Answers to exercises

Detailed solutions to the (a) exercises can be found in the *Student's Solutions Manual for Physical Chemistry*, sixth edition, by P.W. Atkins, C.A. Trapp., M. Cady, and C. Giunta

Answers to 'a' exercises

1.1 10 atm.

1.2 (a) 24 atm; (b) 22 atm.

1.3 (a) 2.57 kTorr; (b) 3.38 atm.

1.4 30 K.

1.5 30 lb in^{-2}.

1.6 4.20×10^{-2} atm.

1.7 8.3147 $J K^{-1} mol^{-1}$.

1.8 S_8.

1.9 6.2 kg.

1.10 (a) 0.758, 0.242, 561 Torr, 179 Torr; (b) 0.751, 0.239, 0.010, 556 Torr, 177 Torr, 7.4 Torr.

1.11 169 $g mol^{-1}$.

1.12 −272°C.

1.13 (a) 9.975; (b) 1.

1.14 (a) 72 K; (b) 0.95 $km s^{-1}$; (c) 72 K.

1.15 81 mPa.

1.16 9.7×10^{-7} m.

1.17 (a) 5×10^{10} s^{-1}; (b) 5×10^{9} s^{-1}; (c) 5×10^{3} s^{-1}.

1.18 (a) 6.7 nm; (b) 67 nm; (c) 6.7 cm.

1.19 9.06×10^{-3}.

1.20 (a) 1.0 atm, 8.2×10^{2} atm; (b) 1.0 atm, 1.7×10^{3} atm.

1.21 67.8 mL mol^{-1}, 54.5 atm, 120 K.
1.22 (a) 0.88; (b) 1.2 L.
1.23 140 atm.
1.24 (a) 0.1353 L mol^{-1}, 0.6957; (b) 0.649.
1.25 (a) 50.7 atm; (b) 34.8 atm, 0.687.
1.26 (a) 0.67, 0.33; (b) 2.0 atm, 1.0 atm; (c) 3.0 atm.
1.27 32.9 cm^3 mol^{-1}, 1.33 L^2 atm mol^{-2}, 0.24 nm.
1.28 (a) 1.4 kK; (b) 0.28 nm.
1.29 (a) 3.64 kK, 8.7 atm; (b) 2.60 kK, 4.5 atm; (c) 46.7 K, 0.18 atm.
1.30 4.6×10^{-5} m^3 mol^{-1}, 0.66.

2.1 (a) 98 J; (b) 16 J.
2.2 2.6 kJ.
2.3 -1.0×10^2 J.
2.4 (a) $\Delta U = 0$, $\Delta H = 0$, $q = +1.57$ kJ, $w = -1.57$ kJ; (b) $\Delta U = 0$, $\Delta H = 0$, $q = +1.13$ kJ, $w = -1.13$ kJ; (c) all 0.
2.5 1.33 atm, $\Delta U = +1.25$ kJ, $w = 0$, $q = +1.25$ kJ.
2.6 (a) -88 J; (b) -167 J.
2.7 +123 J.
2.8 $\Delta U = -37.55$ kJ, $\Delta H = -40.656$ kJ, $q = -40.656$ kJ, $w = +3.10$ kJ.
2.9 -1.5 kJ.
2.10 85.0 MJ.
2.11 (a) $\Delta U = +26.8$ kJ, $\Delta H = +28.3$ kJ, $q = +28.3$ kJ, $w = -1.45$ kJ; (b) $\Delta U = +26.8$ kJ, $\Delta H = +28.3$ kJ, $q = +26.8$ kJ, $w = 0$.
2.12 131 K.
2.13 194 J.
2.14 22 kPa.
2.15 0.45 atm.
2.16 -125 kJ mol^{-1}.
2.17 $C_{p,m} = 30$ J K^{-1} mol^{-1}, $C_{V,m} = 22$ J K^{-1} mol^{-1}.
2.18 80 J K^{-1}.
2.19 $\Delta U = +1.6$ kJ, $\Delta H = +2.2$ kJ, $q = +2.2$ kJ.
2.20 $w = -3.2$ kJ, $q = 0$, $\Delta T = -38$ K, $\Delta U = -3.2$ kJ, $\Delta H = -4.5$ kJ.
2.21 $w = +4.1$ kJ, $q = 0$, $\Delta U = +4.1$ kJ, $\Delta H = +5.4$ kJ, $p_f = 5.2$ atm, $V_f = 11.8$ L.
2.22 9.4 L, 288 K, -0.46 kJ.
2.23 +0.9 mm^3.
2.24 $q = 0$, $w = \Delta U = -20$ J, $\Delta T = -0.35$ K, $\Delta H = -26$ J.
2.25 (a) 226 K; (b) 238 K.
2.26 $\Delta U = +12$ kJ, $\Delta H = +13$ kJ, $q = +13$ kJ, $w = -1.0$ kJ.
2.27 -4564.7 kJ mol^{-1}.
2.28 -126 kJ mol^{-1}.
2.29 +53 kJ mol^{-1}, -33 kJ mol^{-1}.
2.30 -432 kJ mol^{-1}.
2.31 641 J K^{-1}.
2.32 1.58 kJ K^{-1}, +2.05 K.
2.33 (a) -2.80 MJ mol^{-1}; (b) -2.80 MJ mol^{-1}; (c) -1.28 MJ mol^{-1}.
2.34 +65.49 kJ mol^{-1}.
2.35 -383 kJ mol^{-1}.
2.36 25 kJ, 9.8 m.
2.37 (a) -2205 kJ mol^{-1}; (b) -2200 kJ mol^{-1}.
2.38 (a) $\nu(CO_2) = +1$, $\nu(H_2O) = +2$, $\nu(CH_4) = -1$, $\nu(O_2) = -2$, exothermic; (b) $\nu(C_2H_2) = +1$, $\nu(C) = -2$, $\nu(H_2) = -1$, endothermic; (c) $\nu(Na^+) = +1$, $\nu(Cl^-) = +1$, $\nu(NaCl) = -1$, endothermic.
2.39 (a) -57.20 kJ mol^{-1}; (b) -176.01 kJ mol^{-1}.
2.40 (a) -114.40 kJ mol^{-1}, -109.44 kJ mol^{-1}; (b) -92.31 kJ mol^{-1}, -241.82 kJ mol^{-1}.
2.41 -1368 kJ mol^{-1}.
2.42 (a) -392.1 kJ mol^{-1}; (b) -946.6 kJ mol^{-1}; (c) +52.5 kJ mol^{-1}.
2.43 -56.98 kJ mol^{-1}.
2.44 (a) +131.29 kJ mol^{-1}, +128.81 kJ mol^{-1}; (b) +132.56 kJ mol^{-1}, +129.42 kJ mol^{-1}.
2.45 -1892.2 kJ mol^{-1}.
2.46 (a) -124.2 kJ mol^{-1}; (b) -222.46 kJ mol^{-1}.

3.1 (a) $\partial^2 f/\partial y \partial x = \partial/\partial y(2xy) = 2x$, $\partial^2 f/\partial x \partial y = \partial/\partial x(x^2 + 6y) = 2x$; (b) $\partial^2 f/\partial y \partial x = \partial/\partial y(\cos xy - xy \sin xy) = -x \sin xy - x \sin xy - x^2 y \cos xy = -2x \sin xy - x^2 y \cos xy$, $\partial^2 f/\partial x \partial y = \partial/\partial x(-x^2 \sin xy) = -2x \sin xy - x^2 y \cos xy$.
3.2 $dz = 2axy^3\,dx + 3ax^2y^2\,dy$.
3.3 (a) $dz = (2x - 2y + 2)\,dx + (4y - 2x - 4)\,dy$.
3.4 $dz = (y + 1/x)\,dx + (x - 1)\,dy$.
3.5 $(\partial C_V/\partial V)_T = (\partial(\partial U/\partial V)_T \partial T)_V$.
3.6 $(\partial H/\partial U)_p = 1 + p(\partial V/\partial U)_p$.
3.7 $dV = (\partial V/\partial p)_T\,dp + (\partial V/\partial T)_p\,dT$; $d \ln V = -\kappa_T\,dp + \alpha\,dT$.
3.8 0, 0.
3.10 0.71 K atm^{-1}.
3.11 $\Delta U_m = +137$ J mol^{-1}, $q = +8.05 \times 10^3$ J mol^{-1}, $w = -7.91 \times 10^3$ J mol^{-1}.
3.12 1.31×10^{-3} K^{-1}.
3.13 1×10^3 atm.
3.14 -7.2 J atm^{-1} mol^{-1}, 8.1 kJ.
3.15 -4.2 atm.

4.1 (a) +92 J K^{-1}; (b) +67 J K^{-1}.
4.2 152.67 J K^{-1} mol^{-1}.
4.3 +8.92 J K^{-1}.
4.4 -22.1 J K^{-1}.

4.5 $w = +4.1$ kJ, $q = 0$, $\Delta U = +4.1$ kJ, $\Delta H = +5.4$ kJ, $\Delta S = 0$.
4.6 $+12.9\ \mathrm{J\,K^{-1}}$.
4.7 Not reversible.
4.8 (a) 54.9 kJ; (b) $-195\ \mathrm{J\,K^{-1}}$.
4.9 $+26\ \mathrm{J\,K^{-1}}$.
4.10 6.6 L.
4.11 $+2.8\ \mathrm{J\,K^{-1}}$.
4.12 $\Delta H(\text{overall}) = 0$, $\Delta H(\text{individual}) = \pm 1.9 \times 10^2$ kJ, $\Delta S(\text{overall}) = +93.4\ \mathrm{J\,K^{-1}}$.
4.13 (a) $q = 0$; (b) $w = -20$ J; (c) $\Delta U = -20$ J; (d) $\Delta T = -0.35$ K; (e) $\Delta S = +0.60\ \mathrm{J\,K^{-1}}$.
4.14 (a) $+87.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$; (b) $-87.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
4.15 (a) $-386.1\ \mathrm{J\,K^{-1}\,mol^{-1}}$; (b) $-49.0\ \mathrm{J\,K^{-1}\,mol^{-1}}$; (c) $-153.1\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
4.16 (a) $-521.5\ \mathrm{kJ\,mol^{-1}}$; (b) $+25.8\ \mathrm{kJ\,mol^{-1}}$; (c) $-178.7\ \mathrm{kJ\,mol^{-1}}$.
4.17 (a) $-522.1\ \mathrm{kJ\,mol^{-1}}$; (b) $+25.78\ \mathrm{kJ\,mol^{-1}}$; (c) $-178.6\ \mathrm{kJ\,mol^{-1}}$.
4.18 $-93.05\ \mathrm{kJ\,mol^{-1}}$.
4.19 $-50\ \mathrm{kJ\,mol^{-1}}$.
4.20 (a) $+2.9\ \mathrm{J\,K^{-1}}$, $-2.9\ \mathrm{J\,K^{-1}}$, 0; (b) $+2.9\ \mathrm{J\,K^{-1}}$, 0, $+2.9\ \mathrm{J\,K^{-1}}$; (c) 0, 0, 0.
4.21 $\Delta S = n(C_{V,\mathrm{m}} - R)\ln 2$.
4.22 $817.90\ \mathrm{kJ\,mol^{-1}}$.
4.23 0.11, 0.38.

5.1 $(\partial S/\partial V)_T = \alpha/\kappa_T$.
5.2 -3.8 J.
5.3 $-36.5\ \mathrm{J\,K^{-1}}$.
5.4 $+10$ kJ.
5.5 (a) 15.7 atm; (b) $+8.25$ kJ.
5.6 $+7.3\ \mathrm{kJ\,mol^{-1}}$.
5.7 $-0.55\ \mathrm{kJ\,mol^{-1}}$.
5.8 $-2.63 \times 10^{-8}\ \mathrm{Pa^{-1}}$, 0.88.
5.9 $+10$ kJ.
5.10 $+11\ \mathrm{kJ\,mol^{-1}}$.
5.11 $p = RT/(V_\mathrm{m} - b) - a/V_\mathrm{m}^2$.
5.12 $(\partial S/\partial V)_T = nR/(V - nb)$, ΔS greater for van der Waals gas.

6.1 303 K (30°C).
6.2 $+16\ \mathrm{kJ\,mol^{-1}}$, $+45.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
6.3 $+20.80\ \mathrm{kJ\,mol^{-1}}$.
6.4 (a) $+34.08\ \mathrm{kJ\,mol^{-1}}$; (b) 350.5 K.
6.5 281.8 K (8.7°C).
6.6 $25\ \mathrm{g\,s^{-1}}$.
6.7 (a) 1.7 kg; (b) 31 kg; (c) 1.4 g.
6.8 At 373 K, water vapour condenses to liquid. At 273 K, liquid water freezes. Ice remains at 260 K. There is a pause in the rate of cooling at 373 K and at 273 K.
6.9 (a) $+49\ \mathrm{kJ\,mol^{-1}}$; (b) 216°C; (c) $+99\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
6.10 272.80 K.
6.11 0.07630 (7.6 per cent).
6.12 2.6 kPa.
6.13 $72.8\ \mathrm{mN\,m^{-1}}$.
6.14 728 kPa.

7.1 $886.8\ \mathrm{cm^3}$.
7.2 $56.3\ \mathrm{cm^3\,mol^{-1}}$.
7.3 6.4 MPa.
7.4 0.13 MPa.
7.5 $K_\mathrm{f} = 32\ \mathrm{K\,kg\,mol^{-1}}$, $K_\mathrm{b} = 5.22\ \mathrm{K\,kg\,mol^{-1}}$.
7.6 $82\ \mathrm{g\,mol^{-1}}$.
7.7 $381\ \mathrm{g\,mol^{-1}}$.
7.8 -0.09°C.
7.9 $+1.2\ \mathrm{J\,K^{-1}}$, -0.35 kJ.
7.10 $+4.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
7.11 (a) 1:1; (b) 0.8600.
7.12 (a) $3.4\ \mathrm{mmol\,kg^{-1}}$; (b) $34\ \mathrm{mmol\,kg^{-1}}$.
7.13 $0.17\ \mathrm{mol\,L^{-1}}$.
7.14 -0.16°C.
7.15 $24\ \mathrm{g\,kg^{-1}}$.
7.16 $87\ \mathrm{kg\,mol^{-1}}$.
7.17 Raoult's law basis: $a_\mathrm{A} = 0.833$, $\gamma_\mathrm{A} = 0.93$; Henry's law basis (concentration in mole fractions), $a_\mathrm{B} = 0.125$, $\gamma_\mathrm{B} = 1.25$; (concentration as molality) $a_\mathrm{B} = 2.8$, $\gamma_\mathrm{B} = 1.25$.
7.18 $p(\mathrm{CCl_4}) = 32.2$ Torr, $p(\mathrm{Br_2}) = 6.1$ Torr, $p(\text{Total}) = 38.3$ Torr, $y(\mathrm{CCl_4}) = 0.841$, $y(\mathrm{Br_2}) = 0.16$.
7.19 $a_\mathrm{A} = 0.499$, $a_\mathrm{M} = 0.668$, $\gamma_\mathrm{A} = 1.25$, $\gamma_\mathrm{M} = 1.11$.

8.1 $x_\mathrm{A} = 0.920$, $y_\mathrm{A} = 0.968$.
8.2 440 Torr, $x_\mathrm{A} = 0.268$.
8.3 (a) yes; (b) $y_\mathrm{A} = 0.830$.
8.4 (a) 154 Torr; (b) $y_\mathrm{DE} = 0.67$.
8.5 (a) $y_\mathrm{M} = 0.36$; (b) $y_\mathrm{M} = 0.82$.
8.6 (a) 2; (b) 2.
8.7 2, 2.
8.8 (a) 3, 2; (b) 1.
8.12 At b_3, $C = 2$, $P = 2$, $F = 2$. The compositions of the phases are $x_\mathrm{A} = 0.18$ and $x_\mathrm{A} = 0.70$. At b_2, $C = 2$, $P = 1$, $F = 3$. Between the liquid line and b_1, $C = 2$, $P = 2$, $F = 2$. Above b_1, $C = 1$, $P = 1$, $F = 3$.
8.13 Incongruent melting occurs at 460°C. The composition of the eutectic is 4 per cent by mass of silver; it melts at $\theta_\mathrm{e} = 215$°C.

8.15 (a) ≈80 per cent silver by mass; (b) compound decomposes; (c) ≈82 per cent silver by mass.

8.16 (b) 620 Torr; (c) 490 Torr; (d) $x_{Hexane} = 0.50$, $y_{Hexane} = 0.72$; (e) $y_{Hexane} = 0.50$, $x_{Hexane} = 0.30$; (f) $n_{vap} \approx 1.7$ mol, $n_{liq} \approx 0.3$ mol.

8.19 (a) The mixture has a single liquid phase at all compositions. (b) At $x(C_6F_{14}) = 0.24$, two liquid phases separate with compositions $x = 0.24$ and $x = 0.48$. At $x > 0.48$, a single phase forms.

9.1 $-2.42\ kJ\ mol^{-1}$.

9.2 3.01.

9.3 (a) 2.85×10^{-6}; (b) $+240\ kJ\ mol^{-1}$; (c) 0.

9.4 (a) 0.1411; (b) $+4.855\ kJ\ mol^{-1}$; (c) 14.556.

9.5 (a) $-68.26\ kJ\ mol^{-1}$, 9.2×10^{11}; (b) $-69.7\ kJ\ mol^{-1}$, 1.3×10^{9}.

9.6 (a) 0.087 (A), 0.370 (B), 0.196 (C), 0.438 (D); (b) 0.33; (c) 0.33; (d) $+2.8\ kJ\ mol^{-1}$.

9.7 1.5 kK.

9.8 $+2.77\ kJ\ mol^{-1}$, $-16.5\ J\ K^{-1}\ mol^{-1}$.

9.9 $+12.3\ kJ\ mol^{-1}$.

9.10 50 per cent.

9.11 0.904, 0.096.

9.12 (a, c).

9.13 (b).

9.14 (a) $+53\ kJ\ mol^{-1}$; (b) $-53\ kJ\ mol^{-1}$.

9.15 $-14.38\ kJ\ mol^{-1}$, product formation.

9.16 1110 K.

9.17 (a) 5.40; (b) 3.61.

9.18 (a) 5.13; (b) 8.88; (c) 2.88.

9.19 8.3.

9.21 (a) Na_2HPO_4/H_3PO_4; (b) $H_2PO_4^-/HPO_4^{2-}$.

10.1 $-218.66\ kJ\ mol^{-1}$.

10.2 $1.25 \times 10^{-5}\ mol\ L^{-1}$.

10.3 $-291\ kJ\ mol^{-1}$.

10.4 (a) $I(KCl) = b/b^{\ominus}$; (b) $I(FeCl_3) = 6b/b^{\ominus}$; (c) $I(CuSO_4) = 4b/b^{\ominus}$.

10.5 0.90.

10.6 (a) 2.73 g; (b) 2.92 g.

10.7 $0.25\ mol\ kg^{-1}$.

10.8 $\gamma_{\pm} = (\gamma_+\gamma_-^2)^{1/3}$.

10.9 0.56.

10.10 1×10^4 per cent.

10.11 2.01.

10.12 $-1108\ kJ\ mol^{-1}$.

10.13 +34.2 mV.

10.14 −1.18 V.

10.15 (a) $Ag^+(aq) + e^- \longrightarrow Ag(s)$, $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$, $2Ag^+(aq) + Zn(s) \longrightarrow 2Ag(s) + Zn^{2+}(aq)$, +1.56 V; (b) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$, $Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$, $Cd(s) + 2H^+(aq) \longrightarrow Cd^{2+}(aq) + H_2(g)$, +0.40 V; (c) $Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$, $[Fe(CN)_6]^{3-}(aq) + e^- \longrightarrow [Fe(CN)_6]^{4-}(aq)$, $Cr^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \longrightarrow Cr(s) + 3[Fe(CN)_6]^{3-}(aq)$, −1.10 V.

10.16 (a) $Zn(s)|ZnSO_4(aq)\,\|\,CuSO_4(aq)|Cu(s)$, +1.10 V; (b) $Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)$, +0.22 V; (c) $Pt|H_2(g)|H^+(aq), H_2O(l)|O_2(g)|Pt$, +1.23 V.

10.17 (a) +1.56 V; (b) +0.40 V; (c) −1.10 V.

10.18 (a) +1.10 V; (b) +0.22 V; (c) +1.23 V.

10.19 (a) $-363\ kJ\ mol^{-1}$; (b) $-405\ kJ\ mol^{-1}$.

10.20 (a) +0.324 V; (b) +0.45 V.

10.21 +1.92 V.

10.22 −0.62 V.

10.23 (a) 6.5×10^9; (b) 1.5×10^{12}.

10.24 +0.49 V; 4×10^{16}.

10.25 $1.80 \times 10^{-10} \longrightarrow 1.78 \times 10^{-10}$, $9.04 \times 10^{-7} \longrightarrow 5.1 \times 10^{-7}$.

10.26 $E = E^{\ominus} - (RT/6F)\ \ln[(a(Cr^{3+})^2)/(a(Cr_2O_7^{2-})a(H^+)^{14})]$.

10.27 0.86.

10.28 0.

10.29 (a) $1 \times 10^{-8}\ mol\ kg^{-1}$; (b) 1×10^{-16}.

11.1 1.7 MW.

11.2 1.3×10^{-2} W.

11.3 262 nm.

11.4 $2.42\ cm\ s^{-1}$.

11.5 332 pm.

11.6 $8.83 \times 10^{-28}\ kg\ m\ s^{-1}$, $0.969\ km\ s^{-1}$.

11.7 50.6 nm.

11.8 0.70 nm.

11.9 $E/(10^{-19}\ J)$, $E/(kg\ mol^{-1})$: (a) 3.31, 199; (b) 3.61, 218; (c) 4.97, 299.

11.10 (a) $0.66\ m\ s^{-1}$; (b) $0.72\ m\ s^{-1}$; (c) $0.99\ m\ s^{-1}$.

11.11 $21\ m\ s^{-1}$.

11.12 (a) 2.8×10^{18}; (b) 2.8×10^{20}.

11.13 6 kK.

11.14 (a) no ejection; (b) 3.19×10^{-19} J, $837\ km\ s^{-1}$.

11.15 (a) 7×10^{-19} J, $400\ kJ\ mol^{-1}$; (b) 7×10^{-20} J, $40\ kJ\ mol^{-1}$; (c) 7×10^{-34} J, $4 \times 10^{-13}\ kJ\ mol^{-1}$.

11.16 (a) 6.6×10^{-29} m; (b) 6.6×10^{-36} m; (c) 99.7 pm.

11.17 $1.1 \times 10^{-28}\ m\ s^{-1}$, 1×10^{-27} m.

11.18 1.12×10^{-15} J.

12.1 (a) 1.81×10^{-19} J, $110\ kJ\ mol^{-1}$, 1.1 eV, $9.1 \times 10^3\ cm^{-1}$; (b) 6.6×10^{-19} J, $400\ kJ\ mol^{-1}$, 4.1 eV, $3.3 \times 10^4\ cm^{-1}$.

12.2 (a) 0.04; (b) 0.
12.3 $-(\hbar^2/2m)(d^2\psi/dx^2) = E\psi$, 0, $h^2/4L^2$.
12.4 $L/6$, $L/2$, $5L/6$.
12.5 3.
12.6 23 per cent.
12.7 4.30×10^{-21} J.
12.8 278 N m^{-1}.
12.9 2.63 μm.
12.10 3.72 μm.
12.11 (a) 3.3×10^{-34} J; (b) 3.3×10^{-33} J.
12.13 5.61×10^{-21} J.
12.14 $N = 1/(2\pi)^{1/2}$.
12.15 1.49×10^{-34} J s; 0, $\pm 1.05 \times 10^{-34}$ J s.

13.1 14.0 eV.
13.2 $r = 4a_0$, 0.
13.3 101 pm, 376 pm.
13.4 $N = 2/a_0^{3/2}$.
13.5 $\langle V\rangle = 2E(1s)$, $\langle T\rangle = -E(1s)$.
13.6 $r^* = 5.24a_0/Z$.
13.7 (Angular momentum/$\hbar$, angular nodes, radial nodes) = (a) 0,0,0; (b) 0, 0, 2; (c) $6^{1/2}$, 2, 0.
13.8 (a) $\frac{5}{2}, \frac{3}{2}$; (b) $\frac{7}{2}, \frac{5}{2}$.
13.9 1, 1
13.10 (a) 1; (b) 9; (c) 25.
13.11 $L = 2$, $S = 0$, $J = 2$.
13.12 $r = 0.35a_0$.
13.13 (b, c).
13.14 (a) 2; (b) 6; (c) 10; (d) 18.
13.15 (a) [Ar]$3d^8$; (b) $S = 1$, $M_S = 0, \pm 1$, $S = 0$, $M_S = 0$.
13.16 (a) 1 (3), 0 (1); (b) $\frac{3}{2}$ (4), $\frac{1}{2}$ (2), $\frac{1}{2}$ (2).
13.17 $^3D_3$, $^3D_2$, $^3D_1$, $^1D_2$ with $^3D < {}^1D$.
13.18 (a) 0 (1); (b) $\frac{3}{2}$ (4), $\frac{1}{2}$ (2); (c) 2 (5), 1 (3), 2 (1).
13.19 (a) $^2S_{1/2}$; (b) $^2P_{3/2}$, $^2P_{1/2}$.
13.20 2.1 T.

14.1 (a) $1\sigma^2$ (1); (b) $1\sigma^2 2\sigma^{*2}$ (0); (c) $1\sigma^2 2\sigma^{*2} 1\pi^4$ (2).
14.2 (a) $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$; (b) $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2 2\pi^{*1}$; (c) $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$.
14.3 C_2.
14.4 XeF^+ is shorter.
14.5 (a) g; (c) g; (d) u.
14.6 $\frac{1}{2}$, 0.
14.7 N_2 is shorter.
14.10 (a, c).

15.1 E, C_3, $3\sigma_v$.
15.2 (a, b).
15.3 Yes.
15.6 i, σ_h.
15.8 (a) R_3; (b) C_{2v}; (c) D_{3h}; (d) $D_{\infty h}$.
15.9 (a) C_{2v}; (b) $C_{\infty v}$; (c) C_{3v}; (d) D_{2h}; (e) C_{2v}; (f) C_{2h}.
15.10 (a) C_{2v}; (b) C_{2h}.
15.11 Polar: NO_2, N_2O, $CHCl_3$, and *cis*-CHBr=CHBr. Chiral: none.
15.12 d_{xy}.
15.13 $B_1(x)$, $B_2(y)$, $A_1(z)$.
15.14 (a) E_{1u}, A_{2u}; (b) B_{3u}, B_{2u}, B_{1u}.

16.1 (a) 0.0469 J m^{-3} s; (b) 1.33×10^{-13} J m^{-3} s; (c) 4.50×10^{-16} J m^{-3} s.
16.2 0.409 THz.
16.3 (a) 2.642×10^{-47} kg m^2; (b) 127.4 pm.
16.4 4.442×10^{-47} kg m^2, 165.9 pm.
16.5 232.1 pm.
16.6 106.5 pm, 115.6 pm.
16.7 20475 cm^{-1}.
16.8 2699.77 cm^{-1}.
16.9 0.16 kN m^{-1}.
16.10 1.089 per cent.
16.11 328.7 N m^{-1}.
16.12 $4A_1 + A_2 + 2B_1 + 2B_2$.
16.13 b and d.
16.14 b, c, and d.
16.15 a, b, and d.
16.16 0.999 999 925 × 660 nm.
16.17 2.4×10^7 m s^{-1}, 8.4×10^5 K.
16.18 (a) 5 × 10 ps; (b) 5 ps.
16.19 (a) 53 cm^{-1}; (b) 0.53 cm^{-1}.
16.20 (a) 0.067; (b) 0.20.
16.21 HF (967.0 N m^{-1}), HCl (515.6 N m^{-1}), HBr (411.8 N m^{-1}), HI (314.2 N m^{-1}).
16.22 1580.38 cm^{-1}, 7.644×10^{-3}.
16.23 5.15 eV.
16.24 198.9 pm.
16.25 (a) 3; (b) 6; (c) 12.
16.26 (a) All; (b) symmetric stretch: Raman, antisymmetric stretch and bends: IR.
16.27 Raman active.

17.1 80 per cent.
17.2 6.28×10^3 L mol^{-1} cm^{-1}.
17.3 1.5 mmol L^{-1}.
17.4 5.44×10^7 L mol^{-1} cm^{-2}.
17.5 Diene: 243 nm; butene: 192 nm.
17.6 450 L mol^{-1} cm^{-1}.
17.7 159 L mol^{-1} cm^{-1}, 23 per cent.

17.8 (a) 0.9 m; (b) 3 m.
17.9 (a) 5×10^7 L mol^{-1} cm^{-2}; (b) 2.5×10^6 L mol^{-1} cm^{-2}.

18.1 600 MHz.
18.2 $(-1.625 \times 10^{-26}\ \text{J}) \times m_I$.
18.3 154 MHz.
18.4 (a) proton.
18.5 6.116×10^{-26} J.
18.6 (a) 5.87 T; (b) 38.3 T; (c) 23.4 T.
18.7 (a) 1×10^{-6}; (b) 5.1×10^{-6}; (c) 3.4×10^{-5}.
18.8 10.
18.9 (a) 11 μT; (b) 110 μT.
18.11 6.7×10^2 s^{-1}.
18.14 (b).
18.15 0.59 mT, 20 μs.
18.16 0.2 kT, 10 mT.
18.17 2.0022.
18.18 2.3 mT, 2.003.
18.19 330.2 mT, 332.2 mT, 332.8 mT, 334.8 mT, 1:1:1:1.
18.20 (a) 1:3:3:1; (b) 1:3:6:7:6:3:1.
18.21 (a) 331.9 mT; (b) 1.201 T.
18.22 $\frac{3}{2}$.

19.1 1.
19.2 (a) 2.57×10^{27}; (b) 7.26×10^{27}.
19.3 2.83.
19.4 3.156.
19.5 2.45 kJ mol^{-1}.
19.6 354 K.
19.7 (a) 0.71; (b) 0.996.
19.8 (a) 5×10^{-5}, 0.4, 0.905; (b) 1.4; (c) 22 J mol^{-1}; (d) 1.6 J K^{-1} mol^{-1}; (e) 4.8 J K^{-1} mol^{-1}.
19.9 4303 K.
19.10 (a) 138 J K^{-1} mol^{-1}; (b) 146 J K^{-1} mol^{-1}.
19.11 5.18 J K^{-1} mol^{-1}.
19.12 a, b, and d.

20.1 (a) $5R/2$; (b) $3R$; (c) $3R$.
20.2 NH_3: 1.33 and 1.11 (1.31); CH_4:1.33 and 1.08 (1.31).
20.3 (a) 19.6; (b) 34.3.
20.4 (a) 1; (b) 2; (c) 2; (d) 12; (e) 3.
20.5 43.1, 23.36 K.
20.6 43.76 J K^{-1} mol^{-1}.
20.7 (a) 36.95, 80.08; (b) 36.7, 79.7.
20.8 72.5.
20.9 (a) 14.93 J K^{-1} mol^{-1}; (b) 25.65 J K^{-1} mol^{-1}.
20.10 -13.8 kJ mol^{-1}, -0.20 kJ mol^{-1}.
20.11 (a) $0.236R$; (b) $0.193R$.
20.12 11.5 J K^{-1} mol^{-1}.
20.13 (a) 9 J K^{-1} mol^{-1}; (b) 13 J K^{-1} mol^{-1}; (c) 15 J K^{-1} mol^{-1}.
20.14 9.57×10^{-15} J K^{-1}.
20.15 3.70×10^{-3}.

21.1 $(1, \frac{1}{2}, 0)$, $(1, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.
21.2 (323), (110).
21.3 249 pm, 176 pm, 432 pm.
21.4 70.7 pm.
21.5 16°, 23°, 28°.
21.6 0.215 cm.
21.7 3.96×10^{-28} m^3.
21.8 4, 4.01 g cm^{-3}.
21.9 190 pm.
21.10 (111), (200), (311).
21.11 8.17°, 4.82°, 11.75°.
21.12 fcc.
21.13 $F_{hkl} = f$.
21.14 0.9069.
21.16 (a) 58.0 pm; (b) 102 pm.
21.17 0.340.
21.18 7.654 g cm^{-3}.
21.19 +1.6 per cent.
21.21 7.9 km s^{-1}.
21.22 4.6 kV.
21.23 5.8°, 17°, 0.3°, 0.9°.

22.1 O_3 and H_2O_2, but rotation about the O–O bond in H_2O_2 averages out the polarity.
22.2 1.01×10^{-39} J^{-1} C^2 m^2 (9.1×10^{-24} cm^3), 1.7 D.
22.3 4.8.
22.4 1.42×10^{-39} J^{-1} C^2 m^2 (1.28×10^{-23} cm^3).
22.5 17 per cent, 23 per cent; no correlation.
22.6 (a) 0 (by symmetry); (b) 0.7 D; (c) 0.4 D.
22.7 37 D at 11.7° to x-axis.
22.8 4.9 μD.
22.9 1.34.
22.10 18.
22.11 6.9×10^{-6}.
22.12 3.
22.13 -6.4×10^{-5} cm^3 mol^{-1}.
22.14 2.
22.15 4.326.
22.16 +0.016 cm^3 mol^{-1}.
22.17 222 T.

23.1 70 kg mol^{-1}, 71 kg mol^{-1}.
23.2 24 nm.

23.3 1.37×10^4.
23.4 3.08 μm, 3.08 nm.
23.5 100.
23.6 0.73 mm s^{-1}.
23.7 63 kg mol^{-1}.
23.8 31 kg mol^{-1}.
23.9 (a) 18 kg mol^{-1}; (b) 20 kg mol^{-1}.
23.10 0.24 mmol L^{-1}.
23.11 6.7 mmol L^{-1}.
23.12 3.4 Mg mol^{-1}.
23.13 4.3×10^5 *g*.
23.14 24 ns, 14 ps.

24.1 1.9×10^{20}.
24.2 104 mg.
24.3 4.1×10^{-2} J m^{-2} s^{-1}.
24.4 0.056 nm^2.
24.5 17 W, 17 W.
24.6 43 g mol^{-1}.
24.7 30 h.
24.8 0.142 nm^2.
24.9 205 kPa.
24.10 (a) 130 μP; (b) 130 μP; (c) 240 μP.
24.11 (a) 5.4 mJ K^{-1} m^{-1} s^{-1}, 8.1 mW; (b) 29 mJ K^{-1} m^{-1} s^{-1}, 44 mW.
24.12 138 μP, 390 pm.
24.13 5.4×10^{-3} J K^{-1} m^{-1} s^{-1}.
24.14 (a) 11 m^2 s^{-1}, 4.4×10^2 mol m^{-2} s^{-1}; (b) 1.1×10^{-5} m^2 s^{-1}, 4.4×10^{-3} mol m^{-2} s^{-1}; (c) 1.1×10^{-7} m^2 s^{-1}, 4.4×10^{-5} mol m^{-2} s^{-1}.
24.15 7.63×10^{-3} S m^2 mol^{-1}.
24.16 347 μm s^{-1}.
24.17 0.331.
24.18 13.83 mS m^2 mol^{-1}.
24.19 4.01×10^{-8} m^2 V^{-1} s^{-1}, 5.19×10^{-8} m^2 V^{-1} s^{-1}, 7.62×10^{-8} m^2 V^{-1} s^{-1}.
24.20 1.90×10^{-9} m^2 s^{-1}.
24.21 1.3 ks.
24.22 420 pm.
24.23 27 ps.
24.24 113 μm.
24.25 (a) 78 s; (b) 7.8×10^3 s.

25.1 C: 3.0 mol L^{-1} s^{-1}, D: 1.0 mol L^{-1} s^{-1}, A: 1.0 mol L^{-1} s^{-1}, B: 2.0 mol L^{-1} s^{-1}.
25.2 *v*: 0.50 mol L^{-1} s^{-1}, D: 1.5 mol L^{-1} s^{-1}, A: 1.0 mol L^{-1} s^{-1}, B: 0.50 mol L^{-1} s^{-1}.
25.3 L mol^{-1} s^{-1}; (a) $k[A][B]$; (b) $3k[A][B]$.
25.4 $v = \frac{1}{2}k[A][B][C]$, L^2 mol^{-2} s^{-1}.
25.5 2.
25.6 2.
25.7 10.3 ks; (a) 499.7 Torr; (b) 480 Torr.
25.8 (a) 4.1×10^{-3} L mol^{-1} s^{-1}; (b) A: 2.6 ks, B: 7.4 ks.
25.9 (a) L mol^{-1} s^{-1}, L^2 mol^{-2} s^{-1}; (b) kPa^{-1} s^{-1}, kPa^{-2} s^{-1}.
25.10 2720 y.
25.11 (a) 45, 95 mmol L^{-1}; (b) 1, 51 mmol L^{-1}.
25.12 124 ks.
25.13 64.9 kJ mol^{-1}, 4.32×10^8 mol L^{-1} s^{-1}.
25.14 $v = k_2K^{1/2}[A_2]^{1/2}[B]$.
25.16 1.52 mmol L^{-1} s^{-1}.
25.17 1.9 MPa^{-1} s^{-1}.
25.18 7.1×10^5 s^{-1}, 7.63 ns.

26.1 $v = k_1k_2[O_3]^2/(k_1'[O_2] + k_2[O_3])$.
26.3 0.16 to 4.0 kPa.
26.4 3.3×10^{18}.
26.5 0.518.
26.6 $d[P]/dt = (k_1'/k_3[AH]^2[B])/(k_2[BH]^+ + k_3[AH])$.
26.7 $d[AH]/dt = -k_{eff}[AH]$; k_{eff} is a complex combination of rate constants.

27.1 9.6×10^9 s^{-1}, 1.2×10^{35} m^{-3} s^{-1}.
27.2 (a) 0.018, 0.30; (b) 3.9×10^{-18}, 6.0×10^{-6}.
27.3 (a) 13 per cent, 1.2 per cent; (b) 130 per cent, 12 per cent.
27.4 1.7×10^{-2} L mol^{-1} s^{-1}.
27.5 3×10^{10} L mol^{-1} s^{-1}.
27.6 (a) 6.61×10^6 m^3 mol^{-1} s^{-1}; (b) 3.0×10^7 m^3 mol^{-1} s^{-1}.
27.7 7.4×10^9 L mol^{-1} s^{-1}; 0.14 μs.
27.8 1.2×10^{-3}.
27.9 1.9×10^8 mol L^{-1} s^{-1}.
27.10 69.7 kJ mol^{-1}, −25 J K^{-1} mol^{-1}.
27.11 +71.9 kJ mol^{-1}.
27.12 −96.6 J K^{-1} mol^{-1}.
27.13 −76 J K^{-1} mol^{-1}.
27.14 (a) −45.8 J K^{-1} mol^{-1}; (b) +5.0 kJ mol^{-1}; (c) +18.7 kJ mol^{-1}.
27.15 $k_D/k_H \approx 0.15$.
27.16 20.9 L^2 mol^{-2} min^{-1}.

28.1 (a) 1.07×10^{25} m^{-2} s^{-1}, 1.4×10^{18} m^{-2} s^{-1}; (b) 2.35×10^{24} m^{-2} s^{-1}, 3.1×10^{17} m^{-2} s^{-1}.
28.2 1.3×10^4 Pa.
28.3 3.4×10^5 s^{-1}.
28.4 12.7 m^2.
28.5 20.5 cm^3.
28.6 Chemisorption, 50 s.

28.7 $E_d = 610\ \text{kJ mol}^{-1}$, $\tau_0 = 1.13 \times 10^{-13}\ \text{s}, A = 6.15 \times 10^{12}\ \text{s}^{-1}$.
28.8 (a) 0.21 kPa; (b) 22 kPa.
28.9 0.83, 0.36.
28.10 (a) 40 ps, 0.6 ps; (b) 20 Ts, 7 μs.
28.11 15 kPa.
28.12 0 on gold, 1 on platinum.
28.13 $-13\ \text{kJ mol}^{-1}$.
28.14 $700\ \text{kJ mol}^{-1}$; (a) 1.2×10^{97} min; (b) 2.8×10^{-6} min.

29.1 $0.24\ \text{GV m}^{-1}$.
29.2 138 mV.
29.3 $2.8\ \text{mA cm}^{-2}$.
29.4 Increase ×50.
29.5 (a) $0.17\ \text{mA cm}^{-2}$; (b) $0.17\ \text{mA cm}^{-2}$.
29.6 $0.99\ \text{A m}^{-2}$.
29.7 $0.2\ \mu\text{mol L}^{-1}$.
29.8 (a) $0.31\ \text{mA cm}^{-2}$; (b) $5.41\ \text{mA cm}^{-2}$; (c) $-2.19\ \text{mA cm}^{-2}$.
29.9 $a(Fe^{3+})/a(Fe^{2+}) = 0.1$: $684\ \text{mA cm}^{-2}$; $a(Fe^{3+})/a(Fe^{2+}) = 1$: $215\ \text{mA cm}^{-2}$; $a(Fe^{3+})/a(Fe^{2+}) = 10$: $68\ \text{mA cm}^{-2}$.
29.10 108 mV.
29.11 (a) $4.9 \times 10^{15}\ \text{cm}^{-2}\ \text{s}^{-1}$, $3.8\ \text{s}^{-1}$; (b) $1.6 \times 10^{16}\ \text{cm}^{-2}\ \text{s}^{-1}$, $12\ \text{s}^{-1}$; (c) $3.1 \times 10^{7}\ \text{cm}^{-2}\ \text{s}^{-1}$, $2.4 \times 10^{-8}\ \text{s}^{-1}$.
29.12 (a) 33 Ω; (b) 33 GΩ.
29.15 Yes.
29.16 No.
29.17 +1.30 V, 0.13 W.
29.18 (a) +1.23 V; (b) +1.06 V.
29.19 Fe, Al, Co, Cr if O_2 absent; all if O_2 present.
29.20 $1.2\ \text{mm year}^{-1}$.

Answers to 'b' exercises

1.1 146 kPa.
1.2 (a) 10.5 bar; (b) 10.4 bar.
1.3 (a) 8.04×10^2 Torr; (b) 1.07 bar.
1.4 92.4 K.
1.5 119 kPa.
1.6 2.67×10^3 kg.
1.7 $8.206\,15 \times 10^{-2}\ \text{L atm mol}^{-1}\ \text{K}^{-1}$, $31.9987\ \text{g mol}^{-1}$.
1.8 P_4.
1.9 2.6 kg.
1.10 (a) 3.14 L; (b) 212 Torr.
1.11 $16.4\ \text{g mol}^{-1}$.
1.12 −270°C.
1.13 (a) 7.079, (b) 1.
1.14 (a) $475\ \text{m s}^{-1}$; (b) 40 km; (c) $0.01\ \text{s}^{-1}$.
1.15 2.4×10^7 Pa.
1.16 4.1×10^{-7} m.
1.17 $9.9 \times 10^8\ \text{s}^{-1}$.
1.18 (a) 3.7×10^{-9} m; (b) 5.5×10^{-8} m; (c) 4.1×10^{-5} m.
1.19 9.6×10^{-2}.
1.20 (a) 1.0 atm, 270 atm; (b) 0.99 atm, 180 atm.
1.21 $0.131\ \text{L mol}^{-1}$, 25.7 atm, 109 K.
1.22 (a) 1.12, repulsive; (b) $2.7\ \text{L mol}^{-1}$.
1.23 (a) $0.124\ \text{L mol}^{-1}$; (b) $0.108\ \text{L mol}^{-1}$.
1.24 (a) $31.728\ \text{L mol}^{-1}$, 0.996; (b) 0.996.
1.25 (a) 8.7 mL; (b) $-0.15\ \text{L mol}^{-1}$.
1.26 (a) 0.63, 0.37; (b) $p(N_2) = 2.5$ atm, $p(H_2) = 1.5$ atm; (c) 4.0 atm.
1.27 $a = 3.16\ \text{L}^2\ \text{atm mol}^{-2}$, $b = 0.493\ \text{L mol}^{-1}$, $r = 1.94 \times 10^{-10}$ m.
1.28 (a) 1276 K; (b) 1.286×10^{-10} m.
1.29 (a) 2.6 atm, 881 K; (b) 2.2 atm, 718 K; (c) 1.4 atm, 356 K.
1.30 $0.13\ \text{L mol}^{-1}$, 0.67.

2.1 (a) 4.9×10^3 J; (b) 1.9×10^3 J.
2.2 59 J.
2.3 −91 J.
2.4 $\Delta U = 0$, $\Delta H = 0$; (a) $w = -1.62$ kJ, $q = +1.62$ kJ; (b) $w = -1.38$ kJ, $q = +1.38$ kJ; (c) $w = q = 0$.
2.5 $p_2 = 143$ kPa, $w = 0$, $q = \Delta U = +3.28$ kJ.
2.6 (a) −19 J; (b) −52.8 J.
2.7 6.01 J.
2.8 $q = \Delta H = -70.6$ kJ, $w = +5.60 \times 10^3$ J, $\Delta U = -65.0$ kJ.
2.9 −188 J.
2.10 3.07×10^4 kJ.
2.11 (a) $q = \Delta H = +14.9$ kJ, $w = -831$ J, $\Delta U = +14.1$ kJ; (b) $q = \Delta U = +14.1$ kJ, $w = 0$, $\Delta H = +14.9$ kJ.
2.12 200 K.
2.13 −325 J.
2.14 8.5 Torr.
2.15 $p_i = 1.9$ atm, $p_f = 0.46$ atm.
2.16 $-199\ \text{kJ mol}^{-1}$.
2.17 $C_{p,m} = 53\ \text{J K}^{-1}\ \text{mol}^{-1}$, $C_{V,m} = 45\ \text{J K}^{-1}\ \text{mol}^{-1}$.
2.18 $q_p = \Delta H = -2.3$ kJ, $C = 0.18\ \text{kJ K}^{-1}$.
2.19 $\Delta H = q = +2.0\ \text{kJ mol}^{-1}$, $\Delta U = +1.6\ \text{kJ mol}^{-1}$.
2.20 $q = 0$, $w = \Delta U = -3.5$ kJ, $\Delta T = -24$ K, $\Delta H = -4.5$ kJ.
2.21 $q = 0$, $w = \Delta U = +2.4$ kJ, $\Delta H = +3.1$ kJ, $V_f = 14$ L, $p_f = 3.8 \times 10^5$ Pa.
2.22 20 L, 275 K, −0.75 kJ.
2.23 $1.8 \times 10^{-3}\ \text{cm}^3$.
2.24 $q = 0$, $w = \Delta U = -36$ J, $\Delta T = -0.57$ K, $\Delta H = -50$ J.
2.25 (a) 164 K; (b) 171 K.

2.26 $q = \Delta H = +24$ kJ, $w = -1.6$ kJ, $\Delta H = +22.4$ kJ.
2.27 -3053.6 kJ mol^{-1}.
2.28 -126 kJ mol^{-1}.
2.29 -1152 kJ mol^{-1}.
2.30 -324.83 kJ mol^{-1}.
2.31 451 J K^{-1}.
2.32 69.3 J K^{-1}, 63.1 K.
2.33 (a) -2.81×10^3 kJ mol^{-1}; (b) -2.81×10^3 kJ mol^{-1}; (c) -1.27×10^3 kJ mol^{-1}.
2.34 84.40 kJ mol^{-1}.
2.35 1.90 kJ mol^{-1}.
2.36 39 kJ, 16 m.
2.37 (a) -2857 kJ mol^{-1}; (b) -2851 kJ mol^{-1}.
2.38 (a) $\nu(\mathrm{C(s, diamond)}) = -1$, $\nu(\mathrm{C(s, graphite)}) = +1$, exothermic; (b) $\nu(\mathrm{Fe_3O_4}) = -1$, $\nu(\mathrm{CO}) = -1$, $\nu(\mathrm{FeO}) = +3$, $\nu(\mathrm{CO_2}) = +1$, endothermic; (c) $\nu(\mathrm{FeO}) = -3$, $\nu(\mathrm{CO_2}) = -1$, $\nu(\mathrm{Fe_3O_4}) = +1$, $\nu(\mathrm{CO}) = +1$, exothermic.
2.39 (a) -32.88 kJ mol^{-1}; (b) -55.84 kJ mol^{-1}.
2.40 (a) -589.56 kJ mol^{-1}, -582.13 kJ mol^{-1}; (b) -26.48 kJ mol^{-1}, -241.82 kJ mol^{-1}.
2.41 -760.3 kJ mol^{-1}.
2.42 $+52.5$ kJ mol^{-1}.
2.43 -566.93 kJ mol^{-1}.
2.44 -1745 kJ mol^{-1}, -173 kJ mol^{-1} -176 kJ mol^{-1}.
2.45 -1587 kJ mol^{-1}.
2.46 (a) -229.6 kJ mol^{-1}; (b) -160.5 kJ mol^{-1}.

3.2 $\mathrm{d}z = \mathrm{d}x/[(1+y)^2 - 2x\mathrm{d}y/(1+y)^3]$.
3.3 (a) $(3x^2 - 2y^2)\mathrm{d}x - 4xy\mathrm{d}y$.
3.4 $\mathrm{d}z = (2xy + y^2)\mathrm{d}x + (x^2 + 2xy)\mathrm{d}y$.
3.5 $(\partial C_p/\partial p)_T = [\partial(\partial H/\partial p)_T/\partial T]_p$.
3.7 $\mathrm{d}p = (\partial p/\partial V)_T \mathrm{d}V + (\partial V/\partial T)_V \mathrm{d}T$, $\mathrm{d}\ln p = (1/p\kappa_T)(\alpha \mathrm{d}T - \mathrm{d}V/V)$.
3.8 0, 0.
3.9 $\kappa_T = 1/p$, $\alpha = 1/T$.
3.10 0.48 K atm^{-1}.
3.11 $\Delta U_m = +130$ J mol^{-1}, $q = +7.75$ kJ mol^{-1}, $w = -7.62$ kJ mol^{-1}.
3.12 1.27×10^{-3} K^{-1}.
3.13 3.6×10^2 atm.
3.14 -41.2 J atm^{-1} mol^{-1}, 27.2 kJ.
3.15 -340 kPa.

4.1 (a) 1.8×10^2 J K^{-1}; (b) 1.5×10^2 J K^{-1}.
4.2 152.65 J K^{-1} mol^{-1}.
4.3 9.08 J K^{-1}.
4.4 -7.3 J K^{-1}.
4.5 $q = 0$, $\Delta S = 0$, $\Delta U = w = +2.75$ kJ, $\Delta H = +3.58$ kJ.
4.6 76.9 J K^{-1}.
4.7 Not reversible.
4.8 (a) -58.2 kJ; (b) -193 J K^{-1}.
4.9 17 J K^{-1}.
4.10 6.00 L.
4.11 0.2 J K^{-1}.
4.12 $\Delta H_{\text{total}} = 0$, $\Delta S_{\text{total}} = +24$ J K^{-1}.
4.13 (a) 0; (b) -230 J; (c) -230 J; (d) -5.3 K; (e) $+3.21$ J K^{-1}.
4.14 (a) $+104.6$ J K^{-1}; (b) -104.6 J K^{-1}.
4.15 (a) -21.0 J K^{-1} mol^{-1}; (b) $+512$ J K^{-1} mol^{-1}.
4.16 (a) -212.40 kJ mol^{-1}; (b) -5798 kJ mol^{-1}.
4.17 (a) -212.55 kJ mol^{-1}; (b) -5798 kJ mol^{-1}.
4.18 -86.2 kJ mol^{-1}.
4.19 -197 kJ mol^{-1}.
4.20 (a) $+3.0$ J K^{-1}, -3.0 J K^{-1}, 0; (b) $+3.0$ J K^{-1}, 0, $+3.0$ J K^{-1}; (c) 0, 0, 0.
4.21 $\Delta S = \frac{3}{2} nR \ln 3$.
4.22 2108.11 kJ mol^{-1}.
4.23 (a) 0.500; (b) 0.50 kJ; (c) 0.5 kJ.

5.1 Both (Maxwell relation) $= -\alpha V$.
5.2 -2.0 J.
5.3 -42.8 J K^{-1}.
5.4 3.2 kJ.
5.5 (a) 274 kPa; (b) 3.45 kJ.
5.6 2.71 kJ mol^{-1}.
5.7 -0.93 kJ mol^{-1}.
5.8 -1.92×10^{-7} Pa^{-1}, 10^{-6}.
5.9 200 J.
5.10 $+2.88$ kJ mol^{-1}.
5.11 $V = (RT/p)(1 + B'p/RT + C'p^2/RT + D'p^3/RT)$.

6.1 23°C.
6.2 2.4 kJ mol^{-1}, 5.5 J K^{-1} mol^{-1}.
6.3 25.25 kJ mol^{-1}.
6.4 (a) 31.11 kJ mol^{-1}; (b) 276.9 K.
6.5 272 K.
6.6 3.6 kg s^{-1}.
6.7 Yes, $p \geq 3$ Torr.
6.8 (a) gas expands; (b) gas contracts; (c) gas freezes; (d) solid sublimes; (e) gas expands.
6.9 (a) 29 kJ mol^{-1}; (b) 0.22 atm, 0.76 atm.
6.10 272.40 K.
6.11 6.73×10^{-2}.
6.12 5.92 kPa.
6.13 7.12×10^{-2} N m^{-1}.
6.14 2.04×10^5 Pa.

7.1 843.5 cm^3.
7.2 18 cm^3.
7.3 8.2×10^3 kPa.
7.4 1.5×10^2 kPa.
7.5 7.1 K kg mol^{-1}, 4.99 K kg mol^{-1}.
7.6 270 g mol^{-1}.
7.7 178 g mol^{-1}.
7.8 −0.077°C.
7.9 6.34×10^{-2} J K^{-1}, −17.3 J.
7.10 −3.43 kJ, +11.5 J K^{-1}, 0.
7.11 (a) $n_B/n_E = 1$; (b) $m_B/m_E = 0.7358$.
7.12 N_2: 0.51 mmol kg^{-1}; O_2: 0.27 mmol kg^{-1}.
7.13 0.067 mol L^{-1}.
7.14 −0.52°C.
7.15 11 kg Pb/1 kg Bi.
7.16 14.0 kg mol^{-1}.
7.17 $a = 0.9701$, $\gamma = 0.980$.
7.18 −3.54 kJ mol^{-1}, 212 Torr.
7.19 $a_A = 0.436$, $a_B = 0.755$, $\gamma_A = 1.98$, $\gamma_B = 0.968$.

8.1 $x_A = 0.5$, $y_A = 0.5$.
8.2 73.4 kPa, $x_A = 0.653$.
8.3 (a) yes; (b) $y_A = 0.458$, $y_B = 0.542$.
8.4 (a) 48 Torr; (b) $y_B = 0.77$, $y_T = 0.23$; (c) 34 Torr.
8.5 (a) $y_A = 0.81$; (b) $x_A = 0.67$, $y_A = 0.925$.
8.6 3.
8.7 (a) $C = 1$, $P = 2$; (b) $C = 2$, $P = 2$.
8.8 (a) $C = 2$, $P = 2$; (b) $F = 2$.
8.13 $x_B \approx 0.53$ at T_2 and $x_B = 0.82$ at T_3.
8.15 (a) $x_B \approx 0.75$; (b) $x_{AB_2} \approx 0.8$; (c) $x_{AB_2} \approx 0.6$.
8.16 A solid solution with $x(ZrF_4) = 0.24$ appears at 855°C. The solid solution continues to form, and its ZrF_4 content increases until it reaches $x(ZrF_4) = 0.40$ at 820°C. At that temperature, the entire sample is solid.

9.1 +18.18 kJ mol^{-1}.
9.2 0.98.
9.3 (a) 0; (b) 0.168; (c) 4.41 kJ mol^{-1}.
9.4 (a) 0.24; (b) +19 kJ mol^{-1}; (c) 2.96.
9.5 (a) −308.84 kJ mol^{-1}, 1.3×10^{54}; (b) −306.52 kJ mol^{-1}, 3.5×10^{49}.
9.6 (a) 0.178 (A), 0.31 (B), 0.116 (C), 0.674 (D); (b) 9.6; (c) 9.6; (d) −5.6 kJ mol^{-1}.
9.7 1.4×10^3 K.
9.8 +7.2 kJ mol^{-1}, −21 J K^{-1} mol^{-1}.
9.9 −41.0 kJ mol^{-1}.
9.10 No change.
9.11 1.6×10^{-2}.
9.12 (b).
9.13 (b).
9.14 (a) +39 kJ mol^{-1}; (b) −39 kJ mol^{-1}.
9.15 (a) 9.24; (b) −12.9 kJ mol^{-1}; (c) +161 kJ mol^{-1}; (d) +248 J K^{-1} mol^{-1}.
9.16 397 K.
9.17 (a) 1.5×10^{-5}, 4.82; (b) 3.21.
9.18 (a) 8.37; (b) 8.74; (c) 5.07.
9.19 7.38.
9.21 (a) aniline and anilinium ion; (b) ethylammonium ion and ethylamine.

10.1 −65.49 kJ mol^{-1}.
10.2 9.3×10^{-15} mol kg^{-1}.
10.3 −363 kJ mol^{-1}.
10.4 (a) $3b/b^{\ominus}$; (b) $15b/b^{\ominus}$; (c) $15b/b^{\ominus}$.
10.5 0.320.
10.6 (a) 45 g; (b) 38.8 g.
10.7 0.100 mol kg^{-1}.
10.8 $\gamma_{\pm} = (\gamma_+^2\gamma_-^3)^{1/5}$.
10.9 0.661.
10.10 47.1 per cent.
10.11 1.3.
10.12 −128.8 kJ mol^{-1}.
10.13 +56.3 mV.
10.14 $Cd(s)|CD(OH)_2(s)|OH^-(aq)|Ni(OH)_2(s)|Ni(OH)_3(s)|Pt$,
L: $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$,
R: $Ni(OH)_3(s) + e^- \longrightarrow Ni(OH)_2(s) + OH^-$.
10.15 (a) $Ag_2CrO_4(s) + 2e^- \longrightarrow 2Ag(s) + CrO_4^{2-}(aq)$, $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$, $Ag_2CrO_4(s) + 2Cl^-(aq) \longrightarrow 2Ag(s) + CrO_4^{2-}(aq) + Cl_2(g)$, −0.91 V;
(b) $Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$, $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$, $Sn^{4+}(aq) + 2Fe^{2+}(aq) \longrightarrow Sn^{2+}(aq) + 2Fe^{3+}(aq)$, −0.62 V;
(c) $MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$, $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$, $Cu(s) + MnO_2(s) + 4H^+(aq) \longrightarrow Cu^{2+}(aq) + Mn^{2+}(aq) + 2H_2O(l)$, +0.89 V.
10.16 (a) $Na(s)|NaOH(aq)|H_2(g)|Pt$, +1.88 V;
(b) $Pt|H_2(g)|HI(aq)|I_2(s)|Pt$, +0.54 V;
(c) $Pt|H_2(g)|H_2O(l)|H_2(g)|Pt$ = 0.83 V.
10.17 (a) −0.91 V; (b) −0.62 V; (c) +0.89 V.
10.18 (a) +1.88 V; (b) +0.54 V; (c) +0.83 V.
10.19 (a) −291 kJ mol^{-1}; (b) +122 kJ mol^{-1}.
10.20 (a) −2.455 V; (b) +1.627 V.
10.21 (a) $E = E^{\ominus} - (2RT/F)\ln(\gamma_{\pm}b)$; (b) −89.89 kJ mol^{-1}; (c) +0.223 V.
10.22 −1.24 V, +239 kJ mol^{-1}, +300.3 kJ mol^{-1}, +237 kJ mol^{-1} at 35°C.
10.23 1.7×10^{16}; (b) 8.2×10^{-7}.
10.24 +0.20 V.

10.25 AgI: 1.4×10^{-16}; Bi_2S_3: 3.2×10^{-98}; no significant difference.

10.26 $E = E^{\ominus} - (RT/5F)\ \ln\{a(Mn^{2+})/[a(MnO_4^-)a(H^+)^8]\}$.

10.27 9.72.

10.28 0.

10.29 (a) 10^{-20} mol L^{-1}; (b) 10^{-98}.

11.1 2.5×10^2 W.

11.2 1.36×10^{-8} W.

11.3 1.15 μm.

11.4 1.3×10^{-5} m s^{-1}.

11.5 1.6×10^6 m s^{-1}.

11.6 1.89×10^{-27} kg m s^{-1}, 0.565 m s^{-1}.

11.7 38.4 nm.

11.8 5.8×10^{-6} m.

11.9 (a) 9.93×10^{-19} J, 5.98×10^5 J mol^{-1}; (b) 1.32×10^{-15} J, 7.98×10^8 J mol^{-1}; (c) 1.99×10^{-23} J, 12.0 J mol^{-1}.

11.10 (a) 0.499 m s^{-1}; (b) 665 m s^{-1}; (c) 9.9×10^{-6} m s^{-1}.

11.11 158 m s^{-1}.

11.12 (a) 3.52×10^{17} s^{-1}; (b) 3.52×10^{18} s^{-1}.

11.13 1800 K.

11.14 (a) 0; (b) 6.84×10^{-19} J, 1.23×10^6 m s^{-1}.

11.15 (a) 2.65×10^{-19} J, 160 kJ mol^{-1}; (b) 3.00×10^{-19} J, 181 kJ mol^{-1};
(c) 6.62×10^{-31} J, 4.0×10^{-10} kJ mol^{-1}.

11.16 (a) 1.23×10^{-10} m; (b) 3.9×10^{-11} m; (c) 3.88×10^{-12} m.

11.17 $\Delta x = 100$ pm, $\Delta v = 5.8 \times 10^5$ m s^{-1}.

11.18 1.67×10^{-16} J.

12.1 (a) 2.14×10^{-19} J, 1.29×10^2 kJ mol^{-1}, 1.34 eV, 1.08×10^4 cm^{-1}; (b) 3.48×10^{-19} J, 2.10×10^2 kJ mol^{-1}, 2.10 eV, 1.75×10^4 cm^{-1}.

12.2 (a) 0.03; (b) 0.03.

12.3 $\langle p \rangle = 0, \langle p^2 \rangle = h^2/L^2$.

12.4 $L/10$, $3L/10$, $L/2$, $7L/10$, $9L/10$.

12.5 6.

12.6 $n = 7.26 \times 10^{10}$, $\Delta E = 1.76 \times 10^{-31}$ J, $\lambda = 27.5$ pm; may be treated classically.

12.7 3.92×10^{-21} J.

12.8 260 N m^{-1}.

12.9 13.2 μm.

12.10 18.7 μm.

12.11 (a) 2.2×10^{-29} J; (b) 3.14×10^{-20} J.

12.13 2.3421×10^{-20} J.

12.15 Magnitude: 2.58×10^{-34} J s^{-1}; projections: 0, $\pm 1.0546 \times 10^{-34}$ J s, and 2.11094×10^{-34} J s.

13.1 1.94×10^{-18} J.

13.2 $r = 11.5a_0/Z$, $3.53a_0/Z$, 0.

13.3 $r = 0$, $6a_0$.

13.4 $N = \frac{1}{4}(2\pi a_0^3)^{-1/2}$.

13.5 $\langle E_K \rangle = \hbar^2 Z^2/8ma_0^2$, $\langle V \rangle = -Z^2e^2/16\pi\varepsilon_0 a_0$.

13.6 $P_{3s} = 4\pi r^2(1/4\pi)(1/243)(Z/a_0)^3(6 - 6\rho + \rho^2)^2 e^{-\rho}$, $r = 0.74a_0/Z$, $4.19a_0/Z$, and $13.08\ a_0/Z$.

13.7 (a) 2.45×10^{-34} J s, 2, 1; (b) 1.49×10^{-34} J s, 1, 0; (c) 1.49×10^{-34} J s, 1, 1.

13.8 (a) $\frac{1}{2}$, $\frac{3}{2}$; (b) $\frac{9}{2}$, $\frac{11}{2}$.

13.9 8, 7, 6, 5, 4, 3, 2.

13.10 (a) 1; (b) 64; (c) 25.

13.11 $S = 1$, $L = 3$, $J = 4$, $(2S + 1) = 3$ is the multiplicity.

13.12 (a) 110 pm, 20.1 pm; (b) 86 pm, 29.4 pm.

13.13 (b).

13.14 (a) 2; (b) 10; (c) 14; (d) 22.

13.15 $1s^22s^22p^63s^23p^63d^3$, S: $\frac{1}{2}$ or $\frac{3}{2}$, M_S: $\pm\frac{1}{2}$, $\pm\frac{3}{2}$.

13.16 (a) 2 (5), 1 (3), 0 (1); (b) $\frac{5}{2}$ (6), $\frac{3}{2}$ (4), $\frac{1}{2}$ (2).

13.17 $^1F_3$; $^3F_4$, $^3F_3$, $^3F_2$; $^1D_2$; $^3D_3$, $^3D_2$, $^3D_1$; $^1P_1$; $^3P_2$, $^3P_1$, $^3P_0$; $^3F_2$ is lowest.

13.18 (a) $J = 3$, 2, 1 (7, 5, 3 states);
(b) $J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$ (8, 6, 4, 2 states); (c) $J = \frac{9}{2}, \frac{7}{2}$ (10, 8).

13.19 (a) $^2D_{5/2}$, $^2D_{3/2}$; (b) $^2P_{3/2}$, $^2P_{1/2}$.

13.20 1.68 T.

14.1 (a) $1\sigma^22\sigma^{*1}$; (b) $1\sigma^22\sigma^{*2}1\pi^43\sigma^2$; (c) $1\sigma^22\sigma^{*2}3\sigma^21\pi^42\pi^{*2}$

14.2 (a) $1\sigma^22\sigma^{*2}3\sigma^21\pi^42\pi^{*4}$; (b) $1\sigma^22\sigma^{*2}1\pi^43\sigma^2$; (c) $1\sigma^22\sigma^{*2}3\sigma^21\pi^42\pi^{*3}$.

14.3 (a) C_2, CN; (b) NO, O_2, F_2.

14.4 $1\sigma^21\pi^42\pi^{*2}$, BrCl is shorter.

14.5 a_{2u}, e_{1g}, e_{2u}, b_{2g}; hence parities are u, g, u, g.

14.6 3, u.

14.7 O_2^+, O_2, O_2^-, O_2^{2-}.

14.8 $N = 1/(1 + 2\lambda S + \lambda^2)^{1/2}$.

14.9 $N(0.844A - 0.145B)$.

14.10 none.

14.12 (a) $a_{2u}^2e_{1e}^4e_{2u}^1$, $7\alpha + 7\beta$; (b) $a_{2u}^2e_{1g}^3$, $5\alpha + 7\beta$.

15.1 4 C_3 axes (each C–Cl axis), 4 C_2 axes (bisecting Cl–C–Cl angles), 3 S_4 axes (same as C_2 axes), and 6 dihedral mirror planes (each Cl–C–Cl plane).

15.2 (a).

15.3 necessarily 0.

15.4 forbidden.

15.6 T_d: (S_4 and S_1); T_h: (S_2).

15.8 (a) $C_{\infty v}$; (b) D_3; (c) C_{4v}; (d) C_s.

15.9 (a) 3 C_2 axes, 3 mirror planes, inversion centre; D_{2h};
(b) C_2 axis, $2\sigma_v$; D_{2h}; (c) *ortho* and *meta*: C_2 axis, $2\sigma_v$; C_{2v}.
para: 3 C_2 axes, 3 mirror planes, inversion centre; D_{2h}.

15.10 (a) $C_{\infty v}$; (b) D_{5h}; (c) C_{2v}; (d) D_{3h}; (e) O_h; (f) T_d.

15.11 (a) *o*-dichlorobenzene, *m*-dichlorobenzene HF, XeO_2F_2; (b) none.
15.12 NO_3^-: p_x and p_y; SO_3: all *d*-orbitals except d_{z^2}.
15.13 A_2.
15.14 (a) B_{3u}, B_{2u}, B_{1u}; (b) A_{2u}, E_{1u}.
15.15 yes.

16.1 (a) 7.73×10^{-32} J m^{-3} s; (b) 6.2×10^{-28} J m^{-3} s.
16.2 3.4754×10^{-11} s^{-1}.
16.3 (a) 3.307×10^{-47} kg m^2; (b) 141.4 pm.
16.4 5.420×10^{-46} kg m^2, 162.8 pm.
16.5 116.21 pm.
16.6 116.1 pm, 155.9 pm.
16.7 20 603 cm^{-1}.
16.8 2347.16 cm^{-1}.
16.9 0.71 N m^{-1}.
16.10 28.4 per cent.
16.11 245.9 N m^{-1}.
16.12 $A_{1g} + A_{2g} + E_{1u}$.
16.13 all.
16.14 all but (d) N_2.
16.15 all but (c) SF_6.
16.16 6.36×10^7 m s^{-1}.
16.17 3.59×10^7 m s^{-1}, 1.19×10^6 K.
16.18 (a) 1.59 ns; (b) 2.48 ps.
16.19 (a) 1.6×10^2 MHz; (b) 16 MHz.
16.20 (a) 0.212; (b) 0.561.
16.21 3002.3 cm^{-1} (DF), 2143.7 cm^{-1} (DCl), 1885.8 cm^{-1} (DBr), 1640.1 cm^{-1} (DI).
16.22 2374.05 cm^{-1}, 6.087×10^{-3}.
16.23 3.235×10^4 cm^{-1}, 4.01 eV.
16.24 141.78 pm.
16.25 (a) 30; (b) 42; (c) 13.
16.26 (a) IR: A_2'', E', Raman: A_1', E'; (b) IR: A_1, E, Raman: A_1, E.
16.27 (a) inactive; (b) active.

17.1 22.2 per cent.
17.2 7.9×10^5 cm^2 mol^{-1}.
17.3 1.33×10^{-3} mol L^{-1}.
17.4 1.56×10^8 L mol^{-1} cm^{-2} (1.56×10^9 m mol^{-1}).
17.5 rise.
17.6 552 L mol^{-1} cm^{-1}.
17.7 128 L mol^{-1} cm^{-1}, 0.13.
17.8 (a) 0.020 cm; (b) 0.033 cm.
17.9 1.39×10^8 L mol^{-1} cm^{-2} (1.39×10^9 m mol^{-1}).
17.10 stronger.

18.1 649 MHz.
18.2 $E_{+1} = \mp 2.35 \times 10^{-26}$ J, 0.
18.3 47.3 MHz.
18.4 (b)
18.5 3.523 T.
18.6 (a) 97.5 T, 244 T; (b) 7.49 T, 18.7 T; (c) 17.4 T, 43.5 T.
18.7 (a) 4.3×10^{-7}; (b) 2.2×10^{-6}; (c) 1.34×10^{-5}.
18.8 (a) 1; (b) 10.
18.9 (a) 4.2×10^{-6} T; (b) 3.63×10^{-5} T.
18.10 spectrum appears narrower at 650 MHz.
18.11 2.9×10^3 s^{-1}.
18.12 203 MHz.
18.14 neither.
18.15 9.40×10^{-4} T, 6.25 μs.
18.16 1.3 T.
18.17 2.0022.
18.18 2.2 mT, 1.992.
18.19 eight lines at $(332.8 \pm 1.055 \pm 1.435 \pm 1.445)$ mT, all of equal intensity (in a high resolution spectrometer).
18.20 a triplet (1:2:1) of quartets (1:3:3:1).
18.21 (a) 332.3 mT; (b) 1209 mT.
18.22 1.

19.1 623 K.
19.2 (a) 15.9 pm, 5.04 pm; (b) 2.47×10^{26}, 7.82×10^{27}.
19.3 187.9.
19.4 4.006.
19.5 7.605 kJ mol^{-1}.
19.6 213 K.
19.7 (a) 0.997, 0.994; (b) 0.99999, 0.99998.
19.8 (a) 1.00 K: $n_2/n_1 = 1.39 \times 10^{11}$, $n_3/n_1 = 1.93 \times 10^{-22}$; 25.0 K: $n_2/n_1 = 0.368$, $n_3/n_1 = 0.135$; 100 K: $n_2/n_1 = 0.779$, $n_3/n_1 = 0.607$; (b) 1.503; (c) 88.3 J mol^{-1}; (d) 3.53 J K^{-1} mol^{-1}; (e) 6.92 J K^{-1} mol^{-1}.
19.9 50.2 K.
19.10 (a) 147 J K^{-1} mol^{-1}; (b) 169.6 J K^{-1} mol^{-1}.
19.11 10.7 J K^{-1} mol^{-1}.
19.12 (a).

20.1 (a) 3*R*, 6*R*; (b) 3*R*, 21*R*; (c) 2.5*R*, 6.5*R*. (In each case the first value assumes no vibrational contribution; the second a full vibrational contribution.)
20.2 with: 1.15; without: 1.40; experimental: 1.29.
20.3 (a) 143; (b) 251.
20.4 (a) 2; (b) 2; (c) 6; (d) 24; (e) 4.
20.5 5840, 0.8479 K.
20.6 84.57 J K^{-1} mol^{-1}.
20.7 (a) 2.50×10^3, 5.43×10^3; (b) the same.
20.8 (a) 8.03×10^3; (b) 1.13×10^4.

20.9 (a) 5.70 $JK^{-1}mol^{-1}$; (b) 14.83 $JK^{-1}mol^{-1}$.
20.10 −20.1 $kJ\,mol^{-1}$, −110 $J\,mol^{-1}$.
20.11 −3.65 $kJ\,mol^{-1}$.
20.12 14.90 $JK^{-1}\,mol^{-1}$.
20.14 191.4 $JK^{-1}\,mol^{-1}$, residual entropy is negligible.
20.15 ≈0.25.

21.1 $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$.
21.2 (3, 1, $\bar{3}$), (6, 4, 3).
21.3 214 pm, 174 pm, 87.2 pm.
21.4 86.7 pm.
21.5 38.2°, 44.4°, 64.6°.
21.6 0.054 cm
21.7 1.2582 nm^3.
21.8 5, 2.90 $g\,cm^{-3}$.
21.9 182 pm.
21.10 (110), (110), (200).
21.11 4.166°, 3.000°, 7.057°.
21.12 body-centred cubic.
21.13 2*f* for $h + k + l$ even; 0 for $h + k + l$ odd.
21.14 $\frac{2}{3}$.
21.16 (a) 57 pm; (b) 111 pm.
21.17 0.370.
21.18 3.61×10^5 $g\,mol^{-1}$.
21.19 contraction.
21.21 252 pm.
21.22 (a) 39 pm; (b) 12 pm; (c) 6.1 pm.
21.23 neutron: 0°, 14.0°; electron: 0°, 0.72°.

22.1 SF_4.
22.2 $\alpha = 2.55 \times 10^{-39}$ $C^2\,m^2\,J^{-1}$, $\mu = 3.23 \times 10^{-30}$ C m (3.23 D).
22.3 5.57.
22.4 3.40×10^{-40} $C^2\,m^2\,J^{-1}$.
22.5 μ(C-F) > μ(C-O).
22.6 1.4 D.
22.7 9.45×10^{-29} C m, 194.0°.
22.8 3.71×10^{-36} C m.
22.9 1.10.
22.10 16.
22.11 3.2×10^{-6}.
22.12 5.
22.13 -8.2×10^{-4} $cm^3\,mol^{-1}$.
22.14 1.58×10^{-8} $m^3\,mol^{-1}$, dimerization occurs.
22.15 2.52.
22.16 1.85×10^{-7} $m^3\,mol^{-1}$.
22.17 0.935.

23.1 $\overline{M}_n = 68$ $kg\,mol^{-1}$, $\overline{M}_w = 69$ $kg\,mol^{-1}$.
23.2 38.97 nm.
23.3 1.06×10^4.
23.4 1.26×10^{-6} m, 1.97×10^{-8} m.
23.5 71.
23.6 1.47×10^{-4} $m\,s^{-1}$.
23.7 120 $kg\,mol^{-1}$.
23.8 56 $kg\,mol^{-1}$.
23.9 (a) 8.8 $kg\,mol^{-1}$; (b) 11 $kg\,mol^{-1}$.
23.10 3.4×10^{-3} $mol\,L^{-1}$.
23.11 1.5×10^{-2} $mol\,L^{-1}$.
23.12 3.1×10^3 $kg\,mol^{-1}$.
23.13 3.9×10^5 *g*.

24.1 1.1×10^{21}.
24.2 4.89×10^{-4} kg.
24.3 0.17 $J\,m^{-2}\,s^{-1}$.
24.4 1.61×10^{-19} m^2.
24.5 22 $J\,s^{-1}$
24.6 554 $g\,mol^{-1}$.
24.7 1.5×10^4 s.
24.8 3.00×10^{-19} m^2.
24.9 1.00×10^5 Pa.
24.10 (a) 0.95×10^{-5} $kg\,m^{-1}\,s^{-1}$; (b) 0.99×10^{-5} $kg\,m^{-1}\,s^{-1}$; (c) 1.81×10^{-5} $kg\,m^{-1}\,s^{-1}$.
24.11 (a) 0.0114 $J\,m^{-1}\,s^{-1}\,K^{-1}$, 0.017 $J\,s^{-1}$; (b) 9.0×10^{-3} $J\,m^{-1}\,s^{-1}\,K^{-1}$, 0.014 $J\,s^{-1}$.
24.12 52.0×10^{-7} $kg\,m^{-1}\,s^{-1}$, 923 pm.
24.13 9.0×10^{-3} $J\,m^{-1}\,s^{-1}\,K^{-1}$.
24.14 (a) 0.107 $m^2\,s^{-1}$, 0.87 $mol\,m^{-2}\,s^{-1}$; (b) 1.07×10^{-5} $m^2\,s^{-1}$, 8.7×10^{-5} $mol\,m^{-2}\,s^{-1}$; (c) 7.13×10^{-8} $m^2\,s^{-1}$, 5.8×10^{-7} $mol\,m^{-2}\,s^{-1}$.
24.15 4.09 $mS\,m^2\,mol^{-1}$.
24.16 4.81×10^{-5} $m^2\,V^{-1}\,s^{-1}$.
24.17 0.604.
24.18 25.96 $mS\,m^2\,mol^{-1}$.
24.19 5.74×10^{-8} $m^2\,V^{-1}\,s^{-1}$, 7.913×10^{-8} $m^2\,V^{-1}\,s^{-1}$, 8.09×10^{-8} $m^2\,V^{-1}\,s^{-1}$.
24.20 1.09×10^{-9} $m^2\,s^{-1}$.
24.21 4.1×10^3 s.
24.22 207 pm.
24.23 20 ps.
24.24 5.594×10^{-5} m.
24.25 1.7×10^{-2} s.

25.1 A: 1.0 $mol\,L^{-1}\,s^{-1}$, B: 3.0 $mol\,L^{-1}\,s^{-1}$, C: 1.0 $mol\,L^{-1}\,s^{-1}$, D: 2.0 $mol\,L^{-1}\,s^{-1}$.

25.2 rate of: reaction, 0.33 mol L^{-1} s^{-1}, formation of C, 0.33 mol L^{-1} s^{-1}; formation of D, 0.66 mol L^{-1} s^{-1}; consumption of A, 0.33 mol L^{-1} s^{-1}.
25.3 k: L^2 mol^{-2} s^{-1}; (a) $d[A]/dt = -k[A][B]^2$; (b) $d[C]/dt = k[A][B]^2$.
25.4 k: s^{-1}, $k[A][B][C]^{-1}$.
25.5 2.
25.6 0.
25.7 1.80×10^6 s; (a) 31.5 kPa; (b) 29.0 kPa.
25.8 (a) 3.5×10^{-3} L mol^{-1} s^{-1}; (b) A: 2.4 h; B: 0.44 h.
25.9 m^3 $molecule^{-1}$ s^{-1}, m^6 $molecule^{-2}$ s^{-1}; Pa^{-1} s^{-1}, Pa^{-2} s^{-1}.
25.10 (a) 0.642 μg; (b) 0.177 μg.
25.11 (a) 6.5×10^{-3} mol L^{-1}; (b) 0.025 mol L^{-1}.
25.12 1.5×10^6 s.
25.13 $E_a = 9.9$ kJ mol^{-1}; $A = 0.94$ L mol^{-1} s^{-1}.
25.14 $v = k[A][B]$, $k = k_1 k_2/k_2'$.
25.15 $\{(3^{n-1} - 1)/k(n-1)\}[A]_0^{(1-n)}$.
25.16 2.57×10^{-4} mol L^{-1} s^{-1}.
25.17 9.9×10^{-6} s^{-1} Pa^{-1}.
25.18 $k_r = 1.7 \times 10^{-7}$ s^{-1}, $k_f = 8.3 \times 10^8$ L mol^{-1} s^{-1}.

26.1 $k[N_2O_5] = k_1 k_2 [N_2O_5]/(k_1' + k_2)$.
26.2 $-k_1[R_2] - k_2(k_1/k_4)^{1/2}[R_2]^{3/2}$.
26.3 (a) does not occur; (b) 1.3×10^2 Pa to 3×10^4 Pa.
26.4 1.5×10^{-5} moles of photons.
26.5 1.11.
26.6 $(k_1 k_2 K_a^{1/2}/k_1)[HA]^{3/2}[B]$.
26.7 (1) initiation, (3) retardation, (4) termination; $k_1[A_2]$.

27.1 6.64×10^9 s^{-1}, 8.07×10^{34} m^3 s^{-1}, 1.6 per cent.
27.2 (a) 2.4×10^{-3}, 0.10; (b) 7.7×10^{-27}, 1.6×10^{-10}.
27.3 (a) 1.2, 1.03; (b) 7.4, 1.3.
27.4 1.7×10^{-12} L mol^{-1} s^{-1}.
27.5 3.2×10^7 m^3 mol^{-1} s^{-1}.
27.6 (a) 1.97×10^6 m^3 mol^{-1} s^{-1}; (b) 2.4×10^5 m^3 mol^{-1} s^{-1}.
27.7 1.10×10^7 m^3 mol^{-1} s^{-1}, 5.05×10^{-8} s.
27.8 2.22×10^{-3}.
27.9 1.54×10^8 mol L^{-1} s^{-1}.
27.10 48.52 kJ mol^{-1}, -32.2 J K^{-1} mol^{-1}.
27.11 46.8 kJ mol^{-1}.
27.12 -93 J K^{-1} mol^{-1}.
27.13 -80.0 J K^{-1} mol^{-1}.
27.14 (a) -24.1 J K^{-1} mol^{-1}; (b) 27.5 kJ mol^{-1}; (c) 34.7 kJ mol^{-1}.
27.15 (a) $k_T/k_H \approx 0.06$; (b) $k_{18}/k_{16} \approx 0.89$.
27.16 1.08 L^2 mol^{-2} min^{-1}.

28.1 (a) 2.88×10^{23} m^{-2} s^{-1}, 5.75×10^{17} m^{-2} s^{-1}; (b) 3.81×10^{24} m^{-2} s^{-1}, 7.60×10^{17} m^{-2} s^{-1}.
28.2 7.3×10^2 Pa.
28.3 6.6×10^4 s^{-1}.
28.4 18.8 m^2.
28.5 9.7 cm^3.
28.6 200 s.
28.7 3.7 kJ mol^{-1}.
28.8 (a) 0.32 kPa; (b) 3.9 kPa.
28.9 0.75, 0.25.
28.10 (a) 4.9×10^{-11} s, 2.4×10^{-12} s; (b) 1.6×10^{13} s, 1.4 s.
28.11 6.50 kPa.
28.13 -6.40 kJ mol^{-1}.
28.14 $E_d = 2.85 \times 10^5$ J mol^{-1}; (a) 1.48×10^{36} s; (b) 1.38×10^{-4} s.

29.1 2.8×10^8 V m^{-1}.
29.2 0.37 V.
29.3 1.6 mA cm^{-2}
29.4 8.5 mA cm^{-2}.
29.5 (a) 0.34 A cm^{-2}; (b) 0.34 A cm^{-2}.
29.6 1.3 A m^{-2}.
29.7 4×10^{-6} mol L^{-1}.
29.8 $(2.5 \text{ mA cm}^{-2})[e^{0.42E'/f}(3.41 \times 10^{-6}) - e^{-0.58E'/f}(3.55 \times 10^7)]$.
29.10 0.61 V.
29.11 Cu, $H_2|H^+$: 6.2×10^{-12} s^{-1} cm^{-2}, 4.2×10^{-3} s^{-1}; Pt$|Ce^{4+}, Ce^{3+}$: 2.54×10^{14} s^{-1} cm^{-2}, 0.17 s^{-1}.
29.12 (a) 5.1 GΩ; (b) 10 Ω.
29.15 no.
29.16 no.
29.17 1.80 V, 0.180 W.
29.18 0.97675 V.
29.19 all.
29.20 1.5 mm y^{-1}.