21.4 Discuss the mechanism of proton conduction in liquid water.

21.5 Limit the generality of the following expressions: (a) \[ J = -D \frac{dc}{dx} \], (b) \[ D = kT/\sigma \], and (c) \[ D = kT/6\pi \eta a \].

21.6 Provide a molecular interpretation for the observation that mediated transport across a biological membrane leads to a maximum flux \( f_{\text{max}} \) when the concentration of the transported species becomes very large.

21.7 Discuss how nuclear magnetic resonance spectroscopy, inelastic neutron scattering, and dynamic light scattering may be used to measure the mobility of molecules in liquids.

Exercises

21.1a Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of \( \text{H}_2 \) molecules and \( \text{Hg} \) atoms at 20°C.

21.1b Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of \( \text{He} \) atoms and \( \text{Hg} \) atoms at 25°C.

21.2a A 1.0 dm\(^3\) glass bulb contains \( 1.0 \times 10^{23} \) \( \text{H}_2 \) molecules. If the pressure exerted by the gas is 100 kPa, what are (a) the temperature of the gas, (b) the root mean square speed of the molecules? (c) Would the temperature be different if they were \( \text{O}_2 \) molecules?

21.2b The best laboratory vacuum pump can generate a vacuum of about 1 nTorr. At 25°C and assuming that air consists of \( \text{N}_2 \) molecules with a collision diameter of 395 pm, calculate (a) the mean speed of the molecules, (b) the mean free path, (c) the collision frequency in the gas.

21.3a At what pressure does the mean free path of argon at 25°C become comparable to the size of a 1 dm\(^3\) vessel that contains it? Take \( \sigma = 0.36 \text{ nm}^2 \).

21.3b At what pressure does the mean free path of argon at 25°C become comparable to the diameters of the atoms themselves?

21.4a At an altitude of 20 km the temperature is 217 K and the pressure 0.050 atm. What is the mean free path of \( \text{N}_2 \) molecules? (\( \sigma = 0.43 \text{ nm}^2 \).)

21.4b At an altitude of 15 km the temperature is 217 K and the pressure 12.1 kPa. What is the mean free path of \( \text{N}_2 \) molecules? (\( \sigma = 0.43 \text{ nm}^2 \).)

21.5a How many collisions does a single \( \text{Ar} \) atom make in 1.0 s when the temperature is 25°C and the pressure is (a) 10 atm, (b) 1.0 atm, (c) 1.0 \text{ \mu m} \text{t} \text{ atm} ?

21.5b How many collisions per second does an \( \text{N}_2 \) molecule make at an altitude of 15 km? (See Exercise 21.4b for data.)

21.6a Calculate the mean free path of molecules in air using \( \sigma = 0.43 \text{ nm}^2 \) at 25°C and (a) 10 atm, (b) 1.0 atm, (c) 1.0 \text{ \mu m} \text{t} \text{ atm} .

21.6b Calculate the mean free path of carbon dioxide molecules using \( \sigma = 0.50 \text{ nm}^2 \) at 25°C and (a) 15 atm, (b) 1.0 bar, (c) 1.0 Torr.

21.7a Use the Maxwell distribution of speeds to estimate the fraction of \( \text{N}_2 \) molecules at 500 K that have speeds in the range 290 to 300 m s\(^{-1} \).

21.7b Use the Maxwell distribution of speeds to estimate the fraction of \( \text{CO}_2 \) molecules at 300 K that have speeds in the range 200 to 250 m s\(^{-1} \).

21.8a A solid surface with dimensions 2.5 mm \( \times \) 3.0 mm is exposed to argon gas at 90 Pa and 500 K. How many collisions do the \( \text{Ar} \) atoms make with this surface in 15 s?

21.8b A solid surface with dimensions 3.5 mm \( \times \) 4.0 cm is exposed to helium gas at 111 Pa and 1500 K. How many collisions do the \( \text{He} \) atoms make with this surface in 10 s?

21.9a An effusion cell has a circular hole of diameter 2.50 mm. If the molar mass of the solid in the cell is 260 g mol\(^{-1} \) and its vapour pressure is 0.835 Pa at 400 K, by how much will the mass of the solid decrease in a period of 2.00 h?

21.9b An effusion cell has a circular hole of diameter 3.00 mm. If the molar mass of the solid in the cell is 300 g mol\(^{-1} \) and its vapour pressure is 0.224 Pa at 450 K, by how much will the mass of the solid decrease in a period of 24.00 h?

21.10a A manometer was connected to a bulb containing carbon dioxide under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 75 cm to 50 cm was 52 s. When the experiment was repeated using nitrogen (for which \( M = 28.02 \text{ g mol}^{-1} \)) the same fall took place in 42 s. Calculate the molar mass of carbon dioxide.

21.10b A manometer was connected to a bulb containing nitrogen under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 65.1 cm to 42.1 cm was 18.5 s. When the experiment was repeated using a fluorocarbon gas, the same fall took place in 82.3 s. Calculate the molar mass of the fluorocarbon.

21.11a A space vehicle of internal volume 3.0 m\(^3\) is struck by a meteor and a hole of radius 0.1 mm is formed. If the oxygen pressure within the vehicle is initially 80 kPa and its temperature 298 K, how long will the pressure take to fall to 10 kPa?

21.11b A container of internal volume 22.0 m\(^3\) was punctured, and a hole of radius 0.050 mm was formed. If the nitrogen pressure within the vehicle is initially 122 kPa and its temperature 293 K, how long will the pressure take to fall to 105 kPa?

21.12a Calculate the flux of energy arising from a temperature gradient of 2.5 K m\(^{-1} \) in a sample of argon in which the mean temperature is 273 K.

21.12b Calculate the flux of energy arising from a temperature gradient of 3.5 K m\(^{-1} \) in a sample of hydrogen in which the mean temperature is 260 K.

21.13a Use the experimental value of the thermal conductivity of neon (Table 21.2) to estimate the collision cross-section of Ne atoms at 273 K.

21.13b Use the experimental value of the thermal conductivity of nitrogen (Table 21.2) to estimate the collision cross-section of \( \text{N}_2 \) molecules at 298 K.

21.14a In a double-glazed window, the panes of glass are separated by 5.0 cm. What is the rate of transfer of heat by conduction from the warm room (25°C) to the cold exterior (−10°C) through a window of area 1.0 m\(^2 \)? What power of heater is required to make good the loss of heat?

21.14b Two sheets of copper of area 1.50 m\(^2 \) are separated by 10.0 cm. What is the rate of transfer of heat by conduction from the warm room (25°C) to the cold exterior (−10°C) through a window of area 1.0 m\(^2 \)? What power of heater is required to make good the loss of heat?

21.15a Use the experimental value of the coefficient of viscosity for neon (Table 21.2) to estimate the collision cross-section of Ne atoms at 273 K.

21.15b Use the experimental value of the coefficient of viscosity for nitrogen (Table 21.2) to estimate the collision cross-section of the molecules at 273 K.

21.16a Calculate the inlet pressure required to maintain a flow rate of 9.5 \( \times \) 10\(^{-3} \) dm\(^3\) h\(^{-1} \) of nitrogen at 293 K flowing through a pipe of length 8.50 m...
and diameter 1.00 cm. The pressure of gas as it leaves the tube is 1.00 bar. The volume of the gas is measured at that pressure.

21.16b Calculate the inlet pressure required to maintain a flow rate of 8.70 cm$^3$ s$^{-1}$ of nitrogen at 300 K flowing through a pipe of length 10.5 m and diameter 15 mm. The pressure of gas as it leaves the tube is 1.00 bar. The volume of the gas is measured at that pressure.

21.17a Calculate the viscosity of air at (a) 273 K, (b) 298 K, (c) 1000 K. Take $\sigma = 0.40$ nm$^2$. (The experimental values are 173 $\mu$P at 273 K, 182 $\mu$P at 20°C, and 394 $\mu$P at 600°C.)

21.17b Calculate the viscosity of benzene vapour at (a) 273 K, (b) 298 K, (c) 1000 K. Take $\sigma = 0.88$ nm$^2$.

21.18a Calculate the thermal conductivities of (a) argon, (b) helium at 300 K and 1.0 mbar. Each gas is confined in a cubic vessel of side 10 cm, one wall being at 310 K and the one opposite at 295 K. What is the rate of flow of energy as heat from one wall to the other in each case?

21.18b Calculate the thermal conductivities of (a) neon, (b) nitrogen at 300 K and 15 mbar. Each gas is confined in a cubic vessel of side 15 cm, one wall being at 305 K and the one opposite at 295 K. What is the rate of flow of energy as heat from one wall to the other in each case?

21.19a The viscosity of carbon dioxide was measured by comparing its rate of flow through a long narrow tube (using Poiseuille’s formula) with that of argon. For the same pressure differential, the same volume of carbon dioxide passed through the tube in 55 s as argon in 83 s. The viscosity of argon at 25°C is 208 $\mu$P; what is the viscosity of carbon dioxide? Estimate the molecular diameter of carbon dioxide.

21.19b The viscosity of a chlorofluorocarbon (CFC) was measured by comparing its rate of flow through a long narrow tube (using Poiseuille’s formula) with that of argon. For the same pressure differential, the same volume of the CFC passed through the tube in 72.0 s as argon in 18.0 s. The viscosity of argon at 25°C is 208 $\mu$P; what is the viscosity of the CFC? Estimate the molecular diameter of the CFC.

21.20a Calculate the thermal conductivity of argon ($C_{V,m} = 12.5$ J K$^{-1}$ mol$^{-1}$, $\sigma = 0.36$ nm$^2$) at room temperature (20°C).

21.20b Calculate the thermal conductivity of nitrogen ($C_{V,m} = 20.8$ J K$^{-1}$ mol$^{-1}$, $\sigma = 0.43$ nm$^2$) at room temperature (20°C).

21.21a Calculate the diffusion constant of argon at 25°C and (a) 1.00 Pa, (b) 100 kPa, (c) 10.0 MPa. If a pressure gradient of 0.10 atm cm$^{-1}$ is established in a pipe, what is the flow of gas due to diffusion?

21.21b Calculate the diffusion constant of nitrogen at 25°C and (a) 1.00 Pa, (b) 100 kPa, (c) 15.0 MPa. If a pressure gradient of 0.20 bar m$^{-1}$ is established in a pipe, what is the flow of gas due to diffusion?

21.22a The mobility of a chloride ion in aqueous solution at 25°C is $7.91 \times 10^{-8}$ m$^2$ s$^{-1}$ V$^{-1}$. Calculate the molar ionic conductivity.

21.22b The mobility of an acetate ion in aqueous solution at 25°C is $4.24 \times 10^{-8}$ m$^2$ s$^{-1}$ V$^{-1}$. Calculate the molar ionic conductivity.

21.23a The mobility of a Rb$^+$ ion in aqueous solution is $7.92 \times 10^{-9}$ m$^2$ s$^{-1}$ V$^{-1}$ at 25°C. The potential difference between two electrodes placed in the solution is 35.0 V. If the electrodes are 8.00 mm apart, what is the drift speed of the Rb$^+$ ion?

21.23b The mobility of a Li$^+$ ion in aqueous solution is $4.01 \times 10^{-8}$ m$^2$ s$^{-1}$ V$^{-1}$ at 25°C. The potential difference between two electrodes placed in the solution is 12.0 V. If the electrodes are 1.00 cm apart, what is the drift speed of the ion?

21.24a What fraction of the total current is carried by Li$^+$ when current flows through an aqueous solution of LiBr at 25°C?

21.24b What fraction of the total current is carried by Cl$^-$ when current flows through an aqueous solution of NaCl at 25°C?

21.25a The limiting molar conductivities of KCl, KNO$_3$, and AgNO$_3$ are 14.99 mS m$^2$ mol$^{-1}$, 14.50 mS m$^2$ mol$^{-1}$, and 13.34 mS m$^2$ mol$^{-1}$, respectively (all at 25°C). What is the limiting molar conductivity of AgCl at this temperature?

21.25b The limiting molar conductivities of NaI, NaCH$_3$CO$_2$, and Mg(CH$_3$CO$_2$)$_2$ are 12.69 mS m$^2$ mol$^{-1}$, 9.10 mS m$^2$ mol$^{-1}$, and 18.78 mS m$^2$ mol$^{-1}$, respectively (all at 25°C). What is the limiting molar conductivity of MgI$_2$ at this temperature?

21.26a At 25°C the molar ionic conductivities of Li$^+$, Na$^+$, and K$^+$ are 3.87 mS m$^2$ mol$^{-1}$, 5.01 mS m$^2$ mol$^{-1}$, and 7.35 mS m$^2$ mol$^{-1}$, respectively. What are their mobilities?

21.26b At 25°C the molar ionic conductivities of F$^-$, Cl$^-$, and Br$^-$ are 5.54 mS m$^2$ mol$^{-1}$, 7.635 mS m$^2$ mol$^{-1}$, and 7.81 mS m$^2$ mol$^{-1}$, respectively. What are their mobilities?

21.27a The molarity of a NO$_3^-$ ion in aqueous solution at 25°C is $7.40 \times 10^{-8}$ m$^2$ s$^{-1}$ V$^{-1}$. Calculate its diffusion coefficient in water at 25°C.

21.27b The molarity of a CH$_3$CO$_2^-$ ion in aqueous solution at 25°C is $4.24 \times 10^{-8}$ m$^2$ s$^{-1}$ V$^{-1}$. Calculate its diffusion coefficient in water at 25°C.

21.28a The diffusion coefficient of CCl$_4$ in heptane at 25°C is $3.17 \times 10^{-9}$ m$^2$ s$^{-1}$. Estimate the time required for a CCl$_4$ molecule to have a root mean square displacement of 5.0 mm.

21.28b The diffusion coefficient of I$_2$ in hexane at 25°C is $4.05 \times 10^{-9}$ m$^2$ s$^{-1}$. Estimate the time required for an iodine molecule to have a root mean square displacement of 1.0 cm.

21.29a Estimate the effective radius of a sucrose molecule in water at 25°C given that its diffusion coefficient is $5.2 \times 10^{-10}$ m$^2$ s$^{-1}$ and that the viscosity of water is 1.00 cP.

21.29b Estimate the effective radius of a glycine molecule in water at 25°C given that its diffusion coefficient is $1.055 \times 10^{-9}$ m$^2$ s$^{-1}$ and that the viscosity of water is 1.00 cP.

21.30a The diffusion coefficient for molecular iodine in benzene is $2.13 \times 10^{-9}$ m$^2$ s$^{-1}$. How long does a molecule take to jump through about one molecular diameter (approximately the fundamental jump length for translational motion)?

21.30b The diffusion coefficient for CCl$_4$ in heptane is $3.17 \times 10^{-9}$ m$^2$ s$^{-1}$. How long does a molecule take to jump through about one molecular diameter (approximately the fundamental jump length for translational motion)?

21.31a What are the root mean square distances travelled by an iodine molecule in benzene and by a sucrose molecule in water at 25°C in 1.0 s?

21.31b About how long, on average, does it take for the molecules in Exercise 21.31a to drift to a point (a) 1.0 mm, (b) 1.0 cm from their starting points?
21.1 Instead of the arrangement in Fig. 21.8, the speed of molecules can also be measured with a rotating slotted-disc apparatus, which consists of five coaxial 5.0 cm diameter discs separated by 1.0 cm, the slots in their rims being displaced by 2.0° between neighbours. The relative intensities, I, of the detected beam of Kr atoms for two different temperatures and at a series of rotation rates were as follows:

<table>
<thead>
<tr>
<th>v/Hz</th>
<th>I (40 K)</th>
<th>I (100 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.846</td>
<td>0.592</td>
</tr>
<tr>
<td>40</td>
<td>0.513</td>
<td>0.485</td>
</tr>
<tr>
<td>80</td>
<td>0.069</td>
<td>0.217</td>
</tr>
<tr>
<td>100</td>
<td>0.015</td>
<td>0.119</td>
</tr>
<tr>
<td>120</td>
<td>0.002</td>
<td>0.057</td>
</tr>
</tbody>
</table>

Find the distributions of molecular velocities, f(v), at these temperatures, and check that they conform to the theoretical prediction for a one-dimensional system.

21.2 Cars were timed by police radar as they passed in both directions below a bridge. Their velocities (kilometres per hour, numbers of cars in parentheses) to the east and west were as follows: 80 (E40), 85 (E62), 90 (E53), 95 (E12), 100 (E2); 80 W (38), 85 W (59), 90 W (50), 95 W (10), 100 W (2). What are (a) the mean velocity, (b) the mean speed, (c) the root mean square speed?

21.3 A population consists of people of the following heights (in metres, numbers of individuals in brackets): 1.80 (1), 1.82 (2), 1.84 (4), 1.86 (7), 1.88 (10), 1.90 (15), 1.92 (9), 1.94 (4), 1.96 (10), 1.98 (1). What are (a) the mean height, (b) the root mean square height of the population?

21.4 Calculate the ratio of the thermal conductivities of gaseous hydrogen at 300 K to gaseous hydrogen at 10 K. Be circumspect, and think about the modes of motion that are thermally active at the two temperatures.

21.5 A Knudsen cell was used to determine the vapour pressure of germanium at 1000°C. During an interval of 7200 s the mass loss through a hole of radius 0.50 mm amounted to 43 µg. What is the vapour pressure of germanium at 1000°C? Assume the gas to be monatomic.

21.6 The nuclide 244Bk (berkelium) decays by producing α particles, which capture electrons and form He atoms. Its half-life is 4.4 h. A sample of mass 1.0 mg was placed in a container of volume 1.0 cm³ that was impermeable to α radiation, but there was also a hole of radius 2.0 µm in the wall. What is the pressure of helium at 298 K, inside the container after (a) 1.0 h, (b) 10 h?

21.7 An atomic beam is designed to function with (a) cadmium, (b) mercury. The source is an oven maintained at 380 K, there being a small slit of dimensions 1.0 cm × 1.0 × 10⁻⁶ cm. The vapour pressure of cadmium is 0.13 Pa and that of mercury is 12 Pa at this temperature. What is the atomic current (the number of atoms per unit time) in the beams?

21.8 Conductivities are often measured by comparing the resistance of a cell filled with the sample to its resistance when filled with some standard solution, such as aqueous potassium chloride. The conductivity of water is 76 mS m⁻¹ at 25°C and the conductivity of 0.100 mol dm⁻³ KCl(aq) is 1.1635 S m⁻¹. A cell had a resistance of 33.21 Ω when filled with 0.100 mol dm⁻³ KCl(aq) and 300.0 Ω when filled with 0.100 mol dm⁻³ CH₃COOH. What is the molar conductivity of acetic acid at that concentration and temperature?

21.9 The resistances of a series of aqueous NaCl solutions, formed by successive dilution of a sample, were measured in a cell with cell constant (the constant C in the relation κ = C/İ) equal to 0.2063 cm⁻¹. The following values were found:

<table>
<thead>
<tr>
<th>c/(mol dm⁻³)</th>
<th>0.00050</th>
<th>0.0010</th>
<th>0.0050</th>
<th>0.010</th>
<th>0.020</th>
<th>0.050</th>
</tr>
</thead>
<tbody>
<tr>
<td>R/Ω</td>
<td>3314</td>
<td>1669</td>
<td>342.1</td>
<td>174.1</td>
<td>89.08</td>
<td>37.14</td>
</tr>
</tbody>
</table>

Verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity. Determine the coefficient κ. Use the value of κ (which should depend only on the nature, not the identity of the ions) and the information that λ(Na⁺) = 5.01 mS m⁻¹mol⁻¹ and λ(Cl⁻) = 7.68 mS m⁻²mol⁻¹ to predict (a) the molar conductivity, (b) the conductivity, (c) the resistance it would show in the cell, of 0.010 mol dm⁻³ NaCl(aq) at 25°C.

21.10 After correction for the water conductivity, the conductivity of a saturated aqueous solution of AgCl at 25°C was found to be 0.1887 mS m⁻¹. What is the solubility of silver chloride at this temperature?

21.11 What are the drift speeds of Li⁺, Na⁺, and K⁺ in water when a potential difference of 10 V is applied across a 1.00-cm conductivity cell? How long would it take an ion to move from one electrode to the other? In conductivity measurements it is normal to use alternating current: what are the displacements of the ions in (a) centimetres, (b) solvent diameters, about 300 pm, during a half cycle of 1.0 kHz applied potential?

21.12 The mobilities of H⁺ and Cl⁻ at 25°C in water are 3.623 × 10⁻⁷ m²s⁻¹ V⁻¹ and 7.91 × 10⁻⁸ m²s⁻¹ V⁻¹, respectively. What proportion of the current is carried by the protons in 10⁻⁷ m HCl(aq)? What fraction do they carry when the NaCl is added to the acid so that the solution is 1.0 mol dm⁻³ in the salt? Note how concentration as well as mobility governs the transport of current.

21.13 In a moving boundary experiment on KCl the apparatus consisted of a tube of internal diameter 4.146 mm, and it contained aqueous KCl at a concentration of 0.021 mol dm⁻³. A steady current of 18.2 mA was passed, and the boundary advanced as follows:

<table>
<thead>
<tr>
<th>Δx/mm</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δt/s</td>
<td>64</td>
<td>128</td>
<td>192</td>
<td>254</td>
<td>318</td>
</tr>
</tbody>
</table>

Find the transport number of K⁺, its mobility, and its ionic conductivity.

21.14 The proton possesses abnormal mobility in water, but does it behave normally in liquid ammonia? To investigate this question, a moving-boundary technique was used to determine the transport number of NH₄⁺ in liquid ammonia (the analogue of H₃O⁺ in liquid water) at −40°C (J. Baldwin, J. Evans, and J. B. Gill, J. Chem. Soc., A, 3389 (1971)). A steady current of 5.000 mA was passed for 2500 s, during which time the boundary formed between mercury(II) iodide and ammonium iodide solutions in ammonia moved 286.9 mm in a 0.013 65 mol kg⁻¹ solution and 92.03 mm in a 0.042 55 mol kg⁻¹ solution. Calculate the transport number of NH₄⁺ at these concentrations, and comment on the mobility of the proton in liquid ammonia. The bore of the tube is 4.146 mm and the density of liquid ammonia is 0.682 g cm⁻³.

21.15 A dilute solution of potassium permanganate in water at 25°C was prepared. The solution was in a horizontal tube of length 10 cm, and at first there was a linear gradation of intensity of the purple solution from the left (where the concentration was 0.100 mol dm⁻³) to the right (where the concentration was 0.050 mol dm⁻³). What is the magnitude and sign of the thermodynamic force acting on the solute (a) close to the left face of the container, (b) in the middle, (c) close to the right face? Give the force per mole and force per molecule in each case.

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.
21.16 Estimate the diffusion coefficients and the effective hydrodynamic radii of the alkali metal cations in water from their mobilities at 25°C. Estimate the approximate number of water molecules that are dragged along by the cations. Ionic radii are given Table 20.3.

21.17 Nuclear magnetic resonance can be used to determine the mobility of molecules in liquids. A set of measurements on methane in carbon tetrachloride showed that its diffusion coefficient is $2.05 \times 10^{-9}$ m$^2$ s$^{-1}$ at 0°C and $2.89 \times 10^{-9}$ m$^2$ s$^{-1}$ at 25°C. Deduce what information you can about the mobility of methane in carbon tetrachloride.

21.18 A concentrated sucrose solution is poured into a cylinder of diameter 5.0 cm. The solution consisted of 10 g of sugar in 5.0 cm$^3$ of water. A further 1.0 dm$^3$ of water is then poured very carefully on top of the layer, without disturbing the layer. Ignore gravitational effects, and pay attention only to diffusional processes. Find the concentration at 5.0 cm above the lower layer after a lapse of (a) 10 s, (b) 1.0 y.

21.19 In a series of observations on the displacement of rubber latex spheres of radius 0.212 μm, the mean square displacements after selected time intervals were on average as follows:

<table>
<thead>
<tr>
<th>t/s</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{12}$ (Å$^2$)/m$^2$</td>
<td>88.2</td>
<td>113.5</td>
<td>128</td>
<td>144</td>
</tr>
</tbody>
</table>

These results were originally used to find the value of Avogadro’s constant, but there are now better ways of determining $N_a$, so the data can be used to find another quantity. Find the effective viscosity of water at the temperature of this experiment (25°C).

21.20‡ A.K. Srivastava, R.A. Samant, and S.D. Patankar (J. Chem. Eng. Data 41, 431 (1996)) measured the conductance of several salts in a binary solvent mixture of water and a dipolar aprotic solvent 1,3-dioxolan-2-one (ethylene carbonate). They report the following conductances at 25°C in a solvent 80 per cent 1,3-dioxolan-2-one by mass:

- NaI

<table>
<thead>
<tr>
<th>c/(mmol dm$^{-3}$)</th>
<th>32.02</th>
<th>20.28</th>
<th>12.06</th>
<th>8.64</th>
<th>2.85</th>
<th>1.24</th>
<th>0.83</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_m/(S$ cm$^2$ mol$^{-1}$)</td>
<td>50.26</td>
<td>51.99</td>
<td>54.01</td>
<td>55.75</td>
<td>57.99</td>
<td>58.44</td>
<td>58.67</td>
</tr>
</tbody>
</table>

KI

<table>
<thead>
<tr>
<th>c/(mmol dm$^{-3}$)</th>
<th>17.68</th>
<th>10.8</th>
<th>8.79</th>
<th>7.19</th>
<th>6.27</th>
<th>1.28</th>
<th>0.83</th>
<th>0.19</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_m/(S$ cm$^2$ mol$^{-1}$)</td>
<td>42.45</td>
<td>45.91</td>
<td>47.53</td>
<td>51.81</td>
<td>54.09</td>
<td>54.59</td>
<td>57.78</td>
<td>57.42</td>
</tr>
</tbody>
</table>

Calculate $A_m$ for NaI and KI in this solvent and $\lambda^2$(NaI) – $\lambda^2$(K). Compare your results to the analogous quantities in aqueous solution using Table 21.5 in the Data section.

21.21‡ A. Fenghoul, W.A. Wakaham, V. Vesovic, J.T.R. Watson, J. Millat, and E. Vogel (J. Phys. Chem. Ref. Data 24, 1649 (1995)) have compiled an extensive table of viscosity coefficients for ammonia in the liquid and vapour phases. Deduce the effective molecular diameter of NH$\text{I}$ based on each of the following vapour-phase viscosity coefficients: (a) $\eta = 9.08 \times 10^{-6}$ kg m$^{-1}$ s$^{-1}$ at 270 K and 1.00 bar; (b) $\eta = 1.749 \times 10^{-5}$ kg m$^{-1}$ s$^{-1}$ at 490 K and 1.00 bar.

21.22‡ G. Bakale, K. Lacmann, and W.F. Schmidt (J. Phys. Chem. 100, 12477 (1996)) measured the mobility of singly charged $\text{C}_6\text{O}_6$ ions in a variety of nonpolar solvents. In cyclohexane at 22°C, the mobility is 1.1 cm$^2$ V$^{-1}$ s$^{-1}$. Estimate the effective radius of the $\text{C}_6\text{O}_6$ ion. The viscosity of the solvent is 0.93 $\times$ 10$^{-3}$ kg m$^{-1}$ s$^{-1}$ Comment. The researchers interpreted the substantial difference between this number and the van der Waals radius of neutral $\text{C}_6\text{O}_6$ in terms of a solvation layer around the ion.

Theoretical problems

21.23 Start from the Maxwell–Boltzmann distribution and derive an expression for the most probable speed of a gas of molecules at a temperature $T$. Go on to demonstrate the validity of the equipartition conclusion that the average translational kinetic energy of molecules free to move in three dimensions is $\frac{3}{2}kT$.

21.24 Consider molecules that are confined to move in a plane (a two-dimensional gas). Calculate the distribution of speeds and determine the mean speed of the molecules at a temperature $T$.

21.25 A specially constructed velocity-selector accepts a beam of molecules from an oven at a temperature $T$ but blocks the passage of molecules with a speed greater than the mean. What is the mean speed of the emerging beam, relative to the initial value, treated as a one-dimensional problem?

21.26 What is the proportion of gas molecules having (a) more than, (b) less than the root mean square speed? (c) What are the proportions having speeds greater and smaller than the mean speed?

21.27 Calculate the fractions of molecules in a gas that have a speed in a range $\Delta v$ at the speed $v^*$ relative to those in the same range at $v^*$ itself? This calculation can be used to estimate the fraction of very energetic molecules (which is important for reactions). Evaluate the ratio for $n = 3$ and $n = 4$.

21.28 Derive an expression that shows how the pressure of a gas inside an effusion oven (a heated chamber with a small hole in one wall) varies with time if the oven is not replenished as the gas escapes. Then show that $t_{\text{1/2}}$, the time required for the pressure to decrease to half its initial value, is independent of the initial pressure. Hint: Begin by setting up a differential equation relating $dp/dt$ to $p = NKTV$, and then integrating it.

21.29 Show how the ratio of two transport numbers $u'$ and $u''$ for two cations in a mixture depends on their concentrations $c'$ and $c''$ and their mobilities $u'$ and $u''$.

21.30 Confirm that eqn 21.72 is a solution of the diffusion equation with the correct initial value.

21.31 The diffusion equation is valid when many elementary steps are taken in the time interval of interest, but the random walk calculation lets us discuss distributions for short times as well as for long. Use eqn 21.84 to calculate the probability of being six paces from the origin (that is, at $x = 6\lambda$) after (a) four, (b) six, (c) twelve steps.

21.32 Use mathematical software to calculate $P$ in a one-dimensional random walk, and evaluate the probability of being at $x = n\lambda$ for $n = 6, 10, 14, \ldots, 60$. Compare the numerical value with the analytical value in the limit of a large number of steps. At what value of $n$ is the discrepancy no more than 0.1 per cent?

21.33 Supply the intermediate mathematical steps in Justification 21.7.

21.34‡ A dilute solution of a weak (1,1)-electrolyte contains both neutral ion pairs and ions in equilibrium ($\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$). Prove that molar conductivities are related to the degree of ionization by the equations:

$$\frac{1}{A_m} = \frac{1}{A_m(\lambda)} + \frac{(1 - \alpha)A_m}{\alpha^2 A_m(\lambda)^2}$$

$$A_m(\alpha) = \lambda_+ + \lambda_- = A_m(\lambda) - 3(\alpha^2)$$

where $A_m$ is the molar conductivity at infinite dilution and $\alpha$ is the constant in Kohlrausch’s law (eqn 21.29).

Applications: to astrophysics and biochemistry

21.35 Calculate the escape velocity (the minimum initial velocity that will take an object to infinity) from the surface of a planet of radius $R$. What is the value for (a) the Earth, $R = 6.37 \times 10^6$ m, $g = 9.81$ m s$^{-2}$; (b) Mars, $R = 3.38 \times 10^6$ m, $m_{\text{Mars}}/m_{\text{Earth}} = 0.108$. At what temperatures do $\text{H}_2$, $\text{He}$, and $\text{O}_2$ molecules have mean speeds equal to their escape speeds? What proportion of the molecules have enough speed to escape when the temperature is (a) 240 K, (b) 1500 K? Calculations of this kind are very important in considering the composition of planetary atmospheres.
21.36‡ Interstellar space is a medium quite different from the gaseous environments we commonly encounter on Earth. For instance, a typical density of the medium is about 1 atom cm$^{-3}$ and that atom is typically H; the effective temperature due to stellar background radiation is about 10 000 K. Estimate the diffusion coefficient and thermal conductivity of H under these conditions.

Comment. Energy is in fact transferred much more effectively by radiation.

21.37 The principal components of the atmosphere of the Earth are diatomic molecules, which can rotate as well as translate. Given that the translational kinetic energy density of the atmosphere is 0.15 J cm$^{-3}$, what is the total kinetic energy density, including rotation?

21.38‡ In the standard model of stellar structure (I. Nicholson, The sun. Rand McNally, New York (1982)), the interior of the Sun is thought to consist of 36 per cent H and 64 per cent He by mass, at a density of 158 g cm$^{-3}$. Both atoms are completely ionized. The approximate dimensions of the nuclei can be calculated from the formula $r_{\text{nucleus}} = 1.4 \times 10^{-13} A^{1/3}$ m, where $A$ is the mass number. The size of the free electron, $r_e \approx 10^{-18}$ m, is negligible compared to the size of the nuclei. (a) Calculate the excluded volume in 1.0 cm$^3$ of the stellar interior and on that basis decide upon the applicability of the perfect gas law to this system. (b) The standard model suggests that the pressure in the stellar interior is 2.5 $\times$ 10$^{11}$ atm. Calculate the temperature of the Sun’s interior based on the perfect gas model. The generally accepted standard model value is 16 MK. (c) Would a van der Waals type of equation (with $a = 0$) give a better value for $T$?

21.39 Enrico Fermi, the great Italian scientist, was a master at making good approximate calculations based on little or no actual data. Hence, such calculations are often called ‘Fermi calculations’. Do a Fermi calculation on how long it would take for a gaseous air-borne cold virus of molar mass 100 kg mol$^{-1}$ to travel the distance between two conversing people 1.0 m apart by diffusion in still air.

21.40 The diffusion coefficient of a particular kind of t-RNA molecule is $D = 1.0 \times 10^{-11}$ m$^2$ s$^{-1}$ in the medium of a cell interior. How long does it take molecules produced in the cell nucleus to reach the walls of the cell at a distance 1.0 $\mu$m, corresponding to the radius of the cell?

21.41‡ In this problem, we examine a model for the transport of oxygen from air in the lungs to blood. First, show that, for the initial and boundary conditions $c(x,t) = c(x,0) = c_0$ ($0 < x < \infty$) and $c(0,t) = c_s$ ($0 \leq t \leq \infty$) where $c_0$ and $c_s$ are constants, the concentration, $c(x,t)$, of a species is given by

$$c(x,t) = c_0 + (c_s - c_0)(1 - \text{erf}\xi) \quad \xi(x,t) = \frac{x}{(4Dt)^{1/2}}$$

where erf$\xi$ is the error function (Justification 9.4) and the concentration $c(x,t)$ evolves by diffusion from the $yz$-plane of constant concentration, such as might occur if a condensed phase is absorbing a species from a gas phase. Now draw graphs of concentration profiles at several different times of your choice for the diffusion of oxygen into water at 298 K (when $D = 2.10 \times 10^{-9}$ m$^2$ s$^{-1}$) on a spatial scale comparable to passage of oxygen from lungs through alveoli into the blood. Use $c_0 = 0$ and set $c_s$ equal to the solubility of oxygen in water. Hint. Use mathematical software.