# 17 Statistical thermodynamics 2: applications

## Answers to discussion questions

**D17.2** The symmetry number, $\sigma$, is a correction factor to prevent the over-counting of rotational states when computing the high temperature form of the rotational partition function. An elementary interpretation of $\sigma$ is that it recognizes that in a homonuclear diatomic molecule AA the orientations AA′ and A′A are indistinguishable, and should not be counted twice, so the quantity $q = kT/hcB$ is replaced by $q = kT/\sigma hcB$ with $\sigma = 2$. A more sophisticated interpretation is that the Pauli principle allows only certain rotational states to be occupied, and the symmetry factor adjusts the high temperature form of the partition function (which is derived by taking a sum over all states), to account for this restriction. In either case the symmetry number is equal to the number of indistinguishable orientations of the molecule. More formally, it is equal to the order of the rotational subgroup of the molecule. (See Chapter 12.)

**D17.4** The temperature is always high enough for the mean translational energy to be $\frac{3}{2}kT$, the equipartition value (provided the gas is above its condensation temperature). Therefore, the molar constant-volume heat capacity for translation is $C_{V,\mathrm{m}}^{\mathrm{T}} = \frac{3}{2}R$.

Translation is the only mode of motion for a monatomic gas, so for such a gas $C_{V,\mathrm{m}} = \frac{3}{2}R = 12.47\ \mathrm{J\,K^{-1}\,mol^{-1}}$. This result is very reliable: helium, for example has this value over a range of 2000 K.

When the temperature is high enough for the rotations of the molecules to be highly excited (when $T \gg \theta_\mathrm{R}$) we can use the equipartition value $kT$ for the mean rotational energy (for a linear rotor) to obtain $C_{V,\mathrm{m}} = R$. For nonlinear molecules, the mean rotational energy rises to $\frac{3}{2}kT$, so the molar rotational heat capacity rises to $\frac{3}{2}R$ when $T \gg \theta_\mathrm{R}$. Only the lowest rotational state is occupied when the temperature is very low, and then rotation does not contribute to the heat capacity. We can calculate the rotational heat capacity at intermediate temperatures by differentiating the equation for the mean rotational energy (eqn 17.26a for a linear molecule). The resulting expression is plotted in Figure 17.10 of the text. Because the translational contribution is always present, we can expect the molar heat capacity of a gas of diatomic molecules ($C_{V,\mathrm{m}}^{\mathrm{T}} + C_{V,\mathrm{m}}^{\mathrm{R}}$) to change from $\frac{3}{2}R$ to $\frac{5}{2}R$ as the temperature is increased above $\theta_\mathrm{R}$.

Molecular vibrations contribute to the heat capacity, but only when the temperature is high enough for them to be significantly excited. For each vibrational mode, the equipartition mean energy is $kT$, so the maximum contribution to the molar heat capacity is $R$. However, it is very unusual for the vibrations to be so highly excited that equipartition is valid, and it is more appropriate to use the full expression for the vibrational heat capacity which is obtained by differentiating eqn 17.28. The curve in Figure 17.12 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Figure 17.13 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_M$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $\frac{3}{2}R$ to the molar heat capacity. If we denote the number of active rotational modes by $\nu_R^*$ (so for most molecules at normal temperatures $\nu_R^* = 2$ for linear molecules, and 3 for nonlinear molecules), then the rotational contribution is $\frac{1}{2}\nu_R^* R$. If the temperature is high enough for $\nu_V^*$ vibrational modes to be active the vibrational contribution to the molar heat capacity is $\nu_R^* R$. In most cases $\nu_V \approx 0$. It follows that the total molar heat capacity is

$$C_{V,m} = \tfrac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$$

**D17.6** The pair distribution function is a statistical method for studying the complex properties of liquids. It is especially important because, being a Fourier transform of the intensity distribution of scattered radiation, the function relates directly to experimental observation. Equations, which use both the pair distribution function and the intermolecular potential, have been derived for the computation of both equilibrium thermodynamic properties and the equation of state for model liquids [17.50 and 17.51]. However, the computational demands of these equations make the Monte Carlo method and methods of molecular dynamics attractive. The Monte Carlo method randomly displaces molecules and accepts, or rejects, the new molecular configuration with a Boltzmann factor test, which has a potential energy change exponent. Thermodynamic properties are computed as a weighted average of the properties of acceptable configurations. Molecular dynamic methods use Newtonian equations of motion and model intermolecular potentials to compute the motion of molecules as a function of time. Since molecular rotational and vibrational motion occur on the order of $10^{13}$ Hz, the time increment for calculations is taken to be about $10^{-15}$ s (a femtosecond, fs). Properties are computed as time averages.

## Solutions to exercises

**E17.1(b)** $C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$ [17.35]

with a mode active if $T > \theta_M$.

(a) $O_3$ : $C_{V,m} = \frac{1}{2}(3 + 3 + 0)R = 3R$ [experimental = $3.7R$]

(b) $C_2H_6$ : $C_{V,m} = \frac{1}{2}(3 + 3 + 2 \times 1)R = 4R$ [experimental = $6.3R$]

(c) $CO_2$ : $C_{V,m} = \frac{1}{2}(3 + 2 + 0)R = \frac{5}{2}R$ [experimental = $4.5R$]

Consultation of the Herzberg references in *Further reading*, Chapters 13 and 14, turns up only one vibrational mode among these molecules whose frequency is low enough to have a vibrational temperature near room temperature. That mode was in $C_2H_6$, corresponding to the "internal rotation" of $CH_3$ groups. The discrepancies between the estimates and the experimental values suggest that there are vibrational modes in each molecule that contribute to the heat capacity—albeit not to the full equipartition value—that our estimates have classified as inactive.

**E17.2(b)** The equipartition theorem would predict a contribution to molar heat capacity of $\frac{1}{2}R$ for every translational and rotational degree of freedom and $R$ for each vibrational mode. For an ideal gas, $C_{p,m} = R + C_{V,m}$. So for $CO_2$

With vibrations

$$C_{V,\mathrm{m}}/R = 3\left(\tfrac{1}{2}\right) + 2\left(\tfrac{1}{2}\right) = (3 \times 4 - 6) = 6.5 \quad \text{and} \quad \gamma = \frac{7.5}{6.5} = \boxed{1.15}$$

Without vibrations $C_{V,\mathrm{m}}/R = 3\left(\tfrac{1}{2}\right) + 2\left(\tfrac{1}{2}\right) = 2.5$ and $\gamma = \dfrac{3.5}{2.5} = \boxed{1.40}$

Experimental $\gamma = \dfrac{37.11\ \mathrm{J\,mol^{-1}K^{-1}}}{(37.11 - 8.3145)\ \mathrm{J\,mol^{-1}K^{-1}}} = \boxed{1.29}$

The experimental result is closer to that obtained by neglecting vibrations, but not so close that vibrations can be neglected entirely.

**E17.3(b)** The rotational partition function of a linear molecule is [Table 17.3]

$$q^{\mathrm{R}} = \frac{0.6950}{\sigma} \times \frac{T/\mathrm{K}}{(B/\mathrm{cm^{-1}})} = \frac{(0.6950) \times (T/\mathrm{K})}{2 \times 1.4457} = 0.2404(T/\mathrm{K})$$

**(a)** At 25 °C: $q^{\mathrm{R}} = (0.2403) \times (298) = \boxed{71.6}$
**(b)** At 250 °C: $q^{\mathrm{R}} = (0.2403) \times (523) = \boxed{126}$

**E17.4(b)** The symmetry number is the order of the rotational subgroup of the group to which a molecule belongs (except for linear molecules, for which $\sigma = 2$ if the molecule has inversion symmetry and 1 otherwise).

**(a)** $CO_2$: full group $D_{\infty\mathrm{h}}$; subgroup $C_2$; hence $\sigma = \boxed{2}$

**(b)** $O_3$: full group $C_{2\mathrm{v}}$; subgroup $C_2$; $\sigma = \boxed{2}$

**(c)** $SO_3$: full group $D_{3\mathrm{h}}$; subgroup $\{E, C_3, C_3^2, 3C_2\}$; $\sigma = \boxed{6}$

**(d)** $SF_6$: full group $O_\mathrm{h}$; subgroup $O$; $\sigma = \boxed{24}$

**(e)** $Al_2Cl_6$: full group $D_{2\mathrm{d}}$; subgroup $D_2$; $\sigma = \boxed{4}$

**E17.5(b)** The rotational partition function of a non-linear molecule is [Table 17.3]

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma} \frac{(T/\mathrm{K})^{3/2}}{(ABC/\mathrm{cm^{-3}})^{1/2}} = \frac{1.0270 \times 298^{3/2}}{(2) \times (2.027\,36 \times 0.344\,17 \times 0.293\,535)^{1/2}}[\sigma = 2] = \boxed{5837}$$

The high-temperature approximation is valid if $T > \theta_\mathrm{R}$, where

$$\begin{aligned}\theta_\mathrm{R} &= \frac{hc(ABC)^{1/3}}{k} \\ &= \frac{(6.626 \times 10^{-34}\ \mathrm{J\,s}) \times (2.998 \times 10^{10}\ \mathrm{cm\,s^{-1}}) \times [(2.027\,36) \times (0.344\,17) \times (0.293\,535)\ \mathrm{cm^{-3}}]^{1/3}}{1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}} \\ &= \boxed{0.8479\ \mathrm{K}}\end{aligned}$$

**E17.6(b)** $q^{\mathrm{R}} = 5837$ [Exercise 17.5(b)]

All rotational modes of $SO_2$ are active at 25 °C; therefore

$$U_m^R - U_m^R(0) = E^R = \frac{3}{2}RT$$

$$S_m^R = \frac{E^R}{T} + R\ln q^R$$

$$= \tfrac{3}{2}R + R\ln(5837) = \boxed{84.57\ \mathrm{J\,K^{-1}\,mol^{-1}}}$$

**E17.7(b)** **(a)** The partition function is

$$q = \sum_{\text{states}} e^{-E_{\text{state}}/kT} = \sum_{\text{levels}} g e^{-E_{\text{level}}/kT}$$

where $g$ is the degeneracy of the level. For rotations of a symmetric rotor such as $CH_3CN$, the energy levels are $E_J = hc[BJ(J+1) + (A-B)K^2]$ and the degeneracies are $g_{J,K} = 2(2J+1)$ if $K \neq 0$ and $2J+1$ if $K = 0$. The partition function, then, is

$$q = 1 + \sum_{J=1}^{\infty}(2J+1)e^{-\{hcBJ(J+1)/kT\}}\left(1 + 2\sum_{K=1}^{J} e^{-\{hc(A-B)K^2/kT\}}\right)$$

To evaluate this sum explicitly, we set up the following columns in a spreadsheet (values for $A = 5.28\ \mathrm{cm^{-1}}$, $B = 5.2412\ \mathrm{cm^{-1}}$, and $T = 298.15$ K)

| $J$ | $J(J+1)$ | $2J+1$ | $e^{-hcBJ(J+1)/kT}$ | $J$ term | $e^{-\{hc(A-B)K^2/kT\}}$ | $K$ sum | $J$ sum |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 1 | 1 | 1 | 1 | 1 | 1 |
| 1 | 2 | 3 | 0.997 | 8.832 | 0.976 | 2.953 | 9.832 |
| 2 | 6 | 5 | 0.991 | 23.64 | 0.908 | 4.770 | 33.47 |
| 3 | 12 | 7 | 0.982 | 43.88 | 0.808 | 6.381 | 77.35 |
| ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ |
| 82 | 6806 | 165 | $4.18 \times 10^{-5}$ | 0.079 | $8 \times 10^{-71}$ | 11.442 | 7498.95 |
| 83 | 6972 | 167 | $3.27 \times 10^{-5}$ | 0.062 | $2 \times 10^{-72}$ | 11.442 | 7499.01 |

The column labeled $K$ sum is the term in large parentheses, which includes the inner summation. The $J$ sum converges (to 4 significant figures) only at about $J = 80$; the $K$ sum converges much more quickly. But the sum fails to take into account nuclear statistics, so it must be divided by the symmetry number ($\sigma = 3$). At 298 K, $q^R = \boxed{2.50 \times 10^3}$. A similar computation at $T = 500$ K yields $q^R = \boxed{5.43 \times 10^3}$.

**(b)** The rotational partition function of a nonlinear molecule is [Table 17.3 with $B = C$]

$$q^R = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(ABC/\mathrm{cm^{-3}})^{1/2}} = \frac{1.0270}{3}\frac{(T/\mathrm{K})^{3/2}}{(5.28 \times 0.307 \times 0.307)^{1/2}} = 0.485 \times (T/\mathrm{K})^{3/2}$$

At 298 K, $q^R = 0.485 \times 298^{3/2} = \boxed{2.50 \times 10^3}$

At 500 K, $q^R = 0.485 \times 500^{3/2} = \boxed{5.43 \times 10^3}$

The high-temperature approximation is certainly valid here.

**E17.8(b)** The rotational partition function of a nonlinear molecule is [Table 17.3]

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(ABC/\mathrm{cm}^{-3})^{1/2}} = \frac{1.0270 \times (T/\mathrm{K})^{3/2}}{(3.1752 \times 0.3951 \times 0.3505)^{1/2}} = 1.549 \times (T/\mathrm{K})^{3/2}$$

**(a)** At 25 °C, $q^{\mathrm{R}} = 1.549 \times (298)^{3/2} = \boxed{7.97 \times 10^3}$

**(b)** At 100 °C, $q^{\mathrm{R}} = 1.549 \times (373)^{3/2} = \boxed{1.12 \times 10^4}$

**E17.9(b)** The molar entropy of a collection of oscillators is given by

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + k \ln Q\ [17.1] = \frac{N_{\mathrm{A}}\langle\varepsilon\rangle}{T} + R \ln q$$

where $\langle\varepsilon\rangle = \dfrac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} = k\dfrac{\theta_{\mathrm{V}}}{e^{\theta_{\mathrm{V}}/T} - 1}$ [17.28], $q = \dfrac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \dfrac{1}{1 - e^{-\theta_{\mathrm{V}}/T}}$ [17.19]

and $\theta_{\mathrm{V}}$ is the vibrational temperature $hc\tilde{\nu}/k$. Thus

$$S_{\mathrm{m}} = \frac{R(\theta_{\mathrm{V}}/T)}{e^{\theta_{\mathrm{V}}/T} - 1} - R\ln(1 - e^{-\theta_{\mathrm{V}}/T})$$

A plot of $S_{\mathrm{m}}/R$ versus $T/\theta_{\mathrm{V}}$ is shown in Figure 17.1.

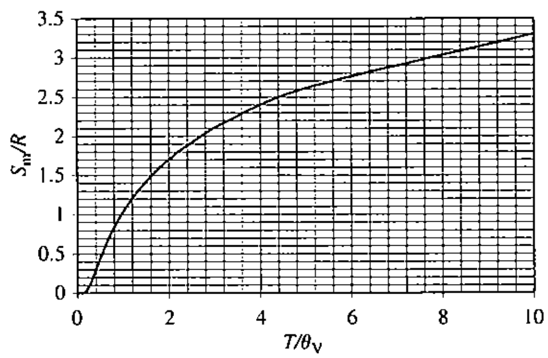



**Figure 17.1**

The vibrational entropy of ethyne is the sum of contributions of this form from each of its seven normal modes. The table below shows results from a spreadsheet programmed to compute $S_{\mathrm{m}}/R$ at a given temperature for the normal-mode wavenumbers of ethyne.

| | | $T = 298$ K | | $T = 500$ K | |
|---|---|---|---|---|---|
| $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\theta_{\mathrm{V}}/\mathrm{K}$ | $T/\theta_{\mathrm{V}}$ | $S_{\mathrm{m}}/R$ | $T/\theta_{\mathrm{V}}$ | $S_{\mathrm{m}}/R$ |
| 612 | 880 | 0.336 | 0.216 | 0.568 | 0.554 |
| 729 | 1049 | 0.284 | 0.138 | 0.479 | 0.425 |
| 1974 | 2839 | 0.105 | 0.000 766 | 0.176 | 0.0229 |
| 3287 | 4728 | 0.0630 | 0.000 002 17 | 0.106 | 0.000 818 |
| 3374 | 4853 | 0.0614 | 0.000 001 46 | 0.103 | 0.000 652 |

The total vibrational heat capacity is obtained by summing the last column (twice for the first two entries, since they represent doubly degenerate modes).

**(a)** At 298 K, $S_m = 0.708R = \boxed{5.88\ \mathrm{J\ mol^{-1}\ K^{-1}}}$

**(b)** At 500 K, $S_m = 1.982R = \boxed{16.48\ \mathrm{J\ mol^{-1}\ K^{-1}}}$

**E17.10(b)** The contributions of rotational and vibrational modes of motion to the molar Gibbs energy depend on the molecular partition functions

$$G_m - G_m(0) = -RT\ln q \text{ [17.9; also see Comment to Exercise 17.6(a)]}$$

The rotational partition function of a nonlinear molecule is given by

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} = \frac{1.0270}{\sigma}\left(\frac{(T/K)^3}{ABC/\mathrm{cm^{-3}}}\right)^{1/2}$$

and the vibrational partition function for each vibrational mode is given by

$$q^V = \frac{1}{1-e^{-\theta/T}} \quad \text{where } \theta = \frac{hc\tilde{\nu}}{k} = \frac{1.4388\,(\tilde{\nu}/\mathrm{cm^{-1}})}{(T/\mathrm{K})}$$

At 298 K $\quad q^R = \dfrac{1.0270}{2}\left(\dfrac{298^3}{(3.553)\times(0.4452)\times(0.3948)}\right)^{1/2} = 3.35\times10^3$

and

$$G_m^R - G_m^R(0) = -(8.3145\ \mathrm{J\ mol^{-1}K^{-1}})\times(298\ \mathrm{K})\ln 3.35\times10^3$$
$$= -20.1\times10^3\ \mathrm{J\ mol^{-1}} = \boxed{-20.1\ \mathrm{kJ\ mol^{-1}}}$$

The vibrational partition functions are so small that we are better off taking

$$\ln q^V = -\ln(1-e^{-\theta/T}) \approx e^{-\theta/T}$$
$$\ln q_1^V \approx e^{-\{1.4388(1110)/298\}} = 4.70\times10^{-3}$$
$$\ln q_2^V \approx e^{-\{1.4388(705)/298\}} = 3.32\times10^{-2}$$
$$\ln q_3^V \approx e^{-\{1.4388(1042)/298\}} = 6.53\times10^{-3}$$

so $\quad G_m^V - G_m^V(0) = -(8.3145\ \mathrm{J\ mol^{-1}K^{-1}})\times(298\ \mathrm{K})$

$$\times(4.70\times10^{-3} + 3.32\times10^{-2} + 6.53\times10^{-3})$$
$$= -110\ \mathrm{J\ mol^{-1}} = \boxed{-0.110\ \mathrm{kJ\ mol^{-1}}}$$

**E17.11(b)** $$q = \sum_j g_j e^{-\beta\varepsilon_j}, \quad \text{where } g = (2S+1) \times \begin{cases} 1 & \text{for } \Sigma \text{ states} \\ 2 & \text{for } \Pi, \Delta, \ldots \text{ states} \end{cases}$$

The $^3\Sigma$ term is triply degenerate (from spin), and the $^1\Delta$ term is doubly (orbitally) degenerate. Hence

$$q = 3 + 2e^{-\beta\varepsilon}$$

At 400 K

$$\beta\varepsilon = \frac{(1.4388\ \text{cm K}) \times (7918.1\ \text{cm}^{-1})}{400\ \text{K}} = 28.48$$

Therefore, the contribution to $G_m$ is

$$G_m - G_m(0) = -RT \ln q \text{ [Table 17.4 for one mole]}$$

$$-RT \ln q = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (400\ \text{K}) \times \ln(3 + 2 \times e^{-28.48})$$

$$= -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (400\ \text{K}) \times (\ln 3) = \boxed{3.65\ \text{kJ mol}^{-1}}$$

**COMMENT.** The contribution of the excited state is negligible at this temperature.

**E17.12(b)** The degeneracy of a species with $S = \frac{5}{2}$ is 6. The electronic contribution to molar entropy is

$$S_m = \frac{U_m - U_m(0)}{T} + R \ln q = R \ln q$$

(The term involving the internal energy is proportional to a temperature-derivative of the partition function, which in turn depends on excited state contributions to the partition function; those contributions are negligible.)

$$S_m = (8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}) \ln 6 = \boxed{14.9\ \text{J mol}^{-1}\ \text{K}^{-1}}$$

**E17.13(b)** Use $S_m = R \ln s$ [17.52b]

Draw up the following table

| $n$: | 0 | 1 | 2 | | | 3 | | | 4 | | | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $o$ | $m$ | $p$ | $a$ | $b$ | $c$ | $o$ | $m$ | $p$ | | |
| $s$ | 1 | 6 | 6 | 6 | 3 | 6 | 6 | 2 | 6 | 6 | 3 | 6 | 1 |
| $S_m/R$ | 0 | 1.8 | 1.8 | 1.8 | 1.1 | 1.8 | 1.8 | 0.7 | 1.8 | 1.8 | 1.1 | 1.8 | 0 |

where $a$ is the 1,2,3 isomer, $b$ the 1,2,4 isomer, and $c$ the 1,3,5 isomer.

**E17.14(b)** We need to calculate

$$K = \prod_J \left(\frac{q^{\ominus}_{J,m}}{N_A}\right)^{\nu_J} \times e^{-\Delta E_0/RT} \text{ [17.54b]} = \frac{q^{\ominus}_m({}^{79}\text{Br}_2)q^{\ominus}_m({}^{81}\text{Br}_2)}{q^{\ominus}_m({}^{79}\text{Br}^{81}\text{Br})^2} e^{-\Delta E_0/RT}$$

Each of these partition functions is a product

$$q_m^{\ominus} = q_m^T q^R q^V q^E$$

with all $q^E = 1$.

The ratio of the translational partition functions is virtually 1 (because the masses nearly cancel; explicit calculation gives 0.999). The same is true of the vibrational partition functions. Although the moments of inertia cancel in the rotational partition functions, the two homonuclear species each have $\sigma = 2$, so

$$\frac{q^R(^{79}Br_2)q^R(^{81}Br_2)}{q^R(^{79}Br^{81}Br)^2} = 0.25$$

The value of $\Delta E_0$ is also very small compared with $RT$, so

$$K \approx \boxed{0.25}$$

## Solutions to problems

### Solutions to numerical problems

**P17.2** $\Delta\varepsilon = \varepsilon = g\mu_B B$ [15.42]

$$q = 1 + e^{-\beta\varepsilon}$$

$$C_{V,m}/R = \frac{x^2 e^{-x}}{(1+e^{-x})^2} \text{ [Problem 17.1]}, \quad x = 2\mu_B B\beta \text{ [} g = 2 \text{ for electrons]}$$

Therefore, if $B = 5.0$ T,

$$x = \frac{(2) \times (9.274 \times 10^{-24}\ \text{J T}^{-1}) \times (5.0\ \text{T})}{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times T} = \frac{6.72}{T/\text{K}}$$

(a) $T = 50$ K, $x = 0.134$, $C_V = 4.47 \times 10^{-3}R$, implying that $C_V = 3.7 \times 10^{-2}\ \text{J K}^{-1}\ \text{mol}^{-1}$. Since the equipartition value is about $3R$ [$\nu_R^* = 3, \nu_V^* \approx 0$], the field brings about a change of about $\boxed{0.1 \text{ per cent}}$

(b) $T = 298$ K, $x = 2.26 \times 10^{-2}$, $C_V = 1.3 \times 10^{-4}R$, implying that $C_V = 1.1\ \text{mJ K}^{-1}\ \text{mol}^{-1}$, a change of about $\boxed{4 \times 10^{-3} \text{ per cent}}$.

***Question.*** What percentage change would a magnetic field of 1 kT cause?

**P17.4** $q = 1 + 5e^{-\beta\varepsilon}$ [$g_J = 2J + 1$]

$$\varepsilon = E(J=2) - E(J=0) = 6hcB \quad [E = hcBJ(J+1)]$$

$$\frac{U - U(0)}{N} = -\frac{1}{q}\frac{\partial q}{\partial \beta} = \frac{5\varepsilon e^{-\beta\varepsilon}}{1 + 5e^{-\beta\varepsilon}}$$

$$C_{V,m} = -k\beta^2 \left(\frac{\partial U_m}{\partial \beta}\right)_V \text{ [17.31a]}$$

$$C_{V,\mathrm{m}}/R = \frac{5\varepsilon^2\beta^2 e^{-\beta\varepsilon}}{(1+5e^{-\beta\varepsilon})^2} = \frac{180(hcB\beta)^2 e^{-6hcB\beta}}{(1+5e^{-6hcB\beta})^2}$$

$$\frac{hcB}{k} = 1.4388 \text{ cm K} \times 60.864 \text{ cm}^{-1} = 87.571 \text{ K}$$

Hence,

$$C_{V,\mathrm{m}}/R = \frac{1.380 \times 10^6 e^{-525.4 \text{ K}/T}}{(1+5e^{-525.4 \text{ K}/T}) \times (T/\text{K})^2}$$

We draw up the following table

| $T/\text{K}$ | 50 | 100 | 150 | 200 | 250 | 300 | 350 | 400 | 450 | 500 |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_{V,\mathrm{m}}/R$ | 0.02 | 0.68 | 1.40 | 1.35 | 1.04 | 0.76 | 0.56 | 0.42 | 0.32 | 0.26 |

These points are plotted in Figure 17.2.

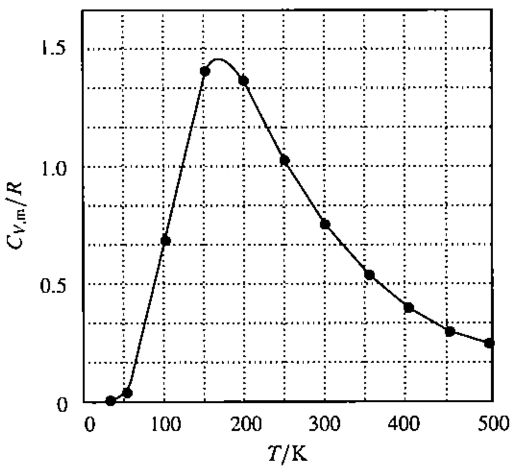



**Figure 17.2**

**P17.6** $$\frac{q_{\mathrm{m}}^{\mathrm{T}}}{N_{\mathrm{A}}} = 2.561 \times 10^{-2} \times (T/\text{K})^{5/2} \times (M/\text{g mol}^{-1})^{3/2} \text{ [Table 17.3]}$$

$$= (2.561 \times 10^{-2}) \times (298)^{5/2} \times (28.02)^{3/2} = 5.823 \times 10^6$$

$$q^{\mathrm{R}} = \frac{0.6950}{\sigma} \times \frac{T/\text{K}}{(B/\text{cm}^{-1})} = \frac{0.6950}{2} \times \frac{298}{1.9987} = 51.81 \text{ [Table 17.3]}$$

$$q^{\mathrm{V}} = \frac{1}{1-e^{-\theta_{\mathrm{V}}/T}} \text{ [Table 17.3]}$$

where $\theta_{\mathrm{V}} = \dfrac{hc\tilde{\nu}}{k} = \dfrac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 2358 \text{ cm}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1}} = 3392 \text{ K}$

so $q^{\mathrm{V}} = \dfrac{1}{1-e^{-3392\text{K}/298\text{K}}} = 1.00$

Therefore

$$\frac{q_{\rm m}^{\ominus}}{N_{\rm A}} = (5.82\overline{3} \times 10^{6}) \times (51.8\overline{1}) \times (1.00) = 3.02 \times 10^{8}$$

$$U_{\rm m} - U_{\rm m}(0) = \frac{3}{2}RT + RT = \frac{5}{2}RT \qquad [T \gg \theta_{\rm T}, \theta_{\rm R}]$$

Hence

$$S_{\rm m}^{\ominus} = \frac{U_{\rm m} - U_{\rm m}(0)}{T} + R\left(\ln\frac{q_{\rm m}^{\ominus}}{N_{\rm A}} + 1\right)$$

$$= \frac{5}{2}R + R\{\ln 3.02 \times 10^{8} + 1\} = 23.03R = \boxed{191.4\ {\rm J\,K^{-1}\,mol^{-1}}}$$

The difference between the experimental and calculated values is negligible, indicating that the residual entropy is negligible.

**P17.8** The vibrational temperature is defined by

$$k\theta_{\rm V} = hc\tilde{\nu},$$

so a vibration with $\theta_{\rm V}$ less than 1000 K has a wavenumber less than

$$\tilde{\nu} = \frac{k\theta_{\rm V}}{hc} = \frac{(1.381 \times 10^{-23}\ {\rm J\,K^{-1}}) \times (1000\,{\rm K})}{(6.626 \times 10^{-34}\ {\rm J\,s}) \times (2.998 \times 10^{10}\ {\rm cm\,s^{-1}})} = 695.2\,{\rm cm^{-1}}$$

There are seven such wavenumbers listed among those for $C_{60}$: two $T_{1u}$, a $T_{2u}$, a $G_u$, and three $H_u$. The number of *modes* involved, $\nu_{\rm V}^{*}$, must take into account the degeneracy of these vibrational energies

$$\nu_{\rm V}^{*} = 2(3) + 1(3) + 1(4) + 3(5) = \boxed{28}$$

The molar heat capacity of a molecule is roughly

$$C_{V,\rm m} = \tfrac{1}{2}(3 + \nu_{\rm R}^{*} + 2\nu_{\rm V}^{*})R\ [17.35] = \tfrac{1}{2}(3 + 3 + 2 \times 28)R = 31R = 31(8.3145\ {\rm J\,mol^{-1}\,K^{-1}})$$

$$= \boxed{258\ {\rm J\,mol^{-1}\,K^{-1}}}$$

**P17.10**

$$K = \frac{q_{\rm m}^{\ominus}({\rm CHD_3})q_{\rm m}^{\ominus}({\rm DCl})}{q_{\rm m}^{\ominus}({\rm CD_4})q_{\rm m}^{\ominus}({\rm HCl})}{\rm e}^{-\beta\Delta E_0}\ [17.54;\ N_{\rm A}\ \text{factors cancel}]$$

Use partition function expressions from Table 17.3. The ratio of translational partition functions is

$$\frac{q_{\rm m}^{\rm T}({\rm CHD_3})q_{\rm m}^{\rm T}({\rm DCl})}{q_{\rm m}^{\rm T}({\rm CD_4})q_{\rm m}^{\rm T}({\rm HCl})} = \left(\frac{M({\rm CHD_3})M({\rm DCl})}{M({\rm CD_4})M({\rm HCl})}\right)^{3/2} = \left(\frac{19.06 \times 37.46}{20.07 \times 36.46}\right)^{3/2} = 0.964$$

The ratio of rotational partition functions is

$$\frac{q^{\rm R}({\rm CHD_3})q^{\rm R}({\rm DCl})}{q^{\rm R}({\rm CD_4})q^{\rm R}({\rm HCl})} = \frac{\sigma({\rm CD_4})}{\sigma({\rm CHD_3})}\frac{(B({\rm CD_4})/{\rm cm^{-1}})^{3/2}B({\rm HCl})/{\rm cm^{-1}}}{(A({\rm CHD_3})B({\rm CHD_3})^2/{\rm cm^{-3}})^{1/2}B({\rm DCl})/{\rm cm^{-1}}}$$

$$= \frac{12}{3} \times \frac{2.63^{3/2} \times 10.59}{(2.63 \times 3.28^2)^{1/2} \times 5.445} = 6.24$$

The ratio of vibrational partition functions (call it $Q$ for convenience below) is

$$Q = \frac{q^{\mathrm{V}}(\mathrm{CHD_3})q^{\mathrm{V}}(\mathrm{DCl})}{q^{\mathrm{V}}(\mathrm{CD_4})q^{\mathrm{V}}(\mathrm{HCl})} = \frac{q(2993)q(2142)q(1003)^3q(1291)^2q(1036)^2q(2145)}{q(2109)q(1092)^2q(2259)^3q(996)^3q(2991)}$$

where $q(x) = \dfrac{1}{1 - \mathrm{e}^{-1.4388x/(T/\mathrm{K})}}$.

We also require $\Delta E_0$, which is equal to the difference in zero point energies

$$\begin{aligned}\frac{\Delta E_0}{hc} &= \frac{1}{2}\{(2993 + 2142 + 3 \times 1003 + 2 \times 1291 + 2 \times 1036 + 2145)\\ &\quad - (2109 + 2 \times 1092 + 3 \times 2259 + 3 \times 996 + 2991)\}\ \mathrm{cm^{-1}}\\ &= -1053\ \mathrm{cm^{-1}}\end{aligned}$$

So the exponent in the energy term is

$$-\beta\Delta E_0 = -\frac{\Delta E_0}{kT} = -\frac{hc}{k} \times \frac{\Delta E_0}{hc} \times \frac{1}{T} = -\frac{1.4388 \times (-1053)}{T/\mathrm{K}} = +\frac{1515}{T/\mathrm{K}}$$

Hence,

$$K = 0.964 \times 6.24 \times Q\mathrm{e}^{+1515/(T/\mathrm{K})} = 6.02Q\mathrm{e}^{+1515/(T/\mathrm{K})}$$

We can now evaluate $K$(on a computer), and obtain the following values

| $T/\mathrm{K}$ | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |
|---|---|---|---|---|---|---|---|---|
| $K$ | 945 | 273 | 132 | 83 | 61 | 49 | 42 | 37 |

The values of $K$ are plotted in Figure 17.3.

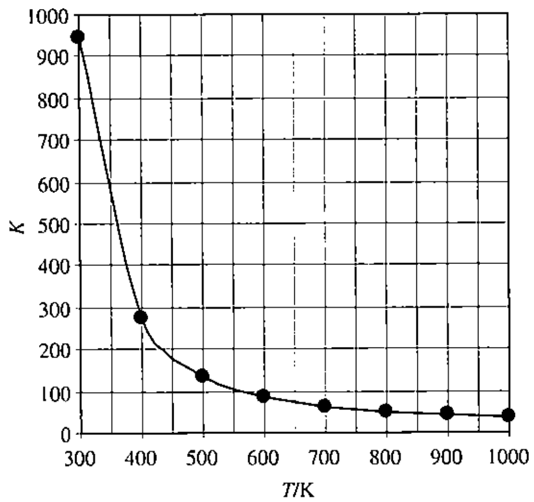



**Figure 17.3**

## Solutions to theoretical problems

**P17.12** A Sackur–Tetrode type of equation describes the translational entropy of the gas. Here

$$q^{\mathrm{T}} = q_x^{\mathrm{T}} q_y^{\mathrm{T}} \quad \text{with } q_x^{\mathrm{T}} = \left(\frac{2\pi m}{\beta h^2}\right)^{1/2} X \ [16.15]$$

where $X$ is the length of the surface. Therefore,

$$q^{\mathrm{T}} = \left(\frac{2\pi m}{\beta h^2}\right) XY = \frac{2\pi m\sigma}{\beta h^2}, \quad \sigma = XY$$

$$U_{\mathrm{m}} - U_{\mathrm{m}}(0) = -\frac{N_{\mathrm{A}}}{q}\left(\frac{\partial q}{\partial \beta}\right) = RT \ \text{[or by equipartition]}$$

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + R(\ln q_{\mathrm{m}} - \ln N_{\mathrm{A}} + 1)\left[q_{\mathrm{m}} = \frac{q}{n}\right]$$

$$= R + R\ln\left(\frac{\mathrm{e}q_{\mathrm{m}}}{N_{\mathrm{A}}}\right) = R\ln\left(\frac{\mathrm{e}^2 q_{\mathrm{m}}}{N_{\mathrm{A}}}\right)$$

$$= \boxed{R\ln\left(\frac{2\pi \mathrm{e}^2 m\sigma_{\mathrm{m}}}{h^2 N_{\mathrm{A}}\beta}\right)}\left[\sigma_{\mathrm{m}} = \frac{\sigma}{n}\right]$$

Call this molar entropy of the mobile two-dimensional film $S_{\mathrm{m}2}$. The molar entropy of condensation is the difference between this entropy and that of a (three-dimensional) gas:

$$\Delta S_{\mathrm{m}} = S_{\mathrm{m}2} - S_{\mathrm{m}3}.$$

The three-dimensional value is given by the Sackur–Tetrode equation

$$S_{\mathrm{m}} = R\ln\left\{\mathrm{e}^{5/2}\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\frac{V_{\mathrm{m}}}{N_{\mathrm{A}}}\right\}$$

So $$\Delta S_{\mathrm{m}} = R\ln\frac{\mathrm{e}^2(2\pi m/h^2\beta)\times(\sigma_{\mathrm{m}}/N_{\mathrm{A}})}{\mathrm{e}^{5/2}(2\pi m/h^2\beta)^{3/2}\times(V_{\mathrm{m}}/N_{\mathrm{A}})} = \boxed{R\ln\left\{\left(\frac{\sigma_{\mathrm{m}}}{V_{\mathrm{m}}}\right)\times\left(\frac{h^2\beta}{2\pi m\mathrm{e}}\right)^{1/2}\right\}}$$

**P17.14** Begin with the partition function of an oscillator (Table 17.3)

$$q = \frac{1}{1-\mathrm{e}^{-x}}, \quad x = \frac{\theta_{\mathrm{V}}}{T} = hc\tilde{\nu}\beta = \hbar\omega\beta$$

Expressions for internal energy and other thermodynamic functions are in Table 17.4.

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_{\mathrm{V}} = -N(1-\mathrm{e}^{-x})\frac{\mathrm{d}}{\mathrm{d}\beta}(1-\mathrm{e}^{-x})^{-1} = \frac{N\hbar\omega\mathrm{e}^{-x}}{1-\mathrm{e}^{-x}} = \boxed{\frac{N\hbar\omega}{\mathrm{e}^{x}-1}}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -k\beta^2\frac{\partial U}{\partial \beta}\ [17.31\mathrm{a}] = -k\beta^2\hbar\omega\frac{\partial U}{\partial x}$$

$$= k(\beta\hbar\omega)^2 N\left\{\frac{\mathrm{e}^{x}}{(\mathrm{e}^{x}-1)^2}\right\} = \boxed{kN\left\{\frac{x^2\mathrm{e}^{x}}{(\mathrm{e}^{x}-1)^2}\right\}}$$

$$H - H(0) = U - U(0)\ [q \text{ is independent of } V] = \boxed{\frac{N\hbar\omega}{e^{x} - 1}}$$

$$S = \frac{U - U(0)}{T} + nR\ln q = \frac{Nkxe^{-x}}{1 - e^{-x}} - Nk\ln(1 - e^{-x})$$

$$= \boxed{Nk\left(\frac{x}{e^{x} - 1} - \ln(1 - e^{-x})\right)}$$

$$A - A(0) = G - G(0) = -nRT\ln q = \boxed{NkT\ln(1 - e^{-x})}$$

The functions are plotted in Figure 17.4.

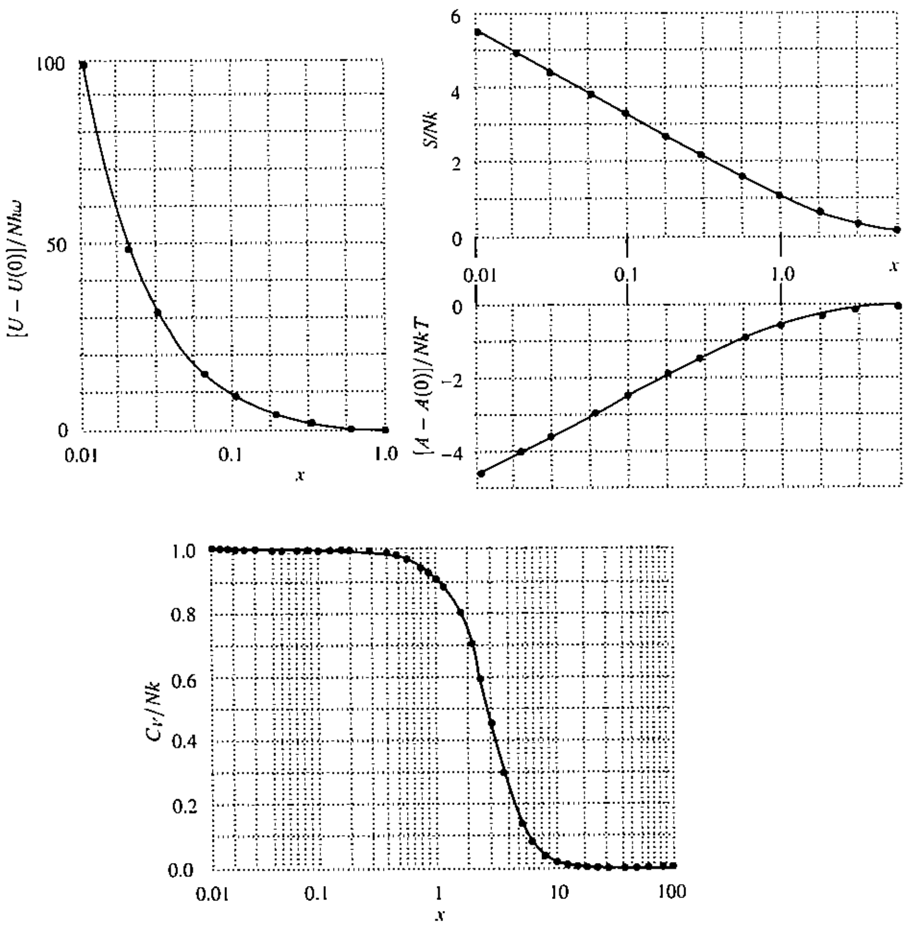



**Figure 17.4**

**P17.16** (a) $$\frac{N_J}{N} = \frac{g_J e^{-\varepsilon_J/kT}}{\sum_J g_J e^{-\varepsilon_J/kT}} = \frac{g_J e^{-\varepsilon_J/kT}}{q}$$

For a linear molecule $g_J = 2J + 1$ and $\varepsilon_J = hcBJ(J + 1)$ [Sections 13.5(c) and d)]. Therefore,

$$N_J \propto (2J + 1)e^{-hcBJ(J+1)/kT}$$

**(b)** $J_{\max}$ occurs when $\mathrm{d}N_J/\mathrm{d}J = 0$.

$$\frac{\mathrm{d}N_J}{\mathrm{d}J} = \frac{N}{q}\frac{\mathrm{d}}{\mathrm{d}J}\left\{(2J+1)\mathrm{e}^{-\left(\frac{hcBJ(J+1)}{kT}\right)}\right\} = 0$$

$$2 - (2J_{\max}+1)\left(\frac{hcB}{kT}\right)(2J_{\max}+1) = 0$$

$$2J_{\max}+1 = \left(\frac{2kT}{hcB}\right)^{1/2}$$

$$\boxed{J_{\max} = \left(\frac{kT}{2hcB}\right)^{1/2} = -\frac{1}{2}}$$

**(c)** $J_{\max} \approx 3$ because the $R$ branch $J = 3 \rightarrow 4$ transition has the least transmittance. Solving the previous equation for $T$ provides the desired temperature estimate.

$$T \approx \frac{hcB}{2k}(2J_{\max}+1)^2$$

$$\approx \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(3.000\times10^{8}\,\mathrm{m\,s^{-1}})\times(10.593\,\mathrm{cm^{-1}})\times\left(\frac{10^2\,\mathrm{cm}}{\mathrm{m}}\right)\times(7)^2}{2(1.380\,66\times10^{-23}\,\mathrm{J\,K^{-1}})}$$

$$\boxed{T \approx 374\,\mathrm{K}}$$

**(d)** For a spherical rotor $g_J = (2J+1)^2$ and $\varepsilon_J = hcBJ(J+1)$ [Sections 13.5(c) and (d)]. Therefore

$$N_J \propto (2J+1)^2\mathrm{e}^{-hcBJ(J+1)/kT}$$

$J_{\max}$ occurs when $\mathrm{d}N_J/\mathrm{d}J = 0$.

$$\frac{\mathrm{d}N_J}{\mathrm{d}J} = \frac{N}{q}\frac{\mathrm{d}}{\mathrm{d}J}\left\{(2J+1)^2\mathrm{e}^{-\left(\frac{hcBJ(J+1)}{kT}\right)}\right\} = 0$$

$$2(2J_{\max}+1)\times2 - (2J_{\max}+1)^2\left(\frac{hcB}{kT}\right)(2J_{\max}+1) = 0$$

Divide both sides by $2J_{\max}+1$:

$$4 - (2J_{\max}+1)^2\left(\frac{hcB}{kT}\right) = 0$$

$$2J_{\max}+1 = \left(\frac{4kT}{hcB}\right)^{1/2}$$

$$\boxed{J_{\max} = \left(\frac{kT}{hcB}\right)^{1/2} - \frac{1}{2}}$$

**P17.18** (a) $$U - U(0) = -\frac{N}{q}\frac{\partial q}{\partial \beta} = -\frac{N}{q}\sum \varepsilon_j e^{-\beta\varepsilon_j} = \frac{NkT}{q}\dot{q} = \boxed{nRT\left(\frac{\dot{q}}{q}\right)}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial \beta}{\partial T}\left(\frac{\partial U}{\partial \beta}\right)_V = \frac{1}{kT^2}\frac{\partial}{\partial \beta}\left(\frac{N}{q}\sum_j \varepsilon_j e^{-\beta\varepsilon_j}\right)$$

$$= \left(\frac{N}{kT^2}\right) \times \left[\frac{1}{q}\sum_j \varepsilon_j^2 e^{-\beta\varepsilon_j} + \frac{1}{q^2}\left(\frac{\partial q}{\partial \beta}\right)\sum_j \varepsilon_j e^{-\beta\varepsilon_j}\right]$$

$$= \left(\frac{N}{kT^2}\right) \times \left[\frac{1}{q}\sum_j \varepsilon_j^2 e^{-\beta\varepsilon_j} - \frac{1}{q^2}\left(\sum_j \varepsilon_j e^{-\beta\varepsilon_j}\right)^2\right]$$

$$= \left(\frac{N}{kT^2}\right) \times \left[\frac{k^2T^2\ddot{q}}{q} - \frac{k^2T^2}{q^2}\dot{q}^2\right]$$

$$= \boxed{nR\left\{\frac{\ddot{q}}{q} - \left(\frac{\dot{q}}{q}\right)^2\right\}}$$

$$S = \frac{U - U(0)}{T} + nR\ln\left(\frac{q}{N} + 1\right) = \boxed{nR\left(\frac{\dot{q}}{q} + \ln\frac{eq}{N}\right)}$$

(b) At 5000 K, $\dfrac{kT}{hc} = 3475\,\text{cm}^{-1}$. We form the sums

$$q = \sum_j e^{-\beta\varepsilon_j} = 1 + e^{-21870/3475} + 3e^{-21870/3475} + \cdots = 1.0167$$

$$\dot{q} = \sum_j \frac{\varepsilon_j}{kT}e^{-\beta\varepsilon_j} = \frac{hc}{kT}\sum_j \tilde{\nu}_j e^{-\beta\varepsilon_j}$$

$$= \left(\frac{1}{3475}\right) \times \{0 + 21850\,e^{-21850/3475} + 3 \times 21870\,e^{-21870/3475} + \cdots\} = 0.1057$$

$$\ddot{q} = \sum_j \left(\frac{\varepsilon_j}{kT}\right)^2 e^{-\beta\varepsilon_j} = \left(\frac{hc}{kT}\right)^2 \sum_j \tilde{\nu}_j^2 e^{-\beta\varepsilon_j}$$

$$= \left(\frac{1}{3475}\right)^2 \times \{0 + 21850^2\,e^{-21850/3475} + 3 \times 21870^2\,e^{-21870/3475} + \cdots\} = 0.6719$$

The electronic contribution to the molar constant-volume heat capacity is

$$C_{V,\text{m}} = R\left\{\frac{\ddot{q}}{q} - \left(\frac{\dot{q}}{q}\right)^2\right\}$$

$$= 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times \left\{\frac{0.6719}{1.0167} - \left(\frac{0.1057}{1.0167}\right)^2\right\} = \boxed{5.41\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

**P17.20** The derivation of

$$C_V = \frac{kN\beta^2}{2}\zeta(\beta)$$

given in P17.19 is completely general. That is, it makes no use of the fact that the energies and degeneracies in question were those of a linear rotor. The derivation and therefore the result can apply equally well to a nonlinear rotor, to electronic energy levels, or to the vibrational energy levels involved in P17.20.

To evaluate contributions of individual excitations to the heat capacity, we re-write $\zeta(\beta)$ in notation associated with vibrational energy levels

$$\zeta(\beta) = \frac{1}{q^2}\sum_{\nu,\nu'}\{\varepsilon(\nu) - \varepsilon(\nu')\}^2 g(\nu)g(\nu')\mathrm{e}^{-\beta[\varepsilon(\nu)+\varepsilon(\nu')]} = \frac{1}{q^2}\sum_{\nu,\nu'}\{\varepsilon(\nu) - \varepsilon(\nu')\}^2\mathrm{e}^{-\beta[\varepsilon(\nu)+\varepsilon(\nu')]}$$

where the levels are nondegenerate, or at least are treated as such because vibrational modes are treated one by one. The energy levels are

$$\varepsilon(\nu) = hc\tilde{\nu}\nu = \theta_V k\nu \quad \text{so} \quad \beta\varepsilon(\nu) = \theta_V \nu/T.$$

The total heat capacity and the contributions of several transitions are plotted in Figure 17.5. For vibration, one can compute $q$ and the total $C_V/R$ analytically, using expressions from Tables 17.3 and 17.5 respectively:

$$q = \frac{1}{1 - \mathrm{e}^{-\theta_V/T}} \quad \text{and} \quad \frac{C_{V,\mathrm{m}}}{R} = \left(\frac{\theta_V}{T}\right)^2 \frac{\mathrm{e}^{-\theta_V/T}}{(1 - \mathrm{e}^{-\theta_V/T})^2}$$

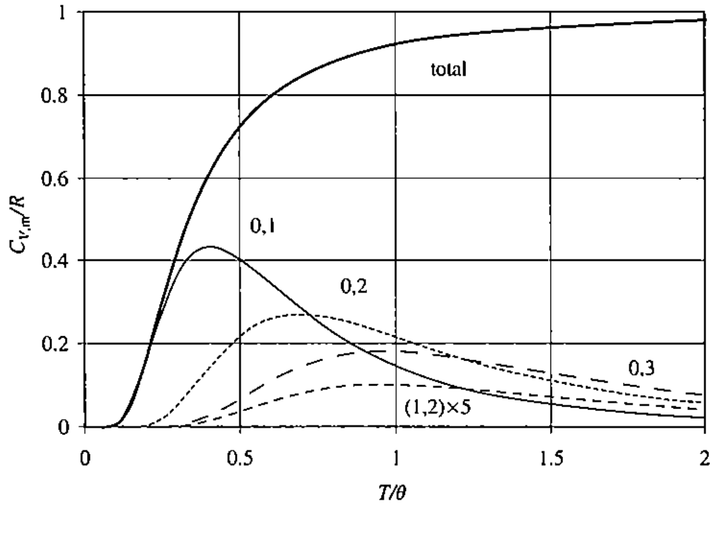



**Figure 17.5**

**P17.22** $$c_s = \left(\frac{\gamma RT}{M}\right)^{1/2}, \quad \gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}}, \quad C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R$$

**(a)** $C_{V,\mathrm{m}} = \frac{1}{2}R(3 + \nu_{\mathrm{R}}^{*} + 2\nu_{\mathrm{V}}^{*}) = \frac{1}{2}R(3+2) = \frac{5}{2}R$

$$C_{p,\mathrm{m}} = \frac{5}{2}R + R = \frac{7}{2}R$$

$$\gamma = \frac{7}{5} = 1.40; \quad \text{hence } \boxed{c_{\mathrm{s}} = \left(\frac{1.40RT}{M}\right)^{1/2}}$$

**(b)** $C_{V,\mathrm{m}} = \dfrac{1}{2}R(3+2) = \dfrac{5}{2}R, \quad \gamma = 1.40, \quad \boxed{c_{\mathrm{s}} = \left(\dfrac{1.40RT}{M}\right)^{1/2}}$

**(c)** $C_{V,\mathrm{m}} = \frac{1}{2}R(3+3) = 3R$

$$C_{p,\mathrm{m}} = 3R + R = 4R, \quad \gamma = \frac{4}{3}, \quad \boxed{c_{\mathrm{s}} = \left(\frac{4RT}{3M}\right)^{1/2}}$$

For air, $M \approx 29\,\mathrm{g\,mol^{-1}}$, $T \approx 298\,\mathrm{K}$, $\gamma = 1.40$

$$c_{\mathrm{s}} = \left(\frac{(1.40) \times (2.48\,\mathrm{kJ\,mol^{-1}})}{29 \times 10^{-3}\,\mathrm{mol^{-1}}}\right)^{1/2} = \boxed{350\,\mathrm{m\,s^{-1}}}$$

## Solutions to applications

**P17.24** (a) The heat capacity is

$$C_V = -k\beta^2 \left(\frac{\partial E}{\partial \beta}\right)_V \quad [17.31\mathrm{a}].$$

First express $E$ as a function of $\beta$:

$$E = \frac{N\varepsilon \mathrm{e}^{-\beta\varepsilon}}{1 + \mathrm{e}^{-\beta\varepsilon}}$$

$$\text{Hence } \frac{C_V}{-k\beta^2} = \left(\frac{\partial E}{\partial \beta}\right)_V = \frac{1}{1 + \mathrm{e}^{-\beta\varepsilon}} \times (-N\varepsilon^2 \mathrm{e}^{-\beta\varepsilon}) - \frac{N\varepsilon}{(1 + \mathrm{e}^{-\beta\varepsilon})^2} \times (-\varepsilon \mathrm{e}^{-\beta\varepsilon})$$

Collecting terms over a common denominator yields

$$C_V = \frac{kN\beta^2\varepsilon^2 \mathrm{e}^{-\beta\varepsilon}}{(1 + \mathrm{e}^{-\beta\varepsilon})^2}(1 + \mathrm{e}^{-\beta\varepsilon} - \mathrm{e}^{-\beta\varepsilon}) = \frac{kN\beta^2\varepsilon^2 \mathrm{e}^{-\beta\varepsilon}}{(1 + \mathrm{e}^{-\beta\varepsilon})^2} = \frac{kN(1/kT)^2\varepsilon^2 \mathrm{e}^{-\varepsilon/kT}}{(1 + \mathrm{e}^{-\varepsilon/kT})^2}$$

Multiply through by $\mathrm{e}^{2\varepsilon/kT}/\mathrm{e}^{2\varepsilon/kT}$:

$$C_V = \frac{kN(1/kT)^2\varepsilon^2 \mathrm{e}^{\varepsilon/kT}}{(\mathrm{e}^{\varepsilon/kT} + 1)^2}$$

The desired expression uses molar rather than molecular quantities:

$$N = N_{\mathrm{A}}, \quad R = N_{\mathrm{A}}k, \quad \text{and} \quad \varepsilon/k = \varepsilon_{\mathrm{m}}/R$$

$$\text{so } C_{V,\text{m}} = \frac{R(\varepsilon_\text{m}/RT)^2 e^{\varepsilon_\text{m}/RT}}{(1 + e^{\varepsilon_\text{m}/RT})^2}$$

**(b)** It is convenient to plot $C_{V,\text{m}}$ (in units of $R$) as a function of $x$ where $x = kT/\varepsilon = RT/\varepsilon_\text{m}$.

$$C_{V,\text{m}} = \frac{Re^{-1/x}}{x^2(1 + e^{-1/x})^2}$$

The molar heat capacity is plotted in Figure 17.6.

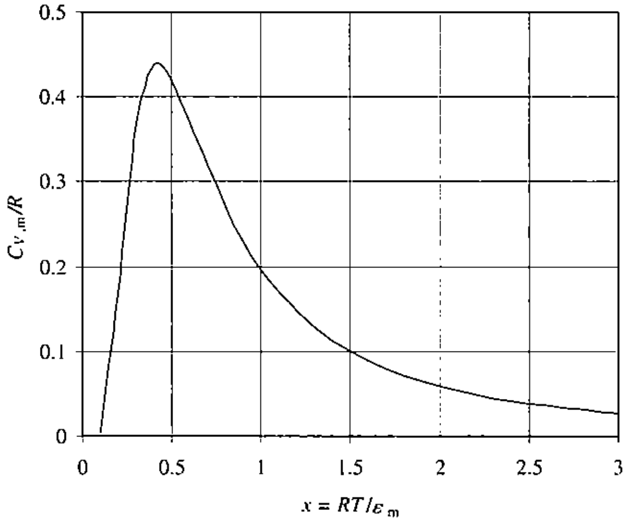



**Figure 17.6**

**(c)** The above plot indicates a maximum heat capacity at about 0.43 $R$ at value for $x$ of about 0.4. The $X - Y$ trace feature of mathematical software may be used to find the more accurate value for $x$ of 0.417. A formula for the maximum is determined by the criterion that $dC_{V,\text{m}}/dx = 0$ at the maximum.

$$\begin{aligned}
\frac{d(C_{V,\text{m}}/R)}{dx} &= \frac{d}{dx}\left\{\frac{e^{-1/x}}{x^2(1 + e^{-1/x})^2}\right\} \\
&= \frac{e^{-1/x}}{x^4(1 + e^{-1/x})^2} - \frac{2e^{-1/x}}{x^3(1 + e^{-1/x})^2} - \frac{2e^{-2/x}}{x^4(1 + e^{-1/x})^3} \\
&= \frac{e^{-1/x}}{x^4(1 + e^{-1/x})^3}\left\{1 - e^{-1/x} - 2x(1 + e^{-1/x}) - 2e^{-1/x}\right\} \\
&= \frac{e^{-1/x}}{x^4(1 + e^{-1/x})^3}\left\{1 - 2x - (1 + 2x)e^{-1/x}\right\}
\end{aligned}$$

Thus, $C_{V,\text{m}}$ is a maximum when $x = x_\text{max}$ satisfies the equation

$$1 - 2x_\text{max} - (1 + 2x_\text{max})e^{-1/x_\text{max}} = 0$$

This is a transcendental equation so it is necessary to solve for $x_\text{max}$ with a numerical method. $x_\text{max}$ may be numerically determined with the numeric solver application of the modern scientific calculator. The Given/Find solve block of Mathcad can be used or a graph containing plots of $f(x) = 1 - x$ and $g(x) = (1 + 2x)e^{-1/x}$ may be prepared. The intercept of $f(x)$ and $g(x)$ determines $x_\text{max}$. Alternatively, expand $e^{-1/x}$ in a Taylor series around $x = 0.4$ within the above equation, discard second order and higher terms (linearize), and solve for $x$. All methods yield $x_{max} \approx 0.417$. The following presents a Mathcad solution

```
x := 2      Estimate for following Solve Block
Given       1 − 2·x − (1 + 2·x)·e^(−1/x) = 0    x > 0   x := Find(x)
x = 0.417
```

**P17.26** The standard molar Gibbs energy is given by

$$G_m^{\ominus} - G_m^{\ominus}(0) = RT \ln \frac{q_m^{\ominus}}{N_A} \quad \text{where } \frac{q_m^{\ominus}}{N_A} = \frac{q_m^{T\ominus}}{N_A} q^R q^V q^E \text{ [17.53]}$$

Translation (see Table 17.3 for all partition functions):

$$\frac{q_m^{T\ominus}}{N_A} = 2.561 \times 10^{-2} (T/\mathrm{K})^{5/2} \, (M/\mathrm{g\,mol^{-1}})^{3/2}$$

$$= 2.561 \times 10^{-2} \times (200.0)^{5/2} \times (102.9)^{3/2} = 1.512 \times 10^{7}$$

Rotation of a nonlinear molecule:

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} = \frac{1.0270}{\sigma} \times \frac{(T/\mathrm{K})^{3/2}}{(ABC/\mathrm{cm^{-3}})^{1/2}}$$

$$= \frac{1.0270}{2} \times \frac{[(200.0) \times (2.998 \times 10^{10}\,\mathrm{cm\,s^{-1}})]^{3/2}}{[(13\,109.4) \times (2409.8) \times (2139.7) \times (10^6\,\mathrm{s^{-1}})^3/\mathrm{cm^{-3}}]^{1/2}} = 2.900 \times 10^{4}$$

Vibration

$$q_1^V = \frac{1}{1 - \exp\left(\dfrac{-1.4388(\tilde{\nu}/\mathrm{cm^{-1}})}{T/\mathrm{K}}\right)} = \frac{1}{1 - \exp\left(\dfrac{-1.4388(753)}{200.0}\right)} = 1.004$$

$$q_2^V = \frac{1}{1 - \exp\left(\dfrac{-1.4388(542)}{200.0}\right)} = 1.021$$

$$q_3^V = \frac{1}{1 - \exp\left(\dfrac{-1.4388(310)}{200.0}\right)} = 1.120$$

$$q_4^V = \frac{1}{1 - \exp\left(\dfrac{-1.4388(127)}{200.0}\right)} = 1.670$$

$$q_5^V = \frac{1}{1 - \exp\left(\dfrac{-1.4388(646)}{200.0}\right)} = 1.010$$

$$q_6^{\mathrm{V}} = \frac{1}{1 - \exp\left(\dfrac{-1.4388(419)}{200.0}\right)} = 1.052$$

$$q^{\mathrm{V}} = \prod_{i=1}^{6} q_i^{\mathrm{V}} = 2.037$$

Putting it all together yields

$$G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) = (8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}) \times (200.0\ \mathrm{K})$$
$$\times \ln[(1.512 \times 10^{7}) \times (2.900 \times 10^{4}) \times (2.037) \times (1)]$$

$$G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) = 4.576 \times 10^{4}\ \mathrm{J\ mol^{-1}} = \boxed{45.76\ \mathrm{kJ\ mol^{-1}}}$$

# 18 Molecular interactions

## Answers to discussion questions

**D18.2** When the applied field changes direction slowly, the permanent dipole moment has time to reorientate–the whole molecule rotates into a new direction–and follow the field. However, when the frequency of the field is high, a molecule cannot change direction fast enough to follow the change in direction of the applied field and the dipole moment then makes no contribution to the polarization of the sample. Because a molecule takes about 1 ps to turn through about 1 radian in a fluid, the loss of this contribution to the polarization occurs when measurements are made at frequencies greater than about $10^{11}$ Hz (in the microwave region). We say that the orientation polarization, the polarization arising from the permanent dipole moments, is lost at such high frequencies.

The next contribution to the polarization to be lost as the frequency is raised is the distortion polarization, the polarization that arises from the distortion of the positions of the nuclei by the applied field. The molecule is bent and stretched by the applied field, and the molecular dipole moment changes accordingly. The time taken for a molecule to bend is approximately the inverse of the molecular vibrational frequency, so the distortion polarization disappears when the frequency of the radiation is increased through the infrared. The disappearance of polarization occurs in stages: as shown in *Justification* 18.3, each successive stage occurs as the incident frequency rises above the frequency of a particular mode of vibration.

At even higher frequencies, in the visible region, only the electrons are mobile enough to respond to the rapidly changing direction of the applied field. The polarization that remains is now due entirely to the distortion of the electron distribution, and the surviving contribution to the molecular polarizability is called the electronic polarizability.

**D18.4** There are three van der Waals type interactions that depend upon distance as $1/r^6$; they are the Keesom interaction between rotating permanent dipoles, the permanent-dipole–induced-dipole-interaction, and the induced-dipole–induced-dipole, or London dispersion, interaction. In each case, we can visualize the distance dependence of the potential energy as arising from the $1/r^3$ dependence of the field (and hence the magnitude of the induced dipole) and the $1/r^3$ dependence of the potential energy of interaction of the dipoles (either permanent or induced).

**D18.6** The increase in entropy of a solution when hydrophobic molecules or groups in molecules cluster together and reduce their structural demands on the solvent (water) is the origin of the hydrophobic interaction that tends to stabilize clustering of hydrophobic groups in solution. A manifestation of the hydrophobic interaction is the clustering together of hydrophobic groups in biological macromolecules. For example, the side chains of amino acids that are used to form the polypeptide chains of proteins are hydrophobic, and the hydrophobic interaction is a major contributor to the tertiary structure of polypeptides. At first thought, this clustering would seem to be a nonspontaneous process as the clustering of the solute results in a decrease in entropy of the solute. However, the clustering of the solute results in greater freedom of movement of the solvent molecules and an accompanying increase in disorder and entropy of the solvent. The total entropy of the system has increased and the process is spontaneous.

## Solutions to exercises

**E18.1(b)** A molecule that has a center of symmetry cannot be polar. $SO_3(D_{3h})$ and $XeF_4(D_{4h})$ cannot be polar. $\boxed{SF_4}$ (see-saw, $C_{2v}$) may be polar.

**E18.2(b)**

$$\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta)^{1/2} \quad [18.2a]$$

$$= [(1.5)^2 + (0.80)^2 + (2) \times (1.5) \times (0.80) \times (\cos 109.5°)]^{1/2}\,\text{D} = \boxed{1.4\,\text{D}}$$

**E18.3(b)** The components of the dipole moment vector are

$$\mu_x = \sum_i q_i x_i = (4e) \times (0) + (-2e) \times (162\,\text{pm})$$
$$+ (-2e) \times (143\,\text{pm}) \times (\cos 30°) = (-572\,\text{pm})e$$

and $\mu_y = \sum_i q_i y_i = (4e) \times (0) + (-2e) \times (0) + (-2e) \times (143\,\text{pm}) \times (\sin 30°) = (-143\,\text{pm})e$

The magnitude is

$$\mu = (\mu_x^2 + \mu_y^2)^{1/2} = ((-570)^2 + (-143)^2)^{1/2}\,\text{pm}\,e = (590\,\text{pm})e$$
$$= (590 \times 10^{-12}\,\text{m}) \times (1.602 \times 10^{-19}\,\text{C}) = \boxed{9.45 \times 10^{-29}\,\text{C m}}$$

and the direction is $\theta = \tan^{-1}\dfrac{\mu_y}{\mu_x} = \tan^{-1}\dfrac{-143\,\text{pm}\,e}{-572\,\text{pm}\,e} = \boxed{194.0°}$ from the $x$-axis (i.e. 14.0° below the negative $x$-axis).

**E18.4(b)** The molar polarization depends on the polarizability through

$$P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

This is a linear equation in $T^{-1}$ with slope

$$m = \frac{N_A\mu^2}{9\varepsilon_0 k} \quad \text{so} \quad \mu = \left(\frac{9\varepsilon_0 km}{N_A}\right)^{1/2} = (4.275 \times 10^{-29}\,\text{C m}) \times (m/(\text{m}^3\,\text{mol}^{-1}\text{K}))^{1/2}$$

and with $y$-intercept

$$b = \frac{N_A\alpha}{3\varepsilon_0} \quad \text{so} \quad \alpha = \frac{3\varepsilon_0 b}{N_A} = (4.411 \times 10^{-35}\,\text{C}^2\,\text{m}^2\,\text{J}^{-1})b/(\text{m}^3\,\text{mol}^{-1})$$

Since the molar polarization is linearly dependent on $T^{-1}$, we can obtain the slope $m$ and the intercept $b$

$$m = \frac{P_{m,2} - P_{m,1}}{T_1^{-1} - T_2^{-1}} = \frac{(75.74 - 71.43)\,cm^3\,mol^{-1}}{(320.0\,K)^{-1} - (421.7\,K)^{-1}} = 5.72 \times 10^3\,cm^3\,mol^{-1}\,K$$

and $b = P_m - mT^{-1} = 75.74\,cm^3\,mol^{-1} - (5.72 \times 10^3\,cm^3\,mol^{-1}\,K) \times (320.0\,K)^{-1}$

$$= 57.9\,cm^3\,mol^{-1}$$

It follows that

$$\mu = (4.275 \times 10^{-29}\,C\,m) \times (5.72 \times 10^{-3})^{1/2} = \boxed{3.23 \times 10^{-30}\,C\,m}$$

and

$$\alpha = (4.411 \times 10^{-35}\,C^2\,m^2\,J^{-1}) \times (57.9 \times 10^{-6}) = \boxed{2.55 \times 10^{-39}\,C^2\,m^2\,J^{-1}}$$

**E18.5(b)** The relative permittivity is related to the molar polarization through

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho P_m}{M} \equiv C \quad \text{so} \quad \varepsilon_r = \frac{2C + 1}{1 - C},$$

$$C = \frac{(1.92\,g\,cm^{-3}) \times (32.16\,cm^3\,mol^{-1})}{85.0\,g\,mol^{-1}} = 0.726$$

$$\varepsilon_r = \frac{2 \times (0.726) + 1}{1 - 0.726} = \boxed{8.97}$$

**E18.6(b)** The induced dipole moment is

$$\mu^* = \alpha\mathcal{E} = 4\pi\varepsilon_0\alpha'\mathcal{E}$$

$$= 4\pi(8.854 \times 10^{-12}\,J^{-1}\,C^2\,m^{-1}) \times (2.22 \times 10^{-30}\,m^3) \times (15.0 \times 10^3\,V\,m^{-1})$$

$$= \boxed{3.71 \times 10^{-36}\,C\,m}$$

**E18.7(b)** If the permanent dipole moment is negligible, the polarizability can be computed from the molar polarization

$$P_m = \frac{N_A\alpha}{3\varepsilon_0} \quad \text{so} \quad \alpha = \frac{3\varepsilon_0 P_m}{N_A}$$

and the molar polarization from the refractive index

$$\frac{\rho P_m}{M} = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{n_r^2 - 1}{n_r^2 + 2} \quad \text{so} \quad \alpha = \frac{3\varepsilon_0 M}{N_A \rho}\left(\frac{n_r^2 - 1}{n_r^2 + 2}\right)$$

$$\alpha = \frac{3 \times (8.854 \times 10^{-12}\,J^{-1}\,C^2\,m^{-1}) \times (65.5\,g\,mol^{-1})}{(6.022 \times 10^{23}\,mol^{-1}) \times (2.99 \times 10^6\,g\,m^{-3})} \times \left(\frac{1.622^2 - 1}{1.622^2 + 2}\right)$$

$$= \boxed{3.40 \times 10^{-40}\,C^2\,m^2\,J^{-1}}$$

**E18.8(b)** The solution to Exercise 18.7(a) showed that

$$\alpha = \left(\frac{3\varepsilon_0 M}{\rho N_A}\right) \times \left(\frac{n_r^2 - 1}{n_r^2 + 2}\right) \quad \text{or} \quad \alpha' = \left(\frac{3M}{4\pi\rho N_A}\right) \times \left(\frac{n_r^2 - 1}{n_r^2 + 2}\right)$$

which may be solved for $n_r$ to yield

$$n_r = \left(\frac{\beta' + 2\alpha'}{\beta' - \alpha'}\right)^{1/2} \quad \text{with } \beta' = \frac{3M}{4\pi\rho N_A}$$

$$\beta' = \frac{(3) \times (72.3\,\mathrm{g\,mol^{-1}})}{(4\pi) \times (0.865 \times 10^6\,\mathrm{g\,m^{-3}}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})} = 3.31\bar{4} \times 10^{-29}\,\mathrm{m^3}$$

$$n_r = \left(\frac{33.1\bar{4} + 2 \times 2.2}{33.1\bar{4} - 2.2}\right)^{1/2} = \boxed{1.10}$$

**E18.9(b)** The relative permittivity is related to the molar polarization through

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho P_m}{M} \equiv C \quad \text{so} \quad \varepsilon_r = \frac{2C + 1}{1 - C}$$

The molar polarization depends on the polarizability through

$$P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right) \quad \text{so} \quad C = \frac{\rho N_A}{3\varepsilon_0 M}\left(4\pi\varepsilon_0\alpha' + \frac{\mu^2}{3kT}\right)$$

$$C = \frac{(1491\,\mathrm{kg\,m^{-3}}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}{3(8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (157.01 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})}$$
$$\times \left(4\pi(8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (1.5 \times 10^{-29}\,\mathrm{m^3}) + \frac{(5.17 \times 10^{-30}\,\mathrm{C\,m})^2}{3(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}\right)$$

$$C = 0.83 \quad \text{and} \quad \varepsilon_r = \frac{2(0.83) + 1}{1 - 0.83} = \boxed{16}$$

**E18.10(b)** $$V_m = \frac{M}{\rho} = \frac{18.02\,\mathrm{g\,mol^{-1}}}{999.4 \times 10^3\,\mathrm{g\,m^{-3}}} = 1.803 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$$

$$\frac{2\gamma V_m}{rRT} = \frac{2\left(7.275 \times 10^{-2}\,\mathrm{N\,m^{-1}}\right) \times \left(1.803 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}\right)}{\left(20.0 \times 10^{-9}\,\mathrm{m}\right) \times \left(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}\right) \times (308.2\,\mathrm{K})}$$
$$= 5.11\bar{9} \times 10^{-2}$$

$$p = (5.623\,\mathrm{kPa})\,e^{0.0511\bar{9}} = \boxed{5.92\,\mathrm{kPa}}$$

**E18.11(b)** $$\gamma = \frac{1}{2}\rho g h r = \frac{1}{2}\left(0.9956\,\mathrm{g\,cm^{-3}}\right) \times \left(9.807\,\mathrm{m\,s^{-2}}\right) \times \left(9.11 \times 10^{-2}\,\mathrm{m}\right)$$
$$\times \left(0.16 \times 10^{-3}\,\mathrm{m}\right) \times \left(\frac{1000\,\mathrm{kg\,m^{-3}}}{\mathrm{g\,cm^{-3}}}\right)$$
$$= \boxed{7.12 \times 10^{-2}\,\mathrm{N\,m^{-1}}}$$

**E18.12(b)** $p_{\text{in}} - p_{\text{out}} = \frac{2\gamma}{r}$ [18.38] $= \frac{(2) \times (22.39 \times 10^{-3}\,\text{N m}^{-1})}{2.20 \times 10^{-7}\,\text{m}} = \boxed{2.04 \times 10^{5}\,\text{Pa}}$

## Solutions to problems

### Solutions to numerical problems

**P18.2** The energy of the dipole $-\mu_1\varepsilon$. To flip it over requires a change in energy of $2\mu_1\varepsilon$. This will occur when the energy of interaction of the dipole with the induced dipole of the Ar atom equals $2\mu_1\varepsilon$. The magnitude of the dipole–induced-dipole interaction is

$$V = \frac{\mu_1^2\alpha_2'}{\pi\varepsilon_0 r^6}\ [18.24] = 2\mu_1\varepsilon\ \text{[after flipping over]}$$

$$r^6 = \frac{\mu_1\alpha_2'}{2\pi\varepsilon_0\varepsilon} = \frac{(6.17 \times 10^{-30}\,\text{C m}) \times (1.66 \times 10^{-30}\,\text{m}^3)}{(2\pi) \times (8.854 \times 10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1}) \times (1.0 \times 10^{3}\,\text{V m}^{-1})}$$

$$= 1.8\bar{4} \times 10^{-52}\,\text{m}^6$$

$$r = 2.4 \times 10^{-9}\,\text{m} = \boxed{2.4\,\text{nm}}$$

**COMMENT.** This distance is about 24 times the radius of the Ar atom.

**P18.4** $$P_{\text{m}} = \left(\frac{M}{\rho}\right) \times \left(\frac{\varepsilon_{\text{r}} - 1}{\varepsilon_{\text{r}} + 2}\right) \quad \text{and} \quad P_{\text{m}} = \frac{4\pi}{3}N_{\text{A}}\alpha' + \frac{N_{\text{A}}\mu^2}{9\varepsilon_0 kT}\ [18.14\text{ and }18.15\text{ with }\alpha = 4\pi\varepsilon_0\alpha']$$

The data have been corrected for the variation in methanol density, so use $\rho = 0.791\ \text{g cm}^{-3}$ for all entries. Obtain $\mu$ and $\alpha'$ from the liquid range ($\theta > -95\,°\text{C}$) results, but note that some molecular rotation occurs even below the freezing point (thus the $-110\,°\text{C}$ value is close to the $-80\,°\text{C}$ value).

Draw up the following table using $M = 32.0\ \text{g mol}^{-1}$.

| $\theta/°\text{C}$ | −80 | −50 | −20 | 0 | 20 |
|---|---|---|---|---|---|
| $T/K$ | 193 | 223 | 253 | 273 | 293 |
| $\frac{1000}{T/K}$ | 5.18 | 4.48 | 3.95 | 3.66 | 3.41 |
| $\varepsilon_r$ | 57 | 49 | 42 | 38 | 34 |
| $\frac{\varepsilon_{\text{r}} - 1}{\varepsilon_{\text{r}} + 2}$ | 0.949 | 0.941 | 0.932 | 0.925 | 0.917 |
| $P_{\text{m}}/(\text{cm}^3\,\text{mol}^{-1})$ | 38.4 | 38.1 | 37.7 | 37.4 | 37.1 |

$P_{\text{m}}$ is plotted against $1/T$ in Figure 18.1.

The extrapolated intercept at $1/T = 0$ is 34.8 (not shown in the figure) and the slope is 721 (from a least-squares analysis). It follows that

$$\alpha' = \frac{3P_{\text{m}}(\text{at intercept})}{4\pi N_{\text{A}}} = \frac{(3) \times (35.0\,\text{cm}^3\,\text{mol}^{-1})}{(4\pi) \times (6.022 \times 10^{23}\,\text{mol}^{-1})} = \boxed{1.38 \times 10^{-23}\,\text{cm}^3}$$

$$\mu = (1.282 \times 10^{-2}\,\text{D}) \times (721)^{1/2}\ [\text{from Problem 18.3}] = \boxed{0.34\,\text{D}}$$

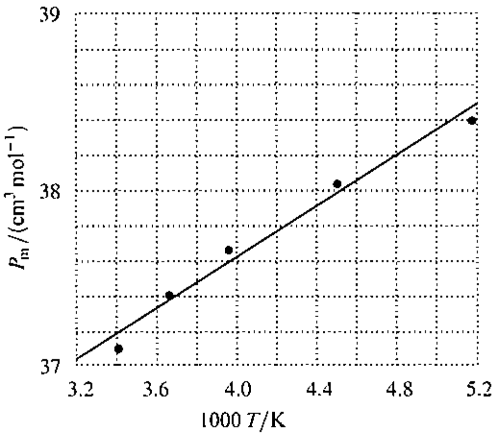



**Figure 18.1**

The jump in $\varepsilon_r$ which occurs below the melting temperature suggests that the molecules can rotate while the sample is still solid.

**P18.6**

$$P_m = \frac{4\pi}{3}N_A\alpha' + \frac{N_A\mu^2}{9\varepsilon_0 kT} \text{ [18.15, with } \alpha = 4\pi\varepsilon_0\alpha'\text{]}$$

Draw up the following table

| $T/K$ | 384.3 | 420.1 | 444.7 | 484.1 | 522.0 |
|---|---|---|---|---|---|
| $1000/(T/K)$ | 2.602 | 2.380 | 2.249 | 2.066 | 1.916 |
| $P_m/(cm^3\ mol^{-1})$ | 57.4 | 53.5 | 50.1 | 46.8 | 43.1 |

The points are plotted in Figure 18.2.

The extrapolated (least-squares) intercept is 3.44 $cm^3\ mol^{-1}$; the slope is $2.08\bar{4} \times 10^4$.

$$\mu = (1.282 \times 10^{-2}\,\text{D}) \times (\text{slope})^{1/2} \text{ [Problem 18.3]} = \boxed{1.85\ \text{D}}$$

$$\alpha' = \frac{3P_m(\text{at intercept})}{4\pi N_A} = \frac{(3) \times (3.44\,\text{cm}^3\,\text{mol}^{-1})}{(4\pi) \times (6.022 \times 10^{23}\,\text{mol}^{-1})} = \boxed{1.36 \times 10^{-24}\ \text{cm}^3}$$

**COMMENT.** The agreement of the value of $\mu$ with Table 18.1 is exact, but the polarizability volumes differ by about 8 percent.

**P18.8** An electric dipole moment may be considered as charge $+q$ and $-q$ separated by a distance $l$ such that

$$\mu = ql \quad \text{so} \quad q = \mu/l = \frac{(1.77\,\text{D}) \times (3.336 \times 10^{-30}\,\text{C m/D})}{299 \times 10^{-12}\,\text{m}} = 1.97 \times 10^{-20}\,\text{C}$$

In units of the electron charge

$$q/e = (1.97 \times 10^{-20}\,\text{C})/(1.602 \times 10^{-19}\,\text{C}) = \boxed{0.123}$$

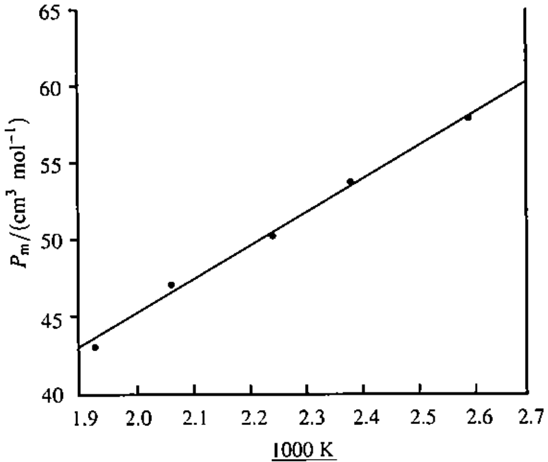



**Figure 18.2**

## Solutions to theoretical problems

**P18.10** (a) Consider the arrangement shown in Figure 18.3(a). There are a total of $3 \times 3 = 9$ Coulombic interactions at the distances shown. The total potential energy of interaction of the two quadrupoles is

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0} \times \left[\left(\frac{1}{r} - \frac{2}{r-l} + \frac{1}{r-2l}\right) - 2\left(\frac{1}{r+l} - \frac{2}{r} + \frac{1}{r-l}\right) + \left(\frac{1}{r+2l} - \frac{2}{r+l} + \frac{1}{r}\right)\right]$$

$$= \frac{q_1 q_2}{4\pi\varepsilon_0 r} \times \left[\left(1 - \frac{2}{1-\lambda} + \frac{1}{1-2\lambda}\right) - 2\left(\frac{1}{1+\lambda} - 2 + \frac{1}{1-\lambda}\right) + \left(\frac{1}{1+2\lambda} - \frac{2}{1+\lambda} + 1\right)\right] \quad \left(\lambda = \frac{l}{r} \ll 1\right)$$

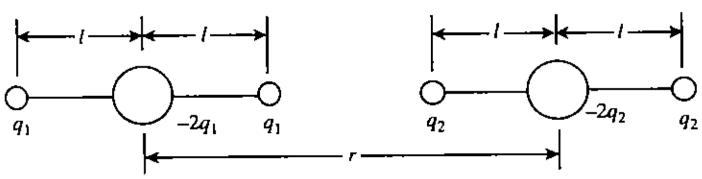



**Figure 18.3(a)**

Expand each term using

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + x^4 - \cdots$$

and keep up to $\lambda^4$ (the preceding terms cancel). The result is

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \times 24\lambda^4 = \frac{6 q_1 q_2 l^4}{\pi\varepsilon_0 r^5}$$

Define the quadrupole moments of the two distributions as

$$Q_1 = q_1 l^2, \qquad Q_2 = q_2 l^2$$

and hence obtain $\boxed{V = \dfrac{6Q_1Q_2}{\pi\varepsilon_0} \times \dfrac{1}{r^5}}$

**(b)** Consider Figure 18.3(b). There are three different distances, $r, r'$, and $r''$. Three interactions are at $r$, four at $r'$, and two at $r''$.

$$r' = (r^2 + l^2)^{1/2} = r(1 + \lambda^2)^{1/2} \approx r\left(1 + \frac{\lambda^2}{2} - \frac{\lambda^4}{8} + \cdots\right)$$

$$r'' = (r^2 + 4l^2)^{1/2} = r(1 + 4\lambda^2)^{1/2} \approx r(1 + 2\lambda^2 - 2\lambda^4 + \cdots)$$

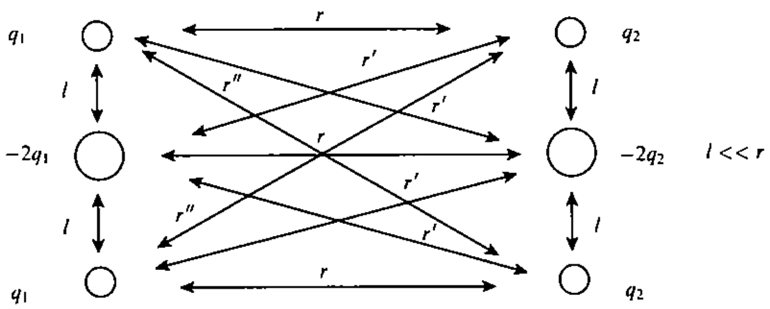



**Figure 18.3(b)**

$$V = \frac{q_1q_2}{4\pi\varepsilon_0} \times \left[\left(\frac{1}{r} - \frac{2}{r'} + \frac{1}{r''}\right) - 2\left(\frac{2}{r'} - \frac{4}{r} + \frac{2}{r'}\right) + \left(\frac{1}{r''} - \frac{2}{r'} + \frac{1}{r}\right)\right]$$

$$= \left(\frac{2q_1q_2}{4\pi\varepsilon_0}\right) \times \left(\frac{3}{r} - \frac{4}{r'} + \frac{1}{r''}\right) = \left(\frac{2q_1q_2}{4\pi\varepsilon_0 r}\right) \times \left(3 - 4\frac{r}{r'} + \frac{r}{r''}\right)$$

Substituting for $r'$ and $r''$ in terms of $r$ and $\lambda$ from above we obtain (dropping terms beyond $\lambda^4$)

$$V = V_0\left(3 - \frac{4}{\left(1 + \frac{\lambda^2}{2} - \frac{\lambda^4}{8}\right)} + \frac{1}{(1 + 2\lambda^2 - 2\lambda^4)}\right) \quad \left[V_0 = \frac{2q_1q_2}{4\pi\varepsilon_0 r}\right]$$

$$= V_0\left[3 - 4\left(1 - \frac{\lambda^2}{2} + \frac{\lambda^4}{8} + \frac{\lambda^4}{4}\right) + (1 - 2\lambda^2 + 2\lambda^4 + 4\lambda^4)\right]$$

The terms in $\lambda^0$ and $\lambda^2$ cancel leaving

$$V = V_0\left(6 - \frac{3}{2}\right)\lambda^4 = \frac{9}{2}V_0\lambda^4 = \frac{9q_1q_2\lambda^4}{4\pi\varepsilon_0 r} = \frac{9q_1q_2l^4}{4\pi\varepsilon_0 r^5} = \boxed{\frac{9Q_1Q_2}{4\pi\varepsilon_0 r^5}}.$$

**P18.12** The dimers should have a zero dipole moment. The strong molecular interactions in the pure liquid probably break up the dimers and produce hydrogen-bonded groups of molecules with a chain-like structure. In very dilute benzene solutions, the molecules should behave much like those in the gas and should tend to form planar dimers. Hence the relative permittivity $\boxed{\text{should decrease}}$ as the dilution increases.

**P18.14** An 'exponential-6' Lennard-Jones potential has the form

$$V = 4\varepsilon\left[\mathrm{A}\mathrm{e}^{-r/\sigma} - \left(\frac{\sigma}{r}\right)^6\right]$$

and is sketched in Figure 18.4.

The minimum occurs where

$$\frac{\mathrm{d}V}{\mathrm{d}r} = 4\varepsilon\left(\frac{-A}{\sigma}\mathrm{e}^{-r/\sigma} + \frac{6\sigma^6}{r^7}\right) = 0$$

which occurs at the solution of

$$\frac{\sigma^7}{r^7} = \frac{\mathrm{A}}{6}\mathrm{e}^{-r/\sigma}$$

Solve this equation numerically. As an example, when $A = \sigma = 1$, a minimum occurs at $r = \boxed{1.63}$

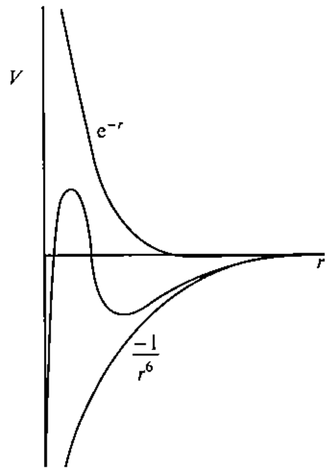



**Figure 18.4**

**P18.16** Refer to Figure 18.5(a).

The scattering angle is $\theta = \pi - 2\alpha$ if specular reflection occurs in the collision (angle of impact equal to angle of departure from the surface). For $b \le R_1 + R_2$, $\sin\alpha = b/(R_1 + R_2)$.

$$\theta = \begin{cases} \pi - 2\arcsin\left(\frac{b}{R_1+R_2}\right) & b \le R_1 + R_2 \\ 0 & b > R_1 + R_2 \end{cases}$$

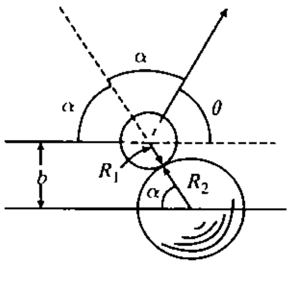



**Figure 18.5(a)**

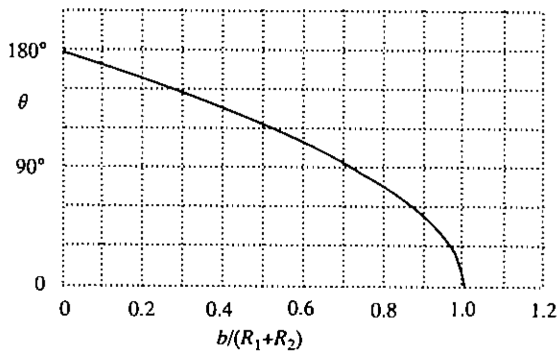



**Figure 18.5(b)**

The function is plotted in the Fig 18.5(b).

**P18.18** The interaction is a dipole–induced-dipole interaction. The energy is given by eqn 18.24:

$$V = -\frac{\mu_1^2\alpha_2'}{4\pi\varepsilon_0 r^6} = -\frac{[(2.7\,\mathrm{D})(3.336\times10^{-30}\,\mathrm{C\,m\,D^{-1}})]^2(1.04\times10^{-29}\,\mathrm{m^3})}{4\pi(8.854\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})(4.0\times10^{-9}\,\mathrm{m})^6}$$

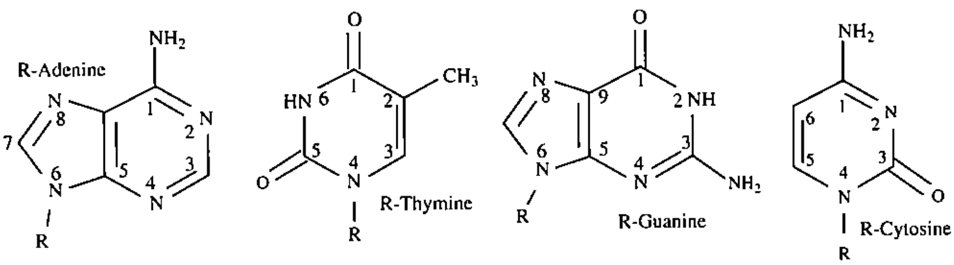
$$V = \boxed{-1.8\times10^{-27}\,\mathrm{J} = -1.1\times10^{-3}\,\mathrm{J\,mol^{-1}}}.$$

**COMMENT.** This value seems exceedingly small. The distance suggested in the problem may be too large compared to typical values.

## Solutions to applications

**P18.20** (a) The table displays computed electrostatic charges (semi-empirical, PM3 level, PC Spartan) of the DNA bases, modified by addition of a methyl group to the position at which the base binds to the DNA backbone. (That is, R = methyl for the computations displayed, but R = DNA backbone in DNA.) See the first set of structures for numbering.

(b) and (c) On purely electrostatic grounds, one would expect the most positively charged hydrogen atoms of one molecule to bind to the most negatively charged atoms of another. The figure below depicts hydrogen atoms as black lines, and has thicker gray lines for the most positively charged hydrogens (those with a charge of at least 0.200); they also happen to be the hydrogens bound to electronegative atoms. The figure also has light gray type for the atoms with the greatest negative charges (more negative than −0.400), with a gray ball on the most negative carbon atoms. In principle, then, any of the thick gray lines of one molecule can line up next to any of the atoms in light gray type of its bonding partner. In practice, the carbon atoms are not good binding sites for steric reasons.

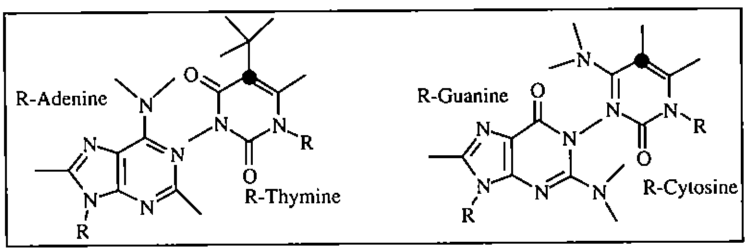



| R-Adenine | | R-Thymine | | R-Guanine | | R-Cytosine | |
|---|---|---|---|---|---|---|---|
| atom | charge | atom | charge | atom | charge | atom | charge |
| C1 | 0.905 | C1 | 0.885 | C1 | 0.720 | C1 | 0.961 |
| amino N | −0.656 | O of C1 | −0.580 | O of C1 | −0.524 | amino N | −0.709 |
| amino H† | 0.288 | C2 | −0.554 | N2 | −0.473 | amino H† | 0.291 |
| N2 | −0.914 | C2 methyl C | 0.180 | H of H2 | 0.233 | N2 | −0.901 |
| C3 | 0.785 | C2 methyl H | −0.003 | C3 | 0.794 | C3 | 0.993 |
| H of C3 | −0.020 | C3 | 0.173 | amino N | −0.693 | O of C3 | −0.609 |
| N4 | −0.835 | H of C3 | 0.111 | amino H† | 0.288 | N4 | −0.286 |
| C5 | 0.639 | N4 | −0.390 | N4 | −0.757 | methyl C* | 0.119 |
| N6 | −0.183 | N4 methyl C* | 0.211 | C5 | 0.325 | methyl H*† | 0.017 |
| methyl C* | 0.113 | N4 methyl H*† | 0.002 | N6 | 0.079 | C5 | 0.205 |
| methyl H*† | 0.022 | C5 | 0.836 | methyl C* | −0.008 | H of C5 | 0.103 |
| C7 | 0.320 | O of C5 | −0.596 | methyl H*† | 0.043 | C6 | −0.684 |
| H of C7 | 0.056 | N6 | −0.540 | C7 | 0.130 | H of C6 | 0.174 |
| N8 | −0.584 | H of N6 | 0.264 | H of C7 | 0.086 | | |
| C9 | −0.268 | | | N8 | −0.470 | | |
| | | | | C9 | −0.146 | | |

* part of R group, so not really available for hydrogen bonding in DNA

† table displays average charge of atoms that are chemically equivalent

**(d)** The naturally occurring pairs are shown below. These configurations are quite accessible sterically, and they have the further advantage of multiple hydrogen bonds.



(e) See above

**P18.22** (a) The hydrocarbons in question form a homologous series. They are straight-chain alkanes of the formula $C_nH_{2n+2}$, or R—H where R = $C_nH_{2n+1}$. Draw up the following table:

| | | | | | |
|---|---|---|---|---|---|
| $n$ | 1 | 2 | 3 | 4 | 5 |
| $\pi$ | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |

The relationship here is evident by inspection: $\pi = n/2$, so we predict for the seven-carbon hydrocarbon in question:

$$\pi = 7/2 = \boxed{3.5}.$$

(b) The plot, shown in Figure 18.6, is consistent with a linear relationship, for $R^2 = 0.997$ is close to unity. The best linear fit is:

$$\log K = -1.95 - 1.49\pi,$$

so $\boxed{\text{slope} = -1.49}$ and $\boxed{\text{intercept} = -1.95}$.

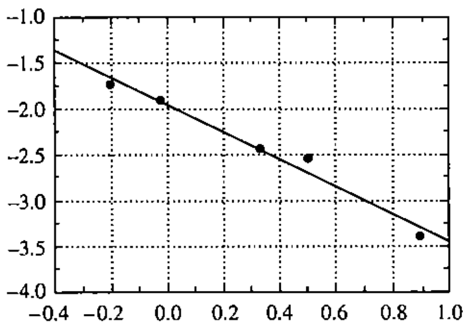


**Figure 18.6**

(c) If we know $\pi$ for the substituent R = H, then we can use the linear SAR just derived. Our best estimate of $\pi$ can be obtained by considering the zero-carbon "alkane" $H_2$, whose radical H ought to have a hydrophobicity constant $\pi = 0/2 = 0$. This value yields

$$\log K = -1.95 - 1.49(0) = -1.95 \text{ so } K = 10^{-1.95} = \boxed{1.12 \times 10^{-2}}.$$

Note: the assumption that R = H is part of the homologous series of straight-chain alkanes is a resonable but questionable one.

# 19 Materials 1: macromolecules and aggregates

## Answers to discussion questions

**D19.2** First, try to understand why different molar mass averages might give different numerical values. Polymers are unlike small molecules in that all small molecules of the same species have nearly identical masses. Polymers vary widely in mass because they can vary in the number of monomeric units they contain. Depending on how a polymer is synthesized and purified, it is entirely possible for one macromolecule to contain 2 monomer units and another 100. We call a polymer sample *polydisperse* if there is a large variation in mass among the molecules of the sample; conversely, a sample is *monodisperse* if its range of masses is narrow.

Even for small molecules, *the* molar mass is an average (over isotopic variants); however, the details of the averaging process make a negligible difference when the distribution of molar masses is narrow. But the different averages can give significantly different answers for highly polydisperse samples. Why should experiments yield one average or another?

The differences in averages are in the weighting factors. We see that the weighting factor for $\overline{M}_n$ is the number of molecules that have a particular mass and (from eqn 19.2) that the weighting factor in $\overline{M}_w$ is the mass fraction of a sample that has a particular mass. Different measurement techniques yield different weighting factors because they are sensitive to different factors (or, more accurately, different combinations of factors). The intensity of a mass spectrometry peak, for instance, is proportional to the number of molecules of a given mass. Some techniques, like light scattering, are more sensitive to the size (volume) and shape of particles, and some, like sedimentation, are more sensitive to the mass. (Discussions in the text reveal, however, that the measurements capture a complicated function of size, shape, mass, and number.)

Experimental techniques for the study of polydisperse polymer solutions are sensitive to a wide range of properties. Osmometry, measuring a colligative property, is sensitive to the number of molecules $N_i$ that have molar mass $M_i$. Consequently, average osmotic properties depend upon the number average molar mass. Light scattering depends upon molecular size and shape, which indirectly depend upon mass, so weight average molar mass becomes important. Other mass averages become important when the technique is sensitive to intermolecular attractions and repulsions, molecular entanglements, gravitational and centrifuge effects.

**D19.4** (a) $\Delta S$ is the change in conformational entropy of a random coil of a polymer chain. It is the statistical entropy arising from the arrangement of bonds, when a coil containing $N$ bonds of length $l$ is stretched or compressed by $nl$, where $n$ is a numerical factor giving the amount of stretching in units of $l$. The amount of stretching relative to the number of monomer units in the chain is $\nu = n/N$.

**(b)** $R_{\text{rms}}$ is one of several measures of the size of a random coil. For a polymer of $N$ monomer units each of length $l$, the root mean square separation, $R_{\text{rms}}$, is a measure of the average separation of the ends of a random coil. It is the square root of the average value of $R^2$, calculated by weighting each possible value of $R^2$ with the probability that $R$ occurs.

**(c)** $R_g$, the radius of gyration, is another measure of the size of a random coil. It is the radius of a thin hollow spherical shell of the same mass and moment of inertia as the polymer molecule.

All of these expressions are derived for the freely jointed random coil model of polymer chains which is the simplest possibility for the conformation of identical units not capable of forming hydrogen bonds or any other type of specific bond. In this model, any bond is free to make any angle with respect to the preceding one (Figure 19.15 of the text). We assume that the residues occupy zero volume, so different parts of the chain can occupy the same region of space. We also assume in the derivation of the expression for the probability of the ends of the chain being a distance $nl$ apart, that the chain is compact in the sense that $n \ll N$. This model is obviously an oversimplification because a bond is actually constrained to a cone of angles around a direction defined by its neighbor (Figure 19.16). In a hypothetical one-dimensional freely jointed chain all the residues lie in a straight line, and the angle between neighbors is either 0° or 180°. The residues in a three-dimensional freely jointed chain are not restricted to lie in a line or a plane.

The random coil model ignores the role of the solvent: a poor solvent will tend to cause the coil to tighten; a good solvent does the opposite. Therefore, calculations based on this model are best regarded as lower bounds to the dimensions of a polymer in a good solvent and as an upper bound for a polymer in a poor solvent. The model is most reliable for a polymer in a bulk solid sample, where the coil is likely to have its natural dimensions.

**D19.6** The formation of micelles is favored by the interaction between hydrocarbon tails and is opposed by charge repulsion of the polar groups which are placed close together at the micelle surface. As salt concentration is increased, the repulsion of head groups is reduced because their charges are partly shielded by the ions of the salt. This favors micelle formation causing the micelles to be larger and the critical micelle concentration to be smaller.

**D19.8** Using symbols that relate to surface properties ($G(\sigma), S(\sigma), n_J(\sigma), \Gamma_S$, etc.) and the symbol $c$ for the surfactant concentration in the bulk solution,

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \gamma\mathrm{d}\sigma + \textstyle\sum_J \mu_J \mathrm{d}n_J \quad \text{(Justification 19.7)}$$

$$\left(\frac{\partial S}{\partial \sigma}\right)_{T,p,n_J} = -\left(\frac{\partial \gamma}{\partial T}\right)_{p,\sigma,n_J} \quad \text{(Maxwell Relationship)}$$

This equation does not give a definitive indication of whether entropy changes are positive (increase) or negative (decrease) when surface area increases at the interface, or when $\Gamma_S > 0$, because the partial derivative of the surface tension with respect to temperature may be either positive or negative. However, the partial of the surface tension (also called interfacial tension) with respect to temperature is usually negative so it seems most likely that the entropy of the interface increases when the surface area increases. The equation for the enthalpy change with surface changes is

$$H = G + TS$$

$$\left(\frac{\partial H}{\partial \sigma}\right)_{T,p,n_J} = \left(\frac{\partial G}{\partial \sigma}\right)_{T,p,n_J} + T\left(\frac{\partial S}{\partial \sigma}\right)_{T,p,n_J} = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{T,\sigma,n_J}$$

Surface tension is always positive and the partial with respect to temperature is usually negative so the enthalpy change is positive for increasing surface area.

Although it is difficult to find general statements concerning thermodynamic properties of surfactants at solution interfaces, a surfactant that forms an ideal solution with one phase and is insoluble in the second phase is expected to exhibit a negative entropy change upon adsorbing at the solution interface. This would happen because the surfactant molecules are relatively disordered in the bulk solution. Upon adsorption, the molecules become self-aligned and ordered. With spontaneous adsorption the free energy of adsorption is negative and, since $\Delta G = \Delta H - T\Delta S$ for an isothermal process, we expect that $\Delta_{\mathrm{ads}}H$ should be exothermic to the extent that $\Delta_{\mathrm{ads}}H < T\Delta_{\mathrm{ads}}S < 0$.

## Solutions to exercises

**E19.1(b)** The number-average molar mass is (eqn 19.1)

$$\overline{M}_{\mathrm{n}} = \frac{1}{N}\sum N_i M_i = \frac{[3 \times (62) + 2 \times (78)]\,\mathrm{kg\,mol^{-1}}}{5} = \boxed{68\,\mathrm{kg\,mol^{-1}}}$$

The mass-average molar mass is (eqn 19.3)

$$\overline{M}_{\mathrm{w}} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{3 \times (62)^2 + 2 \times (78)^2}{3 \times (62) + 2 \times (78)}\,\mathrm{kg\ mol^{-1}} = \boxed{69\,\mathrm{kg\,mol^{-1}}}$$

**E19.2(b)** For a random coil, the radius of gyration is (19.33)

$$R_{\mathrm{g}} = l(N/6)^{1/2} \text{ so } N = 6(R_{\mathrm{g}}/l)^2 = 6 \times (18.9\,\mathrm{nm}/0.450\,\mathrm{nm})^2 = \boxed{1.06 \times 10^4}$$

**E19.3(b)** (a) Osmometry gives the number-average molar mass, so

$$\overline{M}_{\mathrm{n}} = \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2} = \frac{(m_1/M_1)M_1 + (m_2/M_2)M_2}{(m_1/M_1) + (m_2/M_2)} = \frac{m_1 + m_2}{(m_1/M_1) + (m_2/M_2)}$$

$$= \frac{100\,\mathrm{g}}{\left(\dfrac{25\,\mathrm{g}}{22\,\mathrm{kg\,mol^{-1}}}\right) + \left(\dfrac{75\,\mathrm{g}}{22/3\,\mathrm{kg\,mol^{-1}}}\right)} [\text{assume } 100\,\mathrm{g} \text{ of solution}] = \boxed{8.8\,\mathrm{kg\,mol^{-1}}}$$

(b) Light-scattering gives the mass-average molar mass, so

$$\overline{M}_{\mathrm{w}} = \frac{m_1 M_1 + m_2 M_2}{m_1 + m_2} = \frac{(25) \times (22) + (75) \times (22/3)}{25 + 75}\,\mathrm{kg\,mol^{-1}} = \boxed{11\,\mathrm{kg\ mol^{-1}}}$$

**E19.4(b)** The formula for the rotational correlation time is

$$\tau = \frac{4\pi a^3 \eta}{3kT}$$

$\eta(\mathrm{H_2O}, 20\,^{\circ}\mathrm{C}) = 1.00 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$[*CRC Handbook*]

$$\tau = \frac{4\pi \times (4.5 \times 10^{-9}\mathrm{m})^3 \times 1.00 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}}{3 \times 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 293\,\mathrm{K}} = \boxed{9.4 \times 10^{-8}\,\mathrm{s}}$$

**E19.5(b)** The effective mass of the particles is

$$m_{\text{eff}} = bm = (1 - \rho v_{\text{s}})m \ [19.14] = m - \rho v_{\text{s}}m = v\rho_{\text{p}} - v\rho = v(\rho_{\text{p}} - \rho)$$

where $v$ is the particle volume and $\rho_{\text{p}}$ is the particle density. Equating the forces

$$m_{\text{eff}}r\omega^2 = fs = 6\pi\eta as \ [19.15, 19.12]$$

or $v(\rho_{\text{p}} - \rho)r\omega^2 = \frac{4}{3}\pi a^3(\rho_{\text{p}} - \rho)r\omega^2 = 6\pi\eta as$

Solving for $s$ yields

$$s = \frac{2a^2(\rho_p - \rho)r\omega^2}{9\eta}$$

Thus, the relative rates of sedimentation are $\dfrac{s_2}{s_1} = \dfrac{a_2^2(\rho_{\text{p}} - \rho)_2}{a_1^2(\rho_{\text{p}} - \rho)_1} = \left(\dfrac{a_2}{a_1}\right)^2 \dfrac{(\rho_{\text{p}} - \rho)_2}{(\rho_{\text{p}} - \rho)_1}$.

The value of this ratio depends on the density of the solution. For example, in a dilute aqueous solution with $\rho = 1.01\,\text{g cm}^{-3}$ , the difference in polymer densities matters in that the factor involving densities is significantly different than 1:

$$\frac{s_2}{s_1} = (8.4)^2 \frac{(1.10 - 1.01)_2}{(1.18 - 1.01)_1} = \boxed{37}$$

In a less dense organic solution, for example a dilute solution in octane with $\rho = 0.71\,\text{g cm}^{-3}$, the density difference has a smaller effect, for the factor involving densities is closer to 1:

$$\frac{s_2}{s_1} = (8.4)^2 \frac{(1.10 - 0.71)_2}{(1.18 - 0.71)_1} = \boxed{59}$$

In both cases, the larger particle sediments faster.

**E19.6(b)** The molar mass is related to the sedimentation constant through eqns 19.19 and 19.14:

$$\overline{M} = \frac{SRT}{bD} = \frac{SRT}{(1 - \rho v_{\text{s}})D}$$

where we have assumed the data refer to aqueous solution at 298 K.

$$\overline{M}_{\text{n}} = \frac{(7.46 \times 10^{-13}\,\text{s}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{[1 - (1000\,\text{kg m}^{-3}) \times (8.01 \times 10^{-4}\,\text{m}^3\,\text{kg}^{-1})] \times (7.72 \times 10^{-11}\,\text{m}^2\,\text{s}^{-1})}$$

$$= \boxed{120\,\text{kg mol}^{-1}}$$

**E19.7(b)** See the solution to Exercise 19.5(b). In place of the centrifugal force $m_{\text{eff}}r^2$ we have the gravitational force $m_{\text{eff}}g$. The rest of the analysis is similar, leading to

$$s = \frac{2a^2(\rho_{\text{p}} - \rho)g}{9\eta} = \frac{(2) \times (15.5 \times 10^{-6}\,\text{m})^2 \times (1250 - 1000)\,\text{kg m}^{-3} \times (9.81\,\text{m s}^{-2})}{(9) \times (8.9 \times 10^{-4}\,\text{kg m}^{-1}\text{s}^{-1})}$$

$$= \boxed{1.47 \times 10^{-4}\,\text{m s}^{-1}}$$

**E19.8(b)** The molar mass is related to the sedimentation constant through eqns 19.19 and 19.14:

$$\overline{M} = \frac{SRT}{bD} = \frac{SRT}{(1 - \rho v_{\text{s}})D}$$

Assuming that the data refer to an aqueous solution,

$$\overline{M} = \frac{(5.1 \times 10^{-13}\,\text{s}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (293\,\text{K})}{[1 - (0.997\,\text{g cm}^{-3}) \times (0.721\,\text{cm}^3\text{g}^{-1})] \times (7.9 \times 10^{-11}\,\text{m}^2\,\text{s}^{-1})} = \boxed{56\,\text{kg mol}^{-1}}$$

**E19.9(b)** In a sedimentation experiment, the weight-average molar mass is given by (eqn 19.20)

$$\overline{M}_{\text{w}} = \frac{2RT}{(r_2^2 - r_1^2)b\omega^2}\ln\frac{c_2}{c_1} \quad \text{so} \quad \ln\frac{c_2}{c_1} = \frac{\overline{M}_{\text{w}}(r_2^2 - r_1^2)b\omega^2}{2RT}$$

This implies that

$$\ln c = \frac{\overline{M}_{\text{w}}r^2b\omega^2}{2RT} + \text{constant}$$

so the plot of $\ln c$ versus $r^2$ has a slope $m$ equal to

$$m = \frac{\overline{M}_{\text{w}}b\omega^2}{2RT} \text{ and } \overline{M}_{\text{w}} = \frac{2RTm}{b\omega^2}$$

$$\overline{M}_{\text{w}} = \frac{2 \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (293\,\text{K}) \times (821\,\text{cm}^{-2}) \times (100\,\text{cm m}^{-1})^2}{[1 - (1000\,\text{kg m}^{-3}) \times (7.2 \times 10^{-4}\,\text{m}^3\,\text{kg}^{-1})] \times [(1080\,\text{s}^{-1}) \times (2\pi)]^2}$$

$$= \boxed{3.1 \times 10^3\,\text{kg mol}^{-1}}$$

**E19.10(b)** The centrifugal acceleration is

$$a = r\omega^2 \text{ so } a/g = r\omega^2/g$$

$$a/g = \frac{(5.50\,\text{cm}) \times [2\pi \times (1.32 \times 10^3\,\text{s}^{-1})]^2}{(100\,\text{cm m}^{-1}) \times (9.81\,\text{m s}^{-2})} = \boxed{3.86 \times 10^5}$$

**E19.11(b)** For a random coil, the rms separation is [19.31]

$$R_{\text{rms}} = N^{1/2}l = (1200)^{1/2} \times (1.125\,\text{nm}) = \boxed{38.97\,\text{nm}}$$

**E19.12(b)** Polypropylene is $-(CH(CH_3)CH_2)-_N$, where $N$ is given by

$$N = \frac{M_{\text{polymer}}}{M_{\text{monomer}}} = \frac{174\,\text{kg mol}^{-1}}{42.1 \times 10^{-3}\,\text{kg mol}^{-1}} = 4.13 \times 10^3$$

The repeat length $l$ is the length of two C–C bonds. The contour length is [19.30]

$$R_c = Nl = (4.13 \times 10^3) \times (2 \times 1.53 \times 10^{-10}\,\mathrm{m}) = \boxed{1.26 \times 10^{-6}\,\mathrm{m}}$$

The rms seperation is [19.31]

$$R_{rms} = lN^{1/2} = (2 \times 1.53 \times 10^{-10}\,\mathrm{m}) \times (4.13 \times 10^3)^{1/2} = \boxed{1.97 \times 10^{-8}\,\mathrm{m}} = 19.7\,\mathrm{nm}$$

## Solutions to problems

### Solutions to numerical problems

**P19.2** From eqn 19.20, we can relate concentration ratios to the molar mass

$$\ln\frac{c_1}{c_2} = \frac{\overline{M}_w b\omega^2(r_1^2 - r_2^2)}{2RT} = \frac{2\pi^2\overline{M}_w b\nu^2(r_1^2 - r_2^2)}{RT}$$

and hence

$$\nu = \left(\frac{RT\ln\left(\frac{c_1}{c_2}\right)}{2\pi^2\overline{M}_w b\left(r_1^2 - r_2^2\right)}\right)^{1/2}$$

$$= \left(\frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times (\ln 5)}{2\pi^2 \times \left(1 \times 10^2\,\mathrm{kg\,mol^{-1}}\right) \times (1 - 0.75) \times \left(7.0^2 - 5.0^2\right) \times 10^{-4}\,\mathrm{m^2}}\right)^{1/2}$$

$$= 58\,\mathrm{Hz},\ \text{or}\ \boxed{3500\,\mathrm{rpm}}$$

***Question.*** What would the concentration gradient be in this system with a speed of operation of 70 000 rpm in an ultracentrifuge?

**P19.4** We need to determine the intrinsic viscosity from a plot of $((\eta/\eta_0) - 1)/(c/(\mathrm{g\,dm^{-3}}))$ against $c$, extrapolated to $c = 0$ as in Example 19.5. Then from the relation

$$[\eta] = K\overline{M}_V^a \quad [19.25]$$

with $K$ and $a$ from Table 19.4, the viscosity average molar mass $\overline{M}_V$ may be calculated. $\eta/\eta_0$ values are determined from the times of flow using the relation

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \times \frac{\rho}{\rho_0} \approx \frac{t}{t_0} \quad [19.24]$$

noting that in the limit as $c$ approaches 0 the approximation becomes exact. As explained in Example 19.5, $[\eta]$ can also be determined from the limit of $(1/c)\ln(\eta/\eta_0)$ as $c$ approaches 0.

We draw up the following table

| | | | | | |
|---|---|---|---|---|---|
| $c/(\mathrm{g\,dm^{-3}})$ | 0.000 | 2.22 | 5.00 | 8.00 | 10.00 |
| $t/\mathrm{s}$ | 208.2 | 248.1 | 303.4 | 371.8 | 421.3 |
| $\eta/\eta_0$ | — | 1.192 | 1.457 | 1.786 | 2.024 |
| $\dfrac{100\,[(\eta/\eta_0)-1]}{c/(\mathrm{g\,dm^{-3}})}$ | — | 8.63 | 9.15 | 9.82 | 10.24 |
| $\ln(\eta/\eta_0)$ | — | 0.1753 | 0.3766 | 0.5799 | 0.7048 |
| $\dfrac{100\ln(\eta/\eta_0)}{c/(\mathrm{g\,dm^{-3}})}$ | — | 7.89 | 7.52 | 7.24 | 7.05 |

The points are plotted in Figure 19.1.

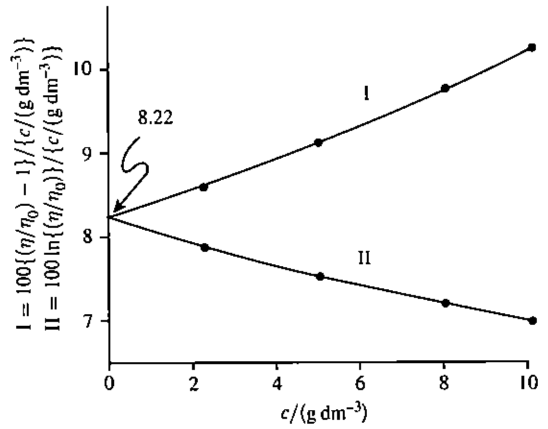



**Figure 19.1**

The intercept as determined from the simultaneous extrapolation of both plots is $0.0822\ \mathrm{dm^3\,g^{-1}}$.

$$\frac{\overline{M}_{\mathrm{V}}}{\mathrm{g\,mol^{-1}}} = \left(\frac{[\eta]}{K}\right)^{1/a} = \left(\frac{0.0822\,\mathrm{dm^3\,g^{-1}}}{9.5\times10^{-6}\,\mathrm{dm^3\,g^{-1}}}\right)^{1/0.74} = \boxed{2.1\times10^5}$$

**P19.6** The relationship (eqn 19.25) between $[\eta]$ and $\overline{M}_{\mathrm{V}}$ can be transformed into a linear one

$$\ln[\eta] = \ln K + a\ln M_{\mathrm{V}}$$

so a plot of $\ln[\eta]$ versus $\ln\overline{M}_{\mathrm{V}}$ will have a slope of $a$ and a $y$-intercept of $\ln K$. The transformed data and plot are shown below (Figure 19.2)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $\overline{M}_{\mathrm{V}}/(\mathrm{kg\,mol^{-1}})$ | 10.0 | 19.8 | 106 | 249 | 359 | 860 | 1800 | 5470 | 9720 | 56 800 |
| $[\eta]/(\mathrm{cm^3\,g^{-1}})$ | 8.90 | 11.9 | 28.1 | 44.0 | 51.2 | 77.6 | 113.9 | 195 | 275 | 667 |
| $\ln\overline{M}_{\mathrm{V}}/(\mathrm{kg\,mol^{-1}})$ | 2.30 | 2.99 | 4.66 | 5.52 | 5.88 | 6.76 | 7.509 | 8.61 | 9.18 | 10.90 |
| $\ln[\eta]/(\mathrm{cm^3\,g^{-1}})$ | 2.19 | 2.48 | 3.34 | 3.78 | 3.94 | 4.35 | 4.749 | 5.27 | 5.62 | 6.500 |

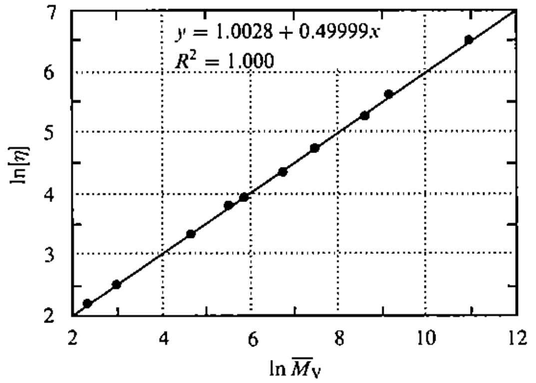



**Figure 19.2**

Thus $a = \boxed{0.500}$ and $K = e^{1.0028}\,\text{cm}^3\,\text{g}^{-1}\,\text{kg}^{-1/2}\,\text{mol}^{1/2} = \boxed{2.73\,\text{cm}^3\,\text{g}^{-1}\,\text{kg}^{-1/2}\,\text{mol}^{1/2}}$

Solving for $\overline{M}_V$ yields

$$\overline{M}_V = \left(\frac{[\eta]}{K}\right)^{1/a} = \left(\frac{100\,\text{cm}^3\,\text{g}^{-1}}{2.73\,\text{cm}^3\,\text{g}^{-1}\,\text{kg}^{-1/2}\,\text{mol}^{1/2}}\right)^2 = \boxed{1.34 \times 10^3\,\text{kg}\,\text{mol}^{-1}}$$

**P19.8** See section 5.5(e) and Example 5.4.

$$\frac{\Pi}{c} = \frac{RT}{\overline{M}_n}\left(1 + B\frac{c}{\overline{M}_n} + \cdots\right) \text{[Example 5.4, with } \Pi = \rho g h\text{]}$$

Therefore, to determine $\overline{M}_n$ and $B$ we need to plot $\Pi/c$ against $c$. We draw up the following table

| | | | | |
|---|---|---|---|---|
| $c/(\text{g}\,\text{dm}^{-3})$ | 1.21 | 2.72 | 5.08 | 6.60 |
| $(\Pi/c)/(\text{Pa}/\text{g}\,\text{dm}^{-3})$ | 111 | 118 | 129 | 136 |

The points are plotted in Figure 19.3

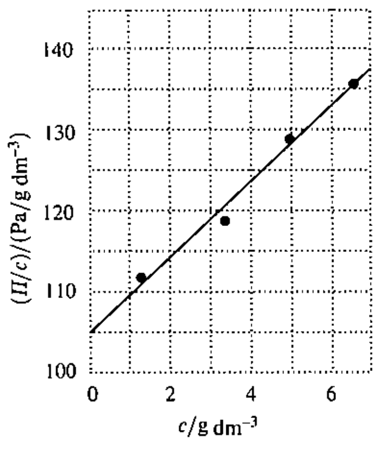



**Figure 19.3**

A least-squares analysis gives an intercept of $105.\bar{4}$ and a slope of 4.64. It follows that

$$\frac{RT}{\overline{M}_n} = 105.\bar{4}\,\mathrm{Pa\,g^{-1}\,dm^3} = 105.\bar{4}\,\mathrm{Pa\,kg^{-1}\,m^3}$$

and hence that $\overline{M}_n = \dfrac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (293\,\mathrm{K})}{105.\bar{4}\,\mathrm{Pa\,kg^{-1}\,m^3}} = \boxed{23.1\,\mathrm{kg\,mol^{-1}}}$

The slope of the graph is equal to $RTB/\overline{M}_n^2$, so

$$\frac{RTB}{\overline{M}_n^2} = 4.64\,\mathrm{Pa\,g^{-2}\,dm^6} = 4.64\,\mathrm{Pa\,kg^{-2}\,m^6}$$

Therefore, $B = \dfrac{(23.1\,\mathrm{kg\,mol^{-1}})^2 \times (4.64\,\mathrm{Pa\,kg^{-2}\,m^6})}{(8.314\,\mathrm{J\,K^{-1}mol^{-1}}) \times (293\,\mathrm{K})} = \boxed{1.02\,\mathrm{m^3\,mol^{-1}}}$

**P19.10** The glass transition temperature $T_g$ is the temperature at which internal bond rotations freeze. In effect, the easier such rotations are, the lower $T_g$. Internal rotations are more difficult for polymers that have bulky side chains than for polymers without such chains because the side chains of neighboring molecules can impede each others' motion. Of the four polymers in this problem, polystyrene has the largest side chain (phenyl) and the largest $T_g$. The chlorine atoms in poly(vinyl chloride) interfere with each other's motion more than the smaller hydrogen atoms that hang from the carbon backbone of polyethylene. Poly(oxymethylene), like polyethylene, has only hydrogen atoms protruding from its backbone; however, poly(oxymethylene) has fewer hydrogen protrusions and a still lower $T_g$ than polyethylene.

## Solutions to theoretical problems

**P19.12**

$$\begin{aligned}\text{SI unit}(\eta/\rho) &= \text{SI unit}(\eta)/\text{SI unit}(\rho) = (\mathrm{Pa})/(\mathrm{kg\,m^{-3}}) = (\mathrm{N\,m^{-2}})/(\mathrm{kg\,m^{-3}})\\ &= (\mathrm{kg\,m^{-1}\,s^{-1}})/(\mathrm{kg\,m^{-3}}) = \mathrm{m^2\,s^{-1}}\end{aligned}$$

We begin by simplifying Poiseuille's formula with the assumptions that $p_2 = p_0$, $p_1 = p_2 + \Delta p$ where $\Delta p < p_2$, and $\Delta p^2 \ll 2p_2\Delta p$ so the second order term may be discarded.

$$\begin{aligned}\frac{dV}{dt} &= \frac{(p_1^2 - p_2^2)\pi r^4}{16\,l\eta p_0} = \frac{\{(p_2+\Delta p)^2 - p_2^2\}\pi r^4}{16\,l\eta p_0}\\ &= \frac{(p_2^2 + 2p_2\Delta p + \Delta p^2 - p_2^2)\pi r^4}{16\,l\eta p_0} \approx \frac{\Delta p\,\pi r^4}{8\,l\eta}\end{aligned}$$

When gravity is the driving force for fluid flow, $\Delta p = F_{\text{gravity}}/(\pi r^2) = mgl/(\pi r^2 l) = \rho g l$ where $g$ is the gravitational acceleration and $dV/dt = V/t = \pi r^2 l/t$.

$$\frac{\pi r^2 l}{t} = \frac{\rho g l\,\pi r^4}{8\,l\eta}$$

$$\frac{\eta/\rho}{t} = \frac{g r^2}{8\,l} = \text{constant}$$

Dividing by the identical expression for a reference liquid gives eqn 19.24.

$$\frac{(\eta/\rho)t_0}{(\eta/\rho)_0 t} = 1 \text{ or } \frac{(\eta/\rho)}{(\eta/\rho)_0} = \frac{t}{t_0}$$

This shows that the drainage time is governed by the kinematic viscosity $(\eta/\rho)$.

**P19.14** Eqn 19.26 gives the probability of finding the end of an $N$-step one-dimensional random walk at a distance $nl$ from the start,

$$P = \left(\frac{2}{\pi N}\right)^{1/2} \mathrm{e}^{-n^2/2N}.$$

We generalize to a continuous version:

$$\mathrm{d}P_x = \left(\frac{2}{\pi N}\right)^{1/2} \mathrm{e}^{-n_x^2/2N}\mathrm{d}n_x.$$

Physically, it is more fundamental to talk of the probability of finding the end "at" a given distance $x = n_x l$ rather than a given number of steps away. $\mathrm{d}x = l\mathrm{d}n_x$. Hence, the probability of finding the end of the polymer in an interval between $x$ and $x + dx$ is

$$\mathrm{d}P_x = \left(\frac{2}{\pi N l^2}\right)^{1/2} \mathrm{e}^{-x^2/2Nl^2}\mathrm{d}x.$$

Building our three-dimensional chain from one-dimensional random walks, we have

$$\mathrm{d}P_x\mathrm{d}P_y\mathrm{d}P_z = \left(\frac{6}{\pi N l^2}\right)^{3/2} \mathrm{e}^{-3(x^2+y^2+z^2)/2Nl^2}\mathrm{d}x\mathrm{d}y\mathrm{d}z$$

(Note that in this step we have replaced $N$ with $N/3$. This allows us to continue to regard $N$ as the total number of units in the polymer, so the number of steps in each dimension, divided equally among this number, becomes $N/3$.) Now change variables to spherical polar coordinates:

$$r^2 = x^2 + y^2 + z^2 \quad \text{and} \quad \mathrm{d}x\mathrm{d}y\mathrm{d}z = r^2 \sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi,$$

$$\text{so} \quad \mathrm{d}P_x\mathrm{d}P_y\mathrm{d}P_z = \left(\frac{6}{\pi N l^2}\right)^{3/2} \mathrm{e}^{-3r^2/2Nl^2} r^2 \sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi.$$

To find the probability of finding the ends of the polymer at a distance between $r$ and $r + \mathrm{d}r$ regardless of angle, integrate over the angles and divide by 8, as stated in the problem, to restrict the integration to positive $x, y, z$:

$$\int_{\substack{\text{positive}\\ x,y,z\\ \text{directions}}} \mathrm{d}P_x\mathrm{d}P_y\mathrm{d}P_z = \frac{1}{8}\left(\frac{6}{\pi N l^2}\right)^{3/2} \mathrm{e}^{-3r^2/2Nl^2} r^2\mathrm{d}r \int_0^{\pi} \sin\theta\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi$$

$$= \frac{4}{8}\pi \left(\frac{6}{\pi N l^2}\right)^{3/2} \mathrm{e}^{-3r^2/2Nl^2} r^2\mathrm{d}r$$

Defining $a = \left(\dfrac{3}{2Nl^2}\right)^{1/2}$ allows us to complete the derivation:

$$\int_{\substack{\text{positive}\\ x,y,z\\ \text{directions}}} \mathrm{d}P_x\mathrm{d}P_y\mathrm{d}P_z = f(r)dr \text{ where } f(r) = \boxed{4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 \mathrm{e}^{-3r^2/2Nl^2}r^2}.$$

**P19.16** A simple procedure is to generate numbers in the range 1 to 8, and to step north for a 1 or 2, east for 3 or 4, south for 5 or 6, and west for 7 or 8 on a uniform grid. One such walk is shown in Figure 19.4.

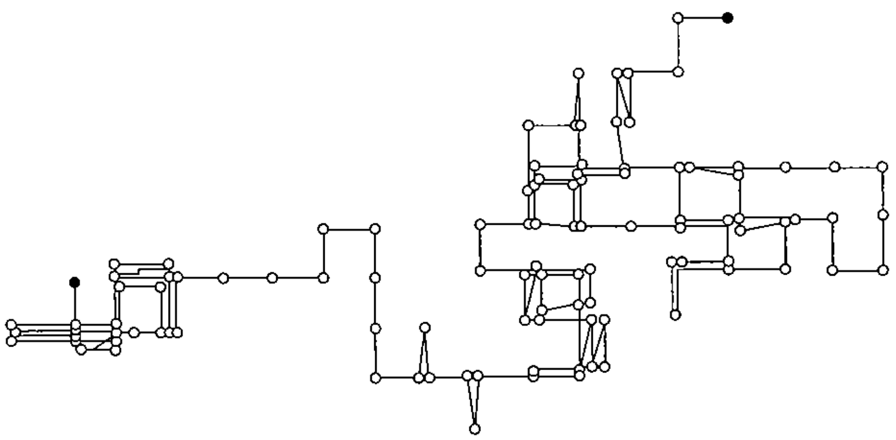


**Figure 19.4**

Roughly, they would appear to vary as $N^{1/2}$

**P19.18** The volume of a spherical molecule of radius $a$ is

$$v_{\text{mol}} = \frac{4\pi a^3}{3}$$

The smallest distance possible between centers of two such molecules is $2a$, so the excluded volume is

$$v_{\text{p}} = \frac{4\pi(2a)^3}{3} = 8v_{\text{mol}}$$

so $B = \dfrac{1}{2}N_{\text{A}}v_{\text{p}} = 4N_{\text{A}}v_{\text{mol}} = \dfrac{16\pi}{2}N_{\text{A}}a_{\text{eff}}^3 = \dfrac{16\pi}{3}N_{\text{A}}\gamma^3R_{\text{g}}^3$

(a) $R_{\text{g}} = \left(\dfrac{N}{6}\right)^{1/2} l$ [19.33]

so $B = \dfrac{16\pi}{3\times 6^{3/2}}\gamma^3l^3N^{3/2}N_{\text{A}} = \boxed{4.22\times 10^{23}\ \text{mol}^{-1}\times(lN^{1/2})^3}$

$= (4.22\times 10^{23}\ \text{mol}^{-1})\times[(154\times 10^{-12}\ \text{m})\times(4000)^{1/2}]^3 = \boxed{0.39\ \text{m}^3\ \text{mol}^{-1}}$

**(b)** $R_g = 2^{1/2} \times R_g(\text{free})$ [19.36]

so $B = 2^{3/2} \times B(\text{free}) = \boxed{1.19 \times 10^{24}\,\text{mol}^{-1} \times (lN^{1/2})^3}$

$= 2^{3/2} \times (0.39\,\text{m}^3\,\text{mol}^{-1}) = \boxed{1.1\,\text{m}^3\,\text{mol}^{-1}}$

**P19.20** Given that $G = U - TS - tl$ and $dU = TdS + tdl$, we take the differential, obtaining

$$dG = dU - TdS - SdT - ldt - tdl$$
$$= TdS + tdl - TdS - SdT - ldt - tdl = \boxed{-SdT - ldt}$$

Since $A = U - TS$, we have $A = G + tl$,

so $dA = dG + tdl + ldt = -SdT - ldt + tdl + ldt = \boxed{-SdT + tdl}$

Since $dA$ and $dG$ are both exact differentials

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial t}{\partial T}\right)_l \quad \text{and} \quad \left(\frac{\partial S}{\partial t}\right)_T = \left(\frac{\partial l}{\partial T}\right)_t$$

Since $dU = TdS + tdl$ [given],

$$\left(\frac{\partial U}{\partial l}\right)_T = T\left(\frac{\partial S}{\partial l}\right)_T + t = \boxed{-T\left(\frac{\partial t}{\partial T}\right)_l + t} \text{[Maxwell relation above]}$$

## Solutions to applications

**P19.22** Molecular mechanics computations with the AMBER force field using the HyperChem package are reported below. The value of the total potential energy will vary between different force fields, as will the shape of the potential energy surface. The local energy minimum at $\phi = -179.6°$ and $\psi = -4.1°$ is found to have a potential energy equal to 28.64 kJ mol$^{-1}$ when R = H. This value is used as a reference to calculate energy differences ($\Delta E$) on the potential energy surface. $\Delta E$ values give the relative stability of different conformations with higher values indicating energetically unstable conformations. Similarly, $\Delta E$ values were calculated with respect to the local energy minimum at $\phi = -152.3°$ and $\psi = 163.2°$ when R = $CH_3$.

| | initial | | optimized | | | |
|---|---|---|---|---|---|---|
| | $\phi$/° | $\psi$/° | $\phi$/° | $\psi$/° | $E$/(kJ mol$^{-1}$) | $\Delta E$/(kJ mol$^{-1}$) |
| **(a)** R = H | 75 | −65 | −176.0 | 8.3 | 28.765 | 0.126 |
| | 180 | 180 | 180 | 180 | 32.154 | 3.515 |
| | 65 | 35 | −179.6 | −4.1 | 28.639 | 0.000 |
| **(b)** R = $CH_3$ | 75 | −65 | 54.5 | 19.7 | 46.338 | 7.531 |
| | 180 | 180 | −152.3 | 163.2 | 38.807 | 0.000 |
| | 65 | 35 | 52.9 | 24.1 | 46.250 | 7.443 |

The computations were set up by using the software's "model build" command, that is, initially setting default values for bond lengths and angles except for the specified initial values of $\phi$ and $\psi$. Care must be taken to build the proper chirality at the central carbon when R = $CH_3$. Then the constraints were removed, and the entire structure was allowed to relax to a minimum energy. Not all of the initial conformations relaxed to the same final conformation. The different final conformations appear to represent local energy minima. It ought not to be surprising that there are several such minima in even a short peptide chain that contains several nearly free internal rotations. It is instructive to compare the all trans ($\phi = \psi = 180°$) initial conformation in the R = H and R = $CH_3$ cases. In the former, neither angle changes, but the resulting structure is not the lowest-energy structure. In the latter, the methyl group appears to push the planes of the peptide link away from each other (albeit not far) due to steric effects; however, the resulting energy is lower than that of the other conformations examined.

Two of the initial conformations of each molecule converge to the same energy minimum. These energy wells are rather broad and the exact angle at which the computation stops within the minimum depends upon details of convergence criteria used in the iterative methodology of the software as well as details of the force field. Both sets of computations also found a second local energy minimum.

An alternative method for studying the energy dependence on $\phi$ and $\psi$ involves a method like that specified above but with the AMBER computation performed at fixed values of both angles. Figure 19.5 summarizes a set of computations with $-180° < \phi < 180°$ and $\psi = 90°$. To characterize the energy surface, one would carry out similar calculations for several values of $\psi$.

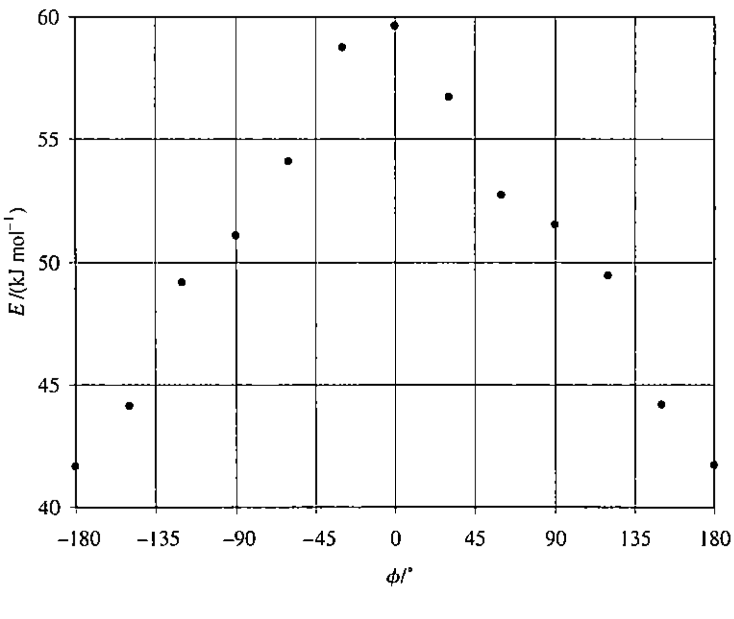



**Figure 19.5**

**P19.24** Assume the solute particles are solid spheres and see how well $R_g$ calculated on the basis of that assumption agrees with experimental values.

$$R_g/\text{nm} = 0.05690 \times \left\{(v_s/\text{cm}^3\,\text{g}^{-1}) \times (M/\text{g mol}^{-1})^{1/3}\right\} \text{[P19.17]}$$

and draw up the following table

| | $M/(\text{g mol}^{-1})$ | $v_s/(\text{cm}^3\ \text{g}^{-1})$ | $(R_g/\text{nm})_{\text{calc}}$ | $(R_g/\text{nm})_{\text{expt}}$ |
|---|---|---|---|---|
| Serum albumin | $66 \times 10^3$ | 0.752 | 2.09 | 2.98 |
| Bushy stunt virus | $10.6 \times 10^6$ | 0.741 | 11.3 | 12.0 |
| DNA | $4 \times 10^6$ | 0.556 | 7.43 | 117.0 |

Therefore, serum albumin and bushy stunt virus resemble solid spheres, but DNA does not.

**P19.26** Rearrange eqn 19.20 to yield

$$\ln c = \text{const.} + \frac{\overline{M}_w b\omega^2 r^2}{2RT}$$

so a plot of $\ln c$ against $r^2$ should be a straight line of slope $\frac{\overline{M}_w b\omega^2}{2RT}$. We construct the following table

| | | | | | |
|---|---|---|---|---|---|
| $r/\text{cm}$ | 5.0 | 5.1 | 5.2 | 5.3 | 5.4 |
| $c/(\text{mg cm}^{-3})$ | 0.536 | 0.284 | 0.148 | 0.077 | 0.039 |
| $r^2/(\text{cm}^2)$ | 25.0 | 26.0 | 27.0 | 28.1 | 29.2 |
| $\ln(c/\text{mg cm}^{-3})$ | −0.624 | −1.259 | −1.911 | −2.564 | −3.244 |

The points are plotted in Figure 19.6. The least-squares slope is −0.623.

Therefore

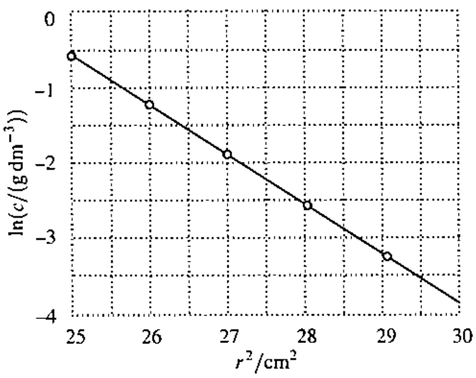



**Figure 19.6**

$$\frac{\overline{M}_w(1-\rho v_s)\omega^2}{2RT} = -0.623\,\text{cm}^{-2} = -0.623 \times 10^4\,\text{m}^{-2}$$

It follows that

$$\overline{M}_w = \frac{(-0.623 \times 10^4\,\text{m}^{-2}) \times (2) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (293\,\text{K})}{\{(1) - (1.001\,\text{g cm}^{-3}) \times (1.112\,\text{cm}^3\,\text{g}^{-1})\} \times [(2\pi) \times (322\,\text{s}^{-1})]^2} = \boxed{65.6\,\text{kg mol}^{-1}}.$$

**P19.28** The sedimentation constant $S$ must first be calculated from the experimental data (eqn 19.16).

$$S = \frac{s}{r\omega^2} = \frac{1}{\omega^2}\frac{\text{d}\ln r}{\text{d}t}\text{[P19.1]}$$

Therefore, the slope of a plot of ln $r$ against $t$ will be related to $S$. We draw up the following table.

| $t/s$ | 0 | 300 | 600 | 900 | 1200 | 1500 | 1800 |
|---|---|---|---|---|---|---|---|
| $r$/cm | 6.127 | 6.153 | 6.179 | 6.206 | 6.232 | 6.258 | 6.284 |
| ln($r$/cm) | 1.813 | 1.817 | 1.821 | 1.826 | 1.830 | 1.834 | 1.838 |

The least-squares slope is $1.408 \times 10^{-5}\,s^{-1}$, so

$$S = \frac{\text{slope}}{\omega^2} = \frac{1.408 \times 10^{-5}\,s^{-1}}{[(2\pi) \times (50 \times 10^3/60\,s)]^2} = 5.14 \times 10^{-13}\,s = \boxed{5.14\,\text{Sv}}$$

$$\text{Then } \overline{M}_n = \frac{SRT}{bD}[19.19] = \frac{(5.14 \times 10^{-13}\,s) \times (8.314\,J\,K^{-1}\,mol^{-1}) \times (293\,K)}{(1 - 0.9981 \times 0.728) \times (7.62 \times 10^{-11}\,m^2\,s)}$$

$$= \boxed{60.1\,kg\,mol^{-1}}$$

We need to determine the ratio of the actual frictional coefficient, $f$, of the macromolecule to that of the frictional coefficient, $f_0$, of a sphere of the same volume, so that by interpolating in Table 19.3 we can obtain the dimensions of the molecular ellipsoid.

$$f = \frac{kT}{D} = \frac{(1.381 \times 10^{-23}\,J\,K^{-1}) \times (293\,K)}{7.62 \times 10^{-11}\,m^2\,s^{-1}} = 5.31 \times 10^{-11}\,kg\,s^{-1}$$

$$V_m = (0.728\,cm^3\,g^{-1}) \times (60.1 \times 10^3\,g\,mol^{-1}) = 43.8 \times 10^3\,cm^3\,mol^{-1}$$

$$= 4.38 \times 10^{-2}\,m^3\,mol^{-1}$$

$$\text{Then, } a = \left(\frac{3V_m}{4\pi N_A}\right)^{1/3} = \left(\frac{(3) \times (4.38 \times 10^{-2}\,m^3\,mol^{-1})}{(4\pi) \times (6.022 \times 10^{23}\,mol^{-1})}\right)^{1/3} = 2.59\,nm$$

$$f_0 = 6\pi a\eta = (6\pi) \times (2.59 \times 10^{-9}\,m) \times (1.00 \times 10^{-3}\,kg\,m^{-1}\,s^{-1}) = 4.89 \times 10^{-11}\,kg\,s^{-1}$$

$$\text{which gives } \frac{f}{f_0} = \frac{5.31}{4.89} = 1.09$$

Therefore, the molecule is either prolate or oblate, with an axial ratio of about 2.8 (Table 19.3).

**P19.30** (a) $S/k_B = \ln(W)$

$$\Delta S/k_B = \ln(W_{\text{circular}}) - \ln(W_{\text{ideal chain}})$$

$W_{\text{circular}}$ is the configuration weight of the DNA molecule that has joined ends ($n = 0$) while $W_{\text{ideal chain}}$ is the configuration weight for the molecule chain for which no segment has a constraint and two possible configurations (right-pointing and left-pointing, see Justification 19.3). $W_{\text{ideal chain}}$ for a molecule of $N$ segments equals $2^N$.

$$W_{\text{circular}} = \frac{N!}{(N/2)!\,(N/2)!}$$

$$\ln(W_{\text{circular}}) = \ln(N!) - 2\ln\{(N/2)!\}$$

$$= \ln(2\pi)^{1/2} + \left(N + \frac{1}{2}\right)\ln(N) - N$$

$$- 2\left\{\ln(2\pi)^{1/2} + \left(\frac{N}{2} + \frac{1}{2}\right)\ln\left(\frac{N}{2}\right) - \frac{N}{2}\right\} \quad \text{(Stirling's approx.)}$$

$$= \ln\left\{2^N\left(\frac{2}{\pi N}\right)^{\frac{1}{2}}\right\}$$

$$\Delta S/k_B = \ln\left\{2^N\left(\frac{2}{\pi N}\right)^{\frac{1}{2}}\right\} - \ln(2^N)$$

$$\Delta S/k_B = \ln\left(\frac{2}{\pi N}\right)^{\frac{1}{2}}$$

Since $2/\pi N < 1$, entropy decreases in forming the closed circular (cc)DNA. The following graph, Figure 19.7, shows the dependence of $\Delta S$ upon $N$ with a plot of $f(N) = \ln(1/N)^{1/2}$ (i.e. $\Delta S/k_B - \ln(2/\pi)^{1/2}$).

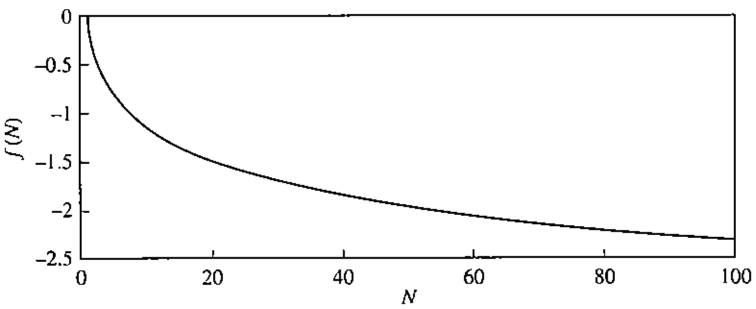



**Figure 19.7**

**(b)** **(i)** A continuous, normalized Gaussian function, which is also called the normal distribution or the bell-curve, has the form: $f(x) = (1/(2\pi\sigma^2)^{1/2})\mathrm{e}^{(x-\langle x\rangle)^2/2\sigma^2}$ where $-\infty < x < \infty$. $\langle x\rangle$ is the mean value of $x$ and $\sigma$ is the standard deviation. It can be shown that $\sigma^2 = \langle x^2\rangle - \langle x\rangle^2$.

The discrete energy distribution for a twisted ccDNA molecule is:

$p_i = \mathrm{e}^{-\beta\varepsilon_i}/q$ [16.7] $= \mathrm{e}^{-\beta k i^2}/q$ where $k$ is an empirical constant and $i = 0, \pm 1, \pm 2, \ldots$

Because it has an exponent in $i^2$, which is comparable to $x^2$ in the above Gaussian function, the energy distribution has the form of a Gaussian function with a maximum value that is centered upon $i = 0$. The standard deviation of the discrete Gaussian distribution is found by comparing the two equations. It is $\sigma = (1/2\beta k)^{1/2}$

**(ii)** The following MathCad worksheet plots the energy distribution at several values of the unitless temperature $T_{\text{ratio}} = 1/\beta k = k_B T/k$. Bar plots (histograms), Figure 19.8(a), are appropriate for discrete distributions in which the argument takes on specific values only ($i = 0, \pm 1, \pm 2, \pm 3, \ldots$). Even though the argument is not defined for non-integer values of $i$, the last graph, Figure 19.8(b) presents line plots with the understanding of discrete values. This reduces the visual confusion of overlapping bars from multiple plots. The plots show that at higher temperatures there are fewer molecules in the lowest energy state $i = 0$ and a greater number of molecules in the high energy states.

$$N_{max} := 10 \quad i := -N_{max}..N_{max} \qquad q(T_{ratio}) := \sum_{i=-75}^{75} e^{-i^2/T_{ratio}} \qquad p(T_{ratio,i}) := \frac{e^{-i^2/T_{ratio}}}{q(T_{ratio})}$$

**(iii)** Cannot be completed unless k is specified. See Figure 19.8 for variation of p with $i$ at several temperatures.

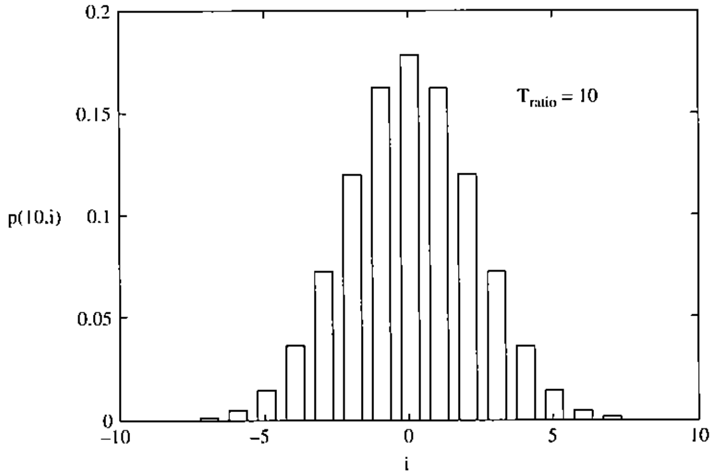



**Figure 19.8**

**P19.32** **(a)** The increase in temperature with the hydrophobic chain length is a result of the increased strength of the van der Waals interaction between long unsaturated portions of the chains that can interlock well with each other. The introduction of double bonds in the chains can affect the interlocking of the parallel chains by putting kinks in the chains, thereby decreasing the strength of the van der Waals interactions between chains. Double bonds can be either *cis* or *trans*. Only *cis*-double bonds produce a kink, but most fatty acids are the *cis*-isomer. So we expect that the transition temperatures will decrease in rough proportion to the number of C=C bonds.

**(b)** The addition of cholesterol is expected to increase the temperature of the transition from the liquid crystalline state to the liquid state by altering the conformations of the hydrocarbon chains. Cholesterol stabilizes extended chain conformations of adjacent hydrocarbon sections by van der Waals interactions relative to the coiled conformations that predominate when cholesterol is absent. The extended chains can pack better than coiled arrangements. However the lower transition temperature, that from the solid crystalline state to the liquid crystalline form, is probably decreased upon addition of cholesterol; its presence prevents the hydrophobic chains from freezing into a solid array by disrupting their packing. This will also spread the melting point over a range of temperatures.

**P19.34** **(a)** $$\frac{\eta}{\eta^*} = \frac{t}{t^*} \approx 1 + [\eta]c + k'[\eta]^2c^2$$

Define $F = \dfrac{t/t^* - 1}{c} = [\eta] + k'[\eta]^2 c$

A linear regression of $F$ against $c$ yields an intercept equal to $[\eta]$ and a slope equal to $k'[\eta]^2$.

(1) *In toluene*: Linear regression ($R = 0.999\,54$) yields

$[\eta] = 0.085\overline{66}\,\mathrm{dm^3\,g^{-1}} = \boxed{0.086\,\mathrm{dm^3\,g^{-1}}}$; standard deviation $= 0.00020\,\mathrm{dm^3\,g^{-1}}$

$k'[\eta]^2 = 0.002\,6\overline{88}\,\mathrm{dm^6\,g^{-2}}$; standard deviation $= 0.000\,057\,\mathrm{dm^6\,g^{-2}}$

Then

$$k' = \frac{0.002\,6\overline{88}\,\mathrm{dm^6\,g^{-2}}}{(0.085\,\overline{66}\,\mathrm{dm^3\,g^{-1}})^2} = \boxed{0.37}$$

(2) *In cyclohexane:* Linear regression ($R = 0.981\,98$) yields

$$[\eta] = 0.041\,\overline{50}\,\mathrm{dm^3\,g^{-1}} = \boxed{0.042\,\mathrm{dm^3\,g^{-1}}};\ \text{standard deviation} = 0.000\,18\,\mathrm{dm^3\,g^{-1}}$$

$$k'[\eta]^2 = 0.006\,0\overline{01}\,\mathrm{dm^6\,g^{-2}};\ \text{standard deviation} = 0.000\,116\,\mathrm{dm^6\,g^{-2}}$$

Then

$$k' = \frac{0.000\,600\overline{1}\,\mathrm{dm^6\,g^{-2}}}{(0.041\,\overline{50}\,\mathrm{dm^3\,g^{-1}})^2} = \boxed{0.35}$$

**(b)** $[\eta] = K\overline{M}_{\mathrm{v}}^{a}$ or $\overline{M}_{\mathrm{v}} = \left(\dfrac{[\eta]}{K}\right)^{1/a}$

(1) *In toluene*

$$\overline{M}_{\mathrm{v}} = \left(\frac{0.085\,\overline{66}\,\mathrm{dm^2\,g^{-1}}}{1.15\times10^{-5}\,\mathrm{dm^3\,g^{-1}}}\right)^{(1/0.72)}\mathrm{g\,mol^{-1}} = \boxed{2.4\times10^5\,\mathrm{g\,mol^{-1}}}$$

(2) *In cyclohexane*

$$\overline{M}_{\mathrm{v}} = \left(\frac{0.041\,\overline{50}\,\mathrm{dm^3\,g^{-1}}}{8.2\times10^{-5}\,\mathrm{dm^3\,g^{-1}}}\right)^{(1/(1/2))}\mathrm{g\,mol^{-1}} = \boxed{2.6\times10^5\,\mathrm{g\,mol^{-1}}}$$

**(c)** $[\eta]/(\mathrm{dm^3\,g^{-1}}) = \Phi(r_{\mathrm{rms}}/\mathrm{m})^3/M,\quad \Phi = 2.84\times10^{26}$

$$r_{\mathrm{rms}} = \left(\frac{[\eta]M}{\Phi}\right)^{1/3}\mathrm{m},\quad \text{where } r_{\mathrm{rms}} = \left\langle r^2\right\rangle^{1/2}$$

$$(1)\ \textit{In toluene: } r_{\mathrm{rms}} = \left(\frac{0.085\,\overline{66}\times2.3\bar{9}\times10^5}{2.84\times10^{26}}\right)^{1/3}\mathrm{m} = \boxed{42\,\mathrm{nm}}$$

$$(2)\ \textit{In cyclohexane: } r_{\mathrm{rms}} = \left(\frac{0.041\,\overline{50}\times2.5\bar{6}\times10^5}{2.84\times10^{26}}\right)^{1/3}\mathrm{m} = \boxed{33\,\mathrm{nm}}$$

**(d)** $M(\text{styrene}) = 104\,\mathrm{g\,mol^{-1}}$

Average number of monomeric units, $\langle n\rangle$ is

$$\langle n\rangle = \frac{\overline{M}_{\mathrm{v}}}{M(\text{styrene})}$$

$$(1)\ \textit{In toluene}\quad \langle n\rangle = \frac{2.3\bar{9}\times10^5\,\mathrm{g\,mol^{-1}}}{104\,\mathrm{g\,mol^{-1}}} = \boxed{2.3\times10^3}$$

$$(2)\ \textit{In cyclohexane:}\quad \langle n\rangle = \frac{2.5\bar{6}\times10^5\,\mathrm{g\,mol^{-1}}}{104\,\mathrm{g\,mol^{-1}}} = \boxed{2.5\times10^3}$$

(e) Consider the geometry in Figure 19.9

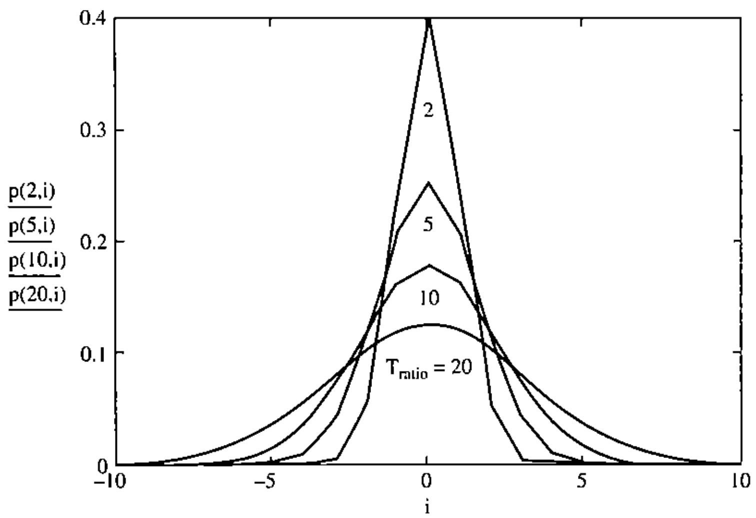



**Figure 19.9**

For a polymer molecule consisting of $\langle n\rangle$ monomers, the maximum molecular length, $L_{max}$, is

$$\begin{aligned} L_{max} &= 2l\,\langle n\rangle \cos\theta \\ &= 2(0.154\,\text{nm})\,\langle n\rangle \cos 35° \\ &= (0.2507\,\text{nm})\,\langle n\rangle \end{aligned}$$

*In toluene*: $L_{max} = (0.2507\text{nm}) \times (2.3\bar{0} \times 10^3) = \boxed{5.8 \times 10^2\ \text{nm}}$

*In cyclohexane*: $L_{max} = (0.2507\,\text{nm}) \times (2.4\bar{6} \times 10^3) = \boxed{6.2 \times 10^2\ \text{nm}}$

**(f)** $R_g = \left(\dfrac{\langle n\rangle}{3}\right)^{1/2} l = (0.0889\,\text{nm})\langle n\rangle^{1/2}$

Kirkwood–Riseman: $r^{KR}_{rms} = \left(\dfrac{[\eta]M}{\Phi}\right)^{1/3} = \left(\dfrac{[\eta]M}{2.84 \times 10^{26}}\right)^{1/3}$

constrained coil: $r_{rms} = (2\langle n\rangle)^{1/2}\, l$ [19.36] or $\langle n\rangle^{1/2} l$ [19.31]

| Solvent | $\langle n\rangle$ | $R_g$/nm | $r^{KR}_{rms}$/nm | $r^{cc}_{rms}$/nm |
|---|---|---|---|---|
| Toluene | $2.3\bar{0} \times 10^3$ | $\boxed{4.3}$ | 42 | $\boxed{10.\bar{4} \text{ or } 7.4}$ |
| Cyclohexane | $2.4\bar{6} \times 10^3$ | $\boxed{4.4}$ | 33 | $\boxed{10.\bar{8} \text{ or } 7.6}$ |

**(g)** There is no reason for them to agree; they are different samples; there is no fixed value of $M$ for polystryene. The manufacturer's claim appears to be valid.

# 20 Materials 2: the solid state

## Answers to discussion questions

**D20.2** We can use the Debye–Scherrer powder diffraction method, follow the procedure of Example 20.3, and in particular look for systematic absences in the diffraction patterns. We can proceed through the following sequence

1. Measure distances of the lines in the diffraction pattern from the center.
2. From the known radius of the camera, convert the distances to angles.
3. Calculate $\sin^2\theta$.
4. Find the common factor $A = \lambda^2/4a^2$ in $\sin^2\theta = (\lambda^2/4a^2)(h^2+k^2+l^2)$.
5. Index the lines using $\sin^2\theta/A = h^2+k^2+l^2$.
6. Look for the systematic absences in $(hkl)$. See Figure 20.22 of the text. For body-centered cubic, diffraction lines corresponding to $h+k+l$ that are odd will be absent. For face-centered cubic, only lines for which $h$, $k$, and $l$ are either all even or all odd will be present, others will be absent.
7. Solve $A = \lambda^2/4a^2$ for $a$.

**D20.4** The phase problem arises with the analysis of data in X-ray diffraction when seeking to perform a Fourier synthesis of the electron density. In order to carry out the sum it is necessary to know the signs of the structure factors; however, because diffraction intensities are proportional to the square of the structure factors, the intensities do not provide information on the sign. For non-centrosymmetric crystals, the structure factors may be complex, and the phase $\alpha$ in the expression $F_{hkl} = |F_{hkl}|e^{i\alpha}$ is indeterminate. The phase problem may be evaded by the use of a Patterson synthesis or tackled directly by using the so-called direct methods of phase allocation.

The Patterson synthesis is a technique of data analysis in X-ray diffraction which helps to circumvent the phase problem. In it, a function $P$ is formed by calculating the Fourier transform of the squares of the structure factors (which are proportional to the intensities):

$$P(r) = \frac{1}{V}\sum_{hkl}|F_{hkl}|^2 e^{-2\pi i(hx+ky+lz)}$$

The outcome is a map of the *separations* of the atoms in the unit cell of the crystal. If some atoms are heavy (perhaps because they have been introduced by isomorphous replacement), they dominate the Patterson function, and their locations can be deduced quite simply. Their locations can then be used in the determination of the locations of lighter atoms.

**D20.6** In a face-centered cubic close-packed lattice, there is an octahedral hole in the center. The rock-salt structure can be thought of as being derived from an fcc structure of $Cl^-$ ions in which $Na^+$ ions have filled the octahedral holes.

The caesium-chloride structure can be considered to be derived from the ccp structure by having $Cl^-$ ions occupy all the primitive lattice points and octahedral sites, with all tetrahedral sites occupied by $Cs^+$ ions. This is exceedingly difficult to visualize and describe without carefully constructed figures or models. Refer to S.-M. Ho and B. E. Douglas, *J. Chem. Educ.* **46**, 208, 1969, for the appropriate diagrams.

**D20.8** Semiconductors generally have lower electrical conductivity than most metals. Additionally, the conductivity of semiconductors increases as the temperature is raised whereas that of metals decreases. The difference occurs because of the relative balance between the excitation of electrons into electrical conductance and the scattering of electrons off the conductance path by collisions with vibrating atoms. The scattering process predominates with increasing temperature of a metal. The excitation process predominates for the semiconductor.

The electronic structure of solids consists of allowed energy bands. The highest energy band of a metal is partially filled. Being approximately filled to the Fermi level only, there is no gap of forbidden energies for excitation. It is easy to promote electrons from the filled level in which all random vector momentums are occupied to levels in which there is a preferred vector momentum. This provides high electrical conductivity. The energy difference between the top of the band and the Fermi level helps to explain their appearance. If sufficiently wide, all incident visible light can be both absorbed and emitted. This gives many metals their shiny, "silver" luster. A narrow width may result in color as a range of visible frequencies are preferentially emitted. An example is the reddish color of copper.

Semiconductors have a band gap, $E_g$, between a filled valence band and an approximately unfilled conductance band above it. Significant energy is needed to promote electrons to the conductance band. The energy may be provided thermally with the application of higher temperature, with electromagnetic radiation of frequency above $\nu_{min} = E_g/h$, or with an applied voltage. The visual appearance of a semiconductor is approximated with $\nu_{min}$. For example, electromagnetic radiation with more energy than green light is absorbed by cadmium sulfide (see *Illustration* 20.2) so the yellow, orange and red visible light are predominately reflected and seen as a yellow-orange color by an observer.

**D20.10** The most obvious difference is that there is no magnetic analog of electric charge; hence, there are no magnetic 'ions.' Both electric and magnetic moments exist and these can be either permanent or induced. Induced magnetic moments in the entire sample can be either parallel or antiparallel to the applied field producing them (paramagnetic or diamagnetic moments), whereas in the electric case they are always parallel. Magnetization, $M$, is the analog of polarization, $P$. Although both magnetization and induced dipole moment are proportional to the fields producing them, they are not analogous quantities, neither are volume magnetic susceptibility, $\chi$, and electric polarizability, $\alpha$. The magnetic quantities refer to the sample as a whole, the electric quantities to the molecules. Molar magnetic susceptibility is analogous to molar polarization as can be seen by comparing eqns 20.30 and 18.15 and magnetizability is analogous to electric polarizability.

## Solutions to exercises

**E20.1(b)** $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$ is the midpoint of a face. All face midpoints are alike, including $\boxed{\left(\frac{1}{2}, \frac{1}{2}, 0\right) \text{ and } \left(0, \frac{1}{2}, \frac{1}{2}\right)}$. There are six faces to each cube, but each face is shared by two cubes. So other face midpoints can be described by one of these three sets of coordinates on an adjacent unit cell.

**E20.2(b)** Taking reciprocals of the coordinates yields $\left(1, \frac{1}{3}, -1\right)$ and $\left(\frac{1}{2}, \frac{1}{3}, \frac{1}{4}\right)$ respectively. Clearing the fractions yields the Miller indices $\boxed{(31\bar{3}) \text{ and } (643)}$

**E20.3(b)** The distance between planes in a cubic lattice is

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

This is the distance between the origin and the plane which intersects coordinate axes at $(h/a, k/a, l/a)$.

$$d_{121} = \frac{523\,\text{pm}}{(1 + 2^2 + 1)^{1/2}} = \boxed{214\,\text{pm}}$$

$$d_{221} = \frac{523\,\text{pm}}{(2^2 + 2^2 + 1)^{1/2}} = \boxed{174\,\text{pm}}$$

$$d_{244} = \frac{523\,\text{pm}}{(2^2 + 4^2 + 4^2)^{1/2}} = \boxed{87.2\,\text{pm}}$$

**E20.4(b)** The Bragg law is

$$n\lambda = 2d \sin\theta$$

Assuming the angle given is for a first-order reflection, the wavelength must be

$$\lambda = 2(128.2\,\text{pm}) \sin 19.76^\circ = \boxed{86.7\,\text{pm}}$$

**E20.5(b)** Combining the Bragg law with Miller indices yields, for a cubic cell

$$\sin\theta_{hkl} = \frac{\lambda}{2a}(h^2 + k^2 + l^2)^{1/2}$$

In a face-centered cubic lattice, $h$, $k$, and $l$ must be all odd or all even. So the first three reflections would be from the (1 1 1), (2 0 0), and (2 2 0) planes. In an fcc cell, the face diagonal of the cube is $4R$, where $R$ is the atomic radius. The relationship of the side of the unit cell to $R$ is therefore

$$(4R)^2 = a^2 + a^2 = 2a^2 \quad \text{so} \quad a = \frac{4R}{\sqrt{2}}$$

Now we evaluate

$$\frac{\lambda}{2a} = \frac{\lambda}{4\sqrt{2}R} = \frac{154\,\text{pm}}{4\sqrt{2}(144\,\text{pm})} = 0.189$$

We set up the following table

| $hkl$ | $\sin\theta$ | $\theta/^\circ$ | $2\theta/^\circ$ |
|---|---|---|---|
| 111 | 0.327 | 19.1 | 38.2 |
| 200 | 0.378 | 22.2 | 44.4 |
| 220 | 0.535 | 32.3 | 64.6 |

**E20.6(b)** In a circular camera, the distance between adjacent lines is $D = R\Delta(2\theta)$, where $R$ is the radius of the camera (distance from sample to film) and $\theta$ is the diffraction angle. Combining these quantities with the Bragg law ($\lambda = 2d\sin\theta$, relating the glancing angle to the wavelength and separation of planes), we get

$$D = 2R\Delta\theta = 2R\Delta\left(\sin^{-1}\frac{\lambda}{2d}\right)$$
$$= 2(5.74\,\text{cm}) \times \left(\sin^{-1}\frac{96.035}{2(82.3\,\text{pm})} - \sin^{-1}\frac{95.401\,\text{pm}}{2(82.3\,\text{pm})}\right) = \boxed{0.054\,\text{cm}}$$

**E20.7(b)** The volume of a hexagonal unit cell is the area of the base times the height $c$. The base is equivalent to two equilateral triangles of side $a$. The altitude of such a triangle is $a\sin 60°$. So the volume is

$$V = 2\left(\tfrac{1}{2}a \times a\sin 60°\right)c = a^2c\sin 60° = (1692.9\,\text{pm})^2 \times (506.96\,\text{pm}) \times \sin 60°$$
$$= 1.2582 \times 10^9\,\text{pm}^3 = \boxed{1.2582\,\text{nm}^3}$$

**E20.8(b)** The volume of an orthorhombic unit cell is

$$V = abc = (589\,\text{pm}) \times (822\,\text{pm}) \times (798\,\text{pm}) = \frac{3.86 \times 10^8\,\text{pm}^3}{(10^{10}\,\text{pm}\,\text{cm}^{-1})^3} = 3.86 \times 10^{-22}\text{cm}^3$$

The mass per formula unit is

$$m = \frac{135.01\,\text{g}\,\text{mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 2.24 \times 10^{-22}\,\text{g}$$

The density is related to the mass $m$ per formula unit, the volume $V$ of the unit cell, and the number $N$ of formula units per unit cell as follows

$$\rho = \frac{Nm}{V} \quad \text{so} \quad N = \frac{\rho V}{m} = \frac{(2.9\,\text{g}\,\text{cm}^{-3}) \times (3.86 \times 10^{-22}\,\text{cm}^3)}{2.24 \times 10^{-22}\,\text{g}} = \boxed{5}$$

A more accurate density, then, is

$$\rho = \frac{5(2.24 \times 10^{-22}\,\text{g})}{3.86 \times 10^{-22}\,\text{cm}^3} = \boxed{2.90\,\text{g}\,\text{cm}^{-3}}$$

**E20.9(b)** The distance between the origin and the plane which intersects coordinate axes at $(h/a, k/b, l/c)$ is given by

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{-1/2} = \left(\frac{3^2}{(679\,\text{pm})^2} + \frac{2^2}{(879\,\text{pm})^2} + \frac{2^2}{(860\,\text{pm})^2}\right)^{-1/2}$$
$$d_{322} = \boxed{182\,\text{pm}}$$

**E20.10(b)** The fact that the 111 reflection is the third one implies that the cubic lattice is simple, where all indices give reflections. The 111 reflection would be the first reflection in a face-centered cubic cell and would be absent from a body-centered cubic.

The Bragg law

$$\sin\theta_{hkl} = \frac{\lambda}{2a}(h^2+k^2+l^2)^{1/2}$$

can be used to compute the cell length

$$a = \frac{\lambda}{2\sin\theta_{hkl}}(h^2+k^2+l^2)^{1/2} = \frac{137\,\text{pm}}{2\sin 17.7°}(1^2+1^2+1^2)^{1/2} = 390\,\text{pm}$$

With the cell length, we can predict the glancing angles for the other reflections expected from a simple cubic

$$\theta_{hkl} = \sin^{-1}\left(\frac{\lambda}{2a}(h^2+k^2+l^2)^{1/2}\right) = \sin^{-1}(0.176(h^2+k^2+l^2)^{1/2})$$

$$\theta_{100} = \sin^{-1}(0.176(1^2+0+0)^{1/2}) = 10.1° \text{ (checks)}$$

$$\theta_{110} = \sin^{-1}(0.176(1^2+1^2+0)^{1/2}) = 14.4° \text{ (checks)}$$

$$\theta_{200} = \sin^{-1}(0.176(2^2+0+0)^{1/2}) = 20.6° \text{ (checks)}$$

These angles predicted for a simple cubic fit those observed, confirming the hypothesis of a simple lattice; the reflections are due to the $\boxed{\text{(100), (110), (111), and (200)}}$ planes.

**E20.11(b)** The Bragg law relates the glancing angle to the separation of planes and the wavelength of radiation

$$\lambda = 2d\sin\theta \quad \text{so} \quad \theta = \sin^{-1}\frac{\lambda}{2d}$$

The distance between the origin and plane which intersects coordinate axes at $(h/a, k/b, l/c)$ is given by

$$d_{hkl} = \left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{-1/2}$$

So we can draw up the following table

| $hkl$ | $d_{hkl}/\text{pm}$ | $\theta_{hkl}/°$ |
|---|---|---|
| 100 | 574.1 | 4.166 |
| 010 | 796.8 | 3.000 |
| 111 | 339.5 | 7.057 |

**E20.12(b)** All of the reflections present have $h+k+l$ even, and all of the even $h+k+l$ are present. The unit cell, then, is $\boxed{\text{body-centered cubic}}$

**E20.13(b)** The structure factor is given by

$$F_{hkl} = \sum_i f_i e^{i\phi_i} \quad \text{where} \quad \phi_i = 2\pi(hx_i+ky_i+lz_i)$$

All eight of the vertices of the cube are shared by eight cubes, so each vertex has a scattering factor of $f/8$.

The coordinates of all vertices are integers, so the phase $\phi$ is a multiple of $2\pi$ and $e^{i\phi} = 1$. The body-center point belongs exclusively to one unit cell, so its scattering factor is $f$. The phase is

$$\phi = 2\pi\left(\tfrac{1}{2}h + \tfrac{1}{2}k + \tfrac{1}{2}l\right) = \pi(h + k + l)$$

When $h + k + l$ is even, $\phi$ is a multiple of $2\pi$ and $e^{i\phi} = 1$; when $h + k + l$ is odd, $\phi$ is $\pi$ + a multiple of $2\pi$ and $e^{i\phi} = -1$. So $e^{i\phi} = (-1)^{h+k+l}$ and

$$F_{hkl} = 8(f/8)(1) + f(-1)^{h+k+l}$$
$$= \boxed{2f \text{ for } h + k + l \text{ even} \quad \text{and} \quad 0 \text{ for } h + k + l \text{ odd}}$$

**E20.14(b)** There are two smaller (white) triangles to each larger (gray) triangle. Let the area of the larger triangle be $A$ and the area of the smaller triangle be $a$. Since $b = \frac{1}{2}B$(base) and $h = \frac{1}{2}H$(height), $a = \frac{1}{4}A$. The white space is then $2NA/4$, for $N$ of the larger triangles. The total space is then $(NA + (NA/2)) = 3NA/2$. Therefore the fraction filled is $NA/(3NA/2) = \boxed{2/3}$

**E20.15(b)** See Figure 20.1.

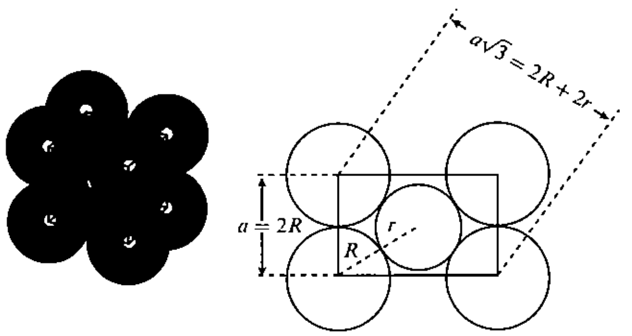



**Figure 20.1**

The body diagonal of a cube is $a\sqrt{3}$. Hence

$$a\sqrt{3} = 2R + 2r \quad \text{or} \quad \sqrt{3}R = R + r \quad [a = 2R]$$
$$\frac{r}{R} = \boxed{0.732}$$

**E20.16(b)** The ionic radius of $K^+$ is 138 pm when it is 6-fold coordinated, 151 pm when it is 8-fold coordinated.

**(a)** The smallest ion that can have 6-fold coordination with it has a radius of $\left(\sqrt{2} - 1\right) \times (138\,\text{pm}) = \boxed{57\,\text{pm}}$.

**(b)** The smallest ion that can have 8-fold coordination with it has a radius of $\left(\sqrt{3} - 1\right) \times (151\,\text{pm}) = \boxed{111\,\text{pm}}$.

**E20.17(b)** The diagonal of the face that has a lattice point in its center is equal to $4r$, where $r$ is the radius of the atom. The relationship between this diagonal and the edge length $a$ is

$$4r = a\sqrt{2} \quad \text{so} \quad a = 2\sqrt{2}r$$

The volume of the unit cell is $a^3$, and each cell contains 2 atoms. (Each of the 8 vertices is shared among 8 cells; each of the 2 face points is shared by 2 cells.) So the packing fraction is

$$\frac{2V_{\text{atom}}}{V_{\text{cell}}} = \frac{2(4/3)\pi r^3}{(2\sqrt{2}r)^3} = \frac{\pi}{3(2)^{3/2}} = \boxed{0.370}$$

**E20.18(b)** The volume of an atomic crystal is proportional to the cube of the atomic radius divided by the packing fraction. The packing fraction for hcp, a close-packed structure, is 0.740; for bcc, it is 0.680. So for titanium

$$\frac{V_{\text{bcc}}}{V_{\text{hcp}}} = \frac{0.740}{0.680}\left(\frac{122\,\text{pm}}{126\,\text{pm}}\right)^3 = 0.99$$

The bcc structure has a smaller volume, so the transition involves a $\boxed{\text{contraction}}$. (Actually, the data are not precise enough to be sure of this. 122 could mean 122.49 and 126 could mean 125.51, in which case an expansion would occur.)

**E20.19(b)** Draw points corresponding to the vectors joining each pair of atoms. Heavier atoms give more intense contributions than light atoms. Remember that there are two vectors joining any pair of atoms ($\overrightarrow{AB}$ and $\overleftarrow{AB}$); don't forget the AA zero vectors for the center point of the diagram. See Figure 20.2 for $C_6H_6$.

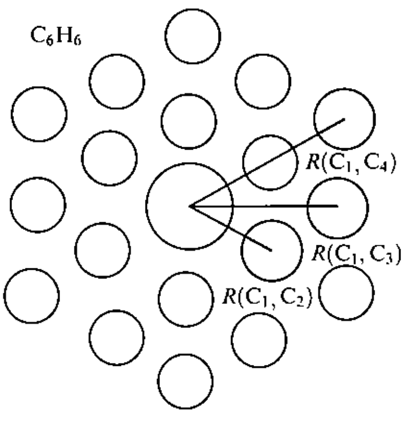



**Figure 20.2**

**E20.20(b)** Combine $E = \frac{1}{2}kT$ and $E = \frac{1}{2}mv^2 = \frac{h^2}{2m\lambda^2}$, to obtain

$$\lambda = \frac{h}{(mkT)^{1/2}} = \frac{6.626 \times 10^{-34}\,\text{J s}}{[(1.675 \times 10^{-27}\,\text{kg}) \times (1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (300\,\text{K})]^{1/2}} = \boxed{252\,\text{pm}}$$

**E20.21(b)** The lattice enthalpy is the difference in enthalpy between an ionic solid and the corresponding isolated ions. In this exercise, it is the enthalpy corresponding to the process

$$MgBr_2(s) \rightarrow Mg^{2+}(g) + 2Br^-(g)$$

The standard lattice enthalpy can be computed from the standard enthalpies given in the exercise by considering the formation of $MgBr_2(s)$ from its elements as occuring through the following steps: sublimation of Mg(s), removing two electrons from Mg(g), vaporization of $Br_2(l)$, atomization of $Br_2(g)$, electron attachment to Br(g), and formation of the solid $MgBr_2$ lattice from gaseous ions

$$\Delta_f H^\ominus(MgBr_2, s) = \Delta_{sub}H^\ominus(Mg, s) + \Delta_{ion}H^\ominus(Mg, g) + \Delta_{vap}H^\ominus(Br_2, l)$$
$$+ \Delta_{at}H^\ominus(Br_2, g) + 2\Delta_{eg}H^\ominus(Br, g) - \Delta_L H^\ominus(MgBr_2, s)$$

So the lattice enthalpy is

$$\Delta_L H^\ominus(MgBr_2, s) = \Delta_{sub}H^\ominus(Mg, s) + \Delta_{ion}H^\ominus(Mg, g) + \Delta_{vap}H^\ominus(Br_2, l)$$
$$+ \Delta_{at}H^\ominus(Br_2, g) + 2\Delta_{eg}H^\ominus(Br, g) - \Delta_f H^\ominus(MgBr_2, s)$$

$$\Delta_L H^\ominus(MgBr_2, s) = [148 + 2187 + 31 + 193 - 2(331) + 524]\,\text{kJ mol}^{-1} = \boxed{2421\,\text{kJ mol}^{-1}}$$

**E20.22(b)** Tension reduces the disorder in the rubber chains; hence, if the rubber is sufficiently stretched, crystallization may occur at temperatures above the normal crystallization temperature. In unstretched rubber the random thermal motion of the chain segments prevents crystallization. In stretched rubber these random thermal motions are drastically reduced. At higher temperatures the random motions may still have been sufficient to prevent crystallization even in the stretched rubber, but lowering the temperature to 0 °C may have resulted in a transition to the crystalline form. Since it is random motion of the chains that resists the stretching force and allows the rubber to respond to forced dimensional changes, this ability ceases when the motion ceases. Hence, the seals failed.

**COMMENT.** The solution to the problem of the cause of the *Challenger* disaster was the final achievement, just before his death, of Richard Feynman, a Nobel prize winner in physics and a person who loved to solve problems. He was an outspoken person who abhorred sham, especially in science and technology. Feynman concluded his personal report on the disaster by saying, 'For a successful technology, reality must take precedence over public relations, for nature cannot be fooled' (James Gleick, *Genius: The Life and Science of Richard Feynman*. Pantheon Books, New York (1992).)

**E20.23(b)** Young's modulus is defined as:

$$E = \frac{\text{normal stress}}{\text{normal strain}}$$

where stress is deforming force per unit area and strain is a fractional deformation. Here the deforming force is gravitational, $mg$, acting across the cross-sectional area of the wire, $\pi r^2$. So the strain induced in the exercise is

$$\text{strain} = \frac{\text{stress}}{E} = \frac{mg}{\pi(d/2)^2 E} = \frac{4mg}{\pi d^2 E} = \frac{4(10.0\,\text{kg})(9.8\,\text{m s}^{-2})}{\pi(0.10 \times 10^{-3}\,\text{m})^2(215 \times 10^9\,\text{Pa})} = \boxed{5.8 \times 10^{-2}}$$

The wire would stretch by 5.8%.

**E20.24(b)** Poisson's ratio is defined as:

$$\nu_P = \frac{\text{transverse strain}}{\text{normal strain}}$$

where normal strain is the fractional deformation along the direction of the deforming force and transverse strain is the fractional deformation in the directions transverse to the deforming force. Here the length of a cube of lead is stretched by 2.0 percent, resulting in a contraction by 0.41 × 2.0 percent, or 0.82 percent, in the width and height of the cube. The relative change in volume is:

$$\frac{V + \Delta V}{V} = (1.020)(0.9918)(0.9918) = 1.003$$

and the absolute change is:

$$\Delta V = (1.003 - 1)(1.0\,\mathrm{dm^3}) = \boxed{0.003\,\mathrm{dm^3}}$$

**E20.25(b)** p-type; the dopant, gallium, belongs to Group 13, whereas germanium belongs to Group 14.

**E20.26(b)** $$E_g = h\nu_{\min} \text{ and } \nu_{\min} = E_g/h = \frac{1.12\,\mathrm{eV}}{6.626 \times 10^{-34}\,\mathrm{J\,s}} \left(\frac{1.602 \times 10^{-19}\,\mathrm{J}}{1\,\mathrm{eV}}\right) = 2.71 \times 10^{14}\,\mathrm{Hz}$$

**E20.27(b)** $$m = g_e\{S(S+1)\}^{1/2}\mu_B \quad [20.34, \text{with } S \text{ in place of } s]$$

Therefore, since $m = 4.00\mu_B$

$$S(S+1) = \left(\tfrac{1}{4}\right) \times (4.00)^2 = 4.00, \quad \text{implying that} \quad S = 1.56$$

Thus $S \approx \frac{3}{2}$, implying three unpaired spins.

In actuality most $Mn^{2+}$ compounds have $\boxed{5}$ unpaired spins.

**E20.28(b)** $$\chi_m = \chi V_m = \frac{\chi M}{\rho} = \frac{(-7.9 \times 10^{-6}) \times (84.15\,\mathrm{g\,mol^{-1}})}{0.811\,\mathrm{g\,cm^{-3}}}$$

$$= \boxed{-8.2 \times 10^{-4}\,\mathrm{cm^3\,mol^{-1}}} = \boxed{-8.2 \times 10^{-10}\,\mathrm{m^3\,mol^{-1}}}$$

**E20.29(b)** The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT}$$

$NO_2$ is an odd-electron species, so it must contain at least one unpaired spin; in its ground state it has one unpaired spin, so $S = \frac{1}{2}$. Therefore,

$$\chi_m = (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (2.0023)^2 \times (4\pi \times 10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3})$$

$$\times \frac{(9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}})^2 \times \left(\frac{1}{2}\right) \times \left(\frac{1}{2} + 1\right)}{3(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}$$

$$= \boxed{1.58 \times 10^{-8}\,\mathrm{m^3\,mol^{-1}}}$$

The expression above does not indicate any pressure-dependence in the molar susceptibility. However, the observed decrease in susceptibility with increased pressure is consistent with the fact that $NO_2$ has a tendency to dimerize, and that dimerization is favored by higher pressure. The dimer has no unpaired electrons, so the dimerization reaction effectively reduced the number of paramagnetic species.

**E20.30(b)** The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \quad \text{so} \quad S(S+1) = \frac{3kT\chi_m}{N_A g_e^2 \mu_0 \mu_B^2}$$

$$S(S+1) = \frac{3(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}{(6.022\times10^{23}\,\mathrm{mol^{-1}})\times(2.0023)^2}$$

$$\times\frac{(6.00\times10^{-8}\,\mathrm{m^3\,mol^{-1}})}{(4\pi\times10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3})\times(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})^2}$$

$$= 2.84 \quad \text{so} \quad S = \frac{-1+\sqrt{1+4(2.84)}}{2} = 1.26$$

corresponding to $\boxed{2.52}$ effective unpaired spins. The theoretical number is $\boxed{2}$. The magnetic moments in a crystal are close together, and they interact rather strongly. The discrepancy is most likely due to an interaction among the magnetic moments.

**E20.31(b)** The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT}$$

$Mn^{2+}$ has five unpaired spins, so $S = 2.5$ and

$$\chi_m = \frac{(6.022\times10^{23}\,\mathrm{mol^{-1}})\times(2.0023)^2\times(4\pi\times10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3})}{3(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})}$$

$$\times\frac{(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})^2\times(2.5)\times(2.5+1)}{(298\,\mathrm{K})}$$

$$= \boxed{1.85\times10^{-7}\,\mathrm{m^3\,mol^{-1}}}$$

**E20.32(b)** The orientational energy of an electron spin system in a magnetic field is

$$E = g_e\mu_B M_S \mathcal{B}$$

The Boltzmann distribution says that the population ratio $r$ of the various states is proportional to

$$r = \exp\left(\frac{-\Delta E}{kT}\right)$$

where $\Delta E$ is the difference between them. For a system with $S = 1$, the $M_S$ states are 0 and $\pm 1$. So between adjacent states

$$r = \exp\left(\frac{-g_e\mu_B M_S \mathcal{B}}{kT}\right) = \exp\left(\frac{-(2.0023) \times (9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}}) \times (1) \times (15.0\,\mathrm{T})}{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}\right)$$

$$= \boxed{0.935}$$

The population of the highest-energy state is $r^2$ times that of the lowest; $r^2 = \boxed{0.873}$

## Solutions to problems

### Solutions to numerical problems

**P20.2** A large separation between the sixth and seventh lines relative to the separation between the fifth and sixth lines is characteristic of a $\boxed{\text{simple (primitive) cubic lattice}}$. This is readily seen without indexing the lines. The conclusion that the unit cell is simple cubic is then confirmed by the presence of reflections from (100) planes.

$$d_{100} = a\ [20.1] = \frac{\lambda}{2\sin\theta}\ [20.5]$$

$$a = \frac{154\,\mathrm{pm}}{(2) \times (0.225)} = \boxed{342\ \mathrm{pm}}$$

**P20.4** Note that since $R = 28.7$ mm, $\theta/\mathrm{deg} = \left(\frac{D}{2R}\right) \times \left(\frac{180}{\pi}\right) = D/\mathrm{mm}$. Then proceed through the following sequence:

1. Measure the distances from the figure.
2. Convert from distances to angle using $\theta/\mathrm{deg} = D/\mathrm{mm}$.
3. Calculate $\sin^2\theta$.
4. Find the common factor $A = \lambda^2/4a^2$ in $\sin^2\theta = \left(\lambda^2/4a^2\right)(h^2 + k^2 + l^2)$.
5. Index the lines using $\sin^2\theta/A = h^2 + k^2 + l^2$.
6. Solve $A = \lambda^2/4a^2$ for $a$.

**(a)**

| $D$/mm | 22 | 30 | 36 | 44 | 50 | 58 | 67 | 77 |
|---|---|---|---|---|---|---|---|---|
| $\theta$/deg | 22 | 30 | 36 | 44 | 50 | 58 | 67 | 77 |
| $10^3 \sin^2\theta$ | 140 | 250 | 345 | 482 | 587 | 719 | 847 | 949 |

Analysis of face-centered cubic possibility

| $(h\,k\,l)$ | (1 1 1) | (2 0 0) | (2 1 1) | (3 1 1) | (2 2 2) | (4 0 0) | (3 3 1) | (4 2 0) |
|---|---|---|---|---|---|---|---|---|
| $10^4 A$ | 467 | 625 | 431 | 438 | 489 | 449 | 446 | 475 |

Analysis of body-centered cubic possibility

| $(h\,k\,l)$ | (1 1 0) | (2 0 0) | (2 1 1) | (2 2 0) | (3 1 0) | (2 2 2) | (3 2 1) | (4 0 0) |
|---|---|---|---|---|---|---|---|---|
| $10^4A$ | 700 | 625 | 575 | 603 | 587 | 599 | 605 | 593 |

Begin by performing steps 1–3 in order to determine $D, \theta$, and $\sin^2\theta$ and place them in tabular form as above. It is now possible to reject the primitive (simple) cubic cell possibility immediately because the separation between the sixth and seventh lines is not significantly larger than the separation between the fifth and sixth lines (see Problem 20.2 and Figure 20.22).

The relatively large uncertainties of the separation measurements force the modification of steps 4 and 5 for the identification of the unit cell as being either face-centered cubic or body-centered cubic. We analyse both possibilities by calculating the common factor $A = \sin^2\theta/h^2 + k^2 + l^2)$ for each datum in each case. Comparison of the standard deviations of the average of $A$ determines the unit cell type.

The analysis of both the face-centered cubic and body-centered cubic possibilities is found in the above table. Successive reflective planes are determined with the rules found in Figure 20.22.

fcc possibility : $A_{\text{av.}} = 0.0478, \quad \sigma_A = 0.0063$ (13 percent)

bcc possibility : $A_{\text{av.}} = 0.0611, \quad \sigma_A = 0.0016$ (6 percent)

These standard deviations ($\sigma_A$) indicate that the cell type is $\boxed{\text{body-centered cubic}}$

The $Q$ test of the (1 1 0) reflection datum for $A$ yields $Q = 0.6$. Consequently this datum may be rejected with better than 95 percent confidence. This yields a better average value for $A$.

$A_{\text{av.}} = 0.0598, \qquad \sigma_A = 0.0016$ (3 percent)

Then $a = \dfrac{\lambda}{2A^{1/2}} = \dfrac{154\,\text{pm}}{(2)\times(0.0598)^{1/2}} = 315\,\text{pm}$

$4R = \sqrt{3}a$, so $\boxed{R = 136\,\text{pm}}$ [Fig. 20.1 above with $r = R$]

**(b)**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| D/mm | 21 | 25 | 37 | 45 | 47 | 59 | 67 | 72 |
| $\theta$/deg | 21 | 25 | 37 | 45 | 47 | 59 | 67 | 72 |
| $10^3\sin^2\theta$ | 128 | 179 | 362 | 500 | 535 | 735 | 847 | 905 |

Analysis of face-centered cubic possibility

| $(h\,k\,l)$ | (1 1 1) | (2 0 0) | (2 2 0) | (3 1 1) | (2 2 2) | (4 0 0) | (3 3 1) | (4 2 0) |
|---|---|---|---|---|---|---|---|---|
| $10^4A$ | 427 | 448 | 453 | 455 | 446 | 459 | 446 | 453 |

Analysis of body-centered cubic possibility

| $(h\,k\,l)$ | (1 1 0) | (2 0 0) | (2 1 1) | (2 2 0) | (3 1 0) | (2 2 2) | (3 2 1) | (400) |
|---|---|---|---|---|---|---|---|---|
| $10^4A$ | 640 | 448 | 603 | 625 | 535 | 613 | 605 | 566 |

Following the procedure established in part (a), the above table is constructed.

$$\text{fcc possibility}: \quad A_{\text{av.}} = 0.0448, \quad \sigma_{\text{A}} = 0.0010 \ (2\,\text{percent})$$

$$\text{bcc possibility}: \quad A_{\text{av.}} = 0.0579, \quad \sigma_{\text{A}} = 0.0063 \ (11\,\text{percent})$$

The standard deviations indicate that the cell type is $\boxed{\text{face-centered cubic}}$

Then $a = \dfrac{\lambda}{2A^{1/2}} = \dfrac{154\,\text{pm}}{(2) \times (0.0448)^{1/2}} = \boxed{364\,\text{pm}}$

$$4R = \sqrt{2}a, \quad \text{so} \quad R = \boxed{129\,\text{pm}}$$

**P20.6** When a very narrow X-ray beam (with a spread of wavelengths) is directed on the center of a genuine pearl, all the crystallites are irradiated parallel to a trigonal axis and the result is a Laue photograph with 6-fold symmetry. In a cultured pearl the narrow beam will have an arbitrary orientation with respect to the crystallite axes (of the central core) and an unsymmetrical Laue photograph will result. (See J. Bijvoet *et al., X-ray Analysis of Crystals*. Butterworth (1951).)

**P20.8**

$$\theta(100\,\text{K}) = 22°2'25'', \quad \theta(300\,\text{K}) = 21°57'59''$$

$$\sin\theta(100\,\text{K}) = 0.37526, \quad \sin\theta(300\,\text{K}) = 0.37406$$

$$\frac{\sin\theta(300\,\text{K})}{\sin\theta(100\,\text{K})} = 0.99681 = \frac{a(100\,\text{K})}{a(300\,\text{K})} \ [\text{see Problem 21.7}]$$

$$a(300\,\text{K}) = \frac{\lambda\sqrt{3}}{2\sin\theta} = \frac{(154.062\,\text{pm}) \times \sqrt{3}}{(2) \times (0.37406)} = 356.67\,\text{pm}$$

$$a(100\,\text{K}) = (0.99681) \times (356.67\,\text{pm}) = 355.53\,\text{pm}$$

$$\frac{\delta a}{a} = \frac{356.67 - 355.53}{355.53} = 3.206 \times 10^{-3}$$

$$\frac{\delta V}{V} = \frac{356.67^3 - 355.53^3}{355.53^3} = 9.650 \times 10^{-3}$$

$$\alpha_{\text{volume}} = \frac{1}{V}\frac{\delta V}{\delta T} = \frac{9.560 \times 10^{-3}}{200\,\text{K}} = \boxed{4.8 \times 10^{-5}\ \text{K}^{-1}}$$

$$\alpha_{\text{volume}} = \frac{1}{a}\frac{\delta a}{\delta T} = \frac{3.206 \times 10^{-3}}{200\,\text{K}} = \boxed{1.6 \times 10^{-5}\ \text{K}^{-1}}$$

**P20.10**

$$V = abc\sin\beta$$

and the information given tells us that $a = 1.377b$, $c = 1.436b$, and $\beta = 122°49'$; hence

$$V = (1.377) \times (1.436b^3)\sin 122°49' = 1.662b^3$$

Since $\rho = NM/VN_{\text{A}} = 2M/(1.662b^3 N_{\text{A}})$ we find that

$$b = \left(\frac{2M}{1.662\rho N_{\text{A}}}\right)^{1/3}$$

$$= \left(\frac{(2) \times (128.18\,\text{g mol}^{-1})}{(1.662) \times (1.152 \times 10^6\,\text{g m}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}\right)^{1/3} = 605.8\,\text{pm}$$

Therefore, $a = \boxed{834\ \text{pm}}$, $b = \boxed{606\ \text{pm}}$, $c = \boxed{870\ \text{pm}}$

**P20.12** As in Example 20.4 of the text we use

$$\rho(x) = \frac{1}{V}\left\{F_0 + 2\sum_{h=1}^{\infty} F_h \cos(2\pi hx)\right\}$$

Because $V$ is unknown we work with

$$V\rho(x) \equiv f(x)$$

$$\begin{aligned} f(x) = {} & 30 + 16.4\cos(2\pi x) + 13\cos(4\pi x) + 8.2\cos(6\pi x) + 11\cos(8\pi x) \\ & - 4.8\cos(10\pi x) + 10.8\cos(12\pi x) + 6.4\cos(14\pi x) - 2\cos(16\pi x) \\ & + 2.2\cos(18\pi x) + 13\cos(20\pi x) + 10.4\cos(22\pi x) - 8.6\cos(24\pi x) \\ & - 2.4\cos(26\pi x) + 0.2\cos(28\pi x) + 4.2\cos(30\pi x) \end{aligned}$$

A plot of $V\rho(x) \equiv f(x)$ is shown in Figure 20.3.

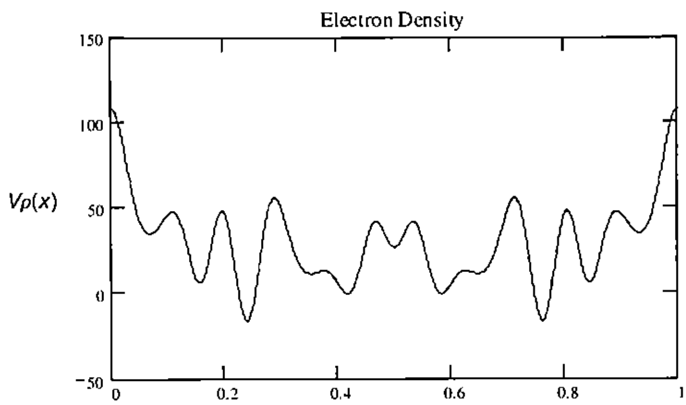



**Figure 20.3**

**P20.14** In a monoclinic cell, the area of parallelogram faces whose sides are $a$ and $c$ is

$$A = ca\cos(\beta - 90°)$$

so the volume of the unit cell is

$$\begin{aligned} V &= abc\cos(\beta - 90°) = (1.0427\ \text{nm}) \times (0.8876\ \text{nm}) \times (1.3777\ \text{nm}) \times \cos(93.254° - 90°) \\ &= 1.2730\ \text{nm}^3 \end{aligned}$$

The mass per unit cell is

$$m = \rho V = (2.024\ \text{g cm}^{-3}) \times (1.2730\ \text{nm}^3) \times (10^{-7}\ \text{cm nm}^{-1})^3 = 2.577 \times 10^{-21}\ \text{g}$$

The monomer is $CuC_7H_{13}N_5O_8S$, so its molar mass is

$$M = 63.546 + 7(12.011) + 13(1.008) + 5(14.007) + 8(15.999) + 32.066\,\mathrm{g\,mol^{-1}}$$
$$= 390.82\,\mathrm{g\,mol^{-1}}$$

The number of monomer units, then, is the mass of the unit cell divided by the mass of the monomer

$$N = \frac{mN_A}{M} = \frac{(2.577 \times 10^{-21}\,\mathrm{g}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}{390.82\,\mathrm{g\,mol^{-1}}} = 3.97 \quad or \quad \boxed{4}$$

**P20.16** The problem asks for an estimate of $\Delta_f H^\ominus(\mathrm{CaCl})$. A Born–Haber cycle would envision formation of CaCl(s) from its elements as sublimation of Ca(s), ionization of Ca(g), atomization of $Cl_2$(g) electrom gain of Cl(g), and formation of CaCl(s) from gaseous ions. Therefore

$$\Delta_f H^\ominus(\mathrm{CaCl, s}) = \Delta_{sub} H^\ominus(\mathrm{Ca, s}) + \Delta_{ion} H^\ominus(\mathrm{Ca, g}) + 2\Delta_f H^\ominus(\mathrm{Cl, g})$$
$$+ 2\Delta_{eg} H^\ominus(\mathrm{Cl, g}) - \Delta_L H^\ominus(\mathrm{CaCl, s})$$

Before we can estimate the lattice enthalpy of CaCl, we select a lattice with the aid of the radius-ratio rule. The ionic radius for $Cl^-$ is 181 pm; use the ionic radius of $K^+$ (1381) for $Ca^+$

$$\gamma = \frac{138\,\mathrm{pm}}{181\,\mathrm{pm}} = 0.762$$

suggesting the CsCl structure. We can interpret the Born–Mayer equation (eqn 20.15) as giving the negative of the lattice enthalpy

$$\Delta_L H^\ominus \approx \frac{A|z_1 z_2|N_A e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)$$

The distance $d$ is

$$d = (138 + 181)\,\mathrm{pm} = 319\,\mathrm{pm}$$

$$\text{so} \quad \Delta_L H^\ominus \approx \frac{(1.763) \times |(1)(-1)| \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (1.602 \times 10^{-9}\,\mathrm{C})^2}{4\pi(8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (319 \times 10^{-12}\,\mathrm{m})}\left(1 - \frac{34.5\,\mathrm{pm}}{319\,\mathrm{pm}}\right)$$

$$\Delta_L H^\ominus \approx 6.85 \times 10^5\,\mathrm{J\,mol^{-1}} = 685\,\mathrm{kJ\,mol^{-1}}$$

The enthalpy of formation, then, is

$$\Delta_f H^\ominus\,(\mathrm{CaCl, s}) \approx [176 + 589.7 + 2(121.7 - 348.7) - 685]\,\mathrm{kJ\,mol^{-1}} = \boxed{-373\,\mathrm{kJ\,mol^{-1}}}.$$

Although formation of CaCl(s) from its elements is exothermic, formation of $CaCl_2$(s) is still more favored energetically. Consider the reaction

$$2\mathrm{CaCl(s)} \rightarrow \mathrm{Ca(s)} + \mathrm{CaCl_2(s)}$$

for which $\Delta H^{\ominus} = \Delta_f H^{\ominus}(\text{Ca}) + \Delta_f H^{\ominus}(\text{CaCl}_2) - 2\Delta_f H^{\ominus}(\text{CaCl})$

$$\approx [0 - 795.8 - 2(-373)]\ \text{kJ mol}^{-1}$$

$$\Delta H^{\ominus} \approx -50\ \text{kJ mol}^{-1}$$

Note: Using the tabulated ionic radius of Ca (i.e. that of $Ca^{2+}$) would be less valid than using the atomic radius of a neighboring monovalent ion, for the problem asks about a hypothetical compound of monovalent calcium. Predictions with the smaller $Ca^{2+}$ radius (100 pm) differ substantially from those listed above: the expected structure changes to rock-salt, the lattice enthalpy to 758 kJ mol$^{-1}$, $\Delta_f H^{\ominus}(\text{CaCl})$ to $-446$ kJ mol$^{-1}$ and the final reaction enthalpy to +96 kJ mol$^{-1}$.

**P20.18**

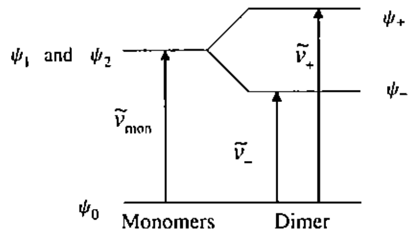



**Figure 20.4(a)**

**(a)**

$$\mu_{+\text{or}-} = \langle \psi_{+\text{or}-} | \mu | \psi_0 \rangle = \langle c_{+\text{or}-,1}\psi_1 + c_{+\text{or}-,2}\psi_2 | \mu | \psi_0 \rangle$$
$$= c_{+\text{or}-,1}\langle \psi_1 | \mu | \psi_0 \rangle + c_{+\text{or}-,2}\langle \psi_2 | \mu | \psi_0 \rangle$$

But $\langle \psi_1 | \mu | \psi_0 \rangle = \langle \psi_2 | \mu | \psi_0 \rangle = \mu_{\text{mon}}$, so

$$\mu_{+\text{or}-} = \left(c_{+\text{or}-,1} + c_{+\text{or}-,2}\right)\mu_{\text{mon}}$$

**(b)**

$$\hat{H}\psi_{+\text{or}-} = \tilde{\nu}_{+\text{or}-}\psi_{+\text{or}-} \quad \text{and} \quad \left(\hat{H} - \tilde{\nu}_{+\text{or}-}\right)\psi_{+\text{or}-} = 0$$

$$\begin{pmatrix} \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-} & \beta \\ \beta & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-} \end{pmatrix}\psi_{+\text{or}-} = 0 \quad \text{where} \quad \beta = \frac{\mu_{\text{mon}}^2}{4\pi\varepsilon_0 hcr^3}\left(1 - 3\cos^2\theta\right)$$

$$\begin{pmatrix} x_{+\text{or}-} & 1 \\ 1 & x_{+\text{or}-} \end{pmatrix}\psi_{+\text{or}-} = 0 \quad \text{where} \quad x_{+\text{or}-} = \left(\tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-}\right)/\beta$$

$$\begin{vmatrix} x_{+\text{or}-} & 1 \\ 1 & x_{+\text{or}-} \end{vmatrix} = x_{+\text{or}-}^2 - 1 = 0$$

$$x_{+\text{or}-} = \left(\tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-}\right)/\beta = \pm 1 \quad \text{and} \quad \tilde{\nu}_{+\text{or}-} = \tilde{\nu}_{\text{mon}} \pm \beta$$

$$\tilde{\nu}_+ = \tilde{\nu}_{\text{mon}} - \beta \quad \text{and} \quad \tilde{\nu}_- = \tilde{\nu}_{\text{mon}} + \beta$$

The ratio of $\mu_+^2/\mu_-^2$ (and the relative intensities of the dimer transitions) doesn't depend upon $\beta$ or $\theta$ because $\mu_+ = 0$. To see this, we use the coefficients of the normalized wavefunctions for $\psi_+$ and $\psi_-$ and the overlap integral $S = \langle \psi_1 | \psi_2 \rangle$.

$$\begin{pmatrix} x_{+\text{or}-} & 1 \\ 1 & x_{+\text{or}-} \end{pmatrix}\begin{pmatrix} c_{+\text{or}-,1} \\ c_{+\text{or}-,2} \end{pmatrix} = 0 \quad \text{where} \quad x_{+\text{or}-} = \pm 1$$

$$x_{+\text{or}-}c_{+\text{or}-,1} + c_{+\text{or}-,2} = 0$$

$$c_{+\text{or}-,2} = -x_{+\text{or}-}c_{+\text{or}-,1} \qquad \text{(i)}$$

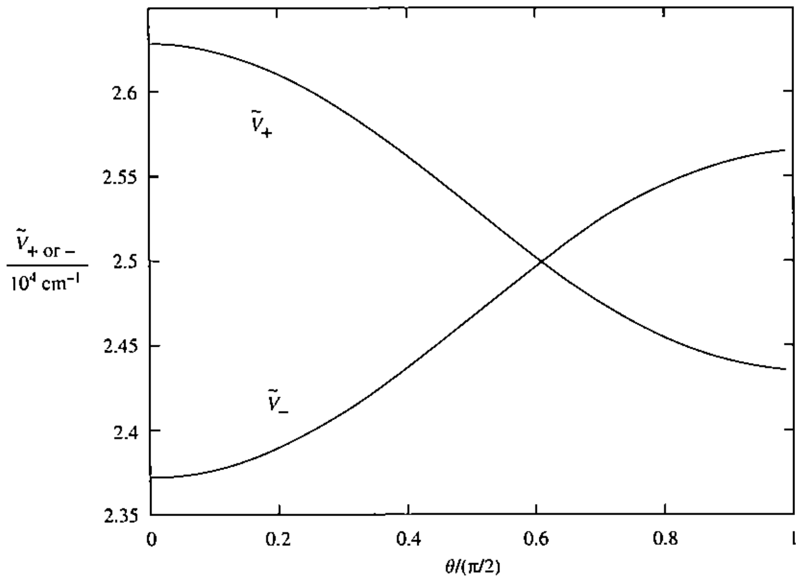



**Figure 20.4(b)**

The coefficients must also satisfy the normalization condition.

$$\begin{aligned}\langle\psi_{+\text{or}-}|\psi_{+\text{or}-}\rangle &= \langle c_{+\text{or}-,1}\psi_1 + c_{+\text{or}-,2}\psi_2|c_{+\text{or}-,1}\psi_1 + c_{+\text{or}-,2}\psi_2\rangle \\ &= c^2_{+\text{or}-,1} + c^2_{+\text{or}-,2} + 2c_{+\text{or}-,1}c_{+\text{or}-,2}S \\ &= c^2_{+\text{or}-,1} + c^2_{+\text{or}-,1} - 2x_{+\text{or}-}c^2_{+\text{or}-,1}S = 1 \qquad \text{(ii)}\end{aligned}$$

Thus,

$$c_{+,1} = \frac{1}{\{2(1-S)\}^{1/2}} \qquad c_{+,2} = -c_{+,1}$$

and

$$c_{-,1} = \frac{1}{\{2(1+S)\}^{1/2}} \qquad c_{-,2} = c_{-,1}$$

$$\frac{\mu_+^2}{\mu_-^2} = \left(\frac{\mu_+}{\mu_-}\right)^2 = \left(\frac{(c_{+,1}+c_{+,2})\,\mu_{\text{mon}}}{(c_{-,1}+c_{-,2})\,\mu_{\text{mon}}}\right)^2 = \left(\frac{c_{+,1}-c_{+,1}}{c_{-,1}+c_{-,1}}\right)^2 = 0$$

(c) The secular determinant for $N$ monomers has the dimension $N \times N$.

$$\begin{vmatrix} \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & V & 0 & \cdots \\ V & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & V & \cdots \\ 0 & V & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{vmatrix} = 0$$

$$\tilde{\nu}_{\text{dimer}} = \tilde{\nu}_{\text{mon}} + 2V\cos\left(\frac{k\pi}{N+1}\right) \qquad k = 1,2,3,\ldots,N \quad [20.21]$$

$$V = \beta(0) = \frac{\mu_{\rm mon}^2}{4\pi\varepsilon_0 hcr^3}\left(1 - 3\cos^2 0\right) = \frac{-\mu_{\rm mon}^2}{2\pi\varepsilon_0 hcr^3}$$

The plot in Figure 20.4(c) shows the dimer transitions for $\theta = 0$ and $N = 15$. The shape of the transition distribution changes slightly with $N$ and transition energies are symmetrically distributed around the monomer transition. The lowest energy transition changes only slightly with $N$ giving a value that goes to $25\,000\ \text{cm}^{-1} + 2V = 25\,000\ \text{cm}^{-1} + 2 \times (-1289\ \text{cm}^{-1}) = 22\,422\ \text{cm}^{-1}$ as $N \to \infty$.

Since the model considers only nearest neighbor interactions, the transition dipole moment of the lowest energy transition doesn't depend upon the size of the chain.

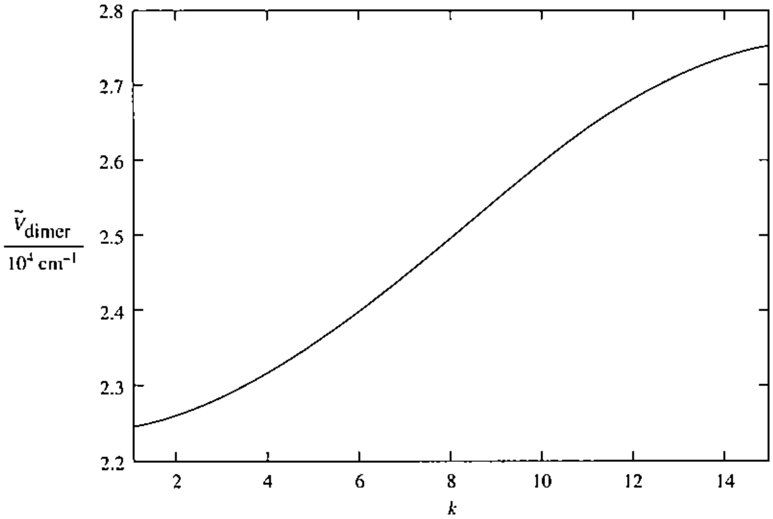



**Figure 20.4(c)**

**P20.20** The relationship between critical temperature and critical magnetic field is given by

$$H_{\rm c}(T) = H_{\rm c}(0)\left(1 - \frac{T^2}{T_{\rm c}^2}\right)$$

Solving for $T$ gives the critical temperature for a given magnetic field:

$$T = T_{\rm c}\left(1 - \frac{H_{\rm c}(T)}{H_{\rm c}(0)}\right)^{1/2} = (7.19\,\text{K}) \times \left(1 - \frac{20 \times 10^3\,\text{A m}^{-1}}{63901\,\text{A m}^{-1}}\right)^{1/2} = \boxed{6.0\,\text{K}}$$

## Solutions to theoretical problems

**P20.22** Consider for simplicity the two-dimensional lattice and planes shown in Figure 20.5.

The $(hk)$ planes cut the $a$ and $b$ axes at $a/h$ and $b/k$, and we have

$$\sin\alpha = \frac{d}{(a/h)} = \frac{hd}{a}, \qquad \cos\alpha = \frac{d}{(b/k)} = \frac{kd}{b}$$

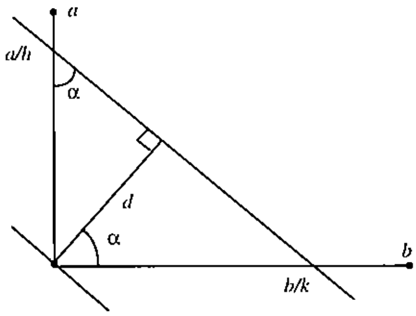



Figure 20.5

Then, since $\sin^2\alpha + \cos^2\alpha = 1$, we can write

$$\left(\frac{hd}{a}\right)^2 + \left(\frac{kd}{b}\right)^2 = 1$$

and therefore

$$\frac{1}{d^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2$$

The same argument extends by analogy (or further trigonometry) to three dimensions, to give

$$\boxed{\frac{1}{d^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}$$

**P20.24** $$f = \frac{NV_a}{V_c}$$

where $N$ is the number of atoms in each unit cell, $V_a$ their individual volumes, and $V_c$ the volume of the unit cell itself. Refer to Figure 20.6.

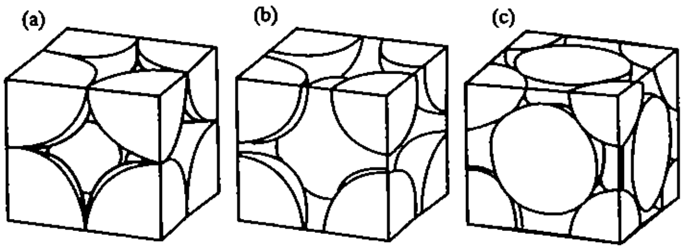



Figure 20.6

**(a)** $N = 1, \quad V_a = \frac{4}{3}\pi r^3, \quad V_c = (2R)^3$

$$f = \frac{\left(\frac{4}{3}\pi R^3\right)}{(2R)^3} = \frac{\pi}{6} = \boxed{0.5236}$$

**(b)** $N = 1, \quad V_a = \frac{4}{3}\pi r^3, \quad V_c = \left(\frac{4R}{\sqrt{3}}\right)^3$ [body diagonal of a unit cube is $\sqrt{3}$]

$$f = \frac{2 \times (4/3)\pi R^3}{\left(4R/\sqrt{3}\right)^3} = \frac{\pi\sqrt{3}}{8} = \boxed{0.6802}$$

**(c)** $N = 4, \quad V_a = \frac{4}{3}\pi R^3, \quad V_c = (2\sqrt{2}R)^3$

$$f = \frac{4 \times (4/3)\pi R^3}{(2\sqrt{2}R)^3} = \frac{\pi}{3\sqrt{2}} = \boxed{0.7405}$$

**P20.26** $F_{hkl} = \sum_i f_i e^{2\pi i(hx_i+ky_i+lz_i)}$ [20.7]

For each A atom use $\frac{1}{8}f_A$ (each A atom shared by eight cells) but use $f_B$ for the central atom (since it contributes solely to the cell).

$$F_{hkl} = \tfrac{1}{8}f_A\left\{1 + e^{2\pi ih} + e^{2\pi ik} + e^{2\pi il} + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(k+l)} + e^{2\pi i(h+k+l)}\right\}$$
$$+ f_B e^{2\pi i(h+k+l)}$$
$$= f_A + (-1)^{(h+k+l)} f_B \quad [h, k, l \text{ are all integers }, e^{i\pi} = -1]$$

**(a)** $f_A = f, \quad f_B = 0; \quad F_{hkl} = f$ $\boxed{\text{no systematic absences}}$

**(b)** $f_B = \frac{1}{2}f_A; \quad F_{hkl} = f_A\left[1 + \frac{1}{2}(-1)^{(h+k+l)}\right]$

Therefore, when $h+k+l$ is odd, $F_{hkl} = f_A\left(1 - \frac{1}{2}\right) = \frac{1}{2}f_A$, and when $h+k+l$ is even, $F_{hkl} = \frac{3}{2}f_A$.

That is, there is an $\boxed{\text{alternation of intensity}}$ $(I \propto F^2)$ according to $\boxed{\text{whether } h+k+l \text{ is odd or even}}$.

**(c)** $f_A = f_B = f; \quad F_{h+k+l} = f\left\{1 + (-1)^{h+k+l}\right\} = 0 \quad \text{if } h+k+l$ is odd.

Thus, $\boxed{\text{all } h+k+l \text{ odd lines are missing}}$.

**P20.28** **(a)** The density of energy levels is:

$$\rho(E) = \frac{dk}{dE} = \left(\frac{dE}{dk}\right)^{-1}$$

where $\dfrac{dE}{dk} = \dfrac{d}{dk}\left(\alpha + 2\beta\cos\dfrac{k\pi}{N+1}\right) = -\dfrac{2\pi\beta}{N+1}\sin\dfrac{k\pi}{N+1}$

so $\rho(E) = -\dfrac{N+1}{2\pi\beta}\left(\sin\dfrac{k\pi}{N+1}\right)^{-1}$

Unlike the expression just derived, the relationship the problem asks us to derive has no trigonometric functions and it contains $E$ and $\alpha$ within a square root. This comparison suggests that the trigonometric identity $\sin^2\theta + \cos^2\theta = 1$ will be of use here. Let $\theta = k\pi/(N+1)$; then

$$\sin\theta = 1(1-\cos^2\theta)^{1/2}$$

however, $\cos\theta$ is related to the energy

$$E = \alpha + 2\beta\cos\theta \quad \text{so} \quad \cos\theta = \frac{E-\alpha}{2\beta}$$

and $\sin\theta = \left[1 - \left(\dfrac{E-\alpha}{2\beta}\right)^2\right]^{1/2}$

Finally, $\boxed{\rho(E) = \dfrac{-(N+1)/2\pi\beta}{\left[1-(E-\alpha/2\beta)^2\right]^{1/2}}}$

**(b)** The denominator of this expression vanishes as the energy approaches $\alpha \pm 2\beta$. Near those limits, $E-\alpha$ becomes $\pm 2\beta$, making the quantity under the square root zero, and $\rho(E)$ approach infinity.

**P20.30** If a substance responds nonlinearly to an electric field $E$, then it induces a dipole moment:

$$\mu = \alpha E + \beta E^2.$$

If the electric field is oscillating at two frequencies, we can write the electric field as

$$E = E_1\cos\omega_1 t + E_2\cos\omega_2 t,$$

and the nonlinear response as

$$\beta E^2 = \beta(E_1\cos\omega_1 t + E_2\cos\omega_2 t)^2,$$
$$\beta E^2 = \beta(E_1^2\cos^2\omega_1 t + E_2^2\cos^2\omega_2 t + 2E_1E_2\cos\omega_1 t\cos\omega_2 t).$$

Application of trigonometric identities allows a product of cosines to be re-written as a sum:

$$\cos A\cos B = \tfrac{1}{2}\cos(A-B) + \tfrac{1}{2}\cos(A+B).$$

Using this result (a special case of which applies to the $\cos^2$ terms), yields:

$$\beta E^2 = \tfrac{1}{2}\beta[E_1^2(1+\cos 2\omega_1 t) + E^2(1+\cos 2\omega_2 t) + 2E_1E_2(\cos(\omega_1+\omega_2)t + \cos(\omega_1-\omega_2)t].$$

This expression includes responses at twice the original frequencies as well as at the sum and difference frequencies.

**P20.32** $N_2O_4(g) \overset{K}{\rightleftharpoons} 2NO_2(g)$

| | | |
|---|---|---|
| $(1-\alpha)n$ | $2\alpha n$ | amounts |
| $\dfrac{1-\alpha}{1+\alpha}$ | $\dfrac{2\alpha}{1+\alpha}$ | mole fractions |

$$\left(\frac{1-\alpha}{1+\alpha}\right)p \quad \left(\frac{2\alpha}{1+\alpha}\right)p \quad \text{partial pressures } [p \equiv p/p^{\ominus} \text{ here}]$$

$$K = \frac{(2\alpha/1+\alpha)^2 p}{(1-\alpha/1+\alpha)} = \frac{4\alpha^2}{1-\alpha^2}p$$

Now solve for $\alpha$.

$$\alpha^2 = \frac{K}{4p+K}, \qquad \alpha = \left(\frac{K}{4p+K}\right)^{1/2}$$

The degree of dimerization is $d = 1 - \alpha = 1 - \left(\frac{K}{4p+K}\right)^{1/2} = \boxed{1 - \left(\frac{1}{4(p/K)+1}\right)^{1/2}}$

The susceptibility varies in proportion to $\alpha = 1 - d$. As pressure increases, $\alpha$ decreases, and the susceptibility $\boxed{\text{decreases}}$.

To determine the effect of temperature we need $\Delta_r H \approx \Delta_r H^{\ominus}$ for the reaction above.

$$\Delta_r H^{\ominus} = 2 \times (33.18\,\text{kJ mol}^{-1}) - 9.16\,\text{kJ mol}^{-1} = +57.2\,\text{kJ mol}^{-1}$$

A positive $\Delta_r H^{\ominus}$ indicates that $NO_2(g)$ is favored as the temperature increases; hence the susceptibility $\boxed{\text{increases}}$ with temperature.

## Solutions to applications

**P20.34** The density of a face-centered cubic crystal is $4m/V$ where $m$ is the mass of the unit hung on each lattice point and $V$ is the volume of the unit cell. (The 4 comes from the fact that each of the cell's 8 vertices is shared by 8 cells, and each of the cell's 6 faces is shared by 2 cells.)

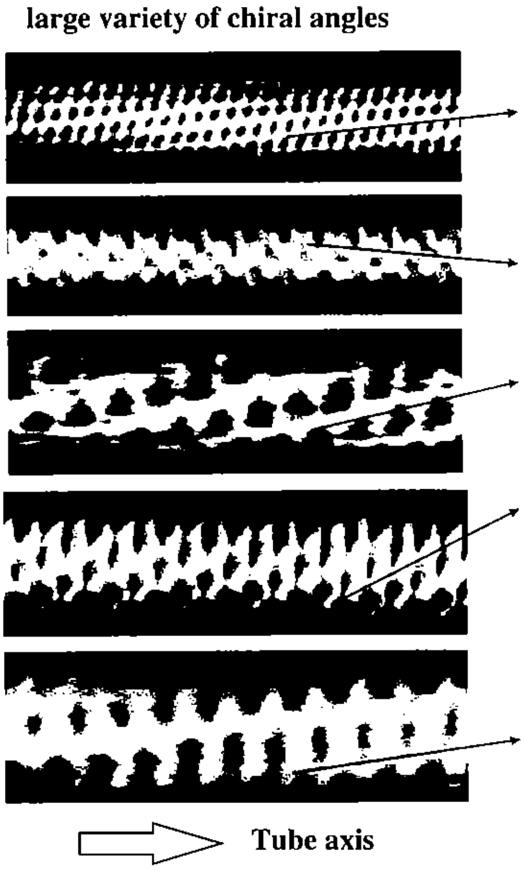
So $\rho = \frac{4m}{a^3} = \frac{4M}{N_A a^3}$ and $M = \frac{1}{4}\rho N_A a^3$

$$M = \tfrac{1}{4}(1.287\,\text{g cm}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \times (12.3 \times 10^{-7}\,\text{cm})^3$$

$$= \boxed{3.61 \times 10^5\,\text{g mol}^{-1}}$$

**P20.36** Single-walled carbon nanotubes (SWNT) may be either conductors or semiconductors depending upon the tube diameter and the chiral angle of the fused benzene rings with respect to the tube axis. Van der Waals forces cause SWNT to stick together in clumps, which are normally mixtures of conductors and semiconductors. SWNT stick to many surfaces and they bend, or drape, around nano-sized features that are upon a surface.

Only the semiconductor SWNT are suitable for the preparation of field-effect transistors (FET) so IBM researchers (*Science*, April 27, 2001) have developed a destructive technique for eliminating conducting tubes from conductor/semiconductor clumps with a current burst. The technique can also be used to remove the outer layers of multiwalled tubes that consist of multiple concentric tubes about a common axis. Bandgaps increase as the diameter of multiwalled tubes is decreased which means that the destructive technique can be used to tailor a semiconductor tube to specific requirements.

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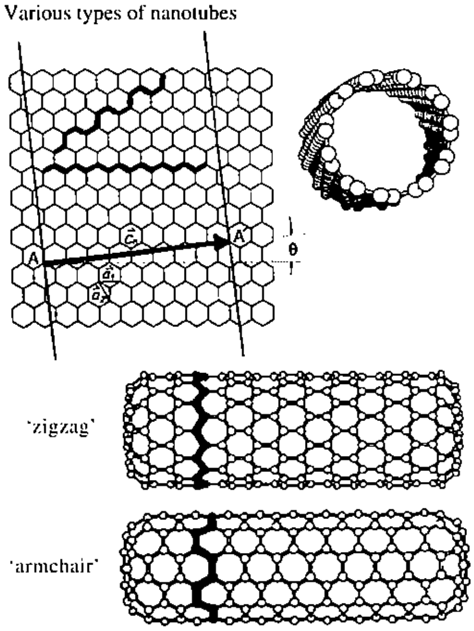


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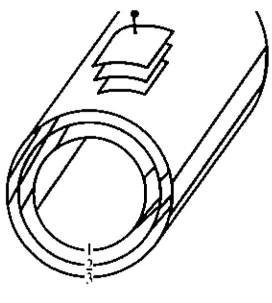



Multiwalled Nanotubes have diameters between 1 nm and 30 nm with an interlayer spacing of 0.34 nm.

http://online.itp.ucsb.edu/online/qhall_c98/dekker/oh/05.html

**Figure 20.7(a)**

Here is a list of ideas for producing transistors with SWNT.

Cees Dekker and students (S.J. Tans *et al.*, *Nature*, **393**, 49 (1998)) have draped a semiconducting carbon nanotube over metal electrodes that are 400 nm apart atop a silicon surface coated with silicon dioxide. A bias voltage between the electrodes provides the source and drain of an FET. The silicon serves as a gate electrode. By adjusting the magnitude of an electric field applied to the gate, current flow across the nanotube may be turned on and off.

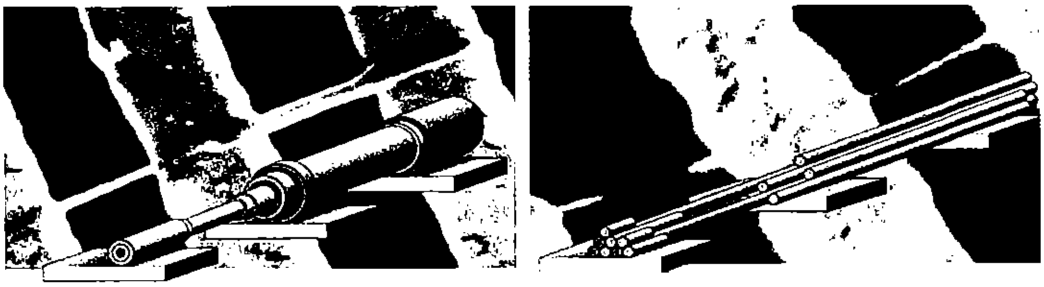
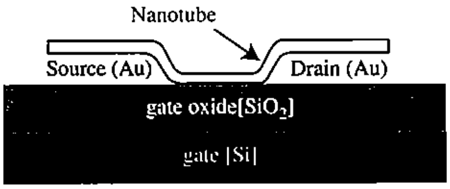


Figure 20.7(b)

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nanoscience/fet.html

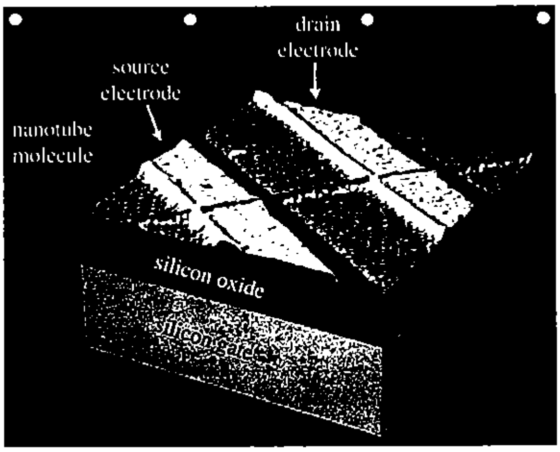


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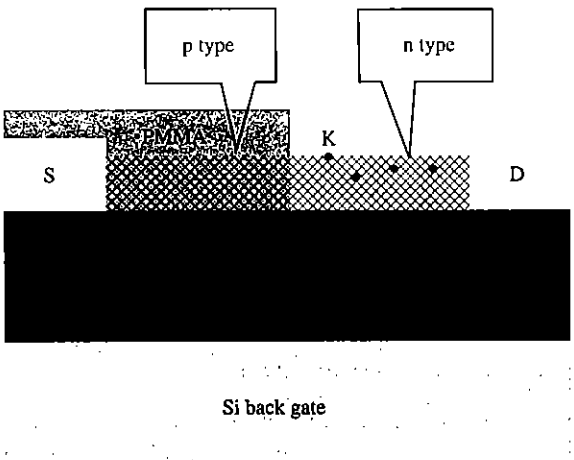
Figure 20.7(c)




http://www.usc.edu/dept/ee/People/Faculty/Zhou/zhougroup/research.html Figure 20.7(d)

A section of a single nanotube may be exposed to potassium vapor to produce a p–n junction.

A single-electron transistor (SET) has been prepared by Cees Dekker and coworkers (*Science*, **293**, 76, (2001)) with a conducting nanotube. The SET is prepared by putting two bends in a tube with the tip of an AFM. Bending causes two buckles that, at a distance of 20 nm, serves as a conductance barrier. When an appropriate voltage is applied to the gate below the barrier, electrons tunnel one at a time across the barrier.

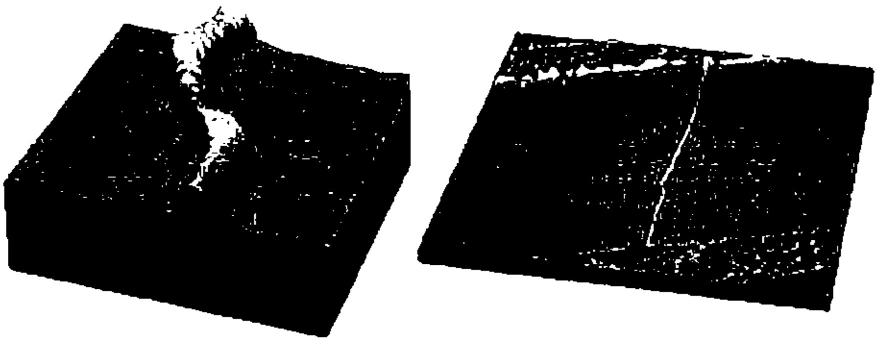
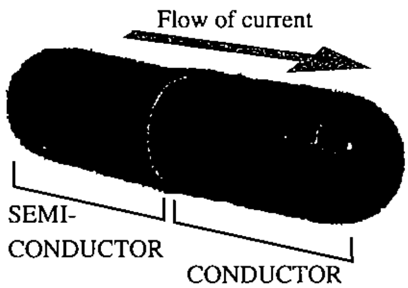


**Figure 20.7(e)**

A semiconductor tube may be fused to a conductor tube to produce a SET similar to an SET.




http://www.geocities.com/
fikrethasmer/physics/
electronic/electronic.html

**Figure 20.7(f)**

# PART 3 Change

# 21 Molecules in motion

## Answers to discussion questions

D21.2 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, also 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 (Figure 21.11 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.

**D21.4** 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 (Figure 21.16a 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 $H_2O\cdots H^+\cdots OH_2$ (Figure 21.16b). 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 (Figure 21.16c). According to this model, there is no coordinated motion of a proton along a chain of molecules, simply a very rapid hopping between neighboring 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.

**D21.6** The maximum flux in mediated transport is achieved at very high concentrations of the transported species. Under such conditions, the transported species A flood the carrier species C, pushing practically all of the latter into the form of the AC complex. (The mathematical condition for saturation of the flux at $J_{max}$ is that $[A] \gg K$, the equilibrium constant for dissociation of the AC complex; this condition puts practically all C into the complex, regardless of its inherent stability.) The value of $J_{max}$ depends on the concentration of carrier species, $[C]_0$. For a given value of $[C]_0, J_{max}$ represents the transport capacity of the "fleet" of carriers. The oversupply of A keeps the carriers transporting at full capacity.

## Solutions to exercises

**E21.1(b)** **(a)** The mean speed of a gas molecule is

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

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

**(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 $\boxed{1}$

**E21.2(b)** **(a)** The mean speed can be calculated from the formula derived in Example 21.1.

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

**(b)** The mean free path is calculated from $\lambda = kT/(2^{1/2}\sigma p)$ [21.13] 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 21.11, but is most easily obtained from eqn 21.12, since $\lambda$ and $\bar{c}$ 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.

**E21.3(b)**

$$p = \frac{kT}{2^{1/2}\sigma\lambda} \quad [21.13]$$

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

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

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.

**E21.4(b)** The mean free path is

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

**E21.5(b)** Obtain data from Exercise 21.4(b)

The expression for $z$ obtained in Exercise 21.5(a) is $z = [16/(\pi mkT)]^{1/2}\,\sigma p$

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

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

$$= \boxed{9.9 \times 10^8\,\text{s}^{-1}}$$

**E21.6(b)** The mean free path is

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

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

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

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

**E21.7(b)** The fraction $F$ of molecules in the speed range from 200 to 250 m s$^{-1}$ is

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

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

$$F \approx 4\pi \left(\frac{44.0 \times 10^{-3}\,\text{kg mol}^{-1}}{2\pi\,(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (300\,\text{K})}\right)^{3/2} \times \left(225\,\text{m s}^{-1}\right)^{2}$$

$$\times \exp\left(\frac{-\left(44.0 \times 10^{-3}\,\text{kg mol}^{-1}\right) \times \left(225\,\text{m s}^{-1}\right)^{2}}{2\,(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (300\,\text{K})}\right) \times \left(50\,\text{m s}^{-1}\right),$$

$$\boxed{F \approx 9.6 \times 10^{-2}}$$

**COMMENT.** The approximation we have employed, taking $f(v)$ to be nearly constant over a narrow range of speeds, might not be accurate enough, for that range of speeds includes about 10 percent of the molecules. You may wish to do the integration without this approximation (a considerably more complicated process) to see how much difference there is.

**E21.8(b)** The number of collisions is

$$N = Z_{W}At = \frac{pAt}{(2\pi mkT)^{1/2}}$$

$$= \frac{(111\,\text{Pa}) \times \left(3.5 \times 10^{-3}\,\text{m}\right) \times \left(4.0 \times 10^{-2}\,\text{m}\right) \times (10\,\text{s})}{\left\{2\pi \times (4.00\,\text{u}) \times \left(1.66 \times 10^{-27}\,\text{kg u}^{-1}\right) \times \left(1.381 \times 10^{-23}\,\text{J K}^{-1}\right) \times (1500\,\text{K})\right\}^{1/2}}$$

$$= \boxed{5.3 \times 10^{21}}$$

**E21.9(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

$$\Delta m = mN = mZ_{\mathrm{W}}At = \frac{mpAt}{(2\pi mkT)^{1/2}} = pAt\left(\frac{m}{2\pi kT}\right)^{1/2} = pAt\left(\frac{M}{2\pi RT}\right)^{1/2}$$

$$= (0.224\,\mathrm{Pa}) \times \pi \times \left(\tfrac{1}{2} \times 3.00 \times 10^{-3}\,\mathrm{m}\right)^2 \times (24.00\,\mathrm{h}) \times \left(3600\,\mathrm{s\,h^{-1}}\right)$$

$$\times \left\{\frac{300 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}}{2\pi \times \left(8.3145\,\mathrm{J\,K^{-1}mol^{-1}}\right) \times (450\,\mathrm{K})}\right\}^{1/2}$$

$$= \boxed{4.98 \times 10^{-4}\,\mathrm{kg}}$$

**E21.10(b)** The time dependence of the pressure of a gas effusing without replenishment is

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

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 $\tau$ 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

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

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

**E21.11(b)** The time dependence of the pressure of a gas effusion without replenishment is

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

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

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

so $t = \left(8.6 \times 10^5\,\mathrm{s}\right) \ln \dfrac{122\,\mathrm{kPa}}{105\,\mathrm{kPa}} = \boxed{1.5 \times 10^4\,\mathrm{s}}$

**E21.12(b)** The flux is

$$J = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{1}{3}\lambda C_{V,\mathrm{m}}\bar{c}\,[\mathrm{X}]\,\frac{\mathrm{d}T}{\mathrm{d}z}$$

where the minus sign indicates flow toward lower temperature and

$$\lambda = \frac{1}{\sqrt{2}N\sigma}, \quad \bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}, \quad \text{and } [\mathrm{M}] = n/V = N/N_{\mathrm{A}}$$

$$\text{So } J = -\frac{2C_{V,\mathrm{m}}}{3\sigma N_{\mathrm{A}}}\left(\frac{RT}{\pi M}\right)^{1/2}\frac{\mathrm{d}T}{\mathrm{d}z}$$

$$= \left(\frac{2 \times (28.832 - 8.3145)\ \mathrm{J\,K^{-1}\,mol^{-1}}}{3 \times \left[0.27 \times \left(10^{-9}\,\mathrm{m}\right)^2\right] \times \left(6.022 \times 10^{23}\,\mathrm{mol^{-1}}\right)}\right)$$

$$\times \left(\frac{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right) \times (260\,\mathrm{K})}{\pi \times \left(2.016 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}\right)}\right)^{1/2} \times \left(3.5\,\mathrm{K\,m^{-1}}\right)$$

$$= \boxed{0.17\,\mathrm{J\,m^{-2}\,s^{-1}}}$$

**E21.13(b)** The thermal conductivity is

$$\kappa = \frac{1}{3}\lambda C_{V,\mathrm{m}}\bar{c}\,[\mathrm{X}] = \frac{2C_{V,\mathrm{m}}}{3\sigma N_{\mathrm{A}}}\left(\frac{RT}{\pi M}\right)^{1/2} \quad \text{so } \sigma = \frac{2C_{V,\mathrm{m}}}{3\kappa N_{\mathrm{A}}}\left(\frac{RT}{\pi M}\right)^{1/2}$$

$$\kappa = \left(0.240\,\mathrm{mJ\,cm^{-2}\,s^{-1}}\right) \times \left(\mathrm{K\,cm^{-1}}\right)^{-1} = 0.240 \times 10^{-1}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$$

$$\text{so } \sigma = \left(\frac{2 \times (29.125 - 8.3145)\,\mathrm{J\,K^{-1}\,mol^{-1}}}{3 \times \left(0.240 \times 10^{-1}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}\right) \times \left(6.022 \times 10^{23}\,\mathrm{mol^{-1}}\right)}\right)$$

$$\times \left(\frac{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right) \times (298\,\mathrm{K})}{\pi \times \left(28.013 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}\right)}\right)^{1/2}$$

$$= \boxed{1.61 \times 10^{-19}\,\mathrm{m^2}}$$

**E21.14(b)** Assuming the space between sheets is filled with air, the flux is

$$J = -k\frac{\mathrm{d}T}{\mathrm{d}z} = \left[\left(0.241 \times 10^{-3}\,\mathrm{J\,cm^{-2}\,s^{-1}}\right) \times \left(\mathrm{K\,cm^{-1}}\right)^{-1}\right] \times \left(\frac{[50 - (-10)\ \mathrm{K}]}{10.0\,\mathrm{cm}}\right)$$

$$= 1.4\bar{5} \times 10^{-3}\,\mathrm{J\,cm^{-2}\,s^{-1}}.$$

So the rate of energy transfer and energy loss is

$$JA = \left(1.4\bar{5} \times 10^{-3}\,\mathrm{J\,cm^{-2}\,s^{-1}}\right) \times \left(1.50\,\mathrm{m^2}\right) \times \left(100\,\mathrm{cm\,m^{-1}}\right)^2 = \boxed{22\,\mathrm{J\,s^{-1}}}$$

**E21.15(b)** The coefficient of viscosity is

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

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

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

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

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

**E21.16(b)** The rate of fluid flow through a tube is described by

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

Several of the parameters need to be converted to SI units

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

$$\text{and } \frac{\text{d}V}{\text{d}t} = 8.70\,\text{cm}^3 \times (10^{-2}\,\text{m cm}^{-1})^3\,\text{s}^{-1} = 8.70 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1}.$$

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

$$\eta\,(300\,\text{K}) = \eta\,(293\,\text{K}) \times \left(\frac{300\,\text{K}}{293\,\text{K}}\right)^{1/2} = (176 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1}) \times \left(\frac{300}{293}\right)^{1/2}$$

$$= 1.78 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1}$$

$$p_{\text{in}} = \left\{\left(\frac{16\,(10.5\,\text{m}) \times (178 \times 10^{-7}\,\text{kg m}^{-1}\text{s}^{-1}) \times (1.00 \times 10^5\,\text{Pa})}{\pi \times (7.5 \times 10^{-3}\,\text{m})^4}\right)\right.$$

$$\left. \times\ (8.70 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1}) + (1.00 \times 10^5\,\text{Pa})^2\right\}^{1/2}$$

$$= \boxed{1.00 \times 10^5\,\text{Pa}}$$

**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!

**E21.17(b)** The coefficient of viscosity is

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

$$= \left(\frac{2}{3\left[0.88 \times (10^{-9}\,\text{m})^2\right]}\right) \times \left(\frac{(78.12 \times 10^{-3}\,\text{kg mol}^{-1}) \times (1.381 \times 10^{-23}\,\text{J K}^{-1})\,T}{\pi \times (6.022 \times 10^{23}\,\text{mol}^{-1})}\right)^{1/2}$$

$$= 5.7\overline{2} \times 10^{-7} \times (T/\text{K})^{1/2}\,\text{kg m}^{-1}\,\text{s}^{-1}$$

(a) At 273 $K$ $\eta = (5.7\bar{2} \times 10^{-7}) \times (273)^{1/2}\ \mathrm{kg\,m^{-1}\,s^{-1}} = \boxed{0.95 \times 10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}}$

(b) At 298 K $\eta = (5.7\bar{2} \times 10^{-7}) \times (298)^{1/2}\ \mathrm{kg\,m^{-1}\,s^{-1}} = \boxed{0.99 \times 10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}}$

(c) At 1000 K $\eta = (5.7\bar{2} \times 10^{-7}) \times (1000)^{1/2}\ \mathrm{kg\,m^{-1}\,s^{-1}} = \boxed{1.81 \times 10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}}$

**E21.18(b)** The thermal conductivity is

$$k = \tfrac{1}{3}\lambda C_{V,\mathrm{m}}\bar{c}\,[\mathrm{X}] = \frac{2C_{V,\mathrm{m}}}{3\sigma N_{\mathrm{A}}}\left(\frac{RT}{\pi M}\right)^{1/2}$$

(a)
$$\kappa = \left(\frac{2 \times \left[(20.786 - 8.3145)\ \mathrm{J\,K^{-1}\,mol^{-1}}\right]}{3\left[0.24 \times \left(10^{-9}\,\mathrm{m}\right)^2\right] \times \left(6.022 \times 10^{23}\,\mathrm{mol^{-1}}\right)}\right)$$
$$\times \left(\frac{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right) \times (300\,\mathrm{K})}{\pi\left(20.18 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}\right)}\right)^{1/2}$$
$$= \boxed{0.011\bar{4}\ \mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}}$$

The flux is

$$J = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} = \left(0.011\bar{4}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}\right) \times \left(\frac{(305 - 295)\ \mathrm{K}}{0.15\,\mathrm{m}}\right) = 0.76\,\mathrm{J\,m^{-2}\,s^{-1}}$$

so the rate of energy loss is

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

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

The flux is

$$J = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} = \left(9.0 \times 10^{-3}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}\right) \times \left(\frac{(305 - 295)\ \mathrm{K}}{0.15\,\mathrm{m}}\right) = 0.60\,\mathrm{J\,m^{-2}\,s^{-1}}$$

so the rate of energy loss is

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

**E21.19(b)** The rate of fluid flow through a tube is described by

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\left(p_{\mathrm{in}}^2 - p_{\mathrm{out}}^2\right)\pi r^4}{16l\eta p_0}$$

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

$$\frac{t_1}{t_2} = \frac{\eta_1}{\eta_2} \quad \text{so } \eta_2 = \frac{\eta_1 t_2}{t_1}$$

$$\eta_{\text{CFC}} = \frac{(208\,\mu\text{P}) \times (18.0\,\text{s})}{72.0\,\text{s}} = \boxed{52.0\,\mu\text{P}} = 52.0 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1}$$

The coefficient of viscosity is

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

so the molecular diameter is

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

**E21.20(b)**

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

**E21.21(b)** The diffusion constant is

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

The flux due to diffusion is

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

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

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

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

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

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

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

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

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

**E21.22(b)** Molar ionic conductivity is related to mobility by

$$\lambda = zuF = (1) \times \left(4.24 \times 10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}\right) \times \left(96485\,\mathrm{C\,mol^{-1}}\right)$$
$$= \boxed{4.09 \times 10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}}$$

**E21.23(b)** The drift speed is given by

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

**E21.24(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 $10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$.)

**E21.25(b)** The limiting molar conductivity of a dissolved salt is the sum of that of its ions, so

$$\Lambda_\mathrm{m}^\circ(\mathrm{MgI_2}) = \lambda\left(\mathrm{Mg^{2+}}\right) + 2\lambda\left(\mathrm{I^-}\right) = \Lambda_\mathrm{m}^\circ(\mathrm{Mg(C_2H_3O_2)_2}) + 2\Lambda_\mathrm{m}^\circ(\mathrm{NaI}) - 2\Lambda_\mathrm{m}^\circ(\mathrm{NaC_2H_3O_2})$$
$$= (18.78 + 2(12.69) - 2(9.10))\ \mathrm{mS\,m^2mol^{-1}} = \boxed{25.96\,\mathrm{mS\,m^2\,mol^{-1}}}$$

**E21.26(b)** Molar ionic conductivity is related to mobility by

$$\lambda = z\mu F \quad \text{so} \quad u = \frac{\lambda}{zF}$$

$$\mathrm{F^-}: \quad u = \frac{5.54 \times 10^{-3}\,\mathrm{S\,m^2mol^{-1}}}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})} = \boxed{5.74 \times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}$$

$$\mathrm{Cl^-}: \quad u = \frac{7.635 \times 10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})} = \boxed{7.913 \times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}$$

$$\mathrm{Br^-}: \quad u = \frac{7.81 \times 10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})} = \boxed{8.09 \times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}$$

**E21.27(b)** The diffusion constant is related to the mobility by

$$D = \frac{uRT}{zF} = \frac{(4.24 \times 10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})}$$

$$= \boxed{1.09 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}}$$

**E21.28(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

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

**E21.29(b)** The diffusion constant is related to the viscosity of the medium and the size of the diffusing molecule as follows

$$D = \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{kT}{6\pi\eta D} = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{6\pi\,(1.00 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}) \times (1.055 \times 10^{-9}\,\mathrm{m^2\,s^{-1}})}$$

$$a = 2.07 \times 10^{-10}\,\mathrm{m} = \boxed{207\,\mathrm{pm}}$$

**E21.30(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

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

$$\text{and } \tau = \frac{(kT)^2}{18(\pi\eta)^2 D^3} = \frac{\left[(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})\right]^2}{18\left[\pi\,(0.387\times10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})\right]^2\times(3.17\times10^{-9}\,\mathrm{m^2\,s^{-1}})^3}$$

$$= \boxed{200\times10^{-11}\,\mathrm{s}} = 20\,\mathrm{ps}$$

**E21.31(b)** The mean square displacement is (from Exercise 21.28(b))

$$\langle r^2\rangle = 6Dt \quad \text{so} \quad t = \frac{\langle r^2\rangle}{6D} = \frac{(1.0\times10^{-6}\,\mathrm{m})^2}{6(1.0\times10^{-11}\,\mathrm{m^2\,s^{-1}})} = \boxed{1.7\times10^{-2}\,\mathrm{s}}$$

## Solutions to problems

### Solutions to numerical problems

**P21.2** For discrete rather than continuous variables the equation analogous to the equation for obtaining $\bar{c}$ (Example 21.1) is $\langle v_x\rangle = \sum_i v_{i,x}\ (N_i/N) = (1/N)\sum_i N_i v_{i,x}$ with $(N_i/N)$ the analogue of $f(v)$

$$N = 40+62+53+12+2+38+59+60+2 = 328$$

(a) $$\langle v_x\rangle = \frac{1}{328}\{40\times80+62\times85+\cdots+2\times100+38\times(-80)$$
$$+59\times(-85)+\cdots+2\times(-100)\}\,\mathrm{km\,h^{-1}}$$
$$= \boxed{2.8\,\mathrm{km\,h^{-1}}}\ \text{east}$$

(b) $$\langle |v_x|\rangle = \frac{1}{328}\{40\times80+62\times85+\cdots+2\times100+38\times80$$
$$+59\times85+\cdots+2\times100\}\,\mathrm{km\,h^{-1}}$$
$$= \boxed{86\,\mathrm{km\,h^{-1}}}$$

(c) $$\langle v_x^2\rangle = \frac{1}{328}\{40\times80^2+62\times85^2+\cdots+2\times100^2\}(\mathrm{km\,h^{-1}})^2 = 7430\,(\mathrm{km\,h^{-1}})^2$$

$$\sqrt{\langle v_x^2\rangle} = \boxed{86\,\mathrm{km\,h^{-1}}} \quad \left[\text{that } \sqrt{\langle v_x^2\rangle} = \langle|v_x|\rangle \text{ in this case is coincidental.}\right]$$

**P21.4** $$\kappa = \tfrac{1}{3}\lambda\bar{c}C_{V,\mathrm{m}}[\mathrm{A}]\ [21.23]$$

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2}[21.7] \propto T^{1/2}$$

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

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

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

**P21.6** Radioactive decay follows first-order kinetics (Chapter 22); hence the two contributions to the rate of change of the number of helium atoms are

$$\frac{dN}{dt} = k_r[\mathrm{Bk}] \text{ (radioactive decay) } \frac{dN}{dt} = -Z_W[A] \quad \text{[Problem21.5]}$$

Therefore, the total rate of change is

$$\frac{dN}{dt} = k_r[\mathrm{Bk}] - Z_W A \text{ with } Z_W = \frac{p}{(2\pi mkT)^{1/2}}$$

$$[\mathrm{Bk}] = [\mathrm{Bk}]_0 e^{-k_r t} \text{ and } p = \frac{nRT}{V} = \frac{nN_A kT}{V} = \frac{NkT}{V}$$

Therefore, the pressure of helium inside the container obeys

$$\frac{dp}{dt} = \frac{kT}{V}\frac{dN}{dt} = \frac{kk_r T}{V}[\mathrm{Bk}]_0 e^{-k_r t} - \frac{(pAkT/V)}{(2\pi mkT)^{1/2}}$$

If we write $a = \dfrac{kk_r T[\mathrm{Bk}]_0}{V}$, $b = \left(\dfrac{A}{V}\right) \times \left(\dfrac{kT}{2\pi m}\right)^{1/2}$, the rate equation becomes

$$\frac{dp}{dt} = ae^{-k_r t} - bp, \quad p = 0 \text{ at } t = 0$$

which is a first-order linear differential equation with the solution

$$p = \left(\frac{a}{k_r - b}\right) \times \left(e^{-bt} - e^{-k_r t}\right)$$

Since $[\mathrm{Bk}] = \frac{1}{2}[\mathrm{Bk}]_0$ when $t = 4.4\,\mathrm{h}$, it follows from the radioactive decay law ($[\mathrm{Bk}] = [\mathrm{Bk}]_0 e^{-k_r t}$) that (Chapter 22)

$$k_r = \frac{\ln 2}{(4.4) \times (3600\,\mathrm{s})} = 4.4 \times 10^{-5}\,\mathrm{s^{-1}}$$

We also know that $[\mathrm{Bk}]_0 = \left(\dfrac{1.0 \times 10^{-3}\,\mathrm{g}}{244\,\mathrm{g\,mol^{-1}}}\right) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) = 2.5 \times 10^{18}$

$$\text{Then, } a = \frac{kk_r T[\mathrm{Bk}]_0}{V} = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (4.4 \times 10^{-5}\,\mathrm{s^{-1}}) \times (298\,\mathrm{K}) \times (2.5 \times 10^{18})}{1.0 \times 10^{-6}\,\mathrm{m^3}}$$

$$= 0.45\,\mathrm{Pa\,s^{-1}}$$

$$\text{and } b = \left(\frac{\pi \times (2.0 \times 10^{-6}\,\mathrm{m})^2}{1.0 \times 10^{-6}\,\mathrm{m^3}}\right) \times \left(\frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{(2\pi) \times (4.0) \times (1.6605 \times 10^{-27}\,\mathrm{kg})}\right)^{1/2} = 3.9 \times 10^{-3}\,\mathrm{s^{-1}}$$

$$\text{Hence, } p = \left(\frac{0.45\,\mathrm{Pa\,s^{-1}}}{[(4.4 \times 10^{-5}) - (3.9 \times 10^{-3})]\,\mathrm{s^{-1}}}\right) \times (e^{-3.9\times10^{-3}(t/s)} - e^{-4.4\times10^{-5}(t/s)})$$

$$= (120\,\mathrm{Pa}) \times (e^{-4.4\times10^{-5}(t/s)} - e^{-3.9\times10^{-3}(t/s)})$$

**(a)** $t = 1\,\text{h}, \quad p = (120\,\text{Pa}) \times (e^{-0.16} - e^{-14}) = \boxed{100\,\text{Pa}}$

**(b)** $t = 10\,\text{h}, \quad p = (120\,\text{Pa}) \times (e^{-1.6} - e^{140}) = \boxed{24\,\text{Pa}}$

**P21.8** $\kappa \propto \dfrac{1}{R}$ [21.27, and the discussion above 21.27]

Because both solutions are aqueous their conductivities include a contribution of $76\,\text{mS m}^{-1}$ from the water. Therefore,

$$\frac{\kappa(\text{acid soln})}{\kappa(\text{KCl soln})} = \frac{\kappa(\text{acid}) + \kappa(\text{water})}{\kappa(\text{KCl}) + \kappa(\text{water})} = \frac{R(\text{KCl soln})}{R(\text{acid soln})} = \frac{33.21\,\Omega}{300.0\,\Omega}$$

Hence, $\kappa(\text{acid}) = \{\kappa(\text{KCl}) + \kappa(\text{water})\} \times \left(\dfrac{33.21}{300.0}\right) - \kappa(\text{water}) = 53\,\text{mS m}^{-1}$

$$\Lambda_{\text{m}} = \frac{\kappa}{c} = \frac{53\,\text{mS m}^{-1}}{1.00 \times 10^{5}\,\text{mol m}^{-3}} = \boxed{5.3 \times 10^{-4}\,\text{mS m}^2\,\text{mol}^{-1}}$$

**P21.10** $c = \dfrac{\kappa}{\Lambda_{\text{m}}}$ [21.28] $\approx \dfrac{\kappa}{\Lambda_{\text{m}}^{\circ}}$ [$c$ small, conductivity of water allowed for in the data]

$$c \approx \frac{1.887 \times 10^{-6}\,\text{S cm}^{-1}}{138.3\,\text{S cm}^2\,\text{mol}^{-1}} \quad \text{[Exercise 21.25(a)]}$$

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

**P21.12** $t(\text{H}^+) = \dfrac{u(\text{H}^+)}{u(\text{H}^+) + u(\text{Cl}^-)}$ [21.49b] $= \dfrac{3.623}{3.623 + 0.791} = \boxed{0.82}$

When a third ion is present we use

$$t(\text{H}^+) = \frac{I(\text{H}^+)}{I(\text{H}^+) + I(\text{Na}^+) + I(\text{Cl}^-)} \quad [21.47]$$

For each $I$, $I = zuvc\,FA\mathcal{E} = \text{constant} \times cu$. Hence, when NaCl is added

$$t(\text{H}^+) = \frac{c(\text{H}^+)\,u(\text{H}^+)}{c(\text{H}^+)\,u(\text{H}^+) + c(\text{Na}^+)\,u(\text{Na}^+) + c(\text{Cl}^-)\,u(\text{Cl}^-)}$$

$$= \frac{(1.0 \times 10^{-3}) \times (3.623)}{(1.0 \times 10^{-3}) \times (3.623) + (1.0) \times (0.519) + (1.001) \times (0.791)} = \boxed{0.0028}$$

**P21.14** $t_+ = \left(\dfrac{zcAF}{I}\right) \times \left(\dfrac{x}{\Delta t}\right)$ [Problem 21.13]

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

$$c/(\text{mol dm}^{-3}) = \rho/(\text{kg dm}^{-3}) \times m/(\text{mol kg}^{-1})$$

which holds for dilute solutions such as these.

$$A = \pi r^2 = \pi \times \left(2.073 \times 10^{-3}\,\text{m}\right)^2 = 1.350 \times 10^{-5}\,\text{m}^2$$

$$\frac{czAF}{I\Delta t} = \frac{(1.350 \times 10^{-5}\,\mathrm{m^2}) \times (9.6485 \times 10^4\,\mathrm{C\,mol^{-1}})}{(5.000 \times 10^{-3}\,\mathrm{A}) \times (2500\,\mathrm{s})} \times c = \left(0.1042\,\mathrm{m^2\,mol^{-1}}\right) \times c$$
$$= \left(0.1042\,\mathrm{m^2\,mol^{-1}}\right) \times \rho \times m = \left(0.1042\,\mathrm{m^2\,mol^{-1}}\right) \times \left(682\,\mathrm{kg\,m^{-3}}\right) \times m$$
$$= \left(71.0\bar{6}\,\mathrm{kg\,m^{-1}\,mol^{-1}}\right) \times m = \left(0.0710\bar{6}\,\mathrm{kg\,mm^{-1}\,mol^{-1}}\right) \times m$$

and so $t_+ = \left(0.0710\bar{6}\,\mathrm{kg\,mm^{-1}mol^{-1}}\right) \times x \times m$

In the first solution $t_+ = \left(0.0710\bar{6}\,\mathrm{kg\,mm^{-1}\,mol^{-1}}\right) \times (286.9\,\mathrm{mm}) \times \left(0.01365\,\mathrm{mol\,kg^{-1}}\right) = \boxed{0.278}$

In the second solution $t_+ = \left(0.0710\bar{6}\,\mathrm{kg\,mm^{-1}\,mol^{-1}}\right) \times (92.03\,\mathrm{mm}) \times \left(0.04255\,\mathrm{mol\,kg^{-1}}\right) = \boxed{0.278}$

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

**P21.16**

$$D = \frac{uRT}{zF}\ [21.63] \quad \text{and} \quad a = \frac{ze}{6\pi\eta u}\ [21.43]$$

$$D = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K}) \times u}{9.6485 \times 10^4\,\mathrm{C\,mol^{-1}}} = 2.569 \times 10^{-2}\,\mathrm{V} \times u$$

so $D/(\mathrm{cm^2\,s^{-1}}) = (2.569 \times 10^{-2}) \times u/(\mathrm{cm^2\,s^{-1}\,V^{-1}})$

$$a = \frac{1.602 \times 10^{-19}\,\mathrm{C}}{(6\pi) \times (0.891 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}) \times u}$$
$$= \frac{9.54 \times 10^{-18}\,\mathrm{C\,kg^{-1}\,ms}}{u} = \frac{9.54 \times 10^{-18}\,\mathrm{V^{-1}\,m^3\,s^{-1}}}{u}(1\,\mathrm{J} = 1\,\mathrm{C\,V}, 1\,\mathrm{J} = 1\,\mathrm{kg\,m^2\,s^{-2}})$$

and so $a/\mathrm{m} = \dfrac{9.54 \times 10^{-14}}{u/\mathrm{cm^2\,s^{-1}\,V^{-1}}}$

and therefore $a/\mathrm{pm} = \dfrac{9.54 \times 10^{-2}}{u/\mathrm{cm^2\,s^{-1}\,V^{-1}}}$

We can now draw up the following table using data from Table 21.6

| | $\mathrm{Li^+}$ | $\mathrm{Na^+}$ | $\mathrm{K^+}$ | $\mathrm{Rb^+}$ |
|---|---|---|---|---|
| $10^4u/(\mathrm{cm^2\,s^{-1}\,V^{-1}})$ | 4.01 | 5.19 | 7.62 | 7.92 |
| $10^5D/\mathrm{cm^2}$ | 1.03 | 1.33 | 1.96 | 2.04 |
| $a/\mathrm{pm}$ | 238 | 184 | 125 | 120 |

The ionic radii themselves (i.e. their crystallographic radii) are

| | $\mathrm{Li^+}$ | $\mathrm{Na^+}$ | $\mathrm{K^+}$ | $\mathrm{Rb^+}$ |
|---|---|---|---|---|
| $r_+/\mathrm{pm}$ | 59 | 102 | 138 | 149 |

and it would seem that $K^+$ and $Rb^+$ have effective hydrodynamic radii that are smaller than their ionic radii. The effective hydrodynamic and ionic volumes of $Li^+$ and $Na^+$ are $(4\pi/3)\pi a^3$ and $(4\pi/3)\pi r_+^3$ respectively, and so the volumes occupied by hydrating water molecules are

(a) $Li^+$ $\Delta V = (4\pi/3) \times (212^3 - 59^3) \times 10^{-36}\,\text{m}^3 = 5.5\bar{6} \times 10^{-29}\,\text{m}^3$

(b) $Na^+$ $\Delta V = (4\pi/3) \times (164^3 - 102^3) \times 10^{-36}\,\text{m}^3 = 2.1\bar{6} \times 10^{-29}\,\text{m}^3$

The volume occupied by a single $H_2O$ molecule is approximately $(4\pi/3) \times (150\,\text{pm})^3 = 1.4 \times 10^{-29}\,\text{m}^3$.

Therefore, $Li^+$ has about $\boxed{\text{four}}$ firmly attached $H_2O$ molecules whereas $Na^+$ has only $\boxed{\text{one to two}}$ (according to this analysis).

**P21.18** This is essentially one-dimensional diffusion and therefore eqn 21.72 applies.

$$c = \frac{n_0 e^{-x^2/4Dt}}{A(\pi Dt)^{1/2}}\ [21.72]$$

and we know that $n_0 = \left(\dfrac{10\,\text{g}}{342\,\text{g mol}^{-1}}\right) = 0.0292\,\text{mol}$

$$A = \pi R^2 = 19.6\,\text{cm}^2,\quad D = 5.21 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}\ [\text{Table21.8}]$$

$$A(\pi Dt)^{1/2} = (19.6\,\text{cm}^2) \times [(\pi) \times (5.21 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}) \times (t)]^{1/2}$$
$$= 7.93 \times 10^{-2}\,\text{cm}^3 \times (t/\text{s})^{1/2}$$

$$\frac{x^2}{4Dt} = \frac{25\,\text{cm}^2}{(4) \times (5.21 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}) \times t} = \frac{1.20 \times 10^6}{(t/\text{s})}$$

$$\text{Therefore, } c = \left(\frac{0.0292\,\text{mol} \times 10^{22}}{(7.93 \times 10^{-2}\,\text{cm}^3) \times (t/\text{s})^{1/2}}\right) \times e^{-1.20\times 10^6/(t/\text{s})}$$
$$= (369\,\text{M}) \times \left(\frac{e^{-1.20\times 10^6/(t/\text{s})}}{(t/\text{s})^{1/2}}\right)$$

(a) $t = 10\,\text{s},\quad c = (369\,\text{M}) \times \left(\dfrac{e^{-1.2\times 10^5}}{10^{1/2}}\right) \approx \boxed{0}$

(b) $t = 1\,\text{yr} = 3.16 \times 10^7\,\text{s},\quad c = (369\,\text{M}) \times \left(\dfrac{e^{-0.038}}{(3.16 \times 10^7)^{1/2}}\right) = \boxed{0.063\,\text{M}}$

**COMMENT.** This problem illustrates the extreme slowness of diffusion through typical macroscopic distances; however, it is rapid enough through distances comparable to the dimensions of a cell. Compare to Problem 21.40.

**P21.20** Kohlrausch's law states that the molar conductance of a strong electrolyte varies with the square root of concentration

$$\Lambda_m = \Lambda_m^\circ - \mathcal{K}c^{1/2}$$

Therefore a pilot of $\Lambda_m$ versus $c^{1/2}$ should be a straight line with $y$-intercept $\Lambda^\circ_m$. The data and plot (Figure 21.1) are shown below

| NaI | | | KI | | |
|---|---|---|---|---|---|
| $c/(\mathrm{m\,mol\,dm^{-3}})$ | $c^{1/2}$ | $\Lambda_m/(\mathrm{S\,cm^2mol^{-1}})$ | $c/(\mathrm{mmol\,dm^{-3}})$ | $c^{1/2}$ | $\Lambda_m/(\mathrm{S\,cm^2\,mol^{-1}})$ |
| 32.02 | 5.659 | 50.26 | 17.68 | 4.205 | 42.45 |
| 20.28 | 4.503 | 51.99 | 10.88 | 3.298 | 45.91 |
| 12.06 | 3.473 | 54.01 | 7.19 | 2.68 | 47.53 |
| 8.64 | 2.94 | 55.75 | 2.67 | 1.63 | 51.81 |
| 2.85 | 1.69 | 57.99 | 1.28 | 1.13 | 54.09 |
| 1.24 | 1.11 | 58.44 | 0.83 | 0.91 | 55.78 |
| 0.83 | 0.91 | 58.67 | 0.19 | 0.44 | 57.42 |

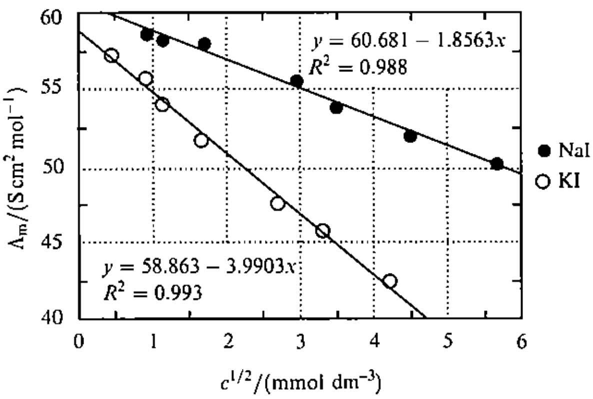



**Figure 21.1**

Thus $\Lambda^\circ_m(\mathrm{NaI}) = \boxed{60.7\ \mathrm{S\,cm^2\,mol^{-1}}}$ and $\Lambda^\circ_m(\mathrm{KI}) = \boxed{58.9\ \mathrm{S\,cm^2\,mol^{-1}}}$

Since these two electrolytes have a common anion, the difference in conductances is due to the cations

$$\lambda^\circ(\mathrm{Na^+}) - \lambda^\circ(\mathrm{K^+}) = \Lambda^\circ_m(\mathrm{NaI}) - \Lambda^\circ_m(\mathrm{KI}) = \boxed{1.8\ \mathrm{S\,cm^2\,mol^{-1}}}$$

The analogous quantities in water are

$$\Lambda^\circ_m(\mathrm{NaI}) = \lambda(\mathrm{Na^+}) + \lambda(\mathrm{I^{-1}}) = (73.50 + 76.8)\ \mathrm{S\,cm^2\,mol^{-1}} = \boxed{126.9\ \mathrm{S\,cm^2\,mol^{-1}}}$$

$$\Lambda^\circ_m(\mathrm{KI}) = \lambda(\mathrm{K^+}) + \lambda(\mathrm{I^{-1}}) = (73.50 + 76.8)\ \mathrm{S\,cm^2mol^{-1}} = \boxed{150.3\ \mathrm{S\,cm^2\,mol^{-1}}}$$

$$\lambda^\circ(\mathrm{Na^+}) - \lambda^\circ(\mathrm{K^+}) = (50.10 - 73.50)\ \mathrm{S\,cm^2mol^{-1}} = \boxed{-23.4\ \mathrm{S\,cm^2\,mol^{-1}}}$$

The ions are considerably more mobile in water than in this solvent. Also, the differences between $\mathrm{Na^+}$ and $\mathrm{K^+}$are minimized and even inverted compared to water.

**P21.22** The diffusion constant of an ion in solution is related to the mobility of the ion and to its radius in separate relations

$$D = \frac{uRT}{zF} = \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{zFk}{6\pi\eta uR} = \frac{ze}{6\pi\eta u}$$

$$a = \frac{(1)\times(1.602\times10^{-19}\,\mathrm{C})}{6\pi\,(0.93\times10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})\times(1.1\times10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}})} = 8.3\times10^{-10}\,\mathrm{m} = \boxed{8.30\,\mathrm{pm}}$$

## Solutions to theoretical problems

**P21.24** We proceed as in Section 21.1(a) except that, instead of taking a product of three one-dimensional distributions in order to get the three-dimensional distribution, we make a product of two one-dimensional distributions.

$$f(v_x, v_y)\mathrm{d}v_x\mathrm{d}v_y = f(v_x^2)f(v_y^2)\mathrm{d}v_x dv_y = \left(\frac{m}{2\pi kT}\right)\mathrm{e}^{-mv^2/2kT}\mathrm{d}v_x\mathrm{d}v_y$$

where $v^2 = v_x^2 + v_y^2$. The probability $f(v)\mathrm{d}v$ that the molecules have a two-dimensional speed, $v$, in the range $v$, $v+\mathrm{d}v$ is sum of the probabilities that it is in any of the area elements $\mathrm{d}v_x\mathrm{d}v_y$ in the circular shell of raidus $v$. The sum of the area elements is the area of the circular shell of radius $v$ and thickness $\mathrm{d}v$ which is $\pi(v+\mathrm{d}v)^2 - \pi v^2 = 2\pi v\,\mathrm{d}v$. Therefore

$$\boxed{f(v) = 2\pi\left(\frac{m}{2\pi kT}\right)v\mathrm{e}^{-mv^2/2kT}} \quad \left[\frac{M}{R} = \frac{m}{k}\right]$$

The mean speed is determined as $\bar{c} = \int_0^\infty vf(v)\,\mathrm{d}v = \int_0^\infty m/(kT)v^2\mathrm{e}^{-mv^2/2kT}\mathrm{d}v$.

Using standard integrals this evaluates to $\boxed{\bar{c} = (\pi kT/2m)^{1/2} = (\pi RT/2M)^{1/2}}$.

**COMMENT.** The two-dimensional gas serves as a model of the motion of molecules of surfaces. See Chapter 24.

**P21.26** Rewriting eqn 21.4 with $(M/R) = (m/k)$

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\mathrm{e}^{-mv^2/2kT}$$

The proportion of molecules with speeds less than $c$ is

$$P = \int_0^c f(v)\,\mathrm{d}v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^c v^2\mathrm{e}^{-mv^2/2kT}\mathrm{d}v$$

Defining $a \equiv \dfrac{m}{2kT}$

$$P = 4\pi\left(\frac{a}{\pi}\right)^{3/2}\int_0^c v^2 e^{-av^2}\,dv = -4\pi\left(\frac{a}{\pi}\right)^{3/2}\frac{d}{da}\int_0^c e^{-av^2}\,dv$$

Defining $x^2 \equiv av^2$, $dv = a^{-1/2}dx$

$$P = -4\pi\left(\frac{a}{\pi}\right)^{3/2}\frac{d}{da}\left\{\frac{1}{a^{1/2}}\int_0^{ca^{1/2}} e^{-x^2}\,dx\right\}$$

$$= -4\pi\left(\frac{a}{\pi}\right)^{3/2}\left\{-\frac{1}{2}\left(\frac{1}{a}\right)^{3/2}\int_0^{ca^{1/2}} e^{-x^2}\,dx + \left(\frac{1}{a}\right)^{1/2}\frac{d}{da}\int_0^{ca^{1/2}} e^{-x^2}\,dx\right\}$$

Then we use $\displaystyle\int_0^{ca^{1/2}} e^{-x^2}\,dx = \left(\pi^{1/2}/2\right)\mathrm{erf}(ca^{1/2})$

$$\frac{d}{da}\int_0^{ca^{1/2}} e^{-x^2}\,dx = \left(\frac{dca^{1/2}}{da}\right)\times(e^{-c^2a}) = \frac{1}{2}\left(\frac{c}{a^{1/2}}\right)e^{-c^2a}$$

where we have used $\displaystyle\frac{d}{dz}\int_0^z f(y)dy = f(z)$

Substituting and cancelling we obtain $P = \mathrm{erf}(ca^{1/2}) - (2ca^{1/2}/\pi^{1/2})\,e^{-c^2a}$

Now, $c = (3kT/m)^{1/2}$, so $ca^{1/2} = (3kT/m)^{1/2} \times (m/2kT)^{1/2} = (3/2)^{1/2}$, and

$$P = \mathrm{erf}\left(\sqrt{\frac{3}{2}}\right) - \left(\frac{6}{\pi}\right)^{1/2} e^{-3/2} = 0.92 - 0.31 = \boxed{0.61}$$

Therefore **(b)** $\boxed{\text{61 percent}}$ of the molecules have a speed less than the root mean square speed and **(a)** $\boxed{\text{39 percent}}$ have a speed greater than the root mean square speed. **(c)** For the proportions in terms of the mean speed $\bar{c}$, replace $c$ by $\bar{c} = (8kT/\pi m)^{1/2} = (8/3\pi)^{1/2}\,c$, so $\bar{c}a^{1/2} = 2/\pi^{1/2}$.

Then $P = \mathrm{erf}(\bar{c}a^{1/2}) - (2\bar{c}a^{1/2}/\pi^{1/2}) \times (e^{-\bar{c}^2a}) = \mathrm{erf}\,(2/\pi^{1/2}) - (4/\pi)e^{-4/\pi} = 0.889 - 0.356 = \boxed{0.533}$

That is, $\boxed{\text{53 percent}}$ of the molecules have a speed less than the mean, and $\boxed{\text{47 percent}}$ have a speed greater than the mean.

**P21.28** An effusion oven has constant volume, fixed temperature, and effusion hole of area $A$. Gas escapes through the hole, which makes the effusion rate negative.

$$-\frac{dN}{dt} = Z_W A = \frac{pAN_A}{(2\pi MRT)^{1/2}} \quad [21.16]$$

For a perfect gas, $pV = nRT = NRT/N_A$ and, therefore, $N = N_ApV/RT$.

Differentiation gives $\frac{dN}{dt} = \frac{N_A V}{RT}\frac{dp}{dt}$. Substitution into the first equation yields:

$$\frac{N_A V}{RT}\frac{dp}{dt} = -\frac{pAN_A}{(2\pi MRT)^{1/2}}$$

$$\frac{dp}{dt} = -\left(\frac{RT}{2\pi M}\right)^{1/2}\frac{A}{V}p = -\frac{p}{\tau} \quad \text{where the time constant is } \tau = \left(\frac{2\pi M}{RT}\right)^{1/2}\frac{V}{A}$$

$$\frac{dp}{p} = -\frac{dt}{\tau}$$

$$\int_{p_0}^{p}\frac{dp}{p} = -\frac{1}{\tau}\int_0^t dt$$

$$\ln\left(\frac{p}{p_0}\right) = -\frac{t}{\tau} \quad \text{or} \quad p = p_0 e^{-t/\tau}$$

When $t = t_{1/2}$, $p = (1/2)p_0$. Substitution into the above equation gives

$$\ln\left(\frac{p_0}{2p_0}\right) = -\frac{t_{1/2}}{\tau} \quad \text{or} \quad t_{1/2} = \tau\ln(2) = \left(\frac{2\pi M}{RT}\right)^{1/2}\frac{V}{A}\ln(2)$$

The final equation indicates that the half-life for effusive loss is independent of $p_0$. Furthermore,the half-life increases with both the $V/A$ and $M^{1/2}$ factors. It decreases with the factor $T^{-1/2}$.

**P21.30** $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$ [21.68] with $c = \frac{n_0 e^{-x^2/4Dt}}{A(\pi Dt)^{1/2}}$ [21.72]

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

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

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

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

$$= -\left(\frac{1}{2Dt}\right)c + \left(\frac{bx^2}{Dt^2}\right)c$$

$$= \frac{1}{D}\frac{\partial c}{\partial t} \text{ as required}$$

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 $\left(e^{-bx^2/t} \to 0 \text{ more strongly that } 1/t^{1/2} \to \infty\right)$

When $x = 0$, $e^{-x^2/4Dt} = 1$. We confirm the correct behavior by noting that $\langle x\rangle = 0$ and $\langle x^2\rangle = 0$ at $t = 0$ [21.82], and so all the material must be at $x = 0$ at $t = 0$.

**P21.32** Draw up the following table based on the third and last equations of *Justification* 21.11

| $N$ | 4 | 6 | 8 | 10 | 20 | 30 | 40 | 60 | 100 |
|---|---|---|---|---|---|---|---|---|---|
| $P(6\lambda)_{\text{Exact}}$ | 0 | 0.016 | 0.0313 | 0.0439 | 0.0739 | 0.0806 | 0.0807 | 0.0763 | 0.0666 |
| $P(6\lambda)_{\text{Approx.}}$ | 0.004 | 0.162 | 0.0297 | 0.0417 | 0.0725 | 0.0799 | 0.0804 | 0.0763 | 0.0666 |

The points are plotted in Figure 21.2.

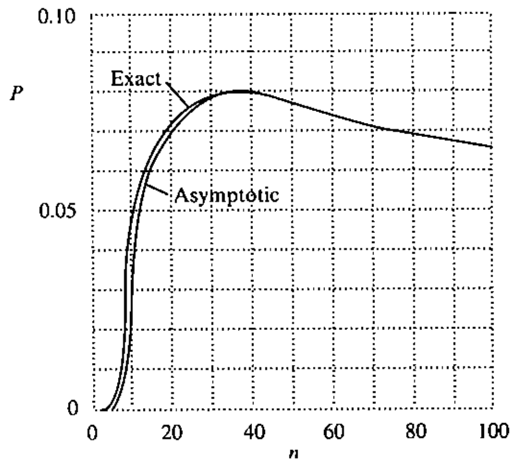



**Figure 21.2**

The discrepancy is less than 0.1 percent when $\boxed{N > 60}$

**P21.34** $AB \rightleftharpoons A^+ + B^-$; $\gamma_{AB} \simeq 1$, because AB interacts weakly with ions.

$$K = \frac{a_{A^+}a_{B^-}}{a_{AB}} = \left(\frac{\gamma_{A^+}\gamma_{B^+}}{\gamma_{AB}}\right) \times \left(\frac{c_{A^+}c_{B^+}}{c_{AB}}\right)$$

$$K = \gamma_\pm^2\left[\frac{(\alpha c)(\alpha c)}{(1-\alpha)c}\right] = \gamma_\pm^2\left(\frac{\alpha^2 c}{1-\alpha}\right) \quad \text{or} \quad \frac{\gamma_\pm^2 c}{K} = \frac{1-\alpha}{\alpha^2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{(\lambda_+ + \lambda_-)c_{\text{ion}}}{c} = \frac{(\lambda_+ + \lambda_-)\alpha c}{c} = (\lambda_+ + \lambda_-)\alpha$$

Let $\Lambda_m^\circ = \lambda_+ + \lambda_-$ be the molar conductivity when the solution is infinitely dilute and $\alpha = 1$ (eqn 21.30). Then, $\alpha = \Lambda_m/(\lambda_+ + \lambda_-) = \Lambda_m/\Lambda_m^\circ$. Substitution into equilibrium expression gives:

$$K = \gamma_\pm^2 c\left(\frac{\Lambda_m}{\Lambda_m^\circ}\right)^2\left(\frac{1}{1-\frac{\Lambda_m}{\Lambda_m^\circ}}\right)$$

$$1 - \frac{\Lambda_m}{\Lambda_m^\circ} = \left(\frac{\Lambda_m}{\Lambda_m^\circ}\right)^2\frac{\gamma_\pm^2 c}{K} = \left(\frac{\Lambda_m}{\Lambda_m^\circ}\right)^2\left(\frac{1-\alpha}{\alpha^2}\right)$$

Division by $\Lambda_m$ gives:

$$\frac{1}{\Lambda_m} - \frac{1}{\Lambda_m^\circ} = \left(\frac{1-\alpha}{\alpha^2}\right)\frac{\Lambda_m}{(\Lambda_m^\circ)^2}$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \left(\frac{1-\alpha}{\alpha^2}\right)\frac{\Lambda_m}{(\Lambda_m^\circ)^2}$$

## Solutions to application

**P21.36** The diffusion coefficient for a perfect gas is

$$D = \tfrac{1}{3}\lambda\bar{c} \quad \text{where } \lambda = (2^{1/2}\sigma\mathcal{N})^{-1} \text{ where } \mathcal{N} \text{ is number density.}$$

The mean speed is

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8(1.381\times10^{-23}\,\text{J K}^{-1})\times(10^4\,\text{K})}{\pi(1\,\text{u})\times(1.66\times10^{-27}\,\text{kg u}^{-1})}\right)^{1/2} = 1.46\times10^4\,\text{m s}^{-1}$$

So $D = \dfrac{\bar{c}}{3\sigma\mathcal{N}2^{1/2}} = \dfrac{1.46\times10^4\,\text{m s}^{-1}}{3(0.21\times10^{-18}\,\text{m}^2)\times(1\times(10^{-2}\,\text{m})^{-3})2^{1/2}} = \boxed{1.\bar{6}\times10^{16}\,\text{m}^2\,\text{s}^{-1}}$.

The thermal conductivity is

$$\kappa = \frac{\bar{c}C_{V,m}}{3\sigma N_A 2^{1/2}} = \frac{(1.46\times10^4\,\text{m s}^{-1})\times(20.784-8.3145)\,\text{J K}^{-1}\,\text{mol}^{-1}}{3(0.21\times10^{-18}\,\text{m}^2)\times(6.022\times10^{23}\,\text{mol}^{-1})2^{1/2}}$$

$$k = \boxed{0.3\bar{4}\,\text{J K}^{-1}\,\text{m}^{-1}\,\text{s}^{-1}}$$

**COMMENT.** The validity of these calculations is in doubt because the kinetic theory of gases assumes the Maxwell–Boltzmann distribution, essentially an equilibrium distribution. In such a dilute medium, the timescales on which particles exchange energy by collision make an assumption of equilibrium unwarranted. It is especially dubious considering that atoms are more likely to interact with photons from stellar radiation than with other atoms.

**P21.38** Concentration of $^1$H nuclei, $[^1\text{H}] = \dfrac{n_\text{H}}{V} = \dfrac{(\text{mass percentage})\times(\text{density})}{100(\text{molar mass})}$

$$= \frac{0.36(158\,\text{g cm}^{-3})}{1.0\,\text{g mol}^{-1}}$$

$$= 57\,\text{mol cm}^{-3}$$

Concentration $^4$He nuclei, $[^4\text{He}] = \dfrac{n_\text{He}}{V} = \dfrac{(\text{mass percentage})\times(\text{density})}{100(\text{molar mass})}$

$$= \frac{0.64(158\,\text{g cm}^{-3})}{4.0\,\text{g mol}^{-1}}$$

$$= 25\,\text{mol cm}^{-3}$$

Concentration of $e^- = [^1\text{H}] + 2[^4\text{He}] = (57 + 2\times25)\,\text{mol cm}^{-3} = 107\,\text{mol cm}^{-3}$

Total concentration of gaseous particles = $(57 + 25 + 107)\ \text{mol cm}^{-3} = 189\ \text{mol cm}^{-3}$

$$r_{\text{H nucleus}} = (1.4 \times 10^{-13}\ \text{cm})(1)^{1/3} = 1.4 \times 10^{-13}\ \text{cm}$$

$$r_{\text{He nucleus}} = (1.4 \times 10^{-13}\ \text{cm})(4)^{1/3} = 2.2 \times 10^{-13}\ \text{cm}$$

**(a)** The excluded volume of a nuclear collisional pair is estimated to be equal to the volume of the dashed sphere in Figure 21.3. The excluded volume of a single nucleus is 1/2 of this.

$$b \approx (N_A) \times \left(\frac{1}{2}\right) \times \left[\frac{4\pi}{3}(2r)^3\right] = \frac{16p}{3}N_A r^3$$

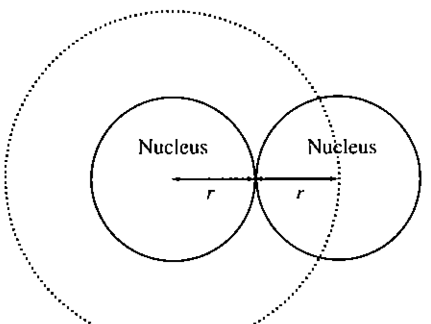



**Figure 21.3**

In this problem we have a mixture of hydrogen and helium nuclei so let us take $r$ to equal the weighted average of hydrogen and helium radii. This is, of course, a very simple estimate. Then

$$r \approx 0.36(1.4 \times 10^{-13}\ \text{cm}) + 0.64(2.2 \times 10^{-13}\ \text{cm})$$

$$r \approx 1.9 \times 10^{-13}\ \text{cm}$$

$$b \approx \frac{16\pi}{3}(6.022 \times 10^{23}\ \text{mol}^{-1}) \times (1.9 \times 10^{-13}\ \text{cm})^3$$

$$\boxed{b \approx 7.1 \times 10^{-14}\ \text{cm}^3\ \text{mol}^{-1}}$$

$$b(\text{per cm}^3) \approx 82\ \text{mol} \times 7.1 \times 10^{-14}\ \text{cm}^3\ \text{mol}^{-1}$$

$$\approx 5.8 \times 10^{-12}\ \text{cm}^3$$

This $b$ is extraordinarily small compared to 1 cm$^3$, so we may treat the nuclei as points within any macroscopic volume. In the sense that the nuclei act as volumeless points, the perfect gas law would seem to be applicable. However, our analysis has not included details of the internuclear forces and these may be appreciably larger than the hard-sphere model estimate.

**(b)** $T_{\text{perfect}} = \dfrac{pV}{nR}$, where $n$ = total number of moles of gaseous particles including the number of moles of electrons

$$= \frac{p}{\left(\frac{n}{V}\right)R}$$

$$= \frac{(2.5 \times 10^{11}\ \text{atm}) \times (1\ \text{dm}^3/10^3\ \text{cm}^3)}{(189\ \text{mol cm}^{-3}) \times (0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1})} = \boxed{1.6 \times 10^7\ \text{K} = T_{\text{perfect}}}$$

(c) $$T_{\text{vanderWaals}} = \frac{V_m - b}{R}\left(p + \frac{a}{V_m^2}\right)$$
$$= \frac{p(V_m - b)}{R} \text{ assuming } \alpha \approx 0$$
$$= \frac{p}{R}\left(\frac{V}{n} - b\right) = \frac{p}{R}\left\{\left(\frac{1}{\frac{n_{\text{total}}}{V}}\right) - b\right\}$$
$$= \left(\frac{2.5 \times 10^{11}\,\text{atm}}{0.0821\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}}\right)$$
$$\times \left\{\frac{1}{189\,\text{mol cm}^{-3}} - 7.1 \times 10^{-14}\,\text{cm}^3\,\text{mol}^{-1}\right\}$$
$$= T_{\text{perfect}} - \frac{(7.1 \times 10^{-14}\,\text{cm}^3\,\text{mol}^{-1}) \times (2.5 \times 10^{11}\,\text{atm})}{(0.0821\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1})}$$

where the last term is negligible. Therefore

$$T_{\text{vanderWaals}} = T_{\text{perfect}}$$

**P21.40** The mean square displacement is (from Exercise 21.28(b))

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