{(100 - 0)^{\circ}\text{C}} = 0.0919 \text{ L atm mol}^{-1} \text{ } ^{\circ}\text{C}^{-1} = R$$

$$a = \frac{PV}{R'} - t = \frac{33.54 \text{ L atm mol}^{-1}}{0.0919 \text{ L atm mol}^{-1} \text{ } ^{\circ}\text{C}^{-1}} - 100^{\circ}\text{C} = 265.0^{\circ}\text{C}$$

- P1.33** Liquid N_2 has a density of 875.4 kg m^{-3} at its normal boiling point. What volume does a balloon occupy at 298 K and a pressure of 1.00 atm if $3.10 \times 10^{-3} \text{ L}$ of liquid N_2 is injected into it? Assume that there is no pressure difference between the inside and outside of the balloon.

$$n_{\text{N}_2} = \frac{\rho_{\text{N}_2} V_{\text{liq}}}{M_{\text{N}_2}}$$

$$V_{\text{N}_2} = \frac{n_{\text{N}_2} RT}{P} = \frac{\rho_{\text{N}_2} V_{\text{liq}} RT}{M_{\text{N}_2} P}$$

$$= \frac{875.4 \text{ g L}^{-1} \times 3.10 \times 10^{-3} \text{ L} \times 8.2057 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{28.01 \text{ g mol}^{-1} \times 1 \text{ atm}} = 2.37 \text{ L}$$

- P1.34** Calculate the volume of all gases evolved by the complete oxidation of 0.375 g of the amino acid alanine $\text{NH}_2\text{CH}(\text{CH}_3)\text{COOH}$ if the products are liquid water, nitrogen gas, and carbon dioxide gas, the total pressure is 1.00 atm , and $T = 298 \text{ K}$.

The initial information allows us to calculate the number of moles of alanine. The number of moles of CO_2 can be calculated from the number of carbon atoms in a molecule of alanine.

$$\begin{aligned}
 n_{\text{alanine}} &= \frac{m_{\text{alanine}}}{M_{\text{alanine}}} = \frac{0.375 \text{ g}}{88.09 \text{ g mol}^{-1}} = 4.26 \times 10^{-4} \text{ mol} \\
 n_{N_2} &= 0.5n_{\text{alanine}} \\
 n_{CO_2} &= 3n_{\text{alanine}} \\
 V_{N_2} &= \frac{n_{N_2}RT}{P} \\
 &= \frac{0.5 \times 4.26 \times 10^{-4} \text{ mol} \times 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ atm}} = 0.0521 \text{ L} \\
 V_{CO_2} &= \frac{n_{CO_2}RT}{P} \\
 &= \frac{3 \times 4.26 \times 10^{-4} \text{ mol} \times 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ atm}} = 0.312 \text{ L} \\
 V_{\text{total}} &= V_{CO_2} + V_{N_2} = 0.364 \text{ L}
 \end{aligned}$$

- P1.35** As a result of photosynthesis, an acre of forest (1 acre = 4047 square meter) can take up 1000. kg of CO_2 . Assuming air is 0.0314% CO_2 by volume, what volume of air is required to provide 350. kg of CO_2 ? Assume $T = 310 \text{ K}$ and $P = 1.00 \text{ atm}$.

$$\begin{aligned}
 V_{CO_2} &= \frac{n_{CO_2}RT}{P} = \frac{\frac{1000. \text{ kg}}{44.01 \times 10^{-3} \text{ kg mol}^{-1}} \times 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 310. \text{ K}}{1 \text{ atm}} \\
 &= 2.02 \times 10^5 \text{ L} \\
 V_{\text{air}} &= \frac{V_{CO_2}}{0.000314} = 6.44 \times 10^8 \text{ L}
 \end{aligned}$$

- P1.36** A glass bulb of volume 0.198 L contains 0.457 g of gas at 759.0 Torr and 134.0°C. What is the molar mass of the gas?

$$\begin{aligned}
 n &= \frac{m}{M} = \frac{PV}{RT}; \quad M = m \frac{RT}{PV} \\
 M &= 0.457 \text{ g} \times \frac{8.2057 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times (273.15 + 134.0) \text{ K}}{\frac{759}{760} \text{ atm} \times 0.198 \text{ L}} = 77.2 \text{ amu}
 \end{aligned}$$

- P1.37** Use L'Hôpital's rule, $\lim_{x \rightarrow 0} [f(x)/g(x)] = \lim_{x \rightarrow 0} \left[\frac{df(x)/dx}{dg(x)/dx} \right]$ to show that the expression derived for P_f in part b of Example Problem 1.1 has the correct limit as $\gamma \rightarrow 0$.

$$\begin{aligned}
 \frac{P_f V_f}{T_f} &= \frac{P_f V_f (1 + \gamma(P_f - P_i))}{T_f} \\
 P_i T_f &= P_f T_i (1 + \gamma(P_f - P_i)) \\
 P_f^2 T_i \gamma + P_f T_i (1 - P_i \gamma) - P_i T_f &= 0 \\
 P_f &= \frac{-T_i (1 - P_i \gamma) \pm \sqrt{T_i^2 (1 - P_i \gamma)^2 + 4 T_i T_f \gamma P_i}}{2 T_i \gamma}
 \end{aligned}$$

$$\begin{aligned} \lim_{\gamma \rightarrow 0} \frac{df(\gamma)/d\gamma}{dg(\gamma)/d\gamma} &= \frac{d\left(-T_i(1-P_i\gamma) \pm \sqrt{T_i^2(1-P_i\gamma)^2 + 4T_iT_f\gamma P_i}\right)/d\gamma}{d(2T_i\gamma)/d\gamma} \\ &= \lim_{\gamma \rightarrow 0} \frac{T_i P_i + \frac{2T_i^2(1-P_i\gamma)(-P_i) + 4T_iT_fP_i}{2\sqrt{T_i^2(1-P_i\gamma)^2 + 4T_iT_f\gamma P_i}}}{2T_i} = \frac{T_i P_i + \frac{2T_i^2(-P_i) + 4T_iT_fP_i}{2T_i}}{2T_i} \\ &= \frac{T_i P_i + -P_i T_i + 2T_f P_i}{2T_i} = \frac{T_f P_i}{T_i} \end{aligned}$$

- P1.38** A 455 cm³ vessel contains a mixture of Ar and Xe. If the mass of the gas mixture is 2.245 g at 25.0°C and the pressure is 760. Torr, calculate the mole fraction of Xe in the mixture.

From the information provided, we can set up two equations for the two unknowns n_{Ar} and n_{Xe} .

$$\begin{aligned} n_{Ar}M_{Ar} + n_{Xe}M_{Xe} &= \text{mass} \\ n_{Ar} + n_{Xe} &= \frac{PV}{RT} \\ 39.95 n_{Ar} + 131.29 n_{Xe} &= 2.245 \text{ g} \\ n_{Ar} + n_{Xe} &= \frac{1 \text{ atm} \times 0.455 \text{ L}}{8.206 \times 10^{-2} \text{ atm L mol}^{-1} \text{ K} \times 298.15 \text{ K}} = 0.186 \text{ mol} \end{aligned}$$

Solving these two equations gives $n_{Ar} = 0.00215$ moles and $n_{Xe} = 0.0164$ moles.

$$x_{Xe} = \frac{n_{Xe}}{n_{Xe} + n_{Ar}} = \frac{0.0164 \text{ mol}}{0.0164 \text{ mol} + 0.00215 \text{ mol}} = 0.884$$

- P1.39** Many processes such as the fabrication of integrated circuits are carried out in a vacuum chamber to avoid reaction of the material with oxygen in the atmosphere. It is difficult to routinely lower the pressure in a vacuum chamber below 1.0×10^{-10} Torr. Calculate the molar density at this pressure at 300. K. What fraction of the gas phase molecules initially present for 1.0 atm in the chamber are present at 1.0×10^{-10} Torr?

$$\begin{aligned} \rho_{\text{molar}} &= \frac{P}{RT} = \frac{1.0 \times 10^{-10} \text{ Torr}}{62.36 \text{ Torr L mol}^{-1} \text{ K} \times 300. \text{ K}} = 5.35 \times 10^{-15} \text{ mol L}^{-1} \\ \text{fraction} &= \frac{P}{P_{\text{atm}}} = \frac{1.0 \times 10^{-10} \text{ Torr}}{760 \text{ Torr}} = 1.32 \times 10^{-13} \end{aligned}$$

- P1.40** Rewrite the van der Waals equation using the molar volume rather than V and n .

$$\begin{aligned} P &= \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \\ &= \frac{RT}{V/n-b} - \frac{a}{V^2/n^2} = \frac{RT}{V_m-b} - \frac{a}{V_m^2} \end{aligned}$$