

Part 3: Change



24 Molecules in motion

Solutions to exercises

Discussion questions

- E24.1(b)** Diffusion is the migration of particles (molecules) down a concentration gradient. Diffusion can be interpreted at the molecular level as being the result of the random jostling of the molecules in a fluid. The motion of the molecules is the result of a series of short jumps in random directions, a so-called random walk.

In the random walk model of diffusion, although a molecule may take many steps in a given time, it has only a small probability of being found far from its starting point because some of the steps lead it away from the starting point but others lead it back. As a result, the net distance traveled increases only as the square root of the time. There is no net flow of molecules unless there is a concentration gradient in the fluid, else there are just as many molecules moving in one direction as another. The rate at which the molecules spread out is proportional to the concentration gradient. The constant of proportionality is called the diffusion coefficient.

On the molecular level in a gas, thermal conduction occurs because of random molecular motions in the presence of a temperature gradient. Across any plane in the gas, there is a net flux of energy from the high temperature side, because molecules coming from that side carry a higher average energy per molecule across the plane than those coming from the low temperature side. In solids, the situation is more complex as energy transport occurs through quantized elastic waves (phonons) and, in metals, also by electrons. Conduction in liquids can occur by all the mechanisms mentioned.

At the molecular (ionic) level, electrical conduction in an electrolytic solution is the net migration of ions in any given direction. When a gradient in electrical potential exists in a conductivity cell there will be a greater flow of positive ions in the direction of the negative electrode than in the direction of the positive electrode, hence there is a net flow of positive charge toward the region of low electrical potential. Likewise a net flow of negative ions in the direction of the positive electrode will occur. In metals, only negatively charged electrons contribute to the current.

To see the connection between the flux of momentum and the viscosity, consider a fluid in a state of *Newtonian* flow, which can be imagined as occurring by a series of layers moving past one another (Fig. 24.11 of the text). The layer next to the wall of the vessel is stationary, and the velocity of successive layers varies linearly with distance, z , from the wall. Molecules ceaselessly move between the layers and bring with them the x -component of linear momentum they possessed in their original layer. A layer is retarded by molecules arriving from a more slowly moving layer because they have a low momentum in the x -direction. A layer is accelerated by molecules arriving from a more rapidly moving layer. We interpret the net retarding effect as the fluid's viscosity.

- E24.2(b)** According to the Grotthuss mechanism, there is an effective motion of a proton that involves the rearrangement of bonds in a group of water molecules. However, the actual mechanism is still highly contentious. Attention now focuses on the H_9O_4^+ unit in which the nearly trigonal planar H_3O^+ ion is linked to three strongly solvating H_2O molecules. This cluster of atoms is itself hydrated, but the hydrogen bonds in the secondary sphere are weaker than in the primary sphere. It is envisaged that the rate-determining step is the cleavage of one of the weaker hydrogen bonds of this secondary sphere (Fig. 24.19a of the text). After this bond cleavage has taken place, and the released molecule has rotated through a few degrees (a process that takes about 1 ps), there is a rapid adjustment of bond lengths and angles in the remaining cluster, to form an H_5O_2^+ cation of structure $\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2$ (Fig. 24.19b). Shortly after this reorganization has occurred, a new H_9O_4^+ cluster forms as other molecules rotate into a position where they can become members of a secondary hydration sphere,

but now the positive charge is located one molecule to the right of its initial location (Fig. 24.19c). According to this model, there is no coordinated motion of a proton along a chain of molecules, simply a very rapid hopping between neighbouring sites, with a low activation energy. The model is consistent with the observation that the molar conductivity of protons increases as the pressure is raised, for increasing pressure ruptures the hydrogen bonds in water.

E24.3(b) Because the drift speed governs the rate at which charge is transported, we might expect the conductivity to decrease with increasing solution viscosity and ion size. Experiments confirm these predictions for bulky ions, but not for small ions. For example, the molar conductivities of the alkali metal ions increase from Li^+ to Cs^+ (Table 24.6) even though the ionic radii increase. The paradox is resolved when we realize that the radius a in the Stokes formula is the hydrodynamic radius (or “Stokes radius”) of the ion, its effective radius in the solution taking into account all the H_2O molecules it carries in its hydration sphere. Small ions give rise to stronger electric fields than large ones, so small ions are more extensively solvated than big ions. Thus, an ion of small ionic radius may have a large hydrodynamic radius because it drags many solvent molecules through the solution as it migrates. The hydrating H_2O molecules are often very labile, however, and NMR and isotope studies have shown that the exchange between the coordination sphere of the ion and the bulk solvent is very rapid.

The proton, although it is very small, has a very high molar conductivity (Table 24.6)! Proton and ^{17}O -NMR show that the times characteristic of protons hopping from one molecule to the next are about 1.5 ps, which is comparable to the time that inelastic neutron scattering shows it takes a water molecule to reorientate through about 1 rad (1–2 ps).

Numerical exercises

E24.4(b) (a) The mean speed of a gas molecule is

$$\bar{c} = \left(\frac{8RT}{\pi M} \right)^{1/2}$$

$$\text{so } \frac{\bar{c}(\text{He})}{\bar{c}(\text{Hg})} = \left(\frac{M(\text{Hg})}{M(\text{He})} \right)^{1/2} = \left(\frac{200.59}{4.003} \right)^{1/2} = \boxed{7.079}$$

(b) The mean kinetic energy of a gas molecule is $\frac{1}{2}mc^2$, where c is the root mean square speed

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

So $\frac{1}{2}mc^2$ is independent of mass, and the ratio of mean kinetic energies of He and Hg is $\boxed{1}$

E24.5(b) (a) The mean speed can be calculated from the formula derived in Example 24.1.

$$\bar{c} = \left(\frac{8RT}{\pi M} \right)^{1/2} = \left(\frac{8 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{\pi \times (28.02 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} = \boxed{4.75 \times 10^2 \text{ m s}^{-1}}$$

(b) The mean free path is calculated from $\lambda = \frac{kT}{2^{1/2}\sigma p}$ [24.14]

$$\text{with } \sigma = \pi d^2 = \pi \times (3.95 \times 10^{-10} \text{ m})^2 = 4.90 \times 10^{-19} \text{ m}^2$$

$$\text{Then, } \lambda = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{2^{1/2} \times (4.90 \times 10^{-19} \text{ m}^2) \times (1 \times 10^{-9} \text{ Torr}) \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right) \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right)}$$

$$= \boxed{4 \times 10^4 \text{ m}}$$

(c) The collision frequency could be calculated from eqn 31, but is most easily obtained from eqn 32,

$$\text{since } \lambda \text{ and } \bar{c} \text{ have already been calculated } z = \frac{\bar{c}}{\lambda} = \frac{4.75 \times 10^2 \text{ m s}^{-1}}{4.46 \times 10^4 \text{ m}} = \boxed{1 \times 10^{-2} \text{ s}^{-1}}$$

Thus there are 100 s between collisions, which is a very long time compared to the usual timescale of molecular events. The mean free path is much larger than the dimensions of the pumping apparatus used to generate the very low pressure.

E24.6(b)
$$p = \frac{kT}{2^{1/2}\sigma\lambda} \quad [24.14]$$

$$\sigma = \pi d^2, \quad d = \left(\frac{\sigma}{\pi}\right)^{1/2} = \left(\frac{0.36 \text{ nm}^2}{\pi}\right)^{1/2} = 0.34 \text{ nm}$$

$$p = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(2^{1/2}) \times (0.36 \times 10^{-18} \text{ m}^2) \times (0.34 \times 10^{-9} \text{ m})} = \boxed{2.4 \times 10^7 \text{ Pa}}$$

This pressure corresponds to about 240 atm, which is comparable to the pressure in a compressed gas cylinder in which argon gas is normally stored.

E24.7(b) The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})}{2^{1/2} [0.43 \times (10^{-9} \text{ m})^2] \times (12.1 \times 10^3 \text{ Pa atm}^{-1})} = \boxed{4.1 \times 10^{-7} \text{ m}}$$

E24.8(b) Obtain data from Exercise 24.7(b)

The expression for z obtained in Exercise 24.8(a) is $z = \left(\frac{16}{\pi m k T}\right)^{1/2} \sigma p$

Substituting $\sigma = 0.43 \text{ nm}^2$, $p = 12.1 \times 10^3 \text{ Pa}$, $m = (28.02 \text{ u})$, and $T = 217 \text{ K}$ we obtain

$$z = \frac{4 \times (0.43 \times 10^{-18} \text{ m}^2) \times (12.1 \times 10^3 \text{ Pa})}{[\pi \times (28.02) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})]^{1/2}} = \boxed{9.9 \times 10^8 \text{ s}^{-1}}$$

E24.9(b) The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (25 + 273) \text{ K}}{2^{1/2} [0.52 \times (10^{-9} \text{ m})^2] p} = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{p}$$

(a)
$$\lambda = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{(15 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1})} = \boxed{3.7 \times 10^{-9} \text{ m}}$$

(b)
$$\lambda = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{(1.0 \text{ bar}) \times (10^5 \text{ Pa bar}^{-1})} = \boxed{5.5 \times 10^{-8} \text{ m}}$$

(c)
$$\lambda = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{(1.0 \text{ Torr}) \times \left(\frac{1.013 \times 10^5 \text{ Pa atm}^{-1}}{760 \text{ Torr atm}^{-1}}\right)} = \boxed{4.1 \times 10^{-5} \text{ m}}$$

E24.10(b) The fraction F of molecules in the speed range from 200 to 250 m s^{-1} is

$$F = \int_{200 \text{ m s}^{-1}}^{250 \text{ m s}^{-1}} f(v) dv$$

where $f(v)$ is the Maxwell distribution. This can be approximated by

$$F \approx f(v) \Delta v = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 \exp \left(\frac{-Mv^2}{2RT} \right) \Delta v,$$

with $f(v)$ evaluated in the middle of the range

$$\begin{aligned} F &\approx 4\pi \left(\frac{44.0 \times 10^{-3} \text{ kg mol}^{-1}}{2\pi (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \right)^{3/2} \times (225 \text{ m s}^{-1})^2 \\ &\quad \times \exp \left(\frac{-(44.0 \times 10^{-3} \text{ kg mol}^{-1}) \times (225 \text{ m s}^{-1})^2}{2(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \right) \times (50 \text{ m s}^{-1}), \\ F &\approx \boxed{9.6 \times 10^{-2}} \end{aligned}$$

Comment. The approximation we have employed, taking $f(v)$ to be nearly constant over a narrow range of speeds, may not be accurate enough, for that range of speeds includes about 10 per cent of the molecules.

Numerical exercises

E24.11(b) The number of collisions is

$$\begin{aligned} N &= Z_W At = \frac{pAt}{(2\pi mkT)^{1/2}} \\ &= \frac{(111 \text{ Pa}) \times (3.5 \times 10^{-3} \text{ m}) \times (4.0 \times 10^{-3} \text{ m}) \times (10 \text{ s})}{\{2\pi \times (4.00 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg u}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (1500 \text{ K})\}^{1/2}} \\ &= \boxed{1.1 \times 10^{21}} \end{aligned}$$

E24.12(b) The mass of the sample in the effusion cell decreases by the mass of the gas which effuses out of it. That mass is the molecular mass times the number of molecules that effuse out

$$\begin{aligned} \Delta m &= mN = mZ_W At = \frac{mpAt}{(2\pi mkT)^{1/2}} = pAt \left(\frac{m}{2\pi kT} \right)^{1/2} = pAt \left(\frac{M}{2\pi RT} \right)^{1/2} \\ &= (0.224 \text{ Pa}) \times \pi \times \left(\frac{1}{2} \times 3.00 \times 10^{-3} \text{ m} \right)^2 \times (24.00 \text{ h}) \times (3600 \text{ s h}^{-1}) \\ &\quad \times \left\{ \frac{300 \times 10^{-3} \text{ kg mol}^{-1}}{2\pi \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})} \right\}^{1/2} \\ &= \boxed{4.89 \times 10^{-4} \text{ kg}} \end{aligned}$$

E24.13(b) The flux is

$$J = -\kappa \frac{dT}{dz} = -\frac{1}{3} \lambda C_{V,m} \langle v \rangle [X] \frac{dT}{dz}$$

where the minus sign indicates flow toward lower temperature and

$$\lambda = \frac{1}{\sqrt{2} N \sigma}, \quad \langle v \rangle = \left(\frac{8kT}{\pi m} \right)^{1/2} = \left(\frac{8RT}{\pi M} \right)^{1/2}, \quad \text{and} \quad [M] = n/V = N/N_A$$

$$\begin{aligned} \text{So } J &= -\frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M} \right)^{1/2} \frac{dT}{dz} \\ &= -\left(\frac{2 \times (28.832 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3 \times [0.27 \times (10^{-9} \text{ m})^2] \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (260 \text{ K})}{\pi \times (2.016 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \times (3.5 \text{ K m}^{-1}) \\ &= \boxed{0.17 \text{ J m}^{-2} \text{ s}^{-1}} \end{aligned}$$

E24.14(b) The thermal conductivity is

$$\begin{aligned} \kappa &= \frac{1}{3} \lambda C_{V,m} \langle v \rangle [X] = \frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M} \right)^{1/2} \quad \text{so} \quad \sigma = \frac{2C_{V,m}}{3\kappa N_A} \left(\frac{RT}{\pi M} \right)^{1/2} \\ &= (0.240 \text{ mJ cm}^{-2} \text{ s}^{-1}) \times (\text{K cm}^{-1})^{-1} = 0.240 \times 10^{-1} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \\ \text{so } \sigma &= \left(\frac{2 \times (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3 \times (0.240 \times 10^{-1} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{1.61 \times 10^{-19} \text{ m}^2} \end{aligned}$$

E24.15(b) Assuming the space between sheets is filled with air, the flux is

$$\begin{aligned} J &= -\kappa \frac{dT}{dz} = [(0.241 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}) \times (\text{K cm}^{-1})^{-1}] \times \left(\frac{[50 - (-10)] \text{ K}}{10.0 \text{ cm}} \right) \\ &= 1.45 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}. \end{aligned}$$

So the rate of energy transfer and energy loss is

$$JA = (1.45 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}) \times (1.50 \text{ m}^2) \times (100 \text{ cm m}^{-1})^2 = \boxed{22 \text{ J s}^{-1}}$$

E24.16(b) The time dependence of the pressure of a gas effusing without replenishment is

$$p = p_0 e^{-t/\tau} \quad \text{where } \tau \propto \sqrt{m}$$

The time t it takes for the pressure to go from any initial pressure p_0 to a prescribed fraction of that pressure fp_0 is

$$t = \tau \ln \frac{fp_0}{p_0} = \tau \ln f$$

so the time is proportional to τ and therefore also to \sqrt{m} . Therefore, the ratio of times it takes two different gases to go from the same initial pressure to the same final pressure is related to their molar masses as follows

$$\frac{t_1}{t_2} = \left(\frac{M_1}{M_2}\right)^{1/2} \quad \text{and} \quad M_2 = M_1 \left(\frac{t_2}{t_1}\right)^2$$

$$\text{So } M_{\text{fluorocarbon}} = (28.01 \text{ g mol}^{-1}) \times \left(\frac{82.3 \text{ s}}{18.5 \text{ s}}\right)^2 = \boxed{554 \text{ g mol}^{-1}}$$

E24.17(b) The time dependence of the pressure of a gas effusion without replenishment is

$$p = p_0 e^{-t/\tau} \quad \text{so} \quad t = \tau \ln p_0/p$$

$$\text{where } \tau = \frac{V}{A_0} \left(\frac{2\pi m}{kT}\right)^{1/2} = \frac{V}{A_0} \left(\frac{2\pi M}{RT}\right)^{1/2}$$

$$= \left(\frac{22.0 \text{ m}^3}{\pi \times (0.50 \times 10^{-3} \text{ m})^2}\right) \times \left(\frac{2\pi \times (28.0 \times 10^{-3} \text{ kg mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}\right)^{1/2} = 2.4 \times 10^5 \text{ s}$$

$$\text{so } t = (8.6 \times 10^5 \text{ s}) \ln \frac{122 \text{ kPa}}{105 \text{ kPa}} = \boxed{1.5 \times 10^4 \text{ s}}$$

E24.18(b) The coefficient of viscosity is

$$\eta = \frac{1}{3} \lambda m N \langle v \rangle = \frac{2}{3\sigma} \left(\frac{mkT}{\pi}\right)^{1/2} \quad \text{so} \quad \sigma = \frac{2}{3\eta} \left(\frac{mkT}{\pi}\right)^{1/2}$$

$$= 1.66 \mu\text{P} = 166 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\text{so } \sigma = \left(\frac{2}{3 \times (166 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1})}\right)$$

$$\times \left(\frac{(28.01 \times 10^{-3} \text{ kg mol}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (273 \text{ K})}{\pi \times (6.022 \times 10^{23} \text{ mol}^{-1})}\right)^{1/2}$$

$$= \boxed{3.00 \times 10^{-19} \text{ m}^2}$$

E24.19(b) The rate of fluid flow through a tube is described by

$$\frac{dV}{dt} = \frac{(p_{\text{in}}^2 - p_{\text{out}}^2) \pi r^4}{16l\eta p_0} \quad \text{so} \quad p_{\text{in}} = \left(\frac{16l\eta p_0}{\pi r^4} \frac{dV}{dt} + p_{\text{out}}^2\right)^{1/2}$$

Several of the parameters need to be converted to MKS units

$$r = \frac{1}{2}(15 \times 10^{-3} \text{ m}) = 7.5 \times 10^{-3} \text{ m}$$

$$\text{and } \frac{dV}{dt} = 8.70 \text{ cm}^3 \times (10^{-2} \text{ m cm}^{-1})^3 \text{ s}^{-1} = 8.70 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}.$$

Also, we have the viscosity at 293 K from the table. According to the $T^{1/2}$ temperature dependence, the viscosity at 300 K ought to be

$$\begin{aligned}\eta(300\text{ K}) &= \eta(293\text{ K}) \times \left(\frac{300\text{ K}}{293\text{ K}}\right)^{1/2} = (176 \times 10^{-7}\text{ kg m}^{-1}\text{ s}^{-1}) \times \left(\frac{300}{293}\right)^{1/2} \\ &= 1.78 \times 10^{-7}\text{ kg m}^{-1}\text{ s}^{-1} \\ p_{\text{in}} &= \left\{ \left(\frac{16(10.5\text{ m}) \times (178 \times 10^{-7}\text{ kg m}^{-1}\text{ s}^{-1}) \times (1.00 \times 10^5\text{ Pa})}{\pi \times (7.5 \times 10^{-3}\text{ m})^4} \right) \right. \\ &\quad \left. \times (8.70 \times 10^{-6}\text{ m}^3\text{ s}^{-1}) + (1.00 \times 10^5\text{ Pa})^2 \right\}^{1/2} \\ &= \boxed{1.00 \times 10^5\text{ Pa}}\end{aligned}$$

Comment. For the exercise as stated the answer is not sensitive to the viscosity. The flow rate is so low that the inlet pressure would equal the outlet pressure (to the precision of the data) whether the viscosity were that of N_2 at 300 K or 293 K—or even liquid water at 293 K!

E24.20(b) The coefficient of viscosity is

$$\begin{aligned}\eta &= \frac{1}{3}\lambda m N \langle v \rangle = \frac{2}{3\sigma} \left(\frac{mkT}{\pi} \right)^{1/2} \\ &= \left(\frac{2}{3[0.88 \times (10^{-9}\text{ m})^2]} \right) \times \left(\frac{(78.12 \times 10^{-3}\text{ kg mol}^{-1}) \times (1.381 \times 10^{-23}\text{ J K}^{-1})T}{\pi \times (6.022 \times 10^{23}\text{ mol}^{-1})} \right)^{1/2} \\ &= 5.72 \times 10^{-7} \times (T/\text{K})^{1/2}\text{ kg m}^{-1}\text{ s}^{-1}\end{aligned}$$

(a) At 273 K $\eta = (5.72 \times 10^{-7}) \times (273)^{1/2}\text{ kg m}^{-1}\text{ s}^{-1} = \boxed{0.95 \times 10^{-5}\text{ kg m}^{-1}\text{ s}^{-1}}$

(b) At 298 K $\eta = (5.72 \times 10^{-7}) \times (298)^{1/2}\text{ kg m}^{-1}\text{ s}^{-1} = \boxed{0.99 \times 10^{-5}\text{ kg m}^{-1}\text{ s}^{-1}}$

(c) At 1000 K $\eta = (5.72 \times 10^{-7}) \times (1000)^{1/2}\text{ kg m}^{-1}\text{ s}^{-1} = \boxed{1.81 \times 10^{-5}\text{ kg m}^{-1}\text{ s}^{-1}}$

E24.21(b) The thermal conductivity is

$$\begin{aligned}\kappa &= \frac{1}{3}\lambda C_{V,m} \langle v \rangle [X] = \frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M} \right)^{1/2} \\ \text{(a)} \quad \kappa &= \left(\frac{2 \times [(20.786 - 8.3145)\text{ J K}^{-1}\text{ mol}^{-1}]}{3[0.24 \times (10^{-9}\text{ m})^2] \times (6.022 \times 10^{23}\text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (300\text{ K})}{\pi(20.18 \times 10^{-3}\text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{0.0114\text{ J m}^{-1}\text{ s}^{-1}\text{ K}^{-1}}\end{aligned}$$

The flux is

$$J = -\kappa \frac{dT}{dz} = (0.0114 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times \left(\frac{(305 - 295) \text{ K}}{0.15 \text{ m}} \right) = 0.76 \text{ J m}^{-2} \text{ s}^{-1}$$

so the rate of energy loss is

$$JA = (0.76 \text{ J m}^{-2} \text{ s}^{-1}) \times (0.15 \text{ m})^2 = \boxed{0.017 \text{ J s}^{-1}}$$

$$\begin{aligned} \text{(b)} \quad \kappa &= \left(\frac{2 \times [(29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}]}{3[0.43 \times (10^{-9} \text{ m})^2] \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times (300 \text{ K})}{\pi (28.013 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}} \end{aligned}$$

The flux is

$$J = -\kappa \frac{dT}{dz} = (9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times \left(\frac{(305 - 295) \text{ K}}{0.15 \text{ m}} \right) = 0.60 \text{ J m}^{-2} \text{ s}^{-1}$$

so the rate of energy loss is

$$JA = (0.60 \text{ J m}^{-2} \text{ s}^{-1}) \times (0.15 \text{ m})^2 = \boxed{0.014 \text{ J s}^{-1}}$$

E24.22(b) The rate of fluid flow through a tube is described by

$$\frac{dV}{dt} = \frac{(p_{\text{in}}^2 - p_{\text{out}}^2)\pi r^4}{16l\eta p_0}$$

so the rate is inversely proportional to the viscosity, and the time required for a given volume of gas to flow through the same tube under identical pressure conditions is directly proportional to the viscosity

$$\begin{aligned} \frac{t_1}{t_2} &= \frac{\eta_1}{\eta_2} \quad \text{so} \quad \eta_2 = \frac{\eta_1 t_2}{t_1} \\ \eta_{\text{CFC}} &= \frac{(208 \text{ } \mu\text{P}) \times (18.0 \text{ s})}{72.0 \text{ s}} = \boxed{52.0 \text{ } \mu\text{P}} = 52.0 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1} \end{aligned}$$

The coefficient of viscosity is

$$\eta = \frac{1}{3}\lambda m N \langle v \rangle = \left(\frac{2}{3\sigma} \right) \times \left(\frac{mkT}{\pi} \right)^{1/2} = \left(\frac{2}{3\pi d^2} \right) \times \left(\frac{mkT}{\pi} \right)^{1/2}$$

so the molecular diameter is

$$\begin{aligned} d &= \left(\frac{2}{3\pi\eta} \right)^{1/2} \times \left(\frac{mkT}{\pi} \right)^{1/4} \\ &= \left(\frac{2}{3\pi(52.0 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1})} \right)^{1/2} \\ &\quad \times \left(\frac{(200 \times 10^{-3} \text{ kg mol}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{\pi \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/4} \\ &= 9.23 \times 10^{-10} \text{ m} = \boxed{923 \text{ pm}} \end{aligned}$$

$$\begin{aligned}
 \text{E24.23(b)} \quad \kappa &= \frac{1}{3} \lambda C_{V,m} \langle v \rangle [X] = \frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M} \right)^{1/2} \\
 &= \left(\frac{2 \times (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3[0.43 \times (10^{-9} \text{ m})^2] \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\
 &= \boxed{9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}}
 \end{aligned}$$

E24.24(b) The diffusion constant is

$$\begin{aligned}
 D &= \frac{1}{3} \lambda \langle v \rangle = \frac{2(RT)^{3/2}}{3\sigma p N_A (\pi M)^{1/2}} \\
 &= \frac{2[(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})]^{3/2}}{3[0.43 \times (10^{-9} \text{ m})^2] p (6.022 \times 10^{23} \text{ mol}^{-1}) \times \left\{ \pi (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \right\}^{1/2}} \\
 &= \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{p/\text{Pa}}
 \end{aligned}$$

The flux due to diffusion is

$$J = -D \frac{d[X]}{dx} = -D \frac{d}{dx} \left(\frac{n}{V} \right) = - \left(\frac{D}{RT} \right) \frac{dp}{dx}$$

where the minus sign indicates flow from high pressure to low. So for a pressure gradient of 0.10 atm cm^{-1}

$$\begin{aligned}
 J &= \left(\frac{D/(\text{m}^2 \text{ s}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right) \times (0.20 \times 10^5 \text{ Pa m}^{-1}) \\
 &= (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (D/(\text{m}^2 \text{ s}^{-1}))
 \end{aligned}$$

$$\text{(a)} \quad D = \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{10.0} = \boxed{0.107 \text{ m}^2 \text{ s}^{-1}}$$

$$\text{and } J = (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (0.107) = \boxed{0.87 \text{ mol m}^{-2} \text{ s}^{-1}}$$

$$\text{(b)} \quad D = \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{100 \times 10^3} = \boxed{1.07 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}}$$

$$\text{and } J = (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (1.07 \times 10^{-5}) = \boxed{8.7 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}}$$

$$\text{(c)} \quad D = \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{15.0 \times 10^6} = \boxed{7.13 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}}$$

$$\text{and } J = (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (7.13 \times 10^{-8}) = \boxed{5.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}}$$

E24.25(b) Molar ionic conductivity is related to mobility by

$$\begin{aligned}
 \lambda &= zuF = (1) \times (4.24 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (96485 \text{ C mol}^{-1}) \\
 &= \boxed{4.09 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}
 \end{aligned}$$

E24.26(b) The drift speed is given by

$$s = u\mathcal{E} = \frac{u\Delta\phi}{l} = \frac{(4.01 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (12.0 \text{ V})}{1.00 \times 10^{-2} \text{ m}} = \boxed{4.81 \times 10^{-5} \text{ m s}^{-1}}$$

E24.27(b) The limiting transport number for Cl^- in aqueous NaCl at 25°C is

$$t_-^\circ = \frac{u_-}{u_+ + u_-} = \frac{7.91}{5.19 + 7.91} = \boxed{0.604}$$

(The mobilities are in $10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$.)

E24.28(b) The limiting molar conductivity of a dissolved salt is the sum of that of its ions, so

$$\begin{aligned} \Lambda_m^\circ(\text{MgI}_2) &= \lambda(\text{Mg}^{2+}) + 2\lambda(\text{I}^-) = \Lambda_m^\circ(\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2) + 2\Lambda_m^\circ(\text{NaI}) - 2\Lambda_m^\circ(\text{NaC}_2\text{H}_3\text{O}_2) \\ &= (18.78 + 2(12.69) - 2(9.10)) \text{ mS m}^2 \text{ mol}^{-1} = \boxed{25.96 \text{ mS m}^2 \text{ mol}^{-1}} \end{aligned}$$

E24.29(b) Molar ionic conductivity is related to mobility by

$$\lambda = zuF \quad \text{so} \quad u = \frac{\lambda}{zF}$$

$$\text{F}^-: \quad u = \frac{5.54 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{(1) \times (96485 \text{ C mol}^{-1})} = \boxed{5.74 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}}$$

$$\text{Cl}^-: \quad u = \frac{7.635 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{(1) \times (96485 \text{ C mol}^{-1})} = \boxed{7.913 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}}$$

$$\text{Br}^-: \quad u = \frac{7.81 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{(1) \times (96485 \text{ C mol}^{-1})} = \boxed{8.09 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}}$$

E24.30(b) The diffusion constant is related to the mobility by

$$\begin{aligned} D &= \frac{uRT}{zF} = \frac{(4.24 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(1) \times (96485 \text{ C mol}^{-1})} \\ &= \boxed{1.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}} \end{aligned}$$

E24.31(b) The mean square displacement for diffusion in one dimension is

$$\langle x^2 \rangle = 2Dt$$

In fact, this is also the mean square displacement in any direction in two- or three-dimensional diffusion from a concentrated source. In three dimensions

$$r^2 = x^2 + y^2 + z^2 \quad \text{so} \quad \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle x^2 \rangle = 6Dt$$

So the time it takes to travel a distance $\sqrt{\langle r^2 \rangle}$ is

$$t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0 \times 10^{-2} \text{ m})^2}{6(4.05 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})} = \boxed{4.1 \times 10^3 \text{ s}}$$

E24.32(b) The diffusion constant is related to the viscosity of the medium and the size of the diffusing molecule as follows

$$\begin{aligned} D &= \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{kT}{6\pi\eta D} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{6\pi(1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) \times (1.055 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})} \\ a &= 2.07 \times 10^{-10} \text{ m} = \boxed{207 \text{ pm}} \end{aligned}$$

E24.33(b) The Einstein–Smoluchowski equation related the diffusion constant to the unit jump distance and time

$$D = \frac{\lambda^2}{2\tau} \quad \text{so} \quad \tau = \frac{\lambda^2}{2D}$$

If the jump distance is about one molecular diameter, or two effective molecular radii, then the jump distance can be obtained by use of the Stokes–Einstein equation

$$D = \frac{kT}{6\pi\eta a} = \frac{kT}{3\pi\eta\lambda} \quad \text{so} \quad \lambda = \frac{kT}{3\pi\eta D}$$

$$\begin{aligned} \text{and } \tau &= \frac{(kT)^2}{18(\pi\eta)^2 D^3} = \frac{[(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})]^2}{18[\pi(0.387 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})]^2 \times (3.17 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})^3} \\ &= \boxed{2.00 \times 10^{-11} \text{ s}} = 20 \text{ ps} \end{aligned}$$

E24.34(b) The mean square displacement is (from Exercise 24.31(b))

$$\langle r^2 \rangle = 6Dt \quad \text{so} \quad t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0 \times 10^{-6} \text{ m})^2}{6(1.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})} = \boxed{1.7 \times 10^{-2} \text{ s}}$$

Solutions to problems

Solutions to numerical problems

P24.3 $\langle X \rangle = \frac{1}{N} \sum_i N_i X_i$ [See Problem 24.2]

$$\text{(a) } \langle h \rangle = \frac{1}{53} \{1.80 \text{ m} + 2 \times (1.82 \text{ m}) + \dots + 1.98 \text{ m}\} = \boxed{1.89 \text{ m}}$$

$$\begin{aligned} \text{(b) } \langle h^2 \rangle &= \frac{1}{53} \left\{ (1.80 \text{ m})^2 + 2 \times (1.82 \text{ m})^2 + \dots + (1.98 \text{ m})^2 \right\} = 3.57 \text{ m}^2 \\ \sqrt{\langle h^2 \rangle} &= \boxed{1.89 \text{ m}} \end{aligned}$$

P24.4 $\kappa = \frac{1}{3} \lambda \bar{c} C_{V,m} [A]$ [24.28]

$$\bar{c} = \left(\frac{8kT}{\pi m} \right)^{1/2} \quad [24.7] \propto T^{1/2}$$

$$\text{Hence, } \kappa \propto T^{1/2} C_{V,m}, \quad \text{so } \frac{\kappa'}{\kappa} = \left(\frac{T'}{T} \right)^{1/2} \times \left(\frac{C'_{V,m}}{C_{V,m}} \right)$$

$$\text{At } 300 \text{ K, } C_{V,m} \approx \frac{3}{2} R + R = \frac{5}{2} R \quad \text{At } 10 \text{ K, } C_{V,m} \approx \frac{3}{2} R \text{ [rotation not excited]}$$

$$\text{Therefore, } \frac{\kappa'}{\kappa} = \left(\frac{300}{10} \right)^{1/2} \times \left(\frac{5}{3} \right) = \boxed{9.1}$$

P24.7 The atomic current is the number of atoms emerging from the slit per second, which is $Z_W A$ with $A = 1 \times 10^{-7} \text{ m}^2$. We use

$$Z_W = \frac{P}{(2\pi mkT)^{1/2}} \quad [24.15]$$

$$\begin{aligned} &= \frac{p/\text{Pa}}{[(2\pi) \times (M/\text{g mol}^{-1}) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (380 \text{ K})]^{1/2}} \\ &= (1.35 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}) \times \left(\frac{p/\text{Pa}}{(M/\text{g mol}^{-1})^{1/2}} \right) \end{aligned}$$

(a) Cadmium:

$$Z_W A = (1.35 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}) \times (1 \times 10^{-7} \text{ m}^2) \times \left(\frac{0.13}{(112.4)^{1/2}} \right) = \boxed{2 \times 10^{14} \text{ s}^{-1}}$$

(b) Mercury:

$$Z_W A = (1.35 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}) \times (1 \times 10^{-7} \text{ m}^2) \times \left(\frac{152}{(200.6)^{1/2}} \right) = \boxed{1 \times 10^{17} \text{ s}^{-1}}$$

P24.10

$$c = \frac{\kappa}{\Lambda_m} [24.98] \approx \frac{\kappa}{\Lambda_m^\circ} [c \text{ small, conductivity of water allowed for in the data}]$$

$$c \approx \frac{1.887 \times 10^{-6} \text{ S cm}^{-1}}{138.3 \text{ S cm}^2 \text{ mol}^{-1}} \text{ [Exercise 24.28(a)]}$$

$$\approx 1.36 \times 10^{-8} \text{ mol cm}^{-3} = \text{solubility} = \boxed{1.36 \times 10^{-5} \text{ M}}$$

P24.12

$$t(\text{H}^+) = \frac{u(\text{H}^+)}{u(\text{H}^+) + u(\text{Cl}^-)} [24.61] = \frac{3.623}{3.623 + 0.791} = \boxed{0.82}$$

When a third ion is present we use

$$t(\text{H}^+) = \frac{I(\text{H}^+)}{I(\text{H}^+) + I(\text{Na}^+) + I(\text{Cl}^-)} [24.58]$$

For each I , $I = z u v c F A E = \text{constant} \times c u$. Hence, when NaCl is added

$$\begin{aligned} t(\text{H}^+) &= \frac{c(\text{H}^+)u(\text{H}^+)}{c(\text{H}^+)u(\text{H}^+) + c(\text{Na}^+)u(\text{Na}^+) + c(\text{Cl}^-)u(\text{Cl}^-)} \\ &= \frac{(1.0 \times 10^{-3}) \times (3.623)}{(1.0 \times 10^{-3}) \times (3.623) + (1.0) \times (0.519) + (1.001) \times (0.791)} = \boxed{0.0028} \end{aligned}$$

P24.14

$$t_+ = \left(\frac{z c A F}{I} \right) \times \left(\frac{x}{\Delta t} \right) \text{ [Problem 24.13]}$$

The density of the solution is 0.682 g cm^{-3} ; the concentration c is related to the molality m by

$$c / (\text{mol L}^{-1}) = \rho / (\text{kg L}^{-1}) \times m / (\text{mol kg}^{-1})$$

which holds for dilute solutions such as these.

$$\begin{aligned} A &= \pi r^2 = \pi \times (2.073 \times 10^{-3} \text{ m})^2 = 1.350 \times 10^{-5} \text{ m}^2 \\ \frac{z c A F}{I \Delta t} &= \frac{(1.350 \times 10^{-5} \text{ m}^2) \times (9.6485 \times 10^4 \text{ C mol}^{-1})}{(5.000 \times 10^{-3} \text{ A}) \times (2500 \text{ s})} \times c = (0.1042 \text{ m}^2 \text{ mol}^{-1}) \times c \\ &= (0.1042 \text{ m}^2 \text{ mol}^{-1}) \times \rho \times m = (0.1042 \text{ m}^2 \text{ mol}^{-1}) \times (682 \text{ kg m}^{-3}) \times m \\ &= (71.06 \text{ kg m}^{-1} \text{ mol}^{-1}) \times m = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times m \end{aligned}$$

and so $t_+ = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times x \times m$

$$\text{In the first solution } t_+ = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times (286.9 \text{ mm}) \times (0.01365 \text{ mol kg}^{-1}) = \boxed{0.278}$$

$$\text{In the second solution } t_+ = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times (92.03 \text{ mm}) \times (0.04255 \text{ mol kg}^{-1}) = \boxed{0.278}$$

Therefore, $t(\text{H}^+) = 0.28$, a value much less than in pure water where $t(\text{H}^+) = 0.63$. Hence, the mobility is much less relative to its counterion, NH_2^- .

P24.17 If diffusion is analogous to viscosity [Section 24.5, eqn 24.36] in that it is also an activation energy controlled process, then we expect

$$D \propto e^{-E_a/RT}$$

Therefore, if the diffusion constant is D at T and D' at T' ,

$$E_a = -\frac{R \ln\left(\frac{D'}{D}\right)}{\left(\frac{1}{T'} - \frac{1}{T}\right)} = -\frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{2.89}{2.05}\right)}{\frac{1}{298 \text{ K}} - \frac{1}{273 \text{ K}}} = 9.3 \text{ kJ mol}^{-1}$$

That is, the activation energy for diffusion is $\boxed{9.3 \text{ kJ mol}^{-1}}$

P24.19 $\langle x^2 \rangle = 2Dt$ [24.91], $D = \frac{kT}{6\pi a\eta}$ [24.83]

$$\begin{aligned} \text{Hence, } \eta &= \frac{kT}{6\pi Da} = \frac{kTt}{3\pi a\langle x^2 \rangle} = \frac{1.381 \times 10^{-23} \text{ J K}^{-1} \times (298.15 \text{ K}) \times t}{(3\pi) \times (2.12 \times 10^{-7} \text{ m}) \times \langle x^2 \rangle} \\ &= (2.06 \times 10^{-15} \text{ J m}^{-1}) \times \left(\frac{t}{\langle x^2 \rangle}\right) \end{aligned}$$

$$\text{and therefore } \eta/(\text{kg m}^{-1} \text{ s}^{-1}) = \frac{2.06 \times 10^{-11} (t/\text{s})}{(\langle x^2 \rangle/\text{cm}^2)}$$

We draw up the following table

t/s	30	60	90	120
$10^8 \langle x^2 \rangle/\text{cm}^2$	88.2	113.4	128	144
$10^3 \eta/(\text{kg m}^{-1} \text{ s}^{-1})$	0.701	1.09	1.45	1.72

Hence, the mean value is $\boxed{1.2 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}}$.

P24.21 The viscosity of a perfect gas is

$$\eta = \frac{1}{3} \mathcal{N} m \lambda \bar{c} = \frac{m\bar{c}}{3\sigma\sqrt{2}} = \frac{2}{3\sigma} \left(\frac{mkT}{\pi}\right)^{1/2} \quad \text{so} \quad \sigma = \frac{2}{3\eta} \left(\frac{mkT}{\pi}\right)^{1/2}$$

The mass is

$$m = \frac{17.03 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.828 \times 10^{-26} \text{ kg}$$

$$\begin{aligned} \text{(a)} \quad \sigma &= \frac{2}{3(9.08 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1})} \\ &\times \left(\frac{(2.828 \times 10^{-26} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (270 \text{ K})}{\pi}\right)^{1/2} \\ &= 4.25 \times 10^{-19} \text{ m}^2 = \pi d^2 \quad \text{so} \quad d = \left(\frac{4.25 \times 10^{-19} \text{ m}^2}{\pi}\right)^{1/2} = \boxed{3.68 \times 10^{-10} \text{ m}} \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \sigma &= \frac{2}{3(17.49 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1})} \\
 &\times \left(\frac{(2.828 \times 10^{-26} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (490 \text{ K})}{\pi} \right)^{1/2} \\
 &= 2.97 \times 10^{-19} \text{ m}^2 = \pi d^2 \quad \text{so} \quad d = \left(\frac{2.97 \times 10^{-19} \text{ m}^2}{\pi} \right)^{1/2} = \boxed{3.07 \times 10^{-10} \text{ m}}
 \end{aligned}$$

Comment. The change in diameter with temperature can be interpreted in two ways. First, it shows the approximate nature of the concept of molecular diameter, with different values resulting from measurements of different quantities. Second, it is consistent with the idea that, at higher temperatures, more forceful collisions contract a molecule's perimeter.

P24.22 The diffusion constant of an ion in solution is related to the mobility of the ion and to its radius in separate relations

$$\begin{aligned}
 D &= \frac{uRT}{zF} = \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{zFk}{6\pi\eta u R} = \frac{ze}{6\pi\eta u} \\
 a &= \frac{(1) \times (1.602 \times 10^{-19} \text{ C})}{6\pi(0.93 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) \times (1.1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1})} = 8.3 \times 10^{-10} \text{ m} = \boxed{830 \text{ pm}}
 \end{aligned}$$

Solutions to theoretical problems

P24.25 Write the mean velocity initially as a ; then in the emerging beam $\langle v_x \rangle = K \int_0^a v_x f(v_x) dv_x$ where K is a constant which ensures that the distribution in the emergent beam is also normalized. That is, $1 = K \int_0^a f(v_x) dv_x = K \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^a e^{-mv_x^2/2kT} dv_x$

This integral cannot be evaluated analytically but it can be related to the error function by defining

$$x^2 = \frac{mv_x^2}{2kT}$$

which gives $dv_x = \left(\frac{2kT}{m} \right)^{1/2} dx$. Then

$$\begin{aligned}
 1 &= K \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{2kT}{m} \right)^{1/2} \int_0^b e^{-x^2} dx \quad [b = (m/2kT)^{1/2} \times a] \\
 &= \frac{K}{\pi^{1/2}} \int_0^b e^{-x^2} dx = \frac{1}{2} K \text{erf}(b)
 \end{aligned}$$

where $\text{erf}(z)$ is the error function [Table 12.2]: $\text{erf}(z) = \frac{2}{\pi^{1/2}} \int_0^z e^{-x^2} dx$

Therefore, $K = \frac{2}{\text{erf}(b)}$

The mean velocity of the emerging beam is

$$\langle v_x \rangle = K \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^a v_x e^{-mv_x^2/2kT} dv_x = K \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{-kT}{m} \right) \int_0^a \frac{d}{dv_x} (e^{-mv_x^2/2kT}) dv_x$$

$$= -K \left(\frac{kT}{2m\pi} \right)^{1/2} (e^{-ma^2/2kT} - 1)$$

$$\text{Now use } a = \langle v_x \rangle_{\text{initial}} = \left(\frac{2kT}{m\pi} \right)^{1/2}$$

This expression for the average magnitude of the one-dimensional velocity in the x direction may be obtained from

$$\begin{aligned} \langle v_x \rangle &= 2 \int_0^\infty v_x f(v_x) dv_x = 2 \int_0^\infty v_x \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/2kT} dv_x \\ &= \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{2kT}{m} \right) = \left(\frac{2kT}{m\pi} \right)^{1/2} \end{aligned}$$

It may also be obtained very quickly by setting $a = \infty$ in the expression for $\langle v_x \rangle$ in the emergent beam with $\text{erf}(b) = \text{erf}(\infty) = 1$.

Substituting $a = \left(\frac{2kT}{m\pi} \right)^{1/2}$ into $\langle v_x \rangle$ in the emergent beam $e^{-ma^2/2kT} = e^{-1/\pi}$ and $\text{erf}(b) = \text{erf}\left(\frac{1}{\pi^{1/2}}\right)$

$$\text{Therefore, } \langle v_x \rangle = \left(\frac{2kT}{m\pi} \right)^{1/2} \times \frac{1 - e^{-1/\pi}}{\text{erf}\left(\frac{1}{\pi^{1/2}}\right)}$$

From tables of the error function (expanded version of Table 12.2), or from readily available software, or by interpolating Table 12.2.

$$\text{erf}\left(\frac{1}{\pi^{1/2}}\right) = \text{erf}(0.56) = 0.57 \text{ and } e^{-1/\pi} = 0.73$$

$$\text{Therefore, } \langle v_x \rangle = \boxed{0.47 \langle v_x \rangle_{\text{initial}}}$$

P24.27 The most probable speed, c^* , was evaluated in Problem 24.23 and is

$$c^* = v(\text{most probable}) = \left(\frac{2kT}{m} \right)^{1/2}$$

Consider a range of speeds Δv around c^* and nc^* , then with $v = c^*$

$$\frac{f(nc^*)}{f(c^*)} = \frac{(nc^*)^2 e^{-mn^2 c^{*2}/2kT}}{c^{*2} e^{-mc^{*2}/2kT}} [24.4] = n^2 e^{-(n^2-1)mc^{*2}/2kT} = \boxed{n^2 e^{(1-n^2)}}$$

$$\text{Therefore, } \frac{f(3c^*)}{f(c^*)} = 9 \times e^{-8} = \boxed{3.02 \times 10^{-3}} \quad \frac{f(4c^*)}{f(c^*)} = 16 \times e^{-15} = \boxed{4.9 \times 10^{-6}}$$

P24.28 The current I_j carried by an ion j is proportional to its concentration c_j , mobility u_j , and charge number $|z_j|$. [Justification 24.9] Therefore

$$I_j = A c_j u_j z_j$$

where A is a constant. The total current passing through a solution is

$$I = \sum_j I_j = A \sum_j c_j u_j z_j$$

The transport number of the ion j is therefore

$$t_j = \frac{I_j}{I} = \frac{Ac_j u_j z_j}{A \sum_j c_j u_j z_j} = \frac{c_j u_j z_j}{\sum_j c_j u_j z_j}$$

If there are two cations in the mixture

$$\frac{t'}{t''} = \frac{\frac{c' u' z'}{c'' u'' z''}}{\frac{c' u' z'}{c'' u'' z''}} = \frac{c' u'}{c'' u''} \quad \text{if } z' = z''$$

P24.29

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} [24.84] \quad \text{with } c = \frac{n_0 e^{-x^2/4Dt}}{A(\pi Dt)^{1/2}} [24.88]$$

$$\text{or } c = \frac{a}{t^{1/2}} e^{-bx^2/t}$$

$$\text{then } \frac{\partial c}{\partial t} = -\left(\frac{1}{2}\right) \times \left(\frac{a}{t^{3/2}}\right) e^{-bx^2/t} + \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{bx^2}{t^2}\right) e^{-bx^2/t} = -\frac{c}{2t} + \frac{bx^2}{t^2} c$$

$$\frac{\partial c}{\partial x} = \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{-2bx}{t}\right) e^{-bx^2/t}$$

$$\begin{aligned} \frac{\partial^2 c}{\partial x^2} &= -\left(\frac{2b}{t}\right) \times \left(\frac{a}{t^{1/2}}\right) e^{-bx^2/t} + \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{2bx}{t}\right)^2 e^{-bx^2/t} = -\left(\frac{2b}{t}\right) c + \left(\frac{2bx}{t}\right)^2 c \\ &= -\left(\frac{1}{2Dt}\right) c + \left(\frac{bx^2}{Dt^2}\right) c \\ &= \frac{1}{D} \frac{\partial c}{\partial t} \text{ as required} \end{aligned}$$

Initially the material is concentrated at $x = 0$. Note that $c = 0$ for $x > 0$ when $t = 0$ on account of the very strong exponential factor ($e^{-bx^2/t} \rightarrow 0$ more strongly than $\frac{1}{t^{1/2}} \rightarrow \infty$). When $x = 0$, $e^{-x^2/4Dt} = 1$. We confirm the correct behaviour by noting that $\langle x \rangle = 0$ and $\langle x^2 \rangle = 0$ at $t = 0$ [24.90], and so all the material must be at $x = 0$ at $t = 0$.

P24.31

Draw up the following table based on the third and last equations of *Justification 24.12*

N	4	6	8	10	20
$P(6\lambda)_{\text{Exact}}$	0	0.016	0.0313	0.0439	0.0739
$P(6\lambda)_{\text{Approx.}}$	0.004	0.162	0.0297	0.0417	0.0725

N	30	40	60	100
$P(6\lambda)_{\text{Exact}}$	0.0806	0.0807	0.0763	0.0666
$P(6\lambda)_{\text{Approx.}}$	0.0799	0.0804	0.0763	0.0666

The points are plotted in Fig. 24.1.

The discrepancy is less than 0.1 per cent when $N > 60$

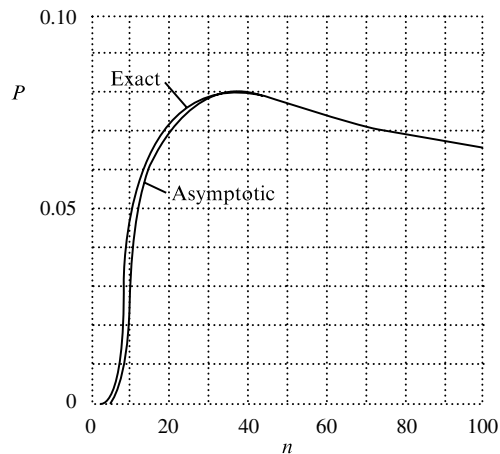


Figure 24.1

Solutions to applications

P24.33

The work required for a mass, m , to go from a distance r from the centre of a planet of mass m' to infinity is

$$w = \int_r^{\infty} F \, dr$$

where F is the force of gravity and is given by Newton's law of universal gravitation, which is

$$F = \frac{Gmm'}{r^2}$$

G is the gravitational constant (not to be confused with g). Then

$$w' = \int_r^{\infty} \frac{Gmm'}{r^2} \, dr = \frac{Gmm'}{r}$$

Since according to Newton's second law of motion, $F = mg$, we may make the identification

$$g = \frac{Gm'}{r^2}$$

Thus, $w = grm$. This is the kinetic energy that the particle must have in order to escape the planet's gravitational attraction at a distance r from the planet's centre; hence $w = \frac{1}{2}mv^2 = mgr$

$$v_e = (2g R_p)^{1/2} \quad [R_p = \text{radius of planet}]$$

which is the escape velocity.

$$(a) \quad v_e = [(2) \times (9.81 \, \text{m s}^{-2}) \times (6.37 \times 10^6 \, \text{m})]^{1/2} = \boxed{11.2 \, \text{km s}^{-1}}$$

$$(b) \quad g(\text{Mars}) = \frac{m(\text{Mars})}{m(\text{Earth})} \times \frac{R(\text{Earth})^2}{R(\text{Mars})^2} \times g(\text{Earth}) = (0.108) \times \left(\frac{6.37}{3.38}\right)^2 \times (9.81 \, \text{m s}^{-2})$$

$$= 3.76 \, \text{m s}^{-2}$$

$$\text{Hence, } v_e = [(2) \times (3.76 \, \text{m s}^{-2}) \times (3.38 \times 10^6 \, \text{m})]^{1/2} = \boxed{5.0 \, \text{km s}^{-1}}$$

$$\text{Since } \bar{c} = \left(\frac{8RT}{\pi M} \right)^{1/2}, T = \frac{\pi M \bar{c}^2}{8R}$$

and we can draw up the following table

$10^{-3} T/\text{K}$	H ₂	He	O ₂	
Earth	11.9	23.7	190	$[\bar{c} = 11.2 \text{ km s}^{-1}]$
Mars	2.4	4.8	38	$[\bar{c} = 5.0 \text{ km s}^{-1}]$

In order to calculate the proportion of molecules that have speeds exceeding the escape velocity, v_e , we must integrate the Maxwell distribution [24.4] from v_e to infinity.

$$P = \int_{v_e}^{\infty} f(v) dv = \int_{v_e}^{\infty} 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \left[\frac{M}{R} = \frac{m}{k} \right]$$

This integral cannot be evaluated analytically and must be expressed in terms of the error function. We proceed as follows.

Defining $\beta = \frac{m}{2kT}$ and $y^2 = \beta v^2$ gives $v = \beta^{-1/2} y$, $v^2 = \beta^{-1} y^2$, $v_e = \beta^{-1/2} y_e$,

$$\begin{aligned} y_e &= \beta^{1/2} v_e, \quad \text{and} \quad dv = \beta^{-1/2} dy \\ P &= 4\pi \left(\frac{\beta}{\pi} \right)^{3/2} \beta^{-1} \beta^{-1/2} \int_{\beta^{1/2} v_e}^{\infty} y^2 e^{-y^2} dy = \frac{4}{\pi^{1/2}} \int_{\beta^{1/2} v_e}^{\infty} y^2 e^{-y^2} dy \\ &= \frac{4}{\pi^{1/2}} \left[\int_0^{\infty} y^2 e^{-y^2} dy - \int_0^{\beta^{1/2} v_e} y^2 e^{-y^2} dy \right] \end{aligned}$$

The first integral can be evaluated analytically; the second cannot.

$$\begin{aligned} \int_0^{\infty} y^2 e^{-y^2} dy &= \frac{\pi^{1/2}}{4}, \text{ hence} \\ P &= 1 - \frac{2}{\pi^{1/2}} \int_0^{\beta^{1/2} v_e} y e^{-y^2} (2y dy) = 1 - \frac{2}{\pi^{1/2}} \int_0^{\beta^{1/2} v_e} y d(-e^{-y^2}) \end{aligned}$$

This integral may be evaluated by parts

$$\begin{aligned} P &= 1 - \frac{2}{\pi^{1/2}} \left[y(-e^{-y^2}) \Big|_0^{\beta^{1/2} v_e} - \int_0^{\beta^{1/2} v_e} (-e^{-y^2}) dy \right] \\ P &= 1 + 2 \left(\frac{\beta}{\pi} \right)^{1/2} v_e e^{-\beta v_e^2} - \frac{2}{\pi^{1/2}} \int_0^{\beta^{1/2} v_e} e^{-y^2} dy = 1 + 2 \left(\frac{\beta}{\pi} \right)^{1/2} v_e e^{-\beta v_e^2} - \text{erf}(\beta^{1/2} v_e) \\ &= \text{erfc}(\beta^{1/2} v_e) + 2 \left(\frac{\beta}{\pi} \right)^{1/2} v_e e^{-\beta v_e^2} \quad [\text{erfc}(z) = 1 - \text{erf}(z)] \end{aligned}$$

From $\beta = \frac{m}{2kT} = \frac{M}{2RT}$ and $v_e = (2gR_p)^{1/2}$

$$\beta^{1/2} v_e = \left(\frac{MgR_p}{RT} \right)^{1/2}$$

For H₂ on Earth at 240 K

$$\beta^{1/2}v_e = \left(\frac{(0.002016 \text{ kg mol}^{-1}) \times (9.807 \text{ m s}^{-2}) \times (6.37 \times 10^6 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (240 \text{ K})} \right)^{1/2} = 7.94$$

$$P = \operatorname{erfc}(7.94) + 2 \left(\frac{7.94}{\pi^{1/2}} \right) e^{-(7.94)^2} = (2.9 \times 10^{-29}) + (3.7 \times 10^{-27}) = \boxed{3.7 \times 10^{-27}}$$

at 1500 K

$$\beta^{1/2}v_e = \left(\frac{(0.002016 \text{ kg mol}^{-1}) \times (9.807 \text{ m s}^{-2}) \times (6.37 \times 10^6 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1500 \text{ K})} \right)^{1/2} = 3.18$$

$$P = \operatorname{erfc}(3.18) + 2 \left(\frac{3.18}{\pi^{1/2}} \right) e^{-(3.18)^2} = (6.9 \times 10^{-6}) + (1.4\bar{6} \times 10^{-4}) = \boxed{1.5 \times 10^{-4}}$$

For H₂ on Mars at 240 K

$$\beta^{1/2}v_e = \left(\frac{(0.002016 \text{ kg mol}^{-1}) \times (3.76 \text{ m s}^{-2}) \times (3.38 \times 10^6 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (240 \text{ K})} \right)^{1/2} = 3.58$$

$$P = \operatorname{erfc}(3.58) + 2 \left(\frac{3.58}{\pi^{1/2}} \right) e^{-(3.58)^2} = (4.13 \times 10^{-7}) + (1.1\bar{0} \times 10^{-5}) = \boxed{1.1 \times 10^{-5}}$$

at 1500 K, $\beta^{1/2}v_e = 1.43$

$$P = \operatorname{erfc}(1.43) + (1.128) \times (1.43) \times e^{-(1.43)^2} = 0.0431 + 0.20\bar{9} = \boxed{0.25}$$

For He on Earth at 240 K

$$\beta^{1/2}v_e = \left(\frac{(0.004003 \text{ kg mol}^{-1}) \times (9.807 \text{ m s}^{-2}) \times (6.37 \times 10^6 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (240 \text{ K})} \right)^{1/2} = 11.1\bar{9}$$

$$P = \operatorname{erfc}(11.2) + (1.128) \times (11.2) \times e^{-(11.2)^2} = 0 + (4 \times 10^{-54}) = \boxed{4 \times 10^{-54}}$$

at 1500 K, $\beta^{1/2}v_e = 4.48$

$$P = \operatorname{erfc}(4.48) + (1.128) \times (4.48) \times e^{-(4.48)^2} = (2.36 \times 10^{-10}) + (9.7\bar{1} \times 10^{-9}) \\ = \boxed{1.0 \times 10^{-8}}$$

For He on Mars at 240 K

$$\beta^{1/2}v_e = \left(\frac{(0.004003 \text{ kg mol}^{-1}) \times (3.76 \text{ m s}^{-2}) \times (3.38 \times 10^6 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (240 \text{ K})} \right)^{1/2} = 5.05$$

$$P = \operatorname{erfc}(5.05) + (1.128) \times (5.05) \times e^{-(5.05)^2} = (9.21 \times 10^{-13}) + (4.7\bar{9} \times 10^{-11}) \\ = \boxed{4.9 \times 10^{-11}}$$

at 1500 K, $\beta^{1/2}v_e = 2.02$

$$P = \operatorname{erfc}(2.02) + (1.128) \times (2.02) \times e^{-(2.02)^2} = (4.28 \times 10^{-3}) + (0.040\bar{1}) = \boxed{0.044}$$

For O₂ on Earth it is clear that $P \approx 0$ at both temperatures.

For O₂ on Mars at 240 K, $\beta^{1/2}v_e = 14.3$

$$P = \operatorname{erfc}(14.3) + (1.128) \times (14.3) \times e^{-(14.3)^2} = 0 + (2.5 \times 10^{-88}) = \boxed{2.5 \times 10^{-88}} \approx 0$$

at 1500 K, $\beta^{1/2}v_e = 5.71$

$$P = \operatorname{erfc}(5.71) + (1.128) \times (5.71) \times e^{-(5.71)^2} = (6.7 \times 10^{-6}) + (4.46 \times 10^{-14}) \\ = \boxed{4.5 \times 10^{-14}}$$

Based on these numbers alone, it would appear that H₂ and He would be depleted from the atmosphere of both Earth and Mars only after many (millions?) years; that the rate on Mars, though still slow, would be many orders of magnitude larger than on Earth; that O₂ would be retained on Earth indefinitely; and that the rate of O₂ depletion on Mars would be very slow (billions of years?), though not totally negligible. The temperatures of both planets may have been higher in past times than they are now.

In the analysis of the data, we must remember that the proportions, P , are not rates of depletion, though the rates should be roughly proportional to P .

The results of the calculations are summarized in the following table

	240 K			1500 K		
	H ₂	He	O ₂	H ₂	He	O ₂
$P(\text{Earth})$	3.7×10^{-27}	4×10^{-54}	0	1.5×10^{-4}	1.0×10^{-8}	0
$P(\text{Mars})$	1.1×10^{-5}	4.9×10^{-11}	0	0.25	0.044	4.5×10^{-14}