Foundations

A Matter

Answers to discussion questions

A.2

	Metals conduct electricity, have luster, and they are malleable and ductile.
	Nonmetals do not conduct electricity and are neither malleable nor ductile.
	Metalloids typically have the appearance of metals but behave chemically like a nonmetal.

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 1.008	Periodic Table of the Elements																2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226	89 Ac (227)															
				58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 145	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5					
				90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np 237	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)					

	Transition metals
	Lanthanoids
	Actinoids

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 1.008	Periodic Table of the Elements																2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86

Cs 132.9	Ba 137.3	La 138.9	Hf 178.5	Ta 180.9	W 183.9	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 197.0	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0	Po (209)	At (210)	Rn (222)
87 Fr (223)	88 Ra 226	89 Ac (227)															
				58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 145	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5					
				90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np 237	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)					

A.4 Valence-shell electron pair repulsion theory (VSEPR theory) predicts molecular shape with the concept that regions of high electron density (as represented by single bonds, multiple bonds, and lone pair) take up orientations around the central atom that maximize their separation. The resulting positions of attached atoms (not lone pairs) are used to classify the shape of the molecule. When the central atom has two or more lone pair, the molecular geometry must minimize repulsion between the relatively diffuse orbitals of the lone pair. Furthermore, it is assumed that the repulsion between a lone pair and a bonding pair is stronger than the repulsion between two bonding pair, thereby, making bond angles smaller than the idealized bond angles that appear in the absence of a lone pair.

Solutions to exercises

A.1(b)

	Example	Element	Ground-state Electronic Configuration
(i)	Group 3	Sc, scandium	$[Ar]3d^14s^2$
(ii)	Group 5	V, vanadium	$[Ar]3d^34s^2$
(iii)	Group 13	Ga, gallium	$[Ar]3d^{10}4s^24p^1$

A.2(b)

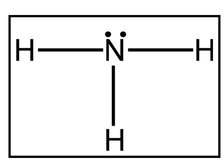
(i) chemical formula and name: CaH_2, calcium hydride
ions: Ca^{2+} and H^-
oxidation numbers of the elements: calcium, +2; hydrogen, –1

(ii) chemical formula and name: CaC_2, calcium carbide
ions: Ca^{2+} and C_2^{2-} (a polyatomic ion)
oxidation numbers of the elements: calcium, +2; carbon, –1

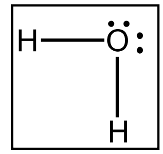
(iii) chemical formula and name: LiN_3, lithium azide
ions: Li^+ and N_3^- (a polyatomic ion)
oxidation numbers of the elements: lithium, +1; nitrogen, –⅓

A.3(b)

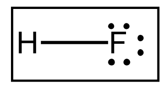
(i) Ammonia, NH_3, illustrates a molecule with one lone pair on the central atom.

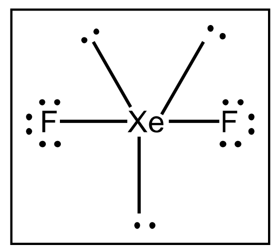


(ii) Water, H_2O, illustrates a molecule with two lone pairs on the central atom.



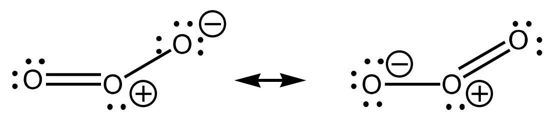
(iii) The hydrogen fluoride molecule, HF, illustrates a molecule with three lone pairs on the central atom. Xenon difluoride has three lone pairs on both the central atom and the two peripheral atoms.



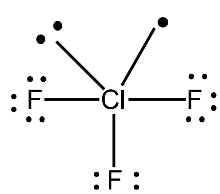


A.4(b)

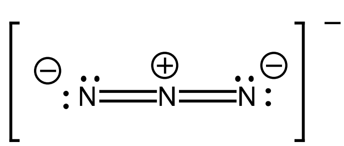
(i) Ozone, O_3. Formal charges (shown in circles) may be indicated.



(ii) ClF_3^+



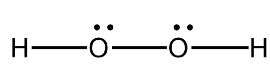
(iii) azide anion, N_3^-



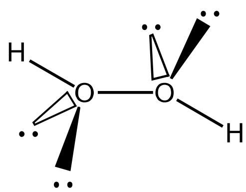
A.5(b) The central atoms in XeF_4, PCl_5, SF_4, and SF_6 are hypervalent.

A.6(b) Molecular and polyatomic ion shapes are predicted by drawing the Lewis structure and applying the concepts of VSEPR theory.

(i) H_2O_2 Lewis structure:

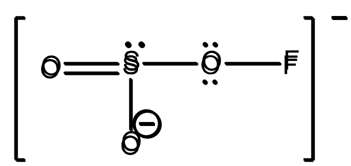


Orientations caused by repulsions between two lone pair and two bonding pair around each oxygen atom:

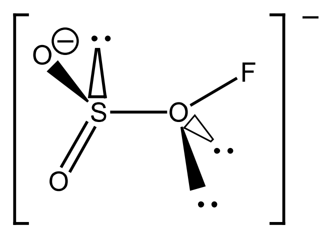


Molecular shape around each oxygen atom: bent (or angular) with bond angles somewhat smaller than 109.5º

(ii) FSO_3^- Lewis structure:
(Formal charge is circled.)

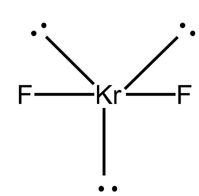


Orientations around the sulfur are caused by repulsions between one lone pair, one double bond, and two single bonds while orientations around the oxygen to which fluorine is attached are caused by repulsions between two lone pair and two single bonds:

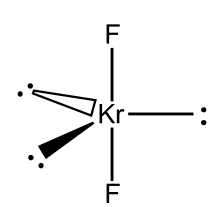


Molecular shape around the sulfur atom is trigonal pyramidal with bond angles somewhat smaller than 109.5º while the shape around the oxygen to which fluorine is attached is bent (or angular) with a bond angle somewhat smaller than 109.5º.

(iii) KrF_2 Lewis structure:

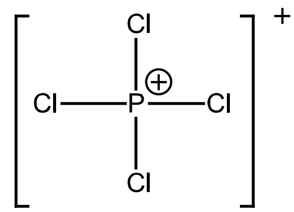


Orientations caused by repulsions between three lone pair and two bonding pair:



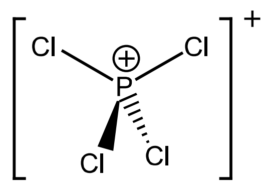
Molecular shape: linear with a 180º bond angle.

(iv) PCl_4^+ Lewis structure:
(Formal charge is shown in a circle.)



Orientations caused by repulsions between four bonding pair (no lone pair):

Molecular shape: tetrahedral and bond angles of 109.5º



A.7(b)

(i) C—H Nonpolar or weakly polar toward the slightly more electronegative carbon.

(ii) $\overset{\delta^+}{P}$—$\overset{\delta^-}{S}$ (c) $\overset{\delta^+}{N}$—$\overset{\delta^-}{Cl}$

A.8(b)

(i) O_3 is a bent molecule that has a small dipole as indicated by consideration of electron densities and formal charge distributions.

(ii) XeF_2 is a linear, nonpolar molecule.

(iii) NO_2 is a bent, polar molecule.

(iv) C_6H_{14} is a nonpolar molecule.

A.9(b) In the order of increasing dipole moment: $XeF_2 \sim C_6H_{14}$, NO_2, O_3

A.10(b)

(i) Pressure is an intensive property.

(ii) Specific heat capacity is an intensive property.

(iii) Weight is an extensive property.

(iv) Molality is an intensive property.

A.11(b)

(i) $$n = \frac{m}{M} = 5.0\text{ g}\left(\frac{1\text{ mol}}{180.16\text{ g}}\right) = \boxed{0.028\text{ mol}} \quad [\text{A.3}]$$

(ii) $$N = nN_\text{A} = 0.028\text{ mol}\left(\frac{6.0221\times10^{23}\text{ molecules}}{\text{mol}}\right) = \boxed{1.7\times10^{22}\text{ molecules}}$$

A.12(b)

(i) $m = nM = 10.0 \text{ mol}\left(\frac{78.11 \text{ g}}{\text{mol}}\right) = \boxed{781. \text{ g}}$ [A.3]

(ii) $\text{weight} = F_{\text{gravity on Mars}} = m\, g_{\text{Mars}}$

$$= (781. \text{ g}) \times (3.72 \text{ m s}^{-2}) \times \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 2.91 \text{ kg m s}^{-2} = \boxed{2.91 \text{ N}}$$

A.13(b) $p = \frac{F}{A} = \frac{mg}{A}$

$$= \frac{(60 \text{ kg}) \times (9.81 \text{ m s}^{-2})}{2 \text{ cm}^2}\left(\frac{1 \text{ cm}^2}{10^{-4} \text{ m}^2}\right) = 3\times10^6 \text{ N m}^{-2} = 3\times10^6 \text{ Pa}\left(\frac{1 \text{ bar}}{10^5 \text{ Pa}}\right)$$

$$= \boxed{30 \text{ bar} \pm 10 \text{ bar}}$$

A.14(b) $(30 \text{ bar} \pm 10 \text{ bar})\left(\frac{1 \text{ atm}}{1.01325 \text{ bar}}\right) = \boxed{30 \text{ atm} \pm 10 \text{ atm}}$

A.15(b)

(i) $222 \text{ atm}\left(\frac{1.01325\times10^5 \text{ Pa}}{1 \text{ atm}}\right) = \boxed{225\times10^5 \text{ Pa}}$

(ii) $222 \text{ atm}\left(\frac{1.01325 \text{ bar}}{1 \text{ atm}}\right) = \boxed{225 \text{ bar}}$

A.16(b) $\theta / ^\circ\text{C} = T/\text{K} - 273.15 = 90.18 - 273.15 = -182.97$ [A.4]

$$\boxed{\theta = -182.97 \text{ }^\circ\text{C}}$$

A.17(b) The absolute zero of temperature is 0 K and 0 ºR. Using the scaling relationship 1 ºF / 1 ºR (given in the exercise) and knowing the scaling ratios 5 ºC / 9 ºF and 1 K / 1 ºC, we find the scaling factor between the Kelvin scale and the Rankine scale to be:

$$\left(\frac{1\ ^\circ\text{F}}{1\ ^\circ\text{R}}\right) \times \left(\frac{5\ ^\circ\text{C}}{9\ ^\circ\text{F}}\right) \times \left(\frac{1 \text{ K}}{1\ ^\circ\text{C}}\right) = \frac{5 \text{ K}}{9\ ^\circ\text{R}}$$

The zero values of the absolute zero of temperature on both the Kelvin and Rankine scales and the value of the scaling relationship implies that:

$$\boxed{T/\text{K} = \tfrac{5}{9} \times (\theta_{\text{R}} / ^\circ\text{R}) \quad \text{or} \quad \theta_{\text{R}} / ^\circ\text{R} = \tfrac{9}{5} \times (T/\text{K})}$$

Normal freezing point of water:

$$\theta_{\text{R}} / ^\circ\text{R} = \tfrac{9}{5} \times (T/\text{K}) = \tfrac{9}{5} \times (273.15) = 491.67$$

$$\theta_{\text{R}} = \boxed{491.67\ ^\circ\text{R}}$$

A.18(b) $n = 0.325\text{ g} \times \left(\dfrac{1\text{ mol}}{20.18\text{ g}}\right) = 0.0161\text{ mol}$

$$p = \frac{nRT}{V}\ [\text{A.5}] = \frac{(0.0161\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(293.15\text{ K})}{2.00\text{ dm}^3}\left(\frac{\text{dm}^3}{10^{-3}\text{ m}^3}\right)$$

$$= 1.96\times10^4\text{ Pa} = \boxed{19.6\text{ kPa}}$$

A.19(b) $pV = nRT\ [\text{A.5}] = \dfrac{mRT}{M}$

$$M = \frac{mRT}{pV} = \frac{\rho RT}{p} \quad \text{where } \rho \text{ is the mass density [A.2]}$$

$$= \frac{(0.6388\text{ kg m}^{-3})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(373.15\text{ K})}{16.0\times10^3\text{ Pa}} = 0.124\text{ kg mol}^{-1} = 124\text{ g mol}^{-1}$$

The molecular mass is four times as large as the atomic mass of phosphorus (30.97 g mol^{-1}) so the molecular formula is $\boxed{P_4}$.

A.20(b) $n = 7.05\text{ g} \times \left(\dfrac{1\text{ mol}}{32.00\text{ g}}\right) = 0.220\text{ mol [A.3]}$

$$p = \frac{nRT}{V}\ [\text{A.5}] = \frac{(0.220\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(373.15.15\text{ K})}{100.\text{ cm}^3}\left(\frac{\text{cm}^3}{10^{-6}\text{ m}^3}\right)$$

$$= 6.83\times10^6\text{ Pa} = \boxed{6.83\text{ MPa}}$$

A.21(b) $n_{O_2} = 0.25\text{ mole}$ and $n_{CO_2} = 0.034\text{ mole}$

$$p_{O_2} = \frac{n_{O_2}RT}{V}\ [\text{A.5}] = \frac{(0.25\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(283.15\text{ K})}{100.\text{ cm}^3}\left(\frac{\text{cm}^3}{10^{-6}\text{ m}^3}\right) = \boxed{5.9\text{ MPa}}$$

Since the ratio of CO_2 moles to O_2 moles is 0.034/0.25, we may scale the oxygen partial pressure by this ratio to find the partial pressure of CO_2.

$$p_{CO_2} = \left(\frac{0.034}{0.25}\right)\times(5.9\text{ MPa}) = \boxed{0.80\text{ MPa}} \qquad p = p_{O_2} + p_{CO_2}\ [1.6] = \boxed{6.7\text{ MPa}}$$

B Energy

Answers to discussion questions

B.2 All objects in motion have the ability to do work during the process of slowing. That is, they have energy, or, more precisely, the energy possessed by a body because of its motion is its **kinetic energy**, E_k. The law of conservation of energy tells us that the kinetic energy of an object equals the work done on the object in order to change its motion from an initial (i) state of $v_i = 0$ to a final (f) state of $v_f = v$. For an object of mass m travelling at a speed v, $E_k = \tfrac{1}{2}mv^2$ [B.8].

The **potential energy**, E_p or more commonly V, of an object is the energy it possesses as a result of its position. For an object of mass m at an altitude h close to the surface of the Earth, the gravitational potential energy is

$$V(h) = mgh \quad \text{[B.11]} \quad \text{where} \quad g = 9.81 \text{ m s}^{-2}$$

Eqn B.11 assigns the gravitational potential energy at the surface of the Earth, $V(0)$, a value equal zero and g is called the **acceleration of free fall**.

The Coulomb potential energy describes the particularly important electrostatic interaction between two point charges Q_1 and Q_2 separated by the distance r:

$$V(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r} \quad \text{in a vacuum [B.14, } \varepsilon_0 \text{ is the vacuum permittivity]}$$

and

$$V(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_r\varepsilon_0 r} \quad \text{in a medium that has the relative permittivity } \varepsilon_r \text{ (formerly, dielectric constant)}$$

Eqn B.14 assigns the Coulomb potential energy at infinite separation, $V(\infty)$, a value equal to zero. Convention assigns a negative value to the Coulomb potential energy when the interaction is attractive and a positive value when it is repulsive. The Coulomb potential energy and the force acting on the charges are related by the expression $F = -\mathrm{d}V/\mathrm{d}r$.

B.4 Quantized energies are certain discrete values that are permitted for particles confined to a region of space.

The quantization of energy is most important—in the sense that the allowed energies are widest apart—for particles of small mass confined to small regions of space. Consequently, quantization is very important for electrons in atoms and molecules. Quantization is important for the electronic states of atoms and molecules and for both the rotational and vibrational states of molecules.

B.6 The Maxwell distribution of speeds indicates that few molecules have either very low or very high speeds. Furthermore, the distribution peaks at lower speeds when either the temperature is low or the molecular mass is high. The distribution peaks at high speeds when either the temperature is high or the molecular mass is low.

Solutions to exercises

B.1(b) $a = \mathrm{d}v/\mathrm{d}t = g$ so $\mathrm{d}v = g\,\mathrm{d}t$. The acceleration of free fall is constant near the surface of the Mars.

$$\int_{v=0}^{v(t)} \mathrm{d}v = \int_{t=0}^{t=t} g\,\mathrm{d}t$$

$$v(t) = g_{\text{Mars}} t$$

(i) $$v(1.0\text{ s}) = (3.72\text{ m s}^{-2}) \times (1.0\text{ s}) = \boxed{3.72\text{ m s}^{-1}}$$

$$E_k = \tfrac{1}{2}mv^2 = \tfrac{1}{2}(0.0010\text{ kg}) \times (3.72\text{ m s}^{-1})^2 = \boxed{6.9\text{ mJ}}$$

(ii) $v(3.0\ \text{s}) = (3.72\ \text{m s}^{-2}) \times (3.0\ \text{s}) = \boxed{11.2\ \text{m s}^{-1}}$

$E_k = \frac{1}{2}mv^2 = \frac{1}{2}(0.0010\ \text{kg}) \times (11.2\ \text{m s}^{-1})^2 = \boxed{63\ \text{mJ}}$

B.2(b) The terminal velocity occurs when there is a balance between the force exerted by the pull of gravity, $mg = V_{\text{particle}}\rho g = {}^4/_3\pi R^3\rho g$, and the force of frictional drag, $6\pi\eta Rs$. It will be in the direction of the gravitational pull and have the magnitude s_{terminal}.

$$\tfrac{4}{3}\pi R^3 \rho g = 6\pi\eta R s_{\text{terminal}}$$

$$\boxed{s_{\text{terminal}} = \frac{2R^2\rho g}{9\eta}}$$

B.3(b) The harmonic oscillator solution $x(t) = A\sin(\omega t)$ has the characteristics that

$$v(t) = \frac{dx}{dt} = A\omega\cos(\omega t) \quad \text{where } \omega = (k_f/m)^{1/2} \text{ or } m\omega^2 = k_f$$

$$x_{\min} = x(t{=}n\pi/\omega, n{=}0,1,2...) = 0 \quad \text{and} \quad x_{\max} = x(t{=}(n{+}\tfrac{1}{2})\pi/\omega, n{=}0,1,2...) = A$$

At $x_{\min}$ the harmonic oscillator restoration force (Hooke's law, $F_x = -k_f x$, Brief illustration B.2) is zero and, consequently, the harmonic potential energy, V, is a minimum that is taken to equal zero while kinetic energy, E_k, is a maximum. As kinetic energy causes movement away from $x_{\min}$, kinetic energy continually converts to potential energy until no kinetic energy remains at $x_{\max}$ where the restoration force changes the direction of motion and the conversion process reverses. We may easily find an expression for the total energy $E(A)$ by examination of either $x_{\min}$ or $x_{\max}$.

Analysis using $x_{\min}$:

$$E = E_k + V = E_{k,\max} + 0 = \tfrac{1}{2}m\,v_{\max}^2 = \tfrac{1}{2}mA^2\omega^2 = \boxed{\tfrac{1}{2}k_f A^2}$$

We begin the analysis that uses $x_{\max}$, by deriving the expression for the harmonic potential energy.

$$dV = -F_x dx\ [\text{B.10}] = k_f x\ dx$$

$$\int_0^{V(x)} dV = \int_0^x k_f x\ dx$$

$$V(x) = \tfrac{1}{2}k_f x^2$$

Thus, $V_{\max} = V(x_{\max}) = \tfrac{1}{2}k_f A^2$ and $E = E_k + V = 0 + V_{\max} = \boxed{\tfrac{1}{2}k_f A^2}$

B.4(b) $w = \tfrac{1}{2}kx^2$ where $x = R - R_e$ is the displacement from equilibrium [Brief illustration B.3]

$$w = \tfrac{1}{2}(510\ \text{N m}^{-1}) \times (20\times10^{-12}\ \text{m})^2 = 1.02\times10^{-19}\ \text{N m} = \boxed{1.02\times10^{-19}\ \text{J}}$$

B.5(b) $E_k = ze\Delta\phi$ where $z = 2$ for $C_6H_4^{2+}$ and $M = 76.03\ \text{g mol}^{-1}$ for the major isotopes

$$\tfrac{1}{2}mv^2 = ze\Delta\phi \quad \text{or} \quad v = \left(\frac{2ze\Delta\phi}{m}\right)^{1/2} \quad \text{where } m = M/N_A$$

$$v = \left(\frac{2 \times 2 \times (1.6022 \times 10^{-19}\ \text{C}) \times (20 \times 10^{3}\ \text{V})}{(0.07603\ \text{kg mol}^{-1})/(6.022 \times 10^{23}\ \text{mol}^{-1})} \right)^{1/2} = 3.2 \times 10^{5} \left(\frac{\text{C V}}{\text{kg}} \right)^{1/2} = 3.2 \times 10^{5} \left(\frac{\text{J}}{\text{kg}} \right)^{1/2}$$

$$= 3.2 \times 10^{5} \left(\frac{\text{kg m}^{2}\ \text{s}^{-2}}{\text{kg}} \right)^{1/2} = \boxed{3.2 \times 10^{5}\ \text{m s}^{-1}}$$

$$E = E_{\text{k}} = ze\Delta\phi = 2e \times (20\ \text{kV}) = \boxed{40\ \text{keV}}$$

B.6(b) The work needed to separate two ions to infinity is identical to the Coulomb potential drop that occurs when the two ions are brought from an infinite separation, where the interaction potential equals zero, to a separation of r.

In a vacuum:

$$w = -V = -\left(\frac{Q_1 Q_2}{4\pi\varepsilon_0 r} \right) [\text{B.14}] = -\left(\frac{(2e) \times (-2e)}{4\pi\varepsilon_0 r} \right) = \frac{4e^2}{4\pi\varepsilon_0 r} = \frac{e^2}{\pi\varepsilon_0 r}$$

$$= \frac{(1.6022 \times 10^{-19}\ \text{C})^2}{\pi(8.85419 \times 10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}) \times (250 \times 10^{-12}\ \text{m})} = \boxed{3.69 \times 10^{-18}\ \text{J}}$$

In water:

$$w = -V = -\left(\frac{Q_1 Q_2}{4\pi\varepsilon r} \right) = -\left(\frac{(2e) \times (-2e)}{4\pi\varepsilon r} \right) = \frac{e^2}{\pi\varepsilon r} = \frac{e^2}{\pi\varepsilon_r \varepsilon_0 r} \ [\text{B.15}] \text{ where } \varepsilon_r = 78 \text{ for water at 25°C}$$

$$= \frac{(1.6022 \times 10^{-19}\ \text{C})^2}{\pi(78) \times (8.85419 \times 10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}) \times (250 \times 10^{-12}\ \text{m})} = \boxed{4.73 \times 10^{-20}\ \text{J}}$$

B.7(b) We will model a solution by assuming that the NaCl pair consists of the two point charge ions Na^+ and Cl^-. The electric potential will be calculated along the line of the ions.

$$\phi = \phi_{\text{Na}^+} + \phi_{\text{Cl}^-} \ [2.17] = \frac{e}{4\pi\varepsilon_0 r_{\text{Na}^+}} + \frac{(-e)}{4\pi\varepsilon_0 r_{\text{Cl}^-}} \ [\text{B.16}] = \frac{e}{4\pi\varepsilon_0} \left(\frac{1}{r_{\text{Na}^+}} - \frac{1}{r_{\text{Cl}^-}} \right)$$

When $r_{\text{Na}^+} = r_{\text{Cl}^-}$, the electric potential equals zero in this model. Likewise, $r_{\text{Na}^+} = r_{\text{Cl}^-}$ at every point both on the line perpendicular to the internuclear line and crossing the internuclear line at the mid-point so electric potential equals $\boxed{\text{zero}}$ at every point on that perpendicular line.

B.8(b) $\Delta U_{\text{ethanol}}$ = energy dissipated by the electric circuit

$$= I\Delta\phi\,\Delta t \text{ [B.20]}$$

$$= (1.12\text{ A})\times(12.5\text{ V})\times(172\text{ s}) = 2.41\times10^{3}\text{ C s}^{-1}\text{ V s} = \boxed{2.41\text{ kJ}}$$

$$\Delta U_{\text{ethanol}} = (nC\Delta T)_{\text{ethanol}} \text{ [B.21]}$$

$$\Delta T = \frac{\Delta U_{\text{ethanol}}}{(nC)_{\text{ethanol}}} = \frac{\Delta U_{\text{ethanol}}}{(mC/M)_{\text{ethanol}}} = \frac{2.41\times10^{3}\text{ J}}{(150\text{ g})\times(111.5\text{ J K}^{-1}\text{ mol}^{-1})/(46.07\text{ g mol}^{-1})}$$

$$= 6.64\text{ K} = \boxed{6.64\text{ °C}}$$

B.9(b) $\Delta T = \dfrac{\Delta U}{C}\text{[B.21]} = \dfrac{50.0\text{ kJ}}{5.77\text{ kJ K}^{-1}} = \boxed{8.67\text{ K or }8.67\text{ °C}}$

B.10(b) $n = 10.0\text{ g}\times\left(\dfrac{1\text{ mol}}{18.01\text{ g}}\right) = 0.555\text{ mol}$

$$\Delta U = C\Delta T\text{ [B.21]} = nC_{\text{m}}\Delta T$$

$$= (0.555\text{ mol})(75.2\text{ J K}^{-1}\text{ mol}^{-1})(10.0\text{ K}) = \boxed{417\text{ J}}$$

B.11(b) $C_{\text{s}} = C_{\text{m}}/M = (28.24\text{ J K}^{-1}\text{ mol}^{-1})\times\left(\dfrac{1\text{ mol}}{22.99\text{ g}}\right) = \boxed{1.228\text{ J K}^{-1}\text{ g}^{-1}}$

B.12(b) $C_{\text{m}} = C_{\text{s}}M = (0.384\text{ J K}^{-1}\text{ g}^{-1})\times\left(\dfrac{63.55\text{ g}}{\text{mol}}\right) = \boxed{24.4\text{ J K}^{-1}\text{ mol}^{-1}}$

B.13(b) $H_{\text{m}} - U_{\text{m}} = pV_{\text{m}}\text{ [B.23]} = \dfrac{pM}{\rho} = \dfrac{(1.00\times10^{5}\text{ Pa})\times(18.02\text{ g mol}^{-1})}{0.997\text{ g cm}^{-3}}\left(\dfrac{10^{-6}\text{ m}^{3}}{\text{cm}^{3}}\right) = \boxed{1.81\text{ J mol}^{-1}}$

B.14(b) $S_{H_2O(l)} > S_{H_2O(s)}$

B.15(b) $S_{H_2O(l,\,100\,°C)} > S_{H_2O(l,\,0\,°C)}$

B.16(b) In a state of static equilibrium there is no net force or torque acting on the system and, therefore, there is no resultant acceleration. Examples:

When holding an object in a steady position above the ground, there is a balance between the downward gravitational force pulling on the object downward and the upward force of the hold. Release the object and it falls.

A movable, but non-moving, piston within a cylinder may be at equilibrium because of equal pressures on each side of the piston. Increase the pressure on one side of the piston and it moves away from that side.

In the Bohr atomic model of 1913 there is a balance between the electrostatic attraction of an electron to the nucleus and the centrifugal force acting on the orbiting electron. Should the electron steadily lose kinetic energy, it spirals into the nucleus.

B.17(b) $\dfrac{N_i}{N_j} = \mathrm{e}^{-(\varepsilon_i-\varepsilon_j)/kT} = \mathrm{e}^{-\Delta\varepsilon_{ij}/kT}$ [B.25a]

(i)

$$\frac{N_2}{N_1} = \mathrm{e}^{-(2.0\ \mathrm{eV})\times(1.602\times10^{-19}\ \mathrm{J\ eV^{-1}})/\{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(200\ \mathrm{K})\}} = 4.2\times10^{-51}$$

(ii)

$$\frac{N_2}{N_1} = \mathrm{e}^{-(2.0\ \mathrm{eV})\times(1.602\times10^{-19}\ \mathrm{J\ eV^{-1}})/\{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(2000\ \mathrm{K})\}} = 9.2\times10^{-6}$$

B.18(b) $\lim_{T\to\infty}\left(\dfrac{N_{\text{upper}}}{N_{\text{lower}}}\right) = \lim_{T\to\infty}\left(\mathrm{e}^{-\Delta\varepsilon/kT}\right)$ [B.25a] $= \mathrm{e}^{-0} = 1$

In the limit of the infinite temperature both the upper and the lower state are equally occupied.

B.19(b) $\Delta\varepsilon = \varepsilon_{\text{upper}} - \varepsilon_{\text{lower}} = h\nu = (6.626\times10^{-34}\ \mathrm{J\ s})(10.0\times10^{9}\ \mathrm{s^{-1}}) = 6.63\times10^{-24}\ \mathrm{J}$

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = \mathrm{e}^{-\Delta\varepsilon/kT}\ [\text{B.25a}] = \mathrm{e}^{-(6.63\times10^{-24}\ \mathrm{J})/\{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(293\ \mathrm{K})\}} = \boxed{0.998}$$

The ratio $N_{\text{upper}}/N_{\text{lower}}$ indicates that the two states are equally populated. A large fraction of gas-phase molecules will be in excited rotational states.

B.20(b) Rates of chemical reaction typically increase with increasing temperature because more molecules have the requisite speed and corresponding kinetic energy to promote excitation and bond breakage during collisions at the high temperatures.

B.21(b) $v_{\text{mean}} \propto (T/M)^{1/2}$ [B.26]

$$\frac{v_{\text{mean}}(T_2)}{v_{\text{mean}}(T_1)} = \frac{(T_2/M)^{1/2}}{(T_1/M)^{1/2}} = \left(\frac{T_2}{T_1}\right)^{1/2}$$

$$\frac{v_{\text{mean}}(303\ \mathrm{K})}{v_{\text{mean}}(293\ \mathrm{K})} = \left(\frac{303\ \mathrm{K}}{293\ \mathrm{K}}\right)^{1/2} = \boxed{1.02}$$

B.22(b) $v_{\text{mean}} \propto (T/M)^{1/2}$ [2.26]

$$\frac{v_{\text{mean}}(M_2)}{v_{\text{mean}}(M_1)} = \frac{(T/M_2)^{1/2}}{(T/M_1)^{1/2}} = \left(\frac{M_1}{M_2}\right)^{1/2}$$

$$\frac{v_{\text{mean}}(\mathrm{H_2})}{v_{\text{mean}}(\mathrm{Hg_2})} = \left(\frac{401.2\ \mathrm{g\ mol^{-1}}}{2.016\ \mathrm{g\ mol^{-1}}}\right)^{1/2} = \boxed{14.11}$$

B.23(b) A gaseous helium atom has three translational degrees of freedom (the components of motion in the *x*, *y*, and *z* directions). Consequently, the equipartition theorem assigns a mean energy of $\frac{3}{2}kT$ to each atom. The molar internal energy is

$$U_m = \tfrac{3}{2}N_A kT = \tfrac{3}{2}RT = \tfrac{3}{2}(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1})(303\ \text{K}) = 3.78\ \text{kJ mol}^{-1}$$

$$U = nU_m = mM^{-1}U_m = (10.0\ \text{g})\left(\frac{1\ \text{mol}}{4.00\ \text{g}}\right)\left(\frac{3.78\ \text{kJ}}{\text{mol}}\right) = \boxed{9.45\ \text{kJ}}$$

B.24(b) A solid state lead atom has three vibrational quadratic degrees of freedom (the components of vibrational motion in the *x*, *y*, and *z* directions). Its potential energy also has a quadratic form in each direction because $V \propto (x - x_{eq})^2$. There is a total of six quadratic degrees of freedom for the atom because the atoms have no translational or rotational motion. Consequently, the equipartition theorem assigns a mean energy of $\frac{6}{2}kT = 3kT$ to each atom. This is the law of Dulong and Petit. The molar internal energy is

$$U_m = 3N_A kT = 3RT = 3(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1})(293\ \text{K}) = 7.31\ \text{kJ mol}^{-1}$$

$$U = nU_m = mM^{-1}U_m = (10.0\ \text{g})\left(\frac{1\ \text{mol}}{207.2\ \text{g}}\right)\left(\frac{7.31\ \text{kJ}}{\text{mol}}\right) = \boxed{0.353\ \text{kJ}}$$

B.25(b) See exercise B.23(b) for the description of the molar internal energy of helium.

$$C_{V,m} = \frac{\partial U_m}{\partial T} = \frac{\partial\left(\frac{3}{2}RT\right)}{\partial T} = \tfrac{3}{2}R = \tfrac{3}{2}(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}) = \boxed{12.47\ \text{J mol}^{-1}\ \text{K}^{-1}}$$

B.26(b)

(i) Water, being a bent molecule, has three quadratic translational and three quadratic rotational degrees of freedom. So,

$$U_m = 3RT \quad \text{for water vapour}$$

$$C_{V,m} = \frac{\partial U_m}{\partial T} = \frac{\partial(3RT)}{\partial T} = 3R = 3(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}) = \boxed{24.94\ \text{J mol}^{-1}\ \text{K}^{-1}}$$

(ii) See exercise B.24(b) for the description of the molar internal energy of lead.

$$U_m = 3RT \quad \text{for Pb(s)}$$

$$C_{V,m} = \frac{\partial U_m}{\partial T} = \frac{\partial(3RT)}{\partial T} = 3R = 3(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}) = \boxed{24.94\ \text{J mol}^{-1}\ \text{K}^{-1}}$$

C Waves

Answers to discussion questions

C.2 The sound of a sudden 'bang' is generated by sharply slapping two macroscopic objects together. This creates a sound wave of displaced air molecules that propagates away from the collision with **intensity**, defined to be the power transferred by the wave through a unit area normal to the direction of propagation. Thus, the SI unit of intensity is the watt per meter squared (W m^{-2}) and 'loudness' increases with increasing intensity. The 'bang' creates a shell of compressed air molecules that propagates away from the source as a shell of higher pressure and density. This longitudinal impulse propagates when gas molecules escape from the high pressure shell into the adjacent, lower pressure shell. Molecular collisions quickly cause momentum transfer from the high density to the low density shell and the effective propagation of the high density shell. The regions over which pressure and density vary during sound propagation are much wider than the molecular mean free path because sound is immediately dissipated by molecular collisions in the case for which pressure and density variations are of the order of the mean free path.

Solutions to exercises

C.1(b) $c_{\text{benzene}} = \dfrac{c}{n_r}\ [\text{C.4}] = \dfrac{3.00\times10^8\ \text{m s}^{-1}}{1.52} = \boxed{1.97\times10^8\ \text{m s}^{-1}}$

C.2(b) $\lambda = \dfrac{1}{\tilde{\nu}}\ [\text{C.5}] = \dfrac{1}{3600\ \text{cm}^{-1}}\left(\dfrac{10^6\ \mu\text{m}}{10^2\ \text{cm}}\right) = \boxed{2.78\ \mu\text{m}}$

$$\nu = \frac{c}{\lambda}\ [\text{C.1}] = \frac{3.00\times10^8\ \text{m s}^{-1}}{2.78\times10^{-6}\ \text{m}} = 1.08\times10^{14}\ \text{s}^{-1} = \boxed{1.08\times10^{14}\ \text{Hz}}$$

Integrated activities

F.2 The plots of Problem F.1 indicate that as temperature increases the peak of the Maxwell–Boltzmann distribution shifts to higher speeds with a decrease in the fraction of molecules that have low speeds and an increase in the fraction that have high speeds. Thus, justifying summary statements like 'temperature is a measure of the average molecular speed and kinetic energy of gas molecules', 'temperature is a positive property because molecular speed is a positive quantity', 'the absolute temperature of 0 K is unobtainable because the area under the plots of Problem F.1 must equal 1'.