

Solutions to odd-numbered problems

Chapter 1

Topic 1A

- P1A.1 -233°N
- P1A.3 -272.95°C
- P1A.5 (a) 0.0245 kPa (b) 9.14 kPa (c) 0.0245 kPa
- P1A.7 $2.8 \times 10^8 \text{ dm}^3 = 2.8 \times 10^5 \text{ m}^3$, $4.1 \times 10^8 \text{ dm}^3 = 4.1 \times 10^5 \text{ m}^3$
- P1A.9 (a) 1.7×10^{-5} (b) 0.72
- P1A.13 51 km, 0.0029 atm

Topic 1B

- P1B.3 $\left(\frac{2RT}{M}\right)^{1/2}$
- P1B.5 $0.47 \langle v_x \rangle_{\text{initial}}$
- P1B.7 $n^2 e^{3(1-n^2)/2}$, 5.53×10^{-5} , 2.71×10^{-9}
- P1B.9 (a) 11.2 km s^{-1} (b) 5.04 km s^{-1}

Topic 1C

- P1C.1 (a) $12.5 \text{ dm}^3 \text{ mol}^{-1}$ (b) $12.3 \text{ dm}^3 \text{ mol}^{-1}$
- P1C.3 (a) $0.941 \text{ dm}^3 \text{ mol}^{-1}$ (b) $2.69 \text{ dm}^3 \text{ mol}^{-1}$, $2.67 \text{ dm}^3 \text{ mol}^{-1}$ (c) $5.11 \text{ dm}^3 \text{ mol}^{-1}$,
inversion temperature
- P1C.5 (a) $0.1353 \text{ dm}^3 \text{ mol}^{-1}$ (b) 0.6957 (c) 0.7158
- P1C.7 $59.4 \text{ cm}^3 \text{ mol}^{-1}$, $5.649 \text{ dm}^6 \text{ atm mol}^{-2}$, 21 atm
- P1C.9 $B = b - \frac{a}{RT}$, $C = b^2$, $34.6 \text{ cm}^3 \text{ mol}^{-1}$, $1.26 \text{ dm}^6 \text{ atm mol}^{-2}$
- P1C.11 $\frac{3C}{B}$, $\frac{B^2}{3RC}$, $\frac{B^3}{27C^2}$, $\frac{1}{3}$

P1C.13 $0.0866 \text{ atm}^{-1}, 2.12 \text{ dm}^3 \text{ mol}^{-1}$

P1C.17 0.011

P1C.21
$$\frac{b\{1 \pm (bRT/a)^{1/2}\}}{1 - bRT/a}$$

Chapter 2

Topic 2A

P2A.1
$$-nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

(a) -1.7 kJ (b) -1.8 kJ (c) -1.5 kJ

P2A.3 (a) -1.5 kJ (b) -1.6 kJ

P2A.5 $\frac{1}{2} k_F x_F^2$

Topic 2B

P2B.1 62.2 kJ mol^{-1}

P2B.3 $w = 0, \Delta U = +2.35 \text{ kJ}, +3.03 \text{ kJ}$

Topic 2C

P2C.1 $-1270 \text{ kJ mol}^{-1}$

P2C.3 $-67.44, n = 0.9253, -6625.5 \text{ kJ mol}^{-1}, 2.17 \text{ per cent}$

P2C.5 $-994.30 \text{ kJ mol}^{-1}$

P2C.7 $-802.31 \text{ kJ mol}^{-1}$

P2C.9 $+37 \text{ K}, 4.09 \text{ kg}$

Topic 2D

P2D.1 $1.6 \text{ m}, 0.80 \text{ m}, 2.8 \text{ m}$

P2D.3 nR

$$P2D.5 \quad T = \left(\frac{p}{nR} \right) \times (V - nb) + \left(\frac{na}{RV^2} \right) \times (V - nb), \quad \left(\frac{\partial T}{\partial p} \right)_V = \frac{V - nb}{nR}$$

$$P2D.7 \quad c_s = \left(\frac{\gamma p}{\rho} \right)^{1/2}, \quad 322 \text{ m s}^{-1}$$

$$P2D.11 \quad \text{(a) } 23.5 \text{ K MPa}^{-1} \quad \text{(b) } 14.0 \text{ K MPa}^{-1}$$

Topic 2E

$$P2E.1 \quad 41.40 \text{ J K}^{-1} \text{ mol}^{-1}$$

Chapter 3

Topic 3A

$$P3A.5 \quad 1.00 \text{ kJ}, 8.4 \text{ kJ}$$

$$P3A.7 \quad 10.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$P3A.9 \quad \text{Path (a) } -2.74 \text{ kJ}, 0, +2.74 \text{ kJ}, +9.13 \text{ J K}^{-1}, 0, -9.13 \text{ J K}^{-1}$$

$$\text{Path (b) } -1.66 \text{ kJ}, 0, +1.66 \text{ kJ}, +9.13 \text{ J K}^{-1}, -5.53 \text{ J K}^{-1}, +3.60 \text{ J K}^{-1}$$

$$P3A.11 \quad nC_{p,m} \ln \frac{T_f}{T_h} + nC_{p,m} \ln \frac{T_f}{T_c}, \quad +22.6 \text{ J K}^{-1}$$

$$P3A.13 \quad 477 \text{ J K}^{-1} \text{ mol}^{-1}$$

Topic 3B

$$P3B.1 \quad \text{(a) } 200.7 \text{ J K}^{-1} \text{ mol}^{-1} \quad \text{(b) } 232.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$P3B.3 \quad +41.16 \text{ kJ mol}^{-1}, +42.08 \text{ J K}^{-1} \text{ mol}^{-1}, +40.84 \text{ kJ mol}^{-1}, +41.08 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$P3B.5 \quad 34.4 \text{ kJ mol}^{-1}, 243 \text{ J K}^{-1} \text{ mol}^{-1}$$

Topic 3C

$$P3C.1 \quad \text{(a) } 50.7 \text{ J K}^{-1}, -11.5 \text{ J K}^{-1} \quad \text{(b) } +3.46 \text{ kJ}, \text{ indeterminate} \quad \text{(c) } 3.46 \times 10^3 \text{ J}, \\ \text{indeterminate} \quad \text{(d) } +39.2 \text{ J K}^{-1}, -39.2 \text{ J K}^{-1}$$

P3C.3 (a) $+35 \text{ J K}^{-1} \text{ mol}^{-1}$ (b) $12 \text{ W m}^{-3}, 1.5 \times 10^4 \text{ W m}^{-3}$ (c) $0.46 \frac{\text{mol ATP}}{\text{mol glutamine}}$

Topic 3D

P3D.1 -501 kJ mol^{-1}

P3D.3 -21 kJ mol^{-1}

P3D.5 $\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_s, \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

P3D.7 $C_p dT - \alpha TV dp, -\alpha TV \Delta p, -0.50 \text{ kJ}$

Chapter 4**Topic 4B**

P4B.1 $196.0 \text{ K}, 11.1 \text{ Torr}$

P4B.3 (a) $+5.56 \times 10^3 \text{ Pa K}^{-1}$ (b) 2.6 per cent

P4B.5 (a) $-1.63 \text{ cm}^3 \text{ mol}^{-1}$ (b) $+30.1 \text{ dm}^3 \text{ mol}^{-1}$ (c) $+6 \times 10^2 \text{ J mol}^{-1}$

P4B.7 22°C

P4B.9 (a) 227.5°C (b) $+53 \text{ kJ mol}^{-1}$

P4B.13 9.8 Torr

P4B.15 363 K

P4B.17 $\frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}}, \frac{dp}{dT} = \frac{C_{p,m2} - C_{p,m1}}{TV_m(\alpha_2 - \alpha_1)}$

Chapter 5**Topic 5A**

P5A.1 $18.079 - 0.11482x^{3/2}$

P5A.3 $15.58 \text{ kPa}, 47.03 \text{ kPa}$

P5A.5 4.6 cm^3

Topic 5B

- P5B.3 $109.0 \text{ cm}^3 \text{ mol}^{-1}, 279.3 \text{ cm}^3 \text{ mol}^{-1}$
- P5B.5 $165 \text{ K}, 0.99978, 19.89 \text{ g solute (100 g solvent)}^{-1}, -\Delta_{\text{fus}}H/R$
- P5B.7 (a) (i) 2 (ii) 3 (b) (ii) 0.19, 0.82, 0.24 (c) $x_{\text{Pb}} = 0.19, x_{\text{Cu}} = 0.18$
- P5B.9 $\frac{\Delta_{\text{fus}}H}{RT^2}, \ln x_A = \frac{-\Delta_{\text{fus}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*} \right)$
- P5B.11 $1.26 \times 10^5 \text{ g mol}^{-1}, 1.23 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$
- P5B.13 $x_A = x_B = 0.5$
- P5B.15 $4.78 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$

Topic 5C

- P5C.1 (b) 391.0 K (c) 0.532
- P5C.7 (b) Ca_2Si and a Ca-rich liquid ($x_{\text{Si}} = 0.13$), 0.5 (c) 0.53, 0.67
- P5C.9 $\frac{x_A p_A^* / p_B^*}{1 + (p_A^* / p_B^* - 1)x_A}$

Topic 5E

- P5E.3 $\Pi = \phi[\text{B}]RT$

Chapter 6

Topic 6A

- P6A.1 (a) $+4.48 \text{ kJ mol}^{-1}$ (b) 0.101 atm
- P6A.3 0.007 mol H_2 , 0.107 mol I_2 , 0.786 mol HI
- P6A.5 $\xi = 1 - \left(\frac{1}{1 + ap / p^\ominus} \right)^{1/2}$

Topic 6B

P6B.1 (a) 1.24×10^{-9} (b) 1.29×10^{-8} (c) 1.8×10^{-4}

P6B.3 $300. \text{ kJ mol}^{-1}$

P6B.5 $0.740, 5.71, -103 \text{ kJ mol}^{-1}$

P6B.7 (a) 1.2×10^8 (b) 2.7×10^3

P6B.9
$$K_c(T) = K_c(T_{\text{ref}}) \times \left(\frac{T_{\text{ref}}}{T}\right)^{\Delta\nu} e^{\frac{\Delta_r H^\ominus}{R} \times \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)}$$

Topic 6C

P6C.1 (a) $+1.23\text{V}$ (b) $+1.09 \text{ V}$

P6C.3 $+14.7 \text{ kJ mol}^{-1}, +18.8 \text{ kJ mol}^{-1}$

Topic 6D

P6D.1 $+0.26843 \text{ V}$

Chapter 7

Topic 7A

P7A.1 (a) $1.6 \times 10^{-33} \text{ J m}^{-3}$ (b) $2.5 \times 10^{-4} \text{ J m}^{-3}$

P7A.3 $\lambda_{\text{max}} T \cong \frac{1}{5} hc / k$

P7A.5 255 K or $18 \text{ }^\circ\text{C}$, $11 \text{ }\mu\text{m}$, $\frac{cE}{4}$

P7A.7 (a) $8\pi hc$, hc (b) $\left(\frac{4}{c}\right) \sigma_{\text{Wien}} T^4$

P7A.9 (a) $223 \bar{1} \text{ K}$, $\theta_E = 0.0315$ (b) 343 K , $\theta_E = 0.897$

Topic 7B

P7B.1 (a) $N = \left(\frac{2}{L}\right)^{1/2}$ (b) $N = \frac{1}{c(2L)^{1/2}}$ (c) $N = \frac{1}{(\pi a^3)^{1/2}}$ (d) $N = \frac{1}{(32\pi a^5)^{1/2}}$

P7B.3 0.0183

P7B.5 (a) 9.0×10^{-6} (b) 1.2×10^{-6}

P7B.7 $x_{\max} = a$

Topic 7C

P7C.1 (a) $\left(-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} - \frac{e^2}{4\pi\epsilon_0 x}\right)\psi = E\psi$ (b) $\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right)\psi = E\psi$ (c) $\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - cx\right)\psi = E\psi$

P7C.3 (a) Yes (b) Yes (c) No (d) No

P7C.5 (a) Yes, $-k^2$ (b) Yes (c) Yes (d) No

(i) (a) and (b) (ii) (c)

P7C.7 (a) $+k\hbar$ (b) 0 (c) 0

P7C.9 $\frac{1}{a}$

P7C.11 (a) (i) $N = (\pi a_0^3)^{-1/2}$ (ii) $N = (32\pi a_0^5)^{-1/2}$ (c) (i) $1.5a_0, 4.5a_0^2$ (ii) $5a_0, 30a_0^2$

P7C.15 $[\hat{x}, \hat{p}_x] = i\hbar$

Chapter 8
Topic 8A

P8A.1 $1.24 \times 10^{-39} \text{ J}, 2.2 \times 10^9, 1.8 \times 10^{-30} \text{ J}$

P8A.3 (a) $\frac{L}{2}, \frac{L}{3^{1/2}}$ (b) $\frac{L}{2}, \left(\frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}\right)^{1/2}$

P8A.5 1.2×10^6

P8A.7 (a) $T = |A_3|^2 = A_3 \times A_3^* = \frac{4k_1^2 k_2^2}{(a^2 + b^2) \sinh^2(k_2 L) + b^2}$
 where $a^2 + b^2 = (k_1^2 + k_2^2)(k_2^2 + k_3^2)$ and $b^2 = k_2^2(k_1 + k_3)^2$

Topic 8B

P8B.1 $\text{HI} < \text{HBr} < \text{HCl} < \text{NO} < \text{CO}$

P8B.5 $\frac{1}{2}\left(v + \frac{1}{2}\right)\hbar\omega$

Topic 8C

P8C.1 (a) $\pm 5.275 \times 10^{-34} \text{ J s}$, $7.89 \times 10^{-19} \text{ J}$ (b) $5.2 \times 10^{14} \text{ Hz}$

P8C.3 (a) $+\hbar$ (b) $-2\hbar$ (c) 0 (d) $\hbar \cos 2\chi$

(a) $\frac{\hbar^2}{2I}$ (b) $\frac{2\hbar^2}{I}$ (c) $\frac{\hbar^2}{2I}$ (d) $\frac{\hbar^2}{2I}$

P8C.5 0, 2.62, 7.86, 15.72

P8C.7 1

P8C.9 $\frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$, $\frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$, $\frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$, $-\frac{\hbar}{i}\hat{L}_z$.

Chapter 9

Topic 9A

P9A.1 $\pm 106 \text{ pm}$

P9A.3 (b) $\rho_{\text{node}} = 3 + \sqrt{3}$ and $\rho_{\text{node}} = 3 - \sqrt{3}$, $\rho_{\text{node}} = 0$ and $\rho_{\text{node}} = 4$, $\rho_{\text{node}} = 0$ (c)

$$\langle r \rangle_{3s} = \frac{27a_0}{2}$$

P9A.7 (a) $\frac{Z}{a_0}$ (b) $\frac{Z}{4a_0}$ (c) $\frac{Z}{4a_0}$ (d) $\frac{Z}{a_0}$

P9A.11 60957.4 cm^{-1} , 60954.7 cm^{-1} , 329170 cm^{-1} , 329155 cm^{-1}

Topic 9B

P9B.1 0.420 pm

Topic 9C

P9C.1 $n_2 \rightarrow 6$

P9C.3 $\tilde{R}_{\text{Li}^{2+}} = 987663 \text{ cm}^{-1}, 137175 \text{ cm}^{-1}, 185187 \text{ cm}^{-1}, 122.5 \text{ eV}$

P9C.5 ${}^2\text{P}_{1/2}$ and ${}^2\text{P}_{3/2}, {}^2\text{D}_{3/2}$ and ${}^2\text{D}_{5/2}, {}^2\text{D}_{3/2}$

P9C.7 $3.3429 \times 10^{-27} \text{ kg}, 1.000272$

P9C.9 (a) 0.9 cm^{-1} (b) small

P9C.11 (a) $2kT$ (b) 23.8 T m^{-1}

Chapter 10

Topic 10A

P10A.1 $\frac{Z^{3/2} e^{-\rho/2}}{(24\pi)^{1/2} a^{3/2}} \left(\frac{2-\rho}{2} + \frac{\rho \sin \theta}{8^{1/2}} \times (-\cos \phi + 3^{1/2} \sin \phi) \right), 120^\circ$

Topic 10B

P10B.1 $1.87 \times 10^6 \text{ J mol}^{-1} = 1.87 \text{ MJ mol}^{-1}$

P10B.3 $E_{\text{HIs}} - \frac{j+k}{1+S} + \frac{j_0}{R}, E_{\text{HIs}} - \frac{j-k}{1-S} + \frac{j_0}{R}$

P10B.5 (b) $2.5a_0 = 1.3 \times 10^{-10} \text{ m}, -0.555j_0/a_0 = -15.1 \text{ eV}, -0.565j_0/a_0 = -15.4 \text{ eV}, 0.055j_0/a_0 = 1.5 \text{ eV}, 0.065j_0/a_0 = 1.8 \text{ eV}$

Topic 10C

P10C.1 $2.1a_0$

P10C.3 (c) $\pi/4$ or $3\pi/4$

Topic 10D

P10D.1 $\frac{\alpha_A + \alpha_B - 2\beta S}{2(1-S^2)} \pm \frac{\alpha_A - \alpha_B}{2(1-S^2)} \left(1 + \frac{4(\beta + \alpha_A S)(\beta + \alpha_B S)}{(\alpha_A - \alpha_B)^2} \right)^{1/2}, \frac{\alpha_A - \beta S}{1-S^2} + \frac{(\beta + \alpha_A S)(\beta + \alpha_B S)}{(\alpha_A - \alpha_B)(1-S^2)},$
 $\frac{\alpha_B - \beta S}{1-S^2} - \frac{(\beta + \alpha_A S)(\beta + \alpha_B S)}{(\alpha_A - \alpha_B)(1-S^2)}$

P10D.3 (i) $E/\text{eV} = -10.7, -8.7, \text{ and } -6.6$ (ii) $E/\text{eV} = -10.8, -8.9, \text{ and } -6.9$

Topic 10E

$$P10E.1 \quad E = \alpha_o, \frac{1}{2} \left(\alpha_o + \alpha_c \pm (\alpha_o - \alpha_c) \sqrt{1 + \frac{12\beta^2}{(\alpha_o - \alpha_c)^2}} \right),$$

$$(\alpha_o - \alpha_c) \left(\sqrt{1 + \frac{12\beta^2}{(\alpha_o - \alpha_c)^2}} - \sqrt{1 + \frac{4\beta^2}{(\alpha_o - \alpha_c)^2}} \right), \frac{4\beta^2}{\alpha_o - \alpha_c}$$

P10E.7 Standard potential increases as the LUMO decreases

P10E.13 (b) 26780 cm^{-1}

Chapter 11**Topic 11A**

P11A.1 (a) D_{3d} (b) D_{3d}, C_{2v} (c) D_{2h} (d) D_3 (e) D_{4d}

P11A.3 S_4, C_2, S_4

Topic 11B

P11B.1 *trans*-CHCl=CHCl

P11B.3 $\Gamma = 3A_1 + B_1 + 2B_2$

P11B.7 +1 or -1, +1, -1

P11B.9 (a) $2A_1 + A_2 + 2B_1 + 2B_2$ (b) $A_1 + 3E$ (c) $A_1 + T_1 + T_2$ (d)
 $A_{2u} + T_{1u} + T_{2u}$

Topic 11C

P11C.1 $A_1 + T_2, s$ and $p, (d_{xy}, d_{yz}, d_{zx})$

Chapter 12**Topic 12A**

P12A.1 4.4×10^3

- P12A.3 $A = \varepsilon'[\mathbf{J}]_0 (1 - e^{-L/\lambda}), A = \varepsilon'[\mathbf{J}]_0$
- P12A.7 $\frac{1}{2} \left(\frac{\pi}{\ln 2} \right)^{1/2} \varepsilon_{\max} \Delta \tilde{\nu}_{1/2}, 5.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$
- P12A.9 (a) receding, $1.128 \times 10^{-3} \text{ c} = 3.381 \times 10^5 \text{ m s}^{-1}$
- P12A.11 $2(kT / mc^2)^{1/2}$

Topic 12B

- P12B.1 $m_{\text{eff}} R^2$

Topic 12C

- P12C.1 596 GHz, 19.9 cm^{-1} , 0.503 mm, 9.941 cm^{-1}
- P12C.3 128.393 pm, 128.13 pm, slightly different
- P12C.5 116.28 pm, 155.97 pm
- P12C.7 14.35 m^{-1} , 26, 15
- P12C.9 $\left(\frac{kT}{2hc\tilde{B}} \right)^{1/2} - \frac{1}{2}, 30, \left(\frac{kT}{hc\tilde{B}} \right)^{1/2} - \frac{1}{2}, 6$

Topic 12D

- P12D.1 $k_f = 2Da^2$.
- P12D.3 142.81 cm^{-1} , 3.36 eV, 93.8 N m^{-1}
- P12D.7 $2\tilde{D}_e / \tilde{\nu} - \frac{1}{2}$
- P12D.9 112.83 pm, 123.52 pm
- P12D.11 $\tilde{B}_0 = 10.433 \text{ cm}^{-1}$, $\tilde{B}_1 = 10.126 \text{ cm}^{-1}$
- P12D.13 $\langle x^2 \rangle = \frac{1}{k_f} (v + \frac{1}{2}) \hbar \omega$., rotational constant B decreases, B decreases with increased anharmonicity

- P12D.15 (a) 2143.26 cm^{-1} (b) $12.8195 \text{ kJ mol}^{-1}$ (c) $1.85563 \times 10^3 \text{ N m}^{-1}$ (d)
 1.91 cm^{-1} (e) 113 pm

Topic 12E

- P12E.1 (a) Cannot undergo simple harmonic motion
- P12E.3 (a) C_{3v} (b) nine (c) $3A_1 + 3E$ (d) all modes are infrared active (e)
 all modes are Raman active

Chapter 13

Topic 13A

- P13A.1 ${}^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$ is allowed
- P13A.3 6808.2 cm^{-1} or 0.84411 eV , 5.08 eV

Topic 13C

- P13C.1 $4 \times 10^{-10} \text{ s}$ or 0.4 ns

Chapter 14

Topic 14A

- P14A.1 10.3 T , 2.42×10^{-5} , β , ($m_l = -\frac{1}{2}$)

Topic 14B

- P14B.1 $29 \mu\text{T m}^{-1}$
- P14B.3 Both fit the data equally well.
- P14B.5 $\cos \phi = B/4C$

Topic 14C

- P14C.1 $400 \times 10^6 \text{ Hz} \pm 8 \text{ Hz}$, 0.29 s

$$P14C.5 \quad \left(\frac{1}{2}\right) \frac{a\tau}{1 + (\omega_0 - \omega)^2 \tau^2}$$

P14C.7 158 pm

P14C.9 0.58 mT

Topic 14D

P14D.1 2.8×10^{13} Hz

P14D.3 6.9 mT, 2.1 mT

Chapter 15

Topic 15A

P15A.1 {2, 2, 0, 1, 0, 0}, {2, 1, 2, 0, 0, 0}

P15A.7 $e^{-Mgh/RT}$, 0.363, 0.57

Topic 15B

P15B.3 (a) (i) 5.00 (ii) 6.26 (b) 1.00, 0.80, 6.58×10^{-11} , 0.122

P15B.5 1.209, 3.004

P15B.7 (a) 1.049 (b) 1.548, 0.953, 0.645, 0.044, 0.230, 0.002, 0.083

P15B.9 (a) 660.6 (b) 4.26×10^4

Topic 15C

P15C.3 (a) 104 K (b) $1 + a$

Topic 15E

P15E.1 0.351, 0.079, 0.029

P15E.3 $4.2 \text{ J K}^{-1} \text{ mol}^{-1}$

P15E.5 28, $258 \text{ J mol}^{-1} \text{ K}^{-1}$

P15E.7 (a) $nRT\left(\frac{\dot{q}}{q}\right)$, $nR\left\{\frac{\ddot{q}}{q}-\left(\frac{\dot{q}}{q}\right)^2\right\}$, $nR\left(\frac{\dot{q}}{q}+\ln\frac{eq}{N}\right)$ (b) $5.41 \text{ J K}^{-1} \text{ mol}^{-1}$

P15E.11 $191 \text{ J K}^{-1} \text{ mol}^{-1}$

P15E.17 (a) 87.55 K , 6330 K (b) and (c) $2\alpha C_{V,m}(\text{H}) + (1-\alpha)C_{V,m}(\text{H}_2)$, $\frac{kT_i(A_{\text{H}_2i})^3 e^{-(D/RT_i)}}{p^\ominus q_i^V q_i^R (A_{\text{H}})^6}$,
 $1.5R$, $2.5R + \left[\frac{\theta^V}{T_i} \times \frac{e^{-(\theta^V/2T_i)}}{1 - e^{\theta^V/T_i}}\right]^2 R$

P15E.19 $9.57 \times 10^{-15} \text{ J K}^{-1}$

Topic 15F

P15F.3 100 T

P15F.5 $45.76 \text{ kJ mol}^{-1}$

Chapter 16

Topic 16A

P16A.1 (a) 0 (b) 0.7 D (c) 0.4 D

P16A.5 $1.00 \mu\text{D}$

P16A.7 $1.2 \times 10^{-23} \text{ cm}^3$, 0.86 D

P16A.9 $2.24 \times 10^{-24} \text{ cm}^3$, 1.58 D , $5.66 \text{ cm}^3 \text{ mol}^{-1}$

P16A.11 $68.8 \text{ cm}^3 \text{ mol}^{-1}$, 4.40 , 2.10 , $8.14 \text{ cm}^3 \text{ mol}^{-1}$, 1.76 , 1.33

P16A.13 Increase in the relative permittivity.

Topic 16B

P16B.1 1.9 nm

P16B.3 $-1.8 \times 10^{-27} \text{ J} = -1.1 \times 10^{-3} \text{ J mol}^{-1}$

P16B.5 $\frac{-6C}{r^7}$

P16B.7 (b) $r_e = 1.3598 r_0$, $A = 1.8531$

Chapter 17**Topic 17A**

P17A.1 (a) $\sqrt{\frac{2}{5}} a$, $0.046460 \times \left\{ \left(\nu_s / \text{cm}^3 \text{ g}^{-1} \right) \times \left(M / \text{g mol}^{-1} \right) \right\}^{1/3}$, 1.96 nm

(b) $\sqrt{\frac{1}{2}} a$, $\sqrt{\frac{1}{12}} l$, 0.35 nm, 46 nm

P17A.3 Nl^2

P17A.5 (a) $\sqrt{\frac{1}{2}} a$, $a/2$ (b) $\sqrt{\frac{1}{2}} a$, $\sqrt{\frac{1}{12}} l$ (c) $\sqrt{\frac{2}{5}} a$

Topic 17B

P17B.1 $\frac{1}{2\pi l} \left(\frac{RT}{M} \right)^{1/2}$, 6.3 GHz

Topic 17D

P17D.1 $\bar{M} + \left(\frac{2\gamma}{\pi} \right)^{1/2}$

P17D.3 (a)

$\theta / ^\circ$	20	45	90
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$I_{\text{rod}} / I_{\text{cc}}$	0.976	0.876	0.514
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(b) 90°

P17D.5 3500 r.p.m.

P17D.7 69 kg mol^{-1} , 3.4 nm

P17D.9 $0.0716 \text{ dm}^3 \text{ g}^{-1}$

P17D.11 $1.6 \times 10^5 \text{ g mol}^{-1}$

Chapter 18**Topic 18A**

P18A.1	$3.61 \times 10^5 \text{ g mol}^{-1}$
P18A.3	$V = (3\sqrt{3}/2)a^2c$
P18A.5	834 pm , 606 pm , 870 pm
P18A.7	4
P18A.9	$\frac{1}{d^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$
P18A.11	Simple (primitive) cubic lattice, $a = 344 \text{ pm}$
P18A.13	629 pm , gave support
P18A.15	0
P18A.17	(a) 14.0° , 24.2° , 0.72° , 1.23° (b) $R_{\text{CCl}} = 176 \text{ pm}$ and $R_{\text{ClCl}} = 289 \text{ pm}$

Topic 18B

P18B.1	0.340
P18B.3	7.654 g cm^{-3}
P18B.7	(a) 0.41421 (b) 0.73205

Topic 18C

P18C.1	μ , $\frac{3\lambda + 2\mu}{3}$
P18C.3	$\lim_{T \rightarrow 0} P(E) = 1$ when $E < \mu$, $\lim_{T \rightarrow 0} f(E) = 0$ when $E > \mu$, $(3N/8\pi)^{2/3} (h^2/2m_e)$, 3.1 eV
P18C.5	0.736 eV
P18C.7	$0.127 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $0.254 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $0.423 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $0.254 \text{ cm}^3 \text{ mol}^{-1}$
P18C.9	0.41

Chapter 19**Topic 19A**

P19A.1 (a) $\sigma = 0.602 \text{ nm}^2$, $d = (\sigma/\pi)^{1/2} = 438 \text{ pm}$ (b) $\sigma = 0.421 \text{ nm}^2$, $d = (\sigma/\pi)^{1/2} = 366 \text{ pm}$

P19A.3 $2.37 \times 10^{17} \text{ m}^2 \text{ s}^{-1}$, $2.85 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$

P19A.5 (a) $1.7 \times 10^{14} \text{ s}^{-1}$ (b) $1.1 \times 10^{16} \text{ s}^{-1}$

Topic 19B

P19B.1 10.2 kJ mol^{-1}

P19B.3 $12.78 \text{ mS m}^2 \text{ mol}^{-1}$, $2.57 \text{ mS m}^2 (\text{mol dm}^{-1})^{-3/2}$

P19B.5 $12.6 \text{ mS m}^2 \text{ mol}^{-1}$, $6.66 \text{ mS m}^2 (\text{mol dm}^{-1})^{-3/2}$ (a) $12.02 \text{ mS m}^2 \text{ mol}^{-1}$ (b) 120 mS m^{-1} (c) 172Ω

P19B.7 0.83 nm

P19B.9 9.3 kJ mol^{-1}

Topic 19C

P19C.1 (a) 12 kN mol^{-1} , $2.0 \times 10^{-20} \text{ N molecule}^{-1}$ (b) 16.5 kN mol^{-1} , $2.7 \times 10^{-20} \text{ N molecule}^{-1}$
 (c) 24.8 kN mol^{-1} , $4.1 \times 10^{-20} \text{ N molecule}^{-1}$

P19C.7 $\langle x^4 \rangle^{1/4} / \langle x^2 \rangle^{1/2} = 3^{1/4}$

P19C.9 (a) 0 (b) 0.0156 (c) 0.0537

P19C.11 $P = \left(\frac{2}{\pi N} \right)^{1/2} e^{-n^2/2N}$

Chapter 20

Topic 20A

P20A.1 Second order

P20A.3 (a) 1, 2, 3 (b) $2.2 \times 10^9 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

Topic 20B

P20B.3 Second-order, $k_r = 0.0594 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$, 2.94 g

- P20B.5 $7.0 \times 10^{-5} \text{ s}^{-1}$, $7.3 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
- P20B.7 $6 \times 10^{-14} \text{ mol dm}^{-3} \text{ s}^{-1}$, $4.4 \times 10^8 \text{ s} = 14 \text{ yr}$
- P20B.9 First-order, $5.84 \times 10^{-3} \text{ s}^{-1}$, $k_r = 2.92 \times 10^{-3} \text{ s}^{-1}$, first-order, 1.98 min
- P20B.11 $3.65 \times 10^{-3} \text{ min}^{-1}$, 190 min, 274 min
- P20B.13 $2.37 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_r = 1.18 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $4.98 \times 10^{-3} \text{ s}$
- P20B.15 First-order, third-order
- P20B.17
$$\left(\frac{1}{3A_0 - 2B_0} \right) \ln \left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)} \right)$$
- P20B.19
$$\frac{2^{n-1} - 1}{\left(\frac{4}{3}\right)^{n-1} - 1}$$

Topic 20C

- P20C.3
$$\frac{k_r'([A]_0 + [B]_0) + (k_r[A]_0 - k_r'[B]_0)e^{-(k_r+k_r')t}}{k_r + k_r'}, \left(\frac{k_r'}{k_r + k_r'} \right) \times ([A]_0 + [B]_0),$$
- $$\left(\frac{k_r}{k_r + k_r'} \right) \times ([A]_0 + [B]_0), \frac{[B]_\infty}{[A]_\infty} = \frac{k_r}{k_r'}$$
- P20C.5 (a) (i) $8k_a k_a' [A]_{\text{tot}} + (k_a')^2$ (c) $1.7 \times 10^7 \text{ s}^{-1}$, $2.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 1.6×10^2

Topic 20D

- P20D.3 16.7 kJ mol^{-1} , $1.14 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
- P20D.5 (a) $2.1 \times 10^{-16} \text{ mol dm}^{-3} \text{ s}^{-1}$ (b) $4.3 \times 10^{11} \text{ kg}$ or 430 Tg

Topic 20E

- P20E.1 Steady-state approximation
- P20E.3 Steady-state intermediate
- P20E.5 $k_r K_1 K_2 [\text{HCl}]^3 [\text{CH}_3\text{CH}=\text{CH}_2]$

Topic 20F

P20F.3 $(1 + 2k_r t[A]_0^2)^{1/2}$

Topic 20G

P20G.1 1.11

P20G.3 (a) 6.7 ns (b) $0.105 \overline{\text{ns}}^{-1}$

P20G.5 $1.98 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

P20G.7 3.5 nm

Topic 20H

P20H.1
$$v = \frac{v_{\max}}{1 + \frac{1}{K[S]_0}}$$
 Rate law based on rapid pre-equilibrium approximation

P20H.5 $2.31 \mu\text{mol dm}^{-3} \text{ s}^{-1}$, 115 s^{-1} , 115 s^{-1} , $1.11 \mu\text{mol dm}^{-3}$, $104 \text{ dm}^3 \mu\text{mol}^{-1} \text{ s}^{-1}$

Chapter 21**Topic 21A**

P21A.1 (a) $4.35 \overline{\times 10^{-20}} \text{ m}^2$ (b) 0.15

P21A.3 $1.7 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, 3.6 ns

P21A.5 $3.12 \times 10^{14} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 193 kJ mol^{-1} , $7.29 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 175 kJ mol^{-1}

Topic 21C

P21C.1 $E_a = 86.0 \text{ kJ mol}^{-1}$, $+83.9 \text{ kJ mol}^{-1}$, $+19.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $+79.0 \text{ kJ mol}^{-1}$

P21C.5 $+60.44 \text{ kJ mol}^{-1}$, $+62.9 \text{ kJ mol}^{-1}$, $-181 \text{ J K}^{-1} \text{ mol}^{-1}$, $+114.7 \text{ kJ mol}^{-1}$

- P21C.7 3×10^7
- P21C.9 Two univalent ions of the same sign
- P21C.11 (a) 0.06 (b) 0.89, 0.83

Topic 21D

- P21D.1 $I = I_0 e^{-\sigma N L}$

Topic 21E

- P21E.1 $k_r \approx (k_{AA} k_{DD} K)^{1/2}$
- P21E.3 1.15 eV

Topic 21F

- P21F.1 0.78, 0.38
- P21F.3 (a) -0.618 V
- P21F.5 2.00×10^{-5} mA m⁻², 0.498, no

Chapter 22

Topic 22A

- P22A.1 -76.9 kJ mol⁻¹, -348.1 kJ mol⁻¹, corner is the likely settling point
- P22A.3 (a) 1.61×10^{15} cm⁻² (b) 1.14×10^{15} cm⁻² (c) 1.86×10^{15} cm⁻²

Topic 22B

- P22B.3 (a) 165, 13.1 cm³ (b) 263, 12.5 cm³
- P22B.5 5.78 mol kg⁻¹, 7.02 Pa⁻¹
- P22B.7 -20.0 kJ mol⁻¹, -63.5 kJ mol⁻¹
- P22B.9 (a) R values in the range 0.975 to 0.991 (b) 3.68×10^{-3} , -8.67 kJ mol⁻¹, 2.62×10^{-5} ppm⁻¹, $\Delta_b H = -15.7$ kJ mol⁻¹

P22B.11 0.138 mg g⁻¹, 0.58

P22B.13 (a) $k = 0.2289$, $n = 0.6180$, $k = 0.2289$, $n = 0.6180$ (c) $k = 0.5227$, $n = 0.7273$

Topic 22C

P22C.1 $-\frac{k_r}{K} \frac{p_{\text{NH}_3}}{p_{\text{H}_2}}$, $k_c = \frac{p - p_0}{t} - \frac{p_0}{t} \ln \frac{p}{p_0}$, $k_c = 2.5 \times 10^{-3} \text{ kPa s}^{-1}$