Solutions to odd-numbered problems

Topic 4

P4.3 $49\overline{6}$ nm, blue-green

Topic 5

P5.1 (a) 0.020 (b) 0.047 (c) 7×10^{-6} (d) 0.5 (e) 0.61

P5.3 $a = \pi / 2^{1/5}$

P5.5 π

P5.7 $x_{\max} = \pm a$

Topic 6

P6.1 (a) $\left(-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}x^2}-\frac{e^2}{4\pi\varepsilon_0 x}\right)\psi = E\psi$ (b) $\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\psi = E\psi$ (c) $\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}-cx\right)\psi = E\psi$

P6.3 (a) –1 (b) +1 (c) not an eigenfunction of $\hat{i}$

Topic 7

P7.1 $\frac{1}{a}$

P7.3 $\frac{\hbar^2 k^2}{2m_e}$

P7.5 (a) (i) $N = \left(\frac{1}{\pi a_0^3}\right)^{1/2}$ (ii) $N = \left(\frac{1}{32\pi a_0^5}\right)^{1/2}$

P7.7 (a) $\frac{-e^2}{4\pi\varepsilon_0 a_0}$ (b) $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$, $-\frac{\hbar^2}{2m}\nabla^2$, $\frac{\hbar^2}{2m_e {a_0}^2}$

Topic 8

P8.3 (a) (i) 0 (ii) $\mathrm{i}\hbar kx$ (b) (i) $-\frac{x\hat{p}_x{}^2}{2m}$ (ii) $-\frac{\mathrm{i}\hbar\hat{p}_x}{2m}$

Topic 9

P9.1 1.24×10^{-39} J, 2.2×10^{9}, 1.8×10^{-30} J

P9.3 (a) $\frac{1}{2}$ (b) $\frac{1}{4}-\frac{1}{2\pi}=0.0908$ (c) $\frac{4\delta x}{L}$

P9.5 $\left(\frac{1}{L}\right)^{1/2}$

Topic 10

P10.1 $\left(\frac{(\mathrm{e}^{\kappa L}-\mathrm{e}^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)}+1\right)^{-1}$, $16\varepsilon(1-\varepsilon)\mathrm{e}^{-2\kappa L}$

P10.3 (a) $T=|A_3|^2=A_3\times A_3^{*}=\frac{4k_1^2k_2^2}{(a^2+b^2)\sinh^2(k_2L)+b^2}$

where $a^2+b^2=(k_1^2+k_2^2)(k_2^2+k_3^2)$ and $b^2=k_2^2(k_1+k_3)^2$

P10.5 1.2×10^{6}

Topic 11

P11.1 8.86×10^{-39} J, 1.11×10^{-30} J

P11.3 1.6×10^{-6} m, 1.6 μm

P11.5 6.9×10^{-10} m, 0.69 nm

P11.7 (a) $n\pi/2$ (b) $\frac{\pi n^2}{6}$

P11.9 $\frac{h^2}{8m}\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)=E$

Topic 12

P12.3 $\frac{1}{2}\left(\frac{mk_{\mathrm{f}}}{\mathrm{h}^2}\right)^{1/2}$

P12.5 $\frac{3}{4}(2v^2+2v+1)\alpha^4$

P12.7 (b) $9V_0$ (c) the oscillations are not excited (d) magnitude of the wavefunction will not fall off so sharply with increasing displacement, so the energy levels will become progressively closer.

P12.11 (a) $e^{-\alpha^2/2}$, $e^{-|\alpha|^2/2}$ (c) $\frac{h}{2}$

Topic 13

P13.1 (a) $N = 1/2$ (b) $-\hbar$, 1/4, $+\hbar$, ¾ (c) $\frac{h^2}{2m_p r^2}$ (d) $\frac{h}{2}$, $\frac{h^2}{2m_p r^2}$

P13.3 1.53×10^{-3} m, 1.53 mm

P13.5 π, $\varphi_0 + \pi$

P13.9 (a) no uncertainty in Δl_z, $\frac{1}{2^{1/2}}$ (b) h, $\frac{1}{2}$

Topic 14

P14.1 7.59×10^{-4} m = 0.759 mm

P14.3 (a) $N = 1/(12)^{1/2}$ (e) $\frac{7h}{4}$, $\frac{17h^2}{6I}$, 3.9×10^{-23} J, $\left(\frac{17}{3}\right)^{1/2}$ h

P14.7 0

P14.9 $\frac{h}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$, $\frac{h}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$, $\frac{h}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$, $-\frac{h}{i}$, l_z

Topic 15

P15.1 (a) $\frac{\varepsilon a}{L} + \frac{\varepsilon}{\pi}\sin\left(\frac{\pi a}{L}\right)$ (b) $\frac{\varepsilon}{10} + \frac{\varepsilon}{\pi}\sin\left(\frac{\pi}{10}\right) = 0.1984\varepsilon$

P15.3 $-\frac{0.08664m^3g^2L^4}{h^2}$, $\frac{32m^2gL^3[(-1)^n+1]n}{\pi^2h^2(n^2-1)^3}$

Topic 17

P17.1 $n_2 \to 6$

P17.3 $a_{\mathrm{Ps}} = 2a_0$, $E_{1,\mathrm{Ps}} = \frac{1}{2}E_{1,\mathrm{H}}$

P17.5 $K = 60$

Topic 18

P18.1 0.420 pm

P18.3 (a) ±106 pm (b) $r = \pm 1.76\ a_0/Z$

P18.5 (b) $\rho_{\mathrm{node}} = 3+\sqrt{3}$ and $\rho_{\mathrm{node}} = 3-\sqrt{3}$, $\rho_{\mathrm{node}} = 0$ and $\rho_{\mathrm{node}} = 4$, $\rho_{\mathrm{node}} = 0$ (c) $\langle r\rangle_{3\mathrm{s}} = \dfrac{27a_0}{2}$

P18.7 $r' = 2.66\,a_0$

P18.9 (a) $\dfrac{Z}{a_0}$ (b) $\dfrac{Z}{4a_0}$ (c) $\dfrac{Z}{4a_0}$

Topic 19

P19.1 $\theta = \cos^{-1}\dfrac{m_l}{\{l(l+1)\}^{1/2}}$, 54°44′, 0

Topic 21

P21.1 $R_{\mathrm{Li}^{2+}} = 987663\,\mathrm{cm}^{-1}$, $137175\,\mathrm{cm}^{-1}$, $185187\,\mathrm{cm}^{-1}$, 122.5 eV

P21.3 $^2\mathrm{P}_{1/2}$ and $^2\mathrm{P}_{3/2}$, $^2\mathrm{D}_{3/2}$ and $^2\mathrm{D}_{5/2}$, $^2\mathrm{D}_{3/2}$

P21.5 3.3429×10^{-27} kg, 1.000272

P21.7 $\Delta l = \pm 1$ and $\Delta m_l = 0$ or ± 1

Topic 22

P22.1 $\dfrac{Z^{3/2}\mathrm{e}^{-\rho/2}}{(24\pi)^{1/2}a^{3/2}}\left(\dfrac{2-\rho}{2}+\dfrac{\rho\sin\theta}{8^{1/2}}\times(-\cos\phi+3^{1/2}\sin\phi)\right)$, 120°

Topic 23

P23.1 1.87×10^6 J mol^{-1} = 1.87 MJ mol^{-1}

P23.3 $E_{\text{H1s}} - \frac{j+k}{1+S} + \frac{j_0}{R}$, $E_{\text{H1s}} - \frac{j-k}{1-S} + \frac{j_0}{R}$

P23.5 (b) $2.5a_0 = 1.3\times10^{-10}$ m, $-0.555j_0/a_0 = -15.1$ eV, $-0.565j_0/a_0 = -15.4$ eV, $0.055j_0/a_0 = 1.5$ eV, $0.065j_0/a_0 = 1.8$ eV

Topic 24

P24.1 $2.1a_0$

P24.3 $\pi/4$ or $3\pi/4$

Topic 25

P25.1 $\frac{\alpha_\text{A}+\alpha_\text{B}-2\beta S}{2(1-S^2)} \pm \frac{\alpha_\text{A}-\alpha_\text{B}}{2(1-S^2)}\left(1+\frac{4(\beta+\alpha_\text{A}S)(\beta+\alpha_\text{B}S)}{(\alpha_\text{A}-\alpha_\text{B})^2}\right)^{1/2}$, $\frac{\alpha_\text{A}-\beta S}{1-S^2} + \frac{(\beta+\alpha_\text{A}S)(\beta+\alpha_\text{B}S)}{(\alpha_\text{A}-\alpha_\text{B})(1-S^2)}$, $\frac{\alpha_\text{B}-\beta S}{1-S^2} - \frac{(\beta+\alpha_\text{A}S)(\beta+\alpha_\text{B}S)}{(\alpha_\text{A}-\alpha_\text{B})(1-S^2)}$

P25.3 (i) E/eV = –10.7, –8.7, and –6.6 (ii) E/eV = –10.8, –8.9, and –6.9

Topic 26

P26.1 $E = \alpha_\text{O}$, $\frac{1}{2}\left(\alpha_\text{O}+\alpha_\text{C} \pm (\alpha_\text{O}-\alpha_\text{C})\sqrt{1+\frac{12\beta^2}{(\alpha_\text{O}-\alpha_\text{C})^2}}\right)$, $(\alpha_\text{O}-\alpha_\text{C})\left(\sqrt{1+\frac{12\beta^2}{(\alpha_\text{O}-\alpha_\text{C})^2}} - \sqrt{1+\frac{4\beta^2}{(\alpha_\text{O}-\alpha_\text{C})^2}}\right)$, $\frac{4\beta^2}{\alpha_\text{O}-\alpha_\text{C}}$

P26.3 (b) 2β, 0.988β, aromatic (c) 1.657β, 1.518β, not aromatic

P26.7 $P_N = xP_{N-1} - P_{N-2}$

P26.9 (a) $\alpha-\beta$, $\alpha-\beta$, and $\alpha+2\beta$ (b) –413 kJ mol^{-1} (c) $-849\,\text{kJ mol}^{-1}$, $3(\alpha/2) - 212\,\text{kJ mol}^{-1}$, $3\alpha - 425\,\text{kJ mol}^{-1}$

Topic 28

P28.1

(a)

Ethanol	AM1*	PM3*	exp

(b)

C_1–C_2 / pm	151.2	151.8	153.0
C_1–O / pm	142.0	141.0	142.5
C_1–H / pm	112.4	110.8	110
C_2–H / pm	111.6	109.7	109
O–H / pm	96.4	94.7	97.1
C $_2$–C_1–O / ^{o}	107.34	107.81	107.8
C_1–O–H / ^{o}	106.65	106.74	
H–C_1–H / ^{o}	108.63	106.98	
H–C_2–H / ^{o}	108.24	107.24	
$\Delta_f H^\ominus(g)$ / kJ mol^{-1}	–262.18	–237.87	–235.10
Dipole / D	1.55	1.45	1.69
*Spartan '10^{TM}			

1,4-dichlorobenzene	AM1*	PM3*	exp
C_1–C_2 / pm	139.9	139.4	138.8
C_2–C_3 / pm	139.3	138.9	138.8
C_1–Cl / pm	169.9	168.5	173.9
C_2–H / pm	110.1	109.6	
Cl–C_1–C_2 / ^{o}	119.71	119.42	
C_1–C_2–H / ^{o}	120.40	120.06	
Cl–C_1–C_2–H / ^{o}	0.00	0.00	
$\Delta_f H^\ominus(g)$ / kJ mol^{-1}	33.36	42.31	24.6
dipole / D	0.00	0.00	0.0
*Spartan '10^{TM}			

Topic 29

P29.1

Features Calculated with Full CI, CCSD(T) and RI–MP2 Methods Bond length (R) in pm and energies in zJ			
He_2	†Full CI	*CCSD(T)/6-311++G(2df,2p)	*RI-MP2/6-311++G(2df,2p)
R	297	321	301
$E_0 - 2E_{He}$	–0.039	–0.00741	–0.165
† T. van Mourik and J.H. van Lenthe, *J. Chem. Phys.*, 102(19), 7479 (15 May 1995). * Spartan '10^{TM}			

P29.3 $\psi_0 = \psi_0^{(0)} + \psi_0^{(1)} = \psi_0^{(0)} + \sum_{n(\neq 0)} \left\{ \frac{\int \psi_n^{(0)} H^{(1)} \psi_0^{(0)} \mathrm{d}\tau}{E_0^{(0)} - E_n^0} \right\} \psi_n^{(0)}$

P29.5 $H_{22} = 2\int \psi_b(1) h_1 \psi_b(1) \mathrm{d}\tau_1 + \frac{1}{2}\{(\mathrm{AA}|\mathrm{AA}) - 4(\mathrm{AA}|\mathrm{AB}) + (\mathrm{AA}|\mathrm{BB}) + 2(\mathrm{AB}|\mathrm{AB})\}$,

$H_{00} = 2E_{\mathrm{H}} + \frac{1}{2}\{(\mathrm{AA}|\mathrm{AA}) + 4(\mathrm{AA}|\mathrm{AB}) + (\mathrm{AA}|\mathrm{BB}) + 2(\mathrm{AB}|\mathrm{AB})\}$, $H_{02} = \frac{1}{2}\{(\mathrm{AA}|\mathrm{AA}) - (\mathrm{AA}|\mathrm{BB})\} = H_{20}$

Topic 30

P30.1 $V_{\mathrm{XC}}(\boldsymbol{r}) = \frac{5}{3}C\rho(\boldsymbol{r})^{2/3}$

Topic 31

P31.1 (a) D_{3d} (b) D_{3d}, C_{2v} (c) D_{2h} (d) D_3 (e) D_{4d}

P31.3 S_4, C_2, S_4

Topic 32

P32.1 *trans*-CHCl=CHCl

P32.3 $\Gamma = 3A_1 + B_1 + 2B_2$

P32.7 $+1$ or -1, $+1$, -1

P32.9 (a) $2A_1 + A_2 + 2B_1 + 2B_2$ (b) $A_1 + 3E$ (c) $A_1 + T_1 + T_2$ (d) $A_{2u} + T_{1u} + T_{2u}$

P32.11 (a) E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$, D_{3h} (d) $A_1' + E'$

Topic 33

P33.1 $A_1 + T_2$, s and p, (d_{xy}, d_{yz}, d_{zx})

P33.7 $4A_1 + 2B_1 + 3B_2 + A_2$

P33.9 (a) $7A_2 + 7B_1$, $\frac{1}{2}(a - a')$, $\frac{1}{2}(b - b'), \ldots, \frac{1}{2}(g - g')$, $\frac{1}{2}(a + a'), \frac{1}{2}(b + b'), \ldots, \frac{1}{2}(g + g')$

Topic 34

P34.1 0.7 D, 0.4 D, 0

P34.5 0.123

P34.7 3.68×10^{-39} J^{-1} C^2 m^2, 3.31×10^{-29} m^3, 1.32 D

Topic 35

P35.1 $-4.3\times10^{-28}\,\mathrm{J} = -2.6\times10^{-4}\,\mathrm{J\,mol^{-1}}$

P35.3 $\dfrac{-6C}{r^7}$

P35.5 $\left(\dfrac{2\pi}{3}\right)\times\left(\dfrac{N_\mathrm{A}\rho}{M}\right)^2\times\left(\dfrac{C_6}{d^3}\right)$

Topic 36

P36.1 $1+\dfrac{b}{V_\mathrm{m}^\mathrm{o}}$, 1.11

P36.3 (a) $8.7\,\mathrm{cm^3}$ (b) $-0.15\,\mathrm{dm^3 mol^{-1}}$

P36.7 $13.6\,\mathrm{dm^3\,mol^{-1}}$, attractive, –2%

Topic 37

P37.1 $3.61\times10^5\,\mathrm{g\,mol^{-1}}$

P37.3 $V=\left(3\sqrt{3}/2\right)a^2c$

P37.5 $834\,\mathrm{pm}$, $606\,\mathrm{pm}$, $870\,\mathrm{pm}$

P37.7 4

P37.9 $\dfrac{1}{d^2}=\left(\dfrac{h}{a}\right)^2+\left(\dfrac{k}{b}\right)^2+\left(\dfrac{l}{c}\right)^2$

P37.11 simple (primitive) cubic lattice, a = 344 pm

P37.13 $628\,\mathrm{pm}$, gave support

P37.15 0

P37.17 (a) 14.0^o, 24.2^o, 0.72^o, 1.23^o (b) R_CCl = 176 pm and R_ClCl = 289 pm

Topic 38

P38.1 0.340

P38.3 $7.654\,\mathrm{g\,cm^{-3}}$

P38.7 $-146\ \text{kJ mol}^{-1}$

P38.9 6.694

Topic 39

P39.7 $8.81\times10^{-9}\ \text{m}^3\ \text{mol}^{-1}$

Topic 40

P40.3 4.4×10^{3}

P40.5 $A=\varepsilon'[\text{J}]_0\left(1-\text{e}^{-L/\lambda}\right)$, $A=\varepsilon'[\text{J}]_0$

P40.9 $\frac{1}{2}\left(\frac{\pi}{\ln 2}\right)^{1/2}\varepsilon_{\max}\Delta\tilde{\nu}_{1/2}$, $5.7\times10^{4}\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-2}$

P40.11 $498\ \text{kg mol}^{-1}$, 51.3 nm

P40.13 (a) receding, 1.128×10^{-3} c = $3.381\times10^{5}\ \text{m s}^{-1}$

P40.15 $2\left(kT/mc^2\right)^{1/2}$

Topic 41

P41.1 $m_{\text{eff}}R^2$

Topic 42

P42.1 596GHZ, $19.9\ \text{cm}^{-1}$, 0.503 mm, $9.941\ \text{cm}^{-1}$

P42.3 128.393pm, 128.13pm

P42.5 116.28 pm, 155.97 pm

P42.7 $14.35\ \text{m}^{-1}$, 26, 15

P42.9 $\left(\frac{kT}{2hcB}\right)^{1/2}-\frac{1}{2}$, 30, $\left(\frac{kT}{hcB}\right)^{1/2}-\frac{1}{2}$, 6

Topic 43

P43.1 $142.81\,\mathrm{cm^{-1}}$, 3.36 eV, $93.8\,\mathrm{N\,m^{-1}}$

P43.5 $2D_e/\tilde{\nu} - \frac{1}{2}$

P43.7 112.83 pm, 123.52 pm

P43.9 B_0 = 10.433 cm^{-1}, B_1 = 10.126 cm^{-1}

P43.11 $\langle x^2 \rangle = \dfrac{1}{k_f}(v+½)\hbar\omega$. Rotational constant *B* decreases, *B* decreases with increased anharmonicity

P43.13 (b) $12.8195\,\mathrm{kJ\,mol^{-1}}$ (c) $1.85563\times10^{3}\,\mathrm{N\,m^{-1}}$ (d) $1.91\,\mathrm{cm^{-1}}$ (e) 113 pm

Topic 44

P44.3 (a) C_{3v} (b) nine (c) $3A_1 + 3E$ (d) all modes are infrared active (e) all modes may be Raman active

Topic 45

P45.1 $1\sigma_g^{\,2}1\sigma_u^{\,2}1\pi_u^{\,4}2\sigma_g^{\,0}1\pi_g^{\,1}$

P45.3 $4936\bar{4}\ \mathrm{cm^{-1}}$

Topic 47

P47.1 (a)

Nuclide	Spin *I*	μ/μ_N	Sensitivity ratio(v)	Sensitivity ratio (B)
^{2}H	1	0.85745	0.409	0.00965
^{13}C	$\frac{1}{2}$	0.7023	0.251	0.01590
^{14}N	1	0.40356	0.193	0.00101
^{19}F	$\frac{1}{2}$	2.62835	0.941	0.83350
^{31}P	$\frac{1}{2}$	1.1317	0.405	0.06654
^{1}H	$\frac{1}{2}$	2.79285		

Topic 48

P48.1 29 $\mu T m^{-1}$

P48.3 Both fit the data equally well

P48.5 $\cos\phi = B/4C$

Topic 49

P49.1 $400\times10^{6}\,\text{Hz}\pm8\,\text{Hz}$, 0.29 s

P49.3 (a) $\Delta\omega_{1/2} = \dfrac{2}{T_2}$ (b) $\Delta\omega_{1/2} = \dfrac{2(\ln 2)^{1/2}}{T_2}$

P49.7 0.58 mT

Topic 50

P50.1 2.8×10^{13} Hz

P50.3 6.9 mT, 2.1 mT

Topic 51

P51.1 (b) {2, 2, 0, 1, 0, 0} and {2, 1, 2, 0, 0, 0}

P51.7 $e^{-Mgh/RT}$, 0.363, 0.57

Topic 52

P52.3 (a) (i) 5.00 (ii) 6.26 (b) 1.00, 0.80, 6.58×10^{-11}, 0.122

P52.5 1.209, 3.004

P52.7 (a) 1.049 (b) 1.548, 0.953, 0.645, 0.044, 0.230, 0.002, 0.083

P52.9 (a) 660.6 (b) 4.26×10^{4}

Topic 53

P53.3 (a) 104 K (b) $1+a$

Topic 54

P54.1 $pV = NkT = nRT$

Topic 55

P55.1 $-nRT\ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - n^2 a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$ (a) –1.7 kJ (b) –1.8 kJ, –1.5 kJ

Topic 56

P56.1 62.2 kJ mol^{-1}

P56.3 $w = 0$, $\Delta U = +2.35$ kJ, +3.03 kJ

P56.5 increase

P56.7 (a) 29.9 K MPa^{-1} (b) –2.99 K

Topic 57

P57.1 –1270 kJ mol^{-1}

P57.3 –67.44, $n = 0.9253$, –6625.5 kJ mol^{-1}, 2.17 per cent

P57.5 –994.30 kJ mol^{-1}

P57.7 –802.31 kJ mol^{-1}

P57.9 +37 K, 4.09 kg

Topic 58

P58.1 1.6 m, 0.80 m, 2.8 m

P58.3 0.385, 0.0786, 0.0206

P58.9 $\frac{N\Delta\varepsilon^2}{kT^2}$

P58.11 $C_{V,\mathrm{m}} = R\left\{1+\frac{1}{45}\left(\frac{\theta_\mathrm{R}}{T}\right)^2+\frac{16}{945}\left(\frac{\theta_\mathrm{R}}{T}\right)^3+\ldots\right\}$,

$C_{V,\mathrm{m}} = R\left\{\left(\frac{1}{xq^\mathrm{R}}\right)^2 12\mathrm{e}^{-2/x}(1+15\mathrm{e}^{-4/x}+20\mathrm{e}^{-6/x}+84\mathrm{e}^{-10/x}+175\mathrm{e}^{-12/x}+105\mathrm{e}^{-16/x}+\ldots)\right\}$,

$C_{V,\mathrm{m}} = R\left\{\left(\frac{1}{xq^\mathrm{R}}\right)^2 12\mathrm{e}^{-2/x}(1+15\mathrm{e}^{-4/x}+20\mathrm{e}^{-6/x}+84\mathrm{e}^{-10/x}+175\mathrm{e}^{-12/x}+105\mathrm{e}^{-16/x}+\ldots)\right\}$

P58.13 $C_{V,\mathrm{m}} = 3R\left\{\left(\frac{\theta_\mathrm{E}}{T}\right)^2\frac{\mathrm{e}^{\theta_\mathrm{E}/T}}{(\mathrm{e}^{\theta_\mathrm{E}/T}-1)^2}\right\}$

P58.15 (a) 87.55 K, 6330 K (b), (c) $\alpha = (K/(K+4))^{1/2}$, $2\alpha C_{V,\mathrm{m}}(\mathrm{H}) + (1-\alpha)C_{V,\mathrm{m}}(\mathrm{H_2})$,
$K_{\mathrm{eq}i} = \frac{kT_i\left(\Lambda_{\mathrm{H}_2 i}\right)^3\mathrm{e}^{-(D/RT_i)}}{p^\ominus q_{\mathrm{V}i}q_{\mathrm{R}i}\left(\Lambda_{\mathrm{H}i}\right)^6}$, $1.5R$, $2.5R+\left[\frac{\theta_\mathrm{V}}{T_i}\times\frac{\mathrm{e}^{-(\theta_\mathrm{V}/2T_i)}}{1-\mathrm{e}^{\theta_\mathrm{V}/T_i}}\right]^2 R$

P58.17 (a) $q^\mathrm{R} = 19.899,\ \dot{q}^\mathrm{R} = 19.558,$ and $\ddot{q}^\mathrm{R} = 576.536$ (b)
$q^\mathrm{R} = 3.007,\ \dot{q}^\mathrm{R} = 2.979,$ and $\ddot{q}^\mathrm{R} = 118.5$

P58.23 nR

P58.25 $T = \left(\frac{p}{nR}\right)\times(V-nb)+\left(\frac{na}{RV^2}\right)\times(V-nb)$, $\left(\frac{\partial T}{\partial p}\right)_V = \frac{V-nb}{nR}$

P58.27 $c = \left(\frac{\gamma p}{\rho}\right)^{1/2}$, 322 m s^{-1}

Topic 60

P60.3 199.4 J mol^{-1} K^{-1}

P60.7 $R\ln\left(\frac{2\pi\mathrm{e}^2 m\sigma_\mathrm{m}}{h^2 N_\mathrm{A}\beta}\right)$, $R\ln\left\{\left(\frac{\sigma_\mathrm{m}}{V_\mathrm{m}}\right)\times\left(\frac{h^2\beta}{2\pi m\mathrm{e}}\right)^{1/2}\right\}$

Topic 61

P61.5 1.00 kJ

Topic 62

P62.1 (a) $-21.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $+21.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $+0.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (b) $+109.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $-111.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $-1.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$

P62.3 (a) $43.9\,\mathrm{kJ}$, $-43.9\,\mathrm{kJ}$, $-118.\dot{1}\,\mathrm{J\,K^{-1}}$, $145.\dot{9}\,\mathrm{J\,K^{-1}}$, $28\,\mathrm{J\,K^{-1}}$ (b) $49.9^{\circ}\mathrm{C} = 323.1\,\mathrm{K}$, $38.4\,\mathrm{kJ}$, $-119.\dot{8}\,\mathrm{J\,K^{-1}}$, $129.\dot{2}\,\mathrm{J\,K^{-1}}$, $9\,\mathrm{J\,K^{-1}}$

P62.5 $+45.4\,\mathrm{J\,K^{-1}}$, $+51.2\,\mathrm{J\,K^{-1}}$

P62.7 $\dfrac{\mathrm{d}S}{\mathrm{d}t} = -CA\ln(T_{\mathrm{i}} - T_{\mathrm{S}})$

Topic 63

P63.1 (a) $200.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (b) $232.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$

P63.3 $+41.16\,\mathrm{kJ\,mol^{-1}}$, $+42.08\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $+40.84\,\mathrm{kJ\,mol^{-1}}$, $+41.08\,\mathrm{J\,K^{-1}\,mol^{-1}}$

P63.5 $34.4\,\mathrm{kJ\,mol^{-1}}$, $243\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Topic 64

P64.1 (a) $50.7\,\mathrm{J\,K^{-1}}$, $-11.5\,\mathrm{J\,K^{-1}}$ (b) $+3.46\,\mathrm{kJ}$, indeterminate (c) $3.46\times10^{3}\,\mathrm{J}$, indeterminate (d) $+39.2\,\mathrm{J\,K^{-1}}$, $-39.2\,\mathrm{J\,K^{-1}}$

P64.3 (a) $+35\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (b) $12\,\mathrm{W\,m^{-3}}$, $1.5\times10^{4}\,\mathrm{W\,m^{-3}}$, $0.46\,\dfrac{\text{mol ATP}}{\text{mol glutamine}}$

Topic 65

P65.1 $513.5\,\mathrm{kJ\,mol^{-1}}$

Topic 66

P66.1 $-501\,\mathrm{kJ\,mol^{-1}}$

P66.3 $-21\,\mathrm{kJ\,mol^{-1}}$

P66.5 $\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S$, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

P66.7 $C_p \mathrm{d}T - \alpha TV\,\mathrm{d}p$, $-\alpha TV\Delta p$, $-0.50\,\mathrm{kJ}$

Topic 67

P67.1 (i) "molten globule" form is not stable

Topic 68

P68.1 (a) $y_\mathrm{M} = 0.36$ (b) $y_\mathrm{M} = 0.81$

Topic 69

P69.1 $196.0\,\mathrm{K}$, $11.1\,\mathrm{Torr}$

P69.3 234.4 K

P69.7 $T_\alpha = T_\beta$

P69.9 $\Delta C_p\ \mathrm{d}\ln\ T$

P69.11 $-\frac{1}{T} \times C_{p,\mathrm{m}}$

Topic 70

P70.1 $15.58\,\mathrm{kPa}$, $47.03\,\mathrm{kPa}$

Topic 71

P71.1 $1.25\times10^5\,\mathrm{g\,mol^{-1}}$, $1.23\times10^4\ \mathrm{dm^3\ mol^{-1}}$

P71.3 $\frac{R(T_\mathrm{b}^*)^2}{\Delta_\mathrm{vap}H} x_\mathrm{B}$

Topic 72

P72.3 (a) $V_1 = V_{m,1} + a_0 x_2^2 + a_1(3x_1 - x_2)x_2^2$, $V_2 = V_{m,2} + a_0 x_1^2 + a_1(x_1 - 3x_2)x_1^2$ (b) 75.63 $cm^3\ mol^{-1}$, 99.06 $cm^3\ mol^{-1}$

P72.7 G^E is reasonably consistent with the model regular solution

P72.9 72.53 $cm^3\ mol^{-1}$

Topic 73

P73.1 (a) +4.48 kJ mol^{-1} (b) 0.102 bar

P73.3 0.02054

P73.5 0.007 mol H_2, 0.107 mol I_2, 0.786 mol HI

P73.7 1.2×10^8, 2.7×10^3

P73.11 (a) K_H(Mb) = 2.0, K_H(Hb) = 36.0

Oxygen partial pressure		*s*	
p / kPa	*p* / Torr	Mb	Hb
1.0	7.5	0.79	0.01
1.5	11.3	0.85	0.04
2.5	18.8	0.90	0.14
4.0	30.0	0.94	0.38
8.0	60.0	0.97	0.81

(b)

p / kPa	*p* / Torr	*s*(Hb)
1.0	7.5	0.002
1.5	11.3	0.01
2.5	18.8	0.07
4.0	30.0	0.33
8.0	60.0	0.89

Topic 74

P74.1

T / K	300	400	500	600	700	800	900	1000
K	945	273	132	83	61	49	42	37

Topic 75

P75.1 (a) 9.24, 31.08 (b) $-12.9\ \text{kJ mol}^{-1}$ (c) $+161\ \text{kJ mol}^{-1}$ (d) $+248\ \text{J K}^{-1}\ \text{mol}^{-1}$

P75.3 $\frac{3}{2}R\times(B-CT)$, $70.5\ \text{J K}^{-1}\ \text{mol}$

P75.5 $78-0.161\times(T/\text{K})$

P75.7 $+156\ \text{kJ mol}^{-1}$

P75.9 $\Delta_{\text{r}}G(T')=\Delta_{\text{r}}G(T)+(T-T')\Delta_{\text{r}}S(T)+\alpha(T',T)\times\Delta a+\beta(T',T)\times\Delta b+\gamma(T',T)\times\Delta c$, $-225.31\ \text{kJ mol}^{-1}$

Topic 76

P76.1 (a) +1.23 V (b) +1.11 V

Topic 77

P77.1a (a) 4.0×10^{-3}, 1.2×10^{-2} (b) 0.74, 0.60 (c) 5.9 (d) +1.102 V (e) +1.079 V

P77.3 (a) $E^{\ominus}-(38.54\ \text{mV})\times\ln(4^{1/3}b)-(38.54\ \text{mV})\ln(\gamma_{\pm})$ (b) 1.0304 V (c) $-236.81\ \text{kJ mol}^{-1}$, $-198.84\ \text{kJ mol}^{-1}$, 6.84×10^{34} (d) 0.763 (e) 0.75 (f) $-87.2\ \text{J K}^{-1}\ \text{mol}^{-1}$, $-262.4\ \text{kJ mol}^{-1}$

P77.5 $+74.9\ \text{kJ mol}^{-1}$, $+80.0\ \text{kJ mol}^{-1}$, $-17.1\ \text{J K}^{-1}\ \text{mol}^{-1}$

P77.7 $-131.25\ \text{kJ mol}^{-1}$, $-167.10\ \text{kJ mol}^{-1}$, $+56.7\ \text{J K}^{-1}\ \text{mol}^{-1}$

P77.11 (b) +0.206 V

Topic 78

P78.3 18.9 s, $v(\text{most probable})=v_{\text{mp}}=\left(\frac{2kT}{m}\right)^{1/2}=\left(\frac{2RT}{M}\right)^{1/2}$

P78.7 $f(v)=\left(\frac{m}{kT}\right)v\text{e}^{-mv^2/2kT}$, $\left(\frac{\pi kT}{2m}\right)^{1/2}$ or $\left(\frac{\pi RT}{2M}\right)^{1/2}$

P78.9 (a) 39% (b) 61% (c) 0.533, 53%, 47%

P78.11 $\frac{2}{\pi^{1/2}}\left(\frac{n+1}{2}\right)!\left(\frac{2kT}{m}\right)^{n/2}$, $\frac{(n+1)!!}{2^{n/2}}\left(\frac{2kT}{m}\right)^{n/2}$

P78.13 (a) 11.2 km s^{-1}, 1.19×10^{4} K, 2.37×10^{4} K, 1.89×10^{5} K (b) 5.04 km s^{-1}, 2.42×10^{3} K, 4.80×10^{3} K, 3.84×10^{4} K

P78.15 0.25 J cm^{-3}

Topic 79

P79.1 (a) $\sigma = 0.602$ nm^2, $d = (\sigma/\pi)^{1/2} = 438$ pm (b) $\sigma = 0.421$ nm^2, $d = (\sigma/\pi)^{1/2} = 366$ pm

P79.3 2.37×10^{17} m^2 s^{-1}, 2.85 J K^{-1} m^{-1} s^{-1}

Topic 80

P80.1 10.2 kJ mol^{-1}

P80.3 12.78 mS m^2 mol^{-1}, 2.57 mS m^2 $(mol\ dm^{-1})^{-3/2}$

P80.5 12.6 mS m^2 mol^{-1}, 6.66 mS m^2 $(mol\ dm^{-1})^{-3/2}$ (a) 12.02 mS m^2 mol^{-1} (b) 120 mS m^{-1} (c) 172 Ω

P80.7 0.83 nm

P80.9 9.3 kJ mol^{-1}

Topic 81

P81.1 (a) 12 kN mol^{-1} or 2.0×10^{-20} N $molecule^{-1}$ (b) $16.\overline{5}$ kN mol^{-1} or 2.7×10^{-20} N $molecule^{-1}$, $24.\overline{8}$ kN mol^{-1}, 4.1×10^{-20} N $molecule^{-1}$

P81.7 $\frac{RT}{2Dt}\boldsymbol{r}$ where $\boldsymbol{r} = x\boldsymbol{i} + y\boldsymbol{j} + z\boldsymbol{k}$

P81.9 $N > 60$

P81.11 1.7×10^{-2} s

P81.13 $Dt = N\lambda^2/6$

Topic 82

P82.1 second order

Topic 83

P83.3 second-order, $k_r = 0.059\overline{4}\,\text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1}$, 2.94 g

P83.5 $7.0\times10^{-5}\,\text{s}^{-1}$, $7.3\times10^{-5}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$

P83.7 $6\times10^{-14}\,\text{mol dm}^{-3}\,\text{s}^{-1}$, $4.\overline{4}\times10^{8}\,\text{s} = 14\,\text{yr}$

P83.9 first-order, $5.84\times10^{-3}\,\text{s}^{-1}$, $k_r = 2.92\times10^{-3}\,\text{s}^{-1}$, first-order, 1.98 min

P83.11 $3.65\times10^{-3}\,\text{min}^{-1}$, 190 min

P83.13 $2.37\times10^{7}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $k_r = 1.18\times10^{7}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $4.98\times10^{-3}\,\text{s}$

P83.15 first-order, third-order

P83.17 $\left(\frac{1}{3A_0 - 2B_0}\right)\ln\left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)}\right)$

P83.19 $\frac{2^{n-1}-1}{\left(\frac{4}{3}\right)^{n-1}-1}$

Topic 84

P84.3 $\left(\frac{k_r' + k_r e^{-(k_r + k_r')t}}{k_r' + k_r}\right)\{[A]_0 + [B]_0\}$, $\frac{k_r'\{[A]_0 + [B]_0\}}{k_r + k_r'}$, $\frac{k_r\{[A]_0 + [B]_0\}}{k_r + k_r'}$

P84.5 (a) $8k_a k_a'[A]_{tot} + (k_a')^2$ (c) $1.\overline{7}\times10^{7}\,\text{s}^{-1}$, $2.\overline{7}\times10^{9}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $1.\overline{6}\times10^{2}$

Topic 85

P85.3 $1.67\times10^{4}\,\text{J mol}^{-1}$, 16.7 kJ mol^{-1}, $1.14\times10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$

P85.5 13.7 kJ mol^{-1}, $8.7\times10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$

Topic 86

P86.1 steady-state approximation

P86.3 steady-state intermediate

P86.5 $k_r K_1 K_2 [HCl]^3 [CH_3CH{=}CH_2]$

Topic 87

P87.1 (a) $4.3\overline{5}\times10^{-20}\ m^2$ (b) 0.15

P87.3 $1.7\times10^{11}\ mol^{-1}\ dm^3\ s^{-1}$, 3.6 ns

P87.5 $3.12\times10^{14}\ dm^3\ mol^{-1}\ s^{-1}$, $193\ kJ\ mol^{-1}$, $7.29\times10^{11}\ dm^3\ mol^{-1}\ s^{-1}$, $175\ kJ\ mol^{-1}$

Topic 88

P88.3 (a) $6.23\times10^6\ m^3\ mol^{-1}\ s^{-1} = 6.23\times10^9\ dm^3\ mol^{-1} s^{-1}$ (b) $4\times10^{-10}\ m = 0.4\ nm$

Topic 89

P89.1 E_a = 86.0 kJ mol^{-1}, +83.9 kJ mol^{-1}, +19.6 J K^{-1} mol^{-1}, +79.0 kJ mol^{-1}

P89.5 two univalent ions of the same sign

P89.7 $\log K_a + \log\dfrac{[HA]}{[A^-]} + 2AI^{1/2}$, $v^\circ\times10^{2AI^{1/2}}$

P89.9 (a) $1.37\times10^6\ dm^3\ mol^{-1}\ s^{-1}$ (b) $1.16\times10^6\ dm^3\ mol^{-1}\ s^{-1}$

P89.11 $\dfrac{v^3}{(v^\ddagger)^2}e^{-\Delta E_0/RT}$ (a) $2.7\times10^{-15}\ m^2\ s^{-1}$ (b) $1.1\times10^{-14}\ m^2\ s^{-1}$

Topic 90

P90.1 $I = I_0 e^{-\sigma\mathcal{N}L}$

Topic 91

P91.1

p/Torr	84.1	11.0	2.89	0.569	0.120	0.067
1/(p/Torr)	0.012	0.091	0.346	1.76	8.33	14.9
$10^4\ k_r$ / s^{-1}	2.98	2.23	1.54	0.857	0.392	0.303

$10^{-4} / (k_r / s^{-1})$	0.336	0.448	0.629	1.17	2.55	3.30

Topic 92

P92.1 $v = \dfrac{v_{max}}{1 + \dfrac{1}{K[S]_0}}$ Rate law based on rapid pre-equilibrium approximation , $k_a' >> k_b$

P92.5 2.31 μmol dm^{-3} s^{-1}, 115 s^{-1}, 115 s^{-1}, 1.11 μmol dm^{-3}, 104 dm^3 μmol^{-1} s^{-1}

P92.7 (b) pH = 7.0

Topic 93

P93.1 1.11

P93.3 (a) 6.9 ns , $0.10\overline{1}$ ns^{-1}

P93.5 1.98×10^9 dm^3 mol^{-1} s^{-1}

P93.7 3.5 nm

Topic 94

P94.1 (e) $k_r \approx (k_{AA} k_{DD} K)^{1/2}$

P94.3 1.15 eV

Topic 95

P95.1 –76.9 kJ mol^{-1} , –348.1 kJ mol^{-1} , corner is the likely settling point

P95.3 (a) 1.61×10^{15} cm^{-2} (b) 1.14×10^{15} cm^{-2} (c) 1.86×10^{15} cm^{-2}

P95.5 $R = R_{eq}\{1 - e^{-k_r t}\}$ where $k_r = k_{on} a_0$, $R = R_{eq} e^{-k_r t}$ where $k_r = k_{off}$

Topic 96

P96.3 (a) 165, 13.1 cm^3 (b) 263, 12.5 cm^3

P96.5 5.78 mol kg^{-1} , 7.02 Pa^{-1}

P96.7 $-20.0\ \text{kJ mol}^{-1}$, $-63.5\ \text{kJ mol}^{-1}$

P96.9 (a) R values in the range 0.975 to 0.991 (b) 3.68×10^{-3}, $-8.67\,\text{kJ mol}^{-1}$, $2.62\times10^{-5}\ \text{ppm}^{-1}$, $\Delta_b H = -15.7\,\text{kJ mol}^{-1}$

Topic 97

P97.1 $-\dfrac{k_r}{K}\dfrac{p_{NH_3}}{p_{H_2}}$, $k_c = \dfrac{p-p_0}{t} - \dfrac{p_0}{t}\ln\dfrac{p}{p_0}$, $k_c = 2.5\times10^{-3}\ \text{kPa s}^{-1}$