

## Solutions to a) exercises

Please note that just the numerical and short-answer solutions are supplied. For full worked solutions to all of the (a) exercises, please refer to the *Solutions Manual* by Charles Trapp, Marshall Cady, and Carmen Giunta (9780198701286).

### Topic 1

#### E1.1a

|     | Example  | Element       | Ground-state electronic configuration                |
|-----|----------|---------------|------------------------------------------------------|
| (a) | Group 2  | Ca, calcium   | [Ar]4s <sup>2</sup>                                  |
| (b) | Group 7  | Mn, manganese | [Ar]3d <sup>5</sup> 4s <sup>2</sup>                  |
| (c) | Group 15 | As, arsenic   | [Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup> |

E1.2a (a) Chemical formula and name: MgCl<sub>2</sub>, magnesium chloride. Ions: Mg<sup>2+</sup> and Cl<sup>−</sup>. Oxidation numbers of the elements: magnesium, +2; chlorine, −1.

(b) Chemical formula and name: FeO, iron(II) oxide. Ions: Fe<sup>2+</sup> and O<sup>2−</sup>. Oxidation numbers of the elements: iron, +2; oxygen, −2.

(c) Chemical formula and name: Hg<sub>2</sub>Cl<sub>2</sub>, mercury(I) chloride. Ions: Cl<sup>−</sup> and Hg<sub>2</sub><sup>2+</sup> (a polyatomic ion). Oxidation numbers of the elements: mercury, +1; chlorine, −1.

#### E1.8a

- (a) CO<sub>2</sub> is a linear, nonpolar molecule.
- (b) SO<sub>2</sub> is a bent, polar molecule.
- (c) N<sub>2</sub>O is linear, polar molecule.
- (d) SF<sub>4</sub> is a seesaw molecule and it is a polar molecule.

E1.9a In the order of increasing dipole moment: CO<sub>2</sub>, N<sub>2</sub>O, SF<sub>4</sub>, SO<sub>2</sub>.

#### E1.10a

- (a) Mass is an extensive property.
- (b) Mass density is an intensive property.
- (c) Temperature is an intensive property.
- (d) Number density is an intensive property.

E1.11a (a) 0.543 mol (b) 3.27 × 10<sup>23</sup> molecules

E1.12a (a) 108. g (b) 1.77 N

E1.13a 0.43 bar

E1.14a 0.42 atm

E1.15a (a)  $1.47 \times 10^5 \text{ Pa}$  (b) 1.47 bar

E1.16a  $T = 310.2 \text{ K}$

E1.17a  $\theta/^{\circ}\text{C} = \frac{5}{9} \times (\theta_{\text{F}}/^{\circ}\text{F} - 32)$  or  $\theta_{\text{F}}/^{\circ}\text{F} = \frac{9}{5} \times \theta/^{\circ}\text{C} + 32$

$$\theta_{\text{F}} = 173^{\circ}\text{F}$$

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

E1.18a 105 kPa

E1.19a  $\text{S}_8$

E1.20a 1.8 MPa

E1.21a  $4.6 \times 10^5 \text{ Pa}$ ,  $6.9 \times 10^5 \text{ Pa}$

## Topic 2

E2.1a (a)  $9.81 \text{ ms}^{-1}$ , 48 mJ (b)  $29.4 \text{ ms}^{-1}$ , 0.43 J

E2.2a  $s_{\text{terminal}} = \frac{zeE}{6\pi\eta R}$

E2.5a  $1.0 \hbar$

E2.6a (a)  $2.25 \times 10^{-20} \text{ J}$  (b)  $9.00 \times 10^{-20} \text{ J}$

E2.7a  $1.88 \times 10^8 \text{ m s}^{-1}$ , 100 keV

E2.8a  $1.15 \times 10^{-18} \text{ J}$ ,  $1.48 \times 10^{-20} \text{ J}$

E2.9a  $-2.40 \text{ V}$

E2.10a 24.1 kJ, 28.8  $^{\circ}\text{C}$

E2.11a 27.2 K or 27.2  $^{\circ}\text{C}$

E2.12a 128 J

E2.13a  $2.4194 \text{ J K}^{-1} \text{ g}^{-1}$

E2.14a  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$

E2.15a  $8.3145 \text{ kJ mol}^{-1}$

E2.16a  $S_{\text{H}_2\text{O(g)}} > S_{\text{H}_2\text{O(l)}}$

E2.17a  $S_{\text{Fe(3000 K)}} > S_{\text{Fe(300 K)}}$

E2.19a (a)  $1.6 \times 10^{-17}$  (b) 0.021

E2.21a  $4.631 \times 10^{-6}$

E2.23a 1.07

E2.24a 1.25

E2.25a 0.47 kJ

E2.26a (a) 1.38 kJ (b) 4.56 kJ

E2.27a  $12.47 \text{ J mol}^{-1} \text{ K}^{-1}$

E2.28a (a)  $20.79 \text{ J mol}^{-1} \text{ K}^{-1}$  (b)  $24.94 \text{ J mol}^{-1} \text{ K}^{-1}$

### Topic 3

E3.1a  $2.26 \times 10^8 \text{ m s}^{-1}$

E3.2a  $4.00 \text{ }\mu\text{m}$ ,  $7.50 \times 10^{13} \text{ Hz}$

### Topic 4

E4.1a (a) 33 zJ,  $20 \text{ kJ mol}^{-1}$  (b)  $3.3 \times 10^{-34} \text{ J}$ ,  $0.20 \text{ nJ mol}^{-1}$

E4.2a (a) No kinetic energy and zero speed (b) 0.452 aJ,  $996 \text{ km s}^{-1}$

E4.3a  $2.23 \text{ }\mu\text{m}$

E4.4a 6.96 keV without a relativist mass correction ; 6.96 keV with the relativistic mass correction

The relativistic mass correction did not make a difference in this exercise.

E4.6a (a)  $3.0 \times 10^{19} \text{ s}^{-1}$  (b)  $7.4 \times 10^{20} \text{ s}^{-1}$

E4.7a (a)  $3.3 \times 10^{-29} \text{ m}$  (b)  $1.3 \times 10^{-36} \text{ m}$  (c) 99.7 pm

E4.8a  $7.27 \times 10^6 \text{ m s}^{-1}$ , 150 V

E4.9a  $1.71 \times 10^6 \text{ m s}^{-1}$

### Topic 5

E5.3a  $N = \left(\frac{1}{2\pi}\right)^{1/2}$

E5.4a  $(1/2\pi) d\phi$

E5.5a  $\frac{1}{2}$

### Topic 6

E6.1a  $\hat{V} = \frac{1}{2} k_f x^2$

E6.2a  $-4$

E6.3a (a)  $ik$  (b) not an eigenfunction of  $d/dx$  (c) not an eigenfunction of  $d/dx$  (d) not an eigenfunction of  $d/dx$  (e) not an eigenfunction of  $d/dx$  (f) not an eigenfunction of  $d/dx$

### Topic 7

E7.3a  $\frac{L}{2}$

E7.4a  $0$

### Topic 8

E8.1a  $52 \text{ pm}$

E8.2a (a)  $1.1 \times 10^{-28} \text{ ms}^{-1}$  (b)  $1 \times 10^{-27} \text{ m}$

E8.3a (a)  $0$  (b)  $0$  (c)  $i\hbar$  (d)  $2ix\hbar$  (e)  $ni x^{n-1}\hbar$

### Topic 9

E9.1a  $3 \times 10^{-34} \text{ kg m s}^{-1}$ ,  $5 \times 10^{-38} \text{ J}$

E9.2a  $Ae^{ikx}$ ,  $2.7 \times 10^{33} \text{ m}^{-1}$

E9.3a (a)  $1.8 \times 10^{-19} \text{ J}$ ,  $1.1 \times 10^2 \text{ kJ mol}^{-1}$ ,  $1.1 \text{ eV}$ ,  $9.1 \times 10^3 \text{ cm}^{-1}$  (b)  $6.6 \times 10^{-19} \text{ J}$ ,  $4.0 \times 10^2 \text{ kJ mol}^{-1}$ ,  $4.1 \text{ eV}$ ,  $3.3 \times 10^4 \text{ cm}^{-1}$

E9.4a (a) 0.04 (b) 0

E9.5a  $\frac{h^2}{4L^2}$

E9.6a  $\frac{\lambda_c}{8^{1/2}}$

E9.7a  $x = \frac{L}{10}, \frac{3L}{10}, \frac{L}{2}, \frac{7L}{10}, \text{ and } \frac{9L}{10}$

## Topic 10

E10.1a 0.8

## Topic 11

E11.1a (a)  $3.6 \times 10^{-19} \text{ J}$ ,  $2.2 \times 10^2 \text{ kJ mol}^{-1}$ ,  $2.3 \text{ eV}$ ,  $1.8 \times 10^4 \text{ cm}^{-1}$  (b)  $1.3 \times 10^{-18} \text{ J}$ ,  $8.0 \times 10^2 \text{ kJ mol}^{-1}$ ,  $8.3 \text{ eV}$ ,  $6.7 \times 10^4 \text{ cm}^{-1}$

E11.2a (a)  $5.5 \times 10^{14} \text{ s}^{-1}$ ,  $5.5 \times 10^{-7} \text{ m}$ ,  $550 \text{ nm}$  (b)  $2.0 \times 10^{15} \text{ s}^{-1}$ ,  $1.5 \times 10^{-7} \text{ m}$ ,  $150 \text{ nm}$

E11.3a (a)  $5.5 \times 10^3 \text{ K}$  (b)  $3.3 \times 10^3 \text{ K}$

E11.4a (a) 0.0016 (b) 0

E11.5a  $(1/8, 1/10)$ ,  $(1/8, 3/10)$ ,  $(1/8, 1/2)$ ,  $(1/8, 7/10)$ ,  $(1/8, 9/10)$

$(3/8, 1/10)$ ,  $(3/8, 3/10)$ ,  $(3/8, 1/2)$ ,  $(3/8, 7/10)$ ,  $(3/8, 9/10)$

$(5/8, 1/10)$ ,  $(5/8, 3/10)$ ,  $(5/8, 1/2)$ ,  $(5/8, 7/10)$ ,  $(5/8, 9/10)$

$(7/8, 1/10)$ ,  $(7/8, 3/10)$ ,  $(7/8, 1/2)$ ,  $(7/8, 7/10)$ ,  $(7/8, 9/10)$

E11.6a  $\frac{x}{L} = 0, \frac{1}{2}, 1$ ,  $\frac{y}{L} = 0, \frac{1}{3}, \frac{2}{3}, 1$

E11.7a  $\frac{h^2}{2L^2}$

E11.8a  $\frac{h}{2m_e c}$ ,  $\frac{\lambda_c}{2}$

E11.10a 3

E11.11a 0.23 or 23 per cent

E11.12a  $n = 9.77 \times 10^{10}$ ,  $1.27 \times 10^{-31}$  J,  $m = 25.8$  pm

## Topic 12

E12.1a  $1.61 \times 10^{-20}$  J

E12.2a  $278 \text{ N m}^{-1}$

E12.3a  $2.63 \text{ }\mu\text{m}$

E12.4a  $3.72 \text{ }\mu\text{m}$

E12.5a  $\pm 0.525\alpha$  or  $\pm 1.65\alpha$

E12.7a  $565 \text{ cm}^{-1}$

E12.8a 0.056

E12.9a  $\langle E_k \rangle = 3\langle V \rangle/2$

## Topic 13

n/a

## Topic 14

E14.1a  $1.49 \times 10^{-34}$  J s, 0 or  $\pm \hbar$

E14.2a (a)  $\pi/4$  radians or  $45^\circ$  (b)  $\pi/2$  radians or  $90^\circ$

E14.3a 7

## Topic 15

E15.1a 0

E15.2a  $\frac{\varepsilon}{2}$

E15.3a  $\frac{\varepsilon}{2}$

E15.4a 0

$$\text{E15.5a } -\frac{mg^2}{2\omega^2}$$

**Topic 16**

$$\text{E16.1a } 4.50 \times 10^{-16} \text{ J m}^{-3} \text{ s}$$

**Topic 17**

$$\text{E17.2a } 14.0 \text{ eV}$$

$$\text{E17.3a } N = \frac{2}{a_0^{3/2}}$$

$$\text{E17.4a } r = 4a_0, r = 0$$

$$\text{E17.5a } r = 6a_0 = 3.175 \times 10^{-10} \text{ m}$$

**Topic 18**

$$\text{E18.1a (a) } l = 0, \text{ so angular momentum} = 0 \quad \text{(b) } l = 1, \text{ so angular momentum} = \sqrt{2}\hbar \quad \text{(c) } l = 3, \text{ so angular momentum} = 2\sqrt{3}\hbar$$

$$\text{E18.2a } 4$$

$$\text{E18.3a (a) } g = 1 \quad \text{(b) } g = 4 \quad \text{(c) } g = 16$$

$$\text{E18.4a } 2E_{1s}, -E_{1s}, -17.4376 \text{ aJ}, 8.7188 \text{ aJ}$$

$$\text{E18.5a } \langle r_{2s} \rangle = \frac{6a_0}{Z}, r^* = (3 + \sqrt{5}) \frac{a}{Z}$$

$$\text{E18.6a } P_{3s} = 4\pi r^2 \left( \frac{1}{4\pi} \right) \times \left( \frac{1}{243} \right) \times \left( \frac{Z}{a_0} \right)^3 \times (6 - 6\rho + \rho^2)^2 e^{-\rho}, r = 0.74a_0/Z, 4.19a_0/Z, \text{ and } 13.08a_0/Z$$

E18.7a  $p_z$  orbital: The nodal plane is the  $xy$  plane and  $\theta = \pi/2$  is an angular node.

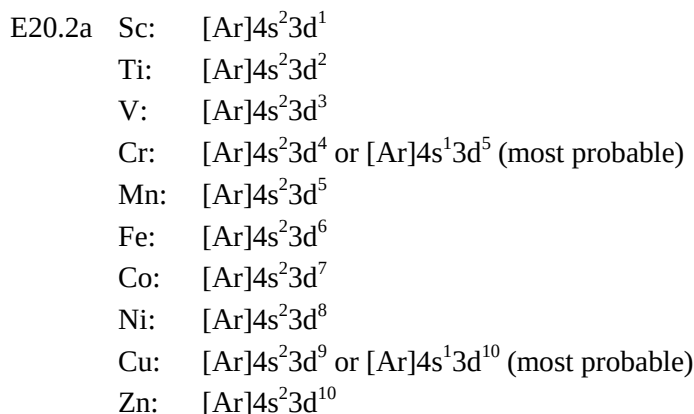
$p_x$  orbital: The nodal plane is the  $yz$  plane and  $\theta = 0$  is an angular node.

$p_y$  orbital: The nodal plane is the  $xz$  plane and  $\theta = 0$  is an angular node.

**Topic 19**

E19.1a  $8.89 \times 10^{10} \text{ m s}^{-1}$

## Topic 20



## Topic 21

E21.1a  $9.118 \times 10^{-6} \text{ cm}$ ,  $1.216 \times 10^{-5} \text{ cm}$

E21.2a  $\tilde{\nu} = 3.292 \times 10^5 \text{ cm}^{-1}$ ,  $\lambda = 3.038 \times 10^{-6} \text{ cm}$ ,  $\nu = 9.869 \times 10^{15} \text{ s}^{-1}$

E21.3a (a) forbidden (b) allowed (c) allowed

E21.4a (a)  $[\text{Kr}]4d^8$  (b)  $S = 1, 0$ ;  $M_S = -1, 0, +1$ ;  $M_S = 0$

E21.5a (a)  $\frac{5}{2}, \frac{3}{2}$  (b)  $\frac{7}{2}, \frac{5}{2}$

E21.6a  $l = 3$  or  $2$ ,  $l = 1$  or  $0$

E21.7a  $J = 3, 2, 1$

E21.8a  $L = 1$ ,  $S = 1$ ,  $J = 2$

E21.9a (a) 1, 0 with multiplicities 3, 1, respectively (b)  $S = \frac{3}{2}, \frac{1}{2}$  [from 1], and  $\frac{1}{2}$  [from 0], with multiplicities 4, 2, 2

E21.10a  $^3D_3, ^3D_2, ^3D_1, ^1D_2, ^3D$  set of terms are the lower in energy

E21.11a (a)  $J = 1$  ( $^3S_1$ ) and there are 3 states (b)  $J = \frac{5}{2}, \frac{3}{2}$ , respectively ( $^2D_{5/2}, ^2D_{3/2}$ ), with 6, and 2 states, respectively (c)  $J = 1$  ( $^1P_1$ ) with 3 states

E21.12a (a)  $^2S_{1/2}$  (b)  $^2D_{5/2}$  and  $^2D_{3/2}$



## Topic 22

E22.1a  $\{s(1)p_z(2)+s(2)p_z(1)\} \times \{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}$

E22.2a  $\psi = a\psi_{\text{VB}} + b\psi_{\text{H}^+\text{F}^+} + c\psi_{\text{H}^+\text{F}^-}$

E22.6a  $N = 3^{-1/2}$ ,  $\psi = 3^{-1/2}(s + 2^{1/2}p)$

## Topic 23

E23.1a  $N = \left( \frac{1}{1 + 2\lambda S + \lambda^2} \right)^{1/2}$

E23.2a  $N = 1.12$ ,  $\psi_1 = 0.163A + 0.947B$ ,  $b = 0.412$ ,  $a = -1.02$ ,  $\psi_2 = -1.02A + 0.412B$

E23.3a 1.9 eV, 130 pm

E23.4a The bonding orbital is odd (u) and the antibonding orbital is even (g).

## Topic 24

24.1a (a)  $1\sigma_g^2$ ,  $b = 1$  (b)  $1\sigma_g^2 1\sigma_u^2$ ,  $b = 0$  (c)  $1\sigma_g^2 1\sigma_u^2 1\pi_u^4$ ,  $b = 2$

24.2a  $C_2$

24.3a  $F_2^+$

24.4a  $b = 1, b = 0, b = 1, b = 2, b = 3, b = 2, b = 1$

24.5a  $2\pi_g$

24.6a  $4 \times 10^5 \text{ m s}^{-1}$

24.7a (a)  $2.1 \times 10^{-10} \text{ m} = 0.21 \text{ nm}$  (b)  $1.0 \times 10^{-10} \text{ m} = 0.10 \text{ nm}$

## Topic 25

E25.1a (a)  $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$  (b)  $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$  (c)  $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$

E25.3a  $\text{NO}^+$

E25.5a 7.2, 8.3

E25.6a -6.6 or -8.9

E25.7a -5.0 or -10.7 eV

## Topic 26

$$\text{E26.1a (a)} \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \quad \text{(b)} \begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix}$$

$$\text{E26.2a (a)} \text{C}_6\text{H}_6^- \text{ (7 electrons): } a_{2u}^2 e_{1g}^4 e_{2u}^1 \quad E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) + (\alpha - \beta) = 7\alpha + 7\beta$$

$$\text{(b) C}_6\text{H}_6^+ \text{ (5 electrons): } a_{2u}^2 e_{1g}^3 \quad E_\pi = 2(\alpha + 2\beta) + 3(\alpha + \beta) = 5\alpha + 7\beta$$

$$\text{E26.3a (a)} 7\beta, 0 \quad \text{(b)} 7\beta, 2\beta$$

$$\text{E26.5a (a)} 14\alpha + 19.314\beta \quad \text{(b)} 14\alpha + 19.448\beta$$

## Topic 27

$$\text{E27.1a } \hat{V} = -3j_0 \left\{ \frac{1}{r_{\text{Li1}}} + \frac{1}{r_{\text{Li2}}} + \frac{1}{r_{\text{Li3}}} + \frac{1}{r_{\text{Li4}}} \right\} - j_0 \left\{ \frac{1}{r_{\text{H1}}} + \frac{1}{r_{\text{H2}}} + \frac{1}{r_{\text{H3}}} + \frac{1}{r_{\text{H4}}} \right\} + j_0 \left\{ \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}} \right\}$$

$$\text{E27.2a } N_e = 2 \text{ for HeH}^+, \quad \hat{H} = -\frac{\hbar^2}{2m_e} \{ \nabla_1^2 + \nabla_2^2 \} - 2j_0 \left\{ \frac{1}{r_{\text{He1}}} + \frac{1}{r_{\text{He2}}} \right\} - j_0 \left\{ \frac{1}{r_{\text{H1}}} + \frac{1}{r_{\text{H2}}} \right\} + j_0 \left\{ \frac{1}{r_{12}} \right\}$$

$$\text{E27.3a } N_e = 2 \text{ for HeH}^+, \quad \Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a^\alpha(1) & \psi_a^\beta(1) \\ \psi_a^\alpha(2) & \psi_a^\beta(2) \end{vmatrix}$$

$$\text{E27.4a } f_1 \psi_a(1) = h_1 \psi_a(1) + J_a(1) \psi_a(1) = \varepsilon_a \psi_a(1)$$

$$\text{E27.6a } F_{\text{AA}} = E_{\text{He}} + c_{\text{Hea}}^2 (\text{HeHe}|\text{HeHe}) + 2c_{\text{Hea}}c_{\text{Ha}} (\text{HeHe}|\text{HeH}) + c_{\text{Ha}}^2 \{ 2(\text{HeHe}|\text{HH}) - (\text{HeH}|\text{HeH}) \}$$

$$F_{\text{AB}} = \int \chi_{\text{He}}(1) h_1 \chi_{\text{H}}(1) d\tau_1 + c_{\text{Hea}}^2 (\text{HeH}|\text{HeHe}) + c_{\text{Hea}}c_{\text{Ha}} \{ 3(\text{HeH}|\text{HeH}) - (\text{HeHe}|\text{HH}) \} + c_{\text{Ha}}^2 (\text{HeH}|\text{HH})$$

$$\text{E27.8a (a)} 17 \text{ basis functions} \quad \text{(b)} 28 \text{ basis functions} \quad \text{(c)} 34 \text{ basis functions}$$

## Topic 28

$$\text{E28.1a } c_{\text{Ha}} = \left( \frac{1}{1 + \left( \frac{\beta}{\alpha_{\text{He}} - \varepsilon_a} \right)^2} \right)^{1/2}, \quad \varepsilon_a = \frac{\alpha_{\text{He}} + \alpha_{\text{H}} - \left( \{ \alpha_{\text{He}} - \alpha_{\text{H}} \}^2 + 4\beta^2 \right)^{1/2}}{2}, \quad c_{\text{Ha}} = \left( \frac{1}{1 + \left( \frac{\beta}{\alpha_{\text{He}} - \varepsilon_a} \right)^2} \right)^{1/2}$$

**Topic 29**

$$\begin{aligned}
 \text{E29.2a } \Psi_1(1 \text{ of } 4) &= (1/2)^{1/2} \begin{vmatrix} \psi_b^\alpha(1) & \psi_a^\beta(1) \\ \psi_b^\alpha(2) & \psi_a^\beta(2) \end{vmatrix}, \quad \Psi_1(2 \text{ of } 4) = (1/2)^{1/2} \begin{vmatrix} \psi_a^\alpha(1) & \psi_b^\beta(1) \\ \psi_a^\alpha(2) & \psi_b^\beta(2) \end{vmatrix}, \\
 \Psi_1(3 \text{ of } 4) &= (1/2)^{1/2} \begin{vmatrix} \psi_a^\alpha(1) & \psi_b^\alpha(1) \\ \psi_a^\alpha(2) & \psi_b^\alpha(2) \end{vmatrix}, \quad \Psi_1(4 \text{ of } 4) = (1/2)^{1/2} \begin{vmatrix} \psi_a^\beta(1) & \psi_b^\beta(1) \\ \psi_a^\beta(2) & \psi_b^\beta(2) \end{vmatrix}, \\
 \Psi &= C_0 \Psi_0 + C_2 \Psi_2 = C_0 \begin{vmatrix} \psi_a^\alpha(1) & \psi_a^\beta(1) \\ \psi_a^\alpha(2) & \psi_a^\beta(2) \end{vmatrix} + C_2 \begin{vmatrix} \psi_b^\alpha(1) & \psi_b^\beta(1) \\ \psi_b^\alpha(2) & \psi_b^\beta(2) \end{vmatrix}
 \end{aligned}$$

E29.3a

$$\Psi = C_0 \Psi_0 + C_1 \{ \Psi_1(1 \text{ of } 2) + \Psi_1(2 \text{ of } 2) \} = C_0 \begin{vmatrix} \psi_a^\alpha(1) & \psi_a^\beta(1) \\ \psi_a^\alpha(2) & \psi_a^\beta(2) \end{vmatrix} + C_1 \left\{ \begin{vmatrix} \psi_b^\alpha(1) & \psi_a^\beta(1) \\ \psi_b^\alpha(2) & \psi_a^\beta(2) \end{vmatrix} + \begin{vmatrix} \psi_a^\alpha(1) & \psi_b^\beta(1) \\ \psi_a^\alpha(2) & \psi_b^\beta(2) \end{vmatrix} \right\}$$

$$\begin{aligned}
 \int \Psi_2 \hat{H}^{(1)} \Psi_0 d\tau &= c_{\text{Hea}}^2 c_{\text{Heb}}^2 (\text{HeHe|HeHe}) + 2(c_{\text{Hea}}^2 c_{\text{Heb}} c_{\text{Hb}} + c_{\text{Hea}} c_{\text{Ha}} c_{\text{Heb}}^2) (\text{HeH|HeHe}) \\
 \text{E29.4a } &+ (c_{\text{Hea}}^2 c_{\text{Hb}}^2 + 2c_{\text{Hea}} c_{\text{Ha}} c_{\text{Heb}} c_{\text{Hb}} + c_{\text{Ha}}^2 c_{\text{Heb}}^2) (\text{HeH|HeH}) + 2c_{\text{Hea}} c_{\text{Ha}} c_{\text{Heb}} c_{\text{Hb}} (\text{HH|HeHe}) \\
 &+ 2(c_{\text{Ha}}^2 c_{\text{Heb}} c_{\text{Hb}} + c_{\text{Hea}} c_{\text{Ha}} c_{\text{Hb}}^2) (\text{HH|HHe}) + c_{\text{Ha}}^2 c_{\text{Hb}}^2 (\text{HH|HH})
 \end{aligned}$$

**Topic 30**

$$\text{E30.2a } 2 \left\{ |\psi_a(\mathbf{r})|^2 + |\psi_b(\mathbf{r})|^2 \right\}$$

**Topic 31**E31.1a The elements, other than the identity  $E$ , are a  $C_3$  axis and three vertical mirror planes  $\sigma_v$ E31.2a There are  $3C_2$  axes, a centre of inversion, and  $3\sigma_h$  mirror planes

E31.3a (a) Sphere: an infinite number of symmetry axes; therefore  $R_3$  (b) Isosceles triangles:  $E$ ,  $C_2$ ,  $\sigma_v$ , and  $\sigma'_v$ ; therefore  $C_{2v}$  (c)  $D_{3h}$  (d)  $D_{\infty h}$

E31.4a (a)  $C_{2v}$  (b)  $C_{\infty v}$  (c)  $C_{3v}$  (d)  $D_{2h}$ E31.5a (a)  $C_{2v}$  (b)  $C_{2h}$ E31.6a (a) pyridine ( $C_{2v}$ ) and (b) nitroethane ( $C_s$ ) are polarE31.8a  $D_{2h}$  contains  $i$  and  $C_{3h}$  contains  $\sigma_h$ **Topic 32**

$$\text{E32.1a } \mathbf{D}(\sigma_h) = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\text{E32.2a } \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \end{pmatrix} = \mathbf{D}(S_3)$$

E32.4a 3

E32.5a 2

### Topic 33

E33.1a Integral must be zero

E33.4a No N orbitals,  $d_{xy}$

E33.6a  $2A_1 + B_1 + E$

E33.7a (a) either  $E_{1u}$  or  $A_{2u}$  (b)  $B_{3u}$  (x-polarized),  $B_{2u}$  (y-polarized),  $B_{1u}$  (z-polarized)

### Topic 34

E34.1a  $\text{ClF}_3$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$

E34.2a 2.8 D

E34.3a -36.1 D, -7.54 D, 36.9 D,  $168^\circ$

E34.4a  $2.19 \times 10^{-36} \text{ C m}$ ,  $0.658 \mu\text{D}$

### Topic 35

E35.1a  $1.07 \times 10^3 \text{ kJ mol}^{-1}$

E35.2a  $\frac{6l^4 Q_1^2}{\pi \epsilon_0 r^5}$

E35.3a  $289 \text{ kJ mol}^{-1}$

### Topic 36

E36.1a 1.24 bar, 1.24 bar

E36.2a 2.75 bar

E36.3a (a) 25 bar (b) 22 bar

E36.4a  $7.61 \times 10^{-2} \text{ kg m}^5 \text{ s}^{-2} \text{ mol}^{-2}$ ,  $2.26 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$

E36.5a (a) 0.92 (b)  $1.6 \text{ dm}^3 \text{ mol}^{-1}$ , attractive forces dominate

E36.6a 140 atm

E36.7a  $1.41 \times 10^3 \text{ K}$

E36.8a 175 pm

E36.9a  $0.046 \text{ dm}^3 \text{ mol}^{-1}$

E36.10a 0.66

### Topic 37

E37.1a  $N = 4$ ,  $4.01 \text{ g cm}^{-3}$

E37.2a (323) and (110)

E37.3a 229 pm, 397 pm, 115 pm

E37.4a 220 pm

E37.5a 291 pm,  $10.1^\circ$ ,  $14.4^\circ$ ,  $17.7^\circ$

E37.6a  $8.16^\circ$ ,  $4.82^\circ$ ,  $11.75^\circ$

E37.7a  $2.14^\circ$

E37.8a  $f_{\text{Br}^-} = 36$

E37.9a  $f$

E37.10a  $3f$  for  $h+k$  even and  $-f$  for  $h+k$  odd

E37.14a  $6.1 \text{ km s}^{-1}$

E37.15a 233 pm

### Topic 38

E38.1a 0.9069

E38.2a (a) 0.5236 (b) 0.6802 (c) 0.7405

E38.3a (a) 74.9 pm (b) 132 pm

E38.4a Expansion

E38.5a 3500 kJ mol<sup>-1</sup>

### Topic 39

E39.1a 3.54 eV

E39.2a Three unpaired spins

E39.3a  $-6.4 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ ,  $-6.4 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$

E39.4a 4.326, 5

E39.5a  $+1.6 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$

### Topic 40

E40.1a 82.9 per cent

E40.2a  $5.34 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

E40.3a  $1.09 \text{ mmol dm}^{-3}$

E40.4a  $1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$

E40.5a  $450 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$

E40.6a  $159 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , 23 per cent

E40.7a (a) 0.87 m (b) 2.9 m

E40.8a  $0.9999 \times \lambda$

E40.9a (a) 27 ps (b) 2.7 ps

E40.10a (a)  $\delta \tilde{\nu} = 53 \text{ cm}^{-1}$  (b)  $\delta \tilde{\nu} = 0.53 \text{ cm}^{-1}$

### Topic 41

E41.1a  $6.33 \times 10^{-46} \text{ kg m}^2$ ,  $0.4421 \text{ cm}^{-1}$

E41.3a (a) asymmetric (b) oblate symmetric (c) spherical (d) prolate symmetric

E41.4a 106.5 pm, 115.6 pm

## Topic 42

E42.2a  $3.07 \times 10^{11} \text{ Hz}$

E42.3a 127.4 pm

E42.4a  $4.442 \times 10^{-47} \text{ kg m}^2$ , 165.9 pm

E42.5a (c)  $\text{CH}_4$  is inactive.

E42.6a  $20\,475 \text{ cm}^{-1}$

E42.7a 198.9 pm

E42.8a  $\frac{5}{3}$

## Topic 43

E43.1a  $16 \text{ N m}^{-1}$

E43.2a 1.077 percent

E43.3a  $328.7 \text{ N m}^{-1}$

E43.4a 967.0, 515.6, 411.8, 314.2

E43.5a  $1580.38 \text{ cm}^{-1}$ ,  $7.644 \times 10^{-3}$

## Topic 44

E44.1a (b) HCl (c)  $\text{CO}_2$  (d)  $\text{H}_2\text{O}$

E44.2a (a) 3 (b) 6 (c) 12

E44.3a 127

E44.4a  $\frac{1}{2}(\tilde{\nu}_1 + \tilde{\nu}_2 + \tilde{\nu}_3)$

E44.5a (a) Nonlinear: all modes are both infrared and Raman active. (b) Linear: the symmetric stretch is infrared inactive but Raman active.

E44.6a Raman active

E44.7a  $4A_1 + A_2 + 2B_1 + 2B_2$

E44.8a  $A_1, B_1$  and  $B_2$  are infrared active; all modes are Raman active.

### Topic 45

E45.1a 3, u

E45.2a (a) allowed (b) allowed (c) forbidden (d) forbidden (e) allowed

E45.3a  $\frac{2\sqrt{2}}{3} e^{-2ax_0^2/3}$

E45.4a  $\frac{1}{32} \left( 3 + \frac{4}{\pi} \right)^2$

E45.5a  $\frac{1}{2} (\tilde{B}' + \tilde{B}) / (\tilde{B}' - \tilde{B})$

E45.6a  $\frac{1}{2} (\tilde{B}' + \tilde{B}) / |(\tilde{B}' - \tilde{B})| - 1, 7$

E45.7a  $30.4 \text{ cm}^{-1} < \tilde{B}' < 40.5 \text{ cm}^{-1}$ , greater

E45.8a  $\Delta_0 = P - \tilde{\nu}$ ,  $14 \times 10^3 \text{ cm}^{-1}$

E45.9a  $\frac{3}{8} \left( \frac{a^3}{b - \frac{1}{2}a} \right)^{1/2}$

E45.10a  $\frac{1}{4} e^{-1/16} a$

### Topic 46

E46.1a (a) lower,  $\tilde{\nu} \approx 1800 \text{ cm}^{-1}$  (b) no information

E46.3a 20 ps, 70 MHz

### Topic 47

E47.1a  $\text{s}^{-1} \text{ T}^{-1}$



E47.2a  $9.133 \times 10^{-35} \text{ J s}$ ,  $\pm 0.9553 \text{ rad} = \pm 54.74^\circ$

E47.3a  $574 \text{ MHz}$

E47.4a  $-1.473 \times 10^{-26} \text{ J} \times m_l$

E47.5a  $165 \text{ MHz}$

E47.6a (a)  $3.98 \times 10^{-25} \text{ J}$  (b)  $6.11 \times 10^{-26} \text{ J}$ , thus the separation in energy is larger for the proton (a).

E47.7a  $16.25 \text{ T}$

E47.9a (a)  $1 \times 10^{-6}$  (b)  $5.1 \times 10^{-6}$  (c)  $3.4 \times 10^{-5}$

E47.10a 13

E47.11a (a)  $2 \times 10^2 \text{ T}$  (b)  $10 \text{ mT}$

### Topic 48

E48.1a (a) independent (b) 13

E48.2a (a)  $11 \mu\text{T}$  (b)  $110 \mu\text{T}$

E48.5a  $753 \text{ MHz}$

E48.7a  $0.39 \text{ ms}$ ,  $2.6 \times 10^3 \text{ s}^{-1}$

### Topic 49

E49.1a  $5.9 \times 10^{-4} \text{ T}$ ,  $20 \mu\text{s}$

### Topic 50

E50.1a 2.0022

E50.2a  $2.3 \text{ mT}$ ,  $2.002\bar{5}$

E50.3a equal intensity,  $330.2 \text{ mT}$ ,  $332.2 \text{ mT}$ ,  $332.8 \text{ mT}$ ,  $334.8 \text{ mT}$

E50.5a (a)  $332.3 \text{ mT}$  (b)  $1.206 \text{ T}$

E50.6a  $I = \frac{3}{2}$

### Topic 51

E51.1a 21 621 600

E51.2a (a) 40 320 (b)  $5.63 \times 10^3$  (c)  $3.99 \times 10^4$

E51.3a 1

E51.4a 524 K

E51.5a 7.43

E51.6a  $35\bar{4}$  K

## Topic 52

E52.1a (a) (i) 8.23 pm (ii) 2.60 pm (b) (i)  $1.79 \times 10^{27}$  (ii)  $5.67 \times 10^{28}$

E52.2a 0.3574

E52.3a 72.2

E52.4a (a)  $7.97 \times 10^3$  (b)  $1.12 \times 10^4$

E52.5a 18 K

E52.6a 37 K

E52.7a 4.5 K

E52.8a (a) 1 (b) 2 (c) 2 (d) 12 (e) 3

E52.9a 660.6

E52.10a 4500 K

E52.11a 2.571

E52.12a 42.3

E52.13a 4.292, 0.0353 to 0.0377 to 1

## Topic 53

E53.1a  $8.16 \times 10^{-22}$  J

E53.2a 18.5 K

E53.3a 25 K

E53.4a 4.5 K

E53.5a 4600 K

E53.6a 10 500 K

E53.7a 6500 K

E53.8a  $4.033 \times 10^{-21}$  J

### Topic 54

E54.1a (a) He gas (b) CO gas (c) H<sub>2</sub>O vapour

### Topic 55

E55.1a (a)  $\frac{7}{2}R$ , 8.671 kJ mol<sup>-1</sup> (b)  $3R$ , 7.436 kJ mol<sup>-1</sup> (c)  $7R$ , 17.35 kJ mol<sup>-1</sup>

E55.2a (a) pressure, (b) temperature, and (d) enthalpy are state functions.

E55.3a  $3.5 \times 10^3$  J needed,  $5.7 \times 10^2$  J needed

E55.4a -75 J

E55.5a (a) -2.68 kJ, +2.68 kJ (b) -1.62 kJ, +1.62 kJ (c)  $w = 0$ , 0

E55.6a 1.33 atm, +1.25 kJ,  $w = 0$ , +1.25 kJ

### Topic 56

E56.1a 30 J K<sup>-1</sup> mol<sup>-1</sup>, 22 J K<sup>-1</sup> mol<sup>-1</sup>

E56.2a (a) +10.7 kJ, -0.624 kJ, +10.1 kJ (b) +10.7 kJ, +10.1 kJ, +10.1 kJ

E56.3a (a) +2.2 kJ, +2.2 kJ, +1.6 kJ

E56.4a -7.2 J atm<sup>-1</sup> mol<sup>-1</sup>, +6.1 kJ

### Topic 57

E57.1a 22.5 kJ, -1.6 kJ, 20.9 kJ

E57.2a -4564.7 kJ mol<sup>-1</sup>

E57.3a  $+53 \text{ kJ mol}^{-1}$ ,  $-33 \text{ kJ mol}^{-1}$

E57.4a  $-167 \text{ kJ mol}^{-1}$

E57.5a  $-5152 \text{ kJ mol}^{-1}$ ,  $1.58 \text{ kJ K}^{-1}$ ,  $+3.08 \text{ K}$

E57.6a (a)  $-114.40 \text{ kJ mol}^{-1}$ ,  $-111.92 \text{ kJ mol}^{-1}$  (b)  $-92.31 \text{ kJ mol}^{-1}$ ,  $-241.82 \text{ kJ mol}^{-1}$

E57.7a  $-1368 \text{ kJ mol}^{-1}$

E57.8a (a)  $+131.29 \text{ kJ mol}^{-1}$ ,  $+128.81 \text{ kJ mol}^{-1}$  (b)  $+134.14 \text{ kJ mol}^{-1}$ ,  $+130.17 \text{ kJ mol}^{-1}$

E57.9a  $-803.07 \text{ kJ mol}^{-1}$

E57.10a  $-1892 \text{ kJ mol}^{-1}$

**Topic 58**

E58.1a (a) 0.236 (b) 0.193

E58.2a

|                        | $C_{V,m}$ | $C_{p,m}$ | $\gamma$ | Exptl |                        |
|------------------------|-----------|-----------|----------|-------|------------------------|
| $\text{NH}_3(v_v^*=0)$ | $3R$      | $4R$      | 1.33     | 1.31  | <a href="#">closer</a> |
| $\text{NH}_3(v_v^*=6)$ | $9R$      | $10R$     | 1.11     |       |                        |
| $\text{CH}_4(v_v^*=0)$ | $3R$      | $4R$      | 1.33     | 1.31  | <a href="#">closer</a> |
| $\text{CH}_4(v_v^*=9)$ | $12R$     | $13R$     | 1.08     |       |                        |

E58.3a  $2.91 \times 10^{-21} \text{ J}$

E58.4a  $131 \text{ K}$

E58.5a  $0.00846 \text{ m}^3$ ,  $257 \text{ K}$ ,  $-0.89 \times 10^3 \text{ J}$

E58.6a  $-194 \text{ J}$

E58.7a  $9.7 \text{ kPa}$

E58.8a  $5.03 \text{ mbar}$

E58.9a  $+1301 \text{ J mol}^{-1}$ ,  $+7.52 \times 10^3 \text{ J mol}^{-1}$ ,  $-7.39 \times 10^3 \text{ J mol}^{-1}$

E58.10a  $1.31 \times 10^{-3} \text{ K}^{-1}$

E58.11a  $2.0 \times 10^3 \text{ atm}$

### Topic 59

E59.1a Not spontaneous

### Topic 60

E60.1a (a)  $126 \text{ J K}^{-1} \text{ mol}^{-1}$  (b)  $169 \text{ J K}^{-1} \text{ mol}^{-1}$

E60.2a  $T = 2.35 \times 10^3 \text{ K}$

E60.3a 43.1, 22.36 K,  $43.76 \text{ J K}^{-1} \text{ mol}^{-1}$

E60.4a  $54.72 \text{ J K}^{-1} \text{ mol}^{-1}$

E60.5a  $11.5 \text{ J K}^{-1} \text{ mol}^{-1}$

E60.6a (a)  $34.72 \text{ J K}^{-1} \text{ mol}^{-1}$  (b)  $119.06 \text{ J K}^{-1} \text{ mol}^{-1}$

### Topic 61

E61.1a  $T_c = 191.2 \text{ K}$

E61.2a (a)  $366 \text{ J K}^{-1}$  (b)  $309 \text{ J K}^{-1}$

### Topic 62

E62.1a  $\text{I}_2(\text{g})$

E62.2a  $3.1 \text{ J K}^{-1}$

E62.3a  $30.0 \text{ kJ mol}^{-1}$

E62.4a  $152.67 \text{ J K}^{-1} \text{ mol}^{-1}$

E62.6a 0, 0

E62.7a  $\Delta H = 0$ ,  $+2.7 \text{ J K}^{-1}$

E62.8a (a)  $+2.9 \text{ J K}^{-1}$ ,  $-2.9 \text{ J K}^{-1}$ , 0 (b)  $+2.9 \text{ J K}^{-1}$ , 0,  $+2.9 \text{ J K}^{-1}$  (c) 0, 0, 0

E62.9a (a)  $+87.8 \text{ J K}^{-1} \text{ mol}^{-1}$  (b)  $-87.8 \text{ J K}^{-1} \text{ mol}^{-1}$

E62.10a  $\Delta S = 92.2 \text{ J K}^{-1}$

### Topic 63

E63.1a (a)  $9.13 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $13.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $14.9 \text{ J K}^{-1} \text{ mol}^{-1}$

E63.2a (a)  $-386.1 \text{ J K}^{-1} \text{ mol}^{-1}$ , (b)  $+92.6 \text{ J K}^{-1} \text{ mol}^{-1}$  (c)  $-153.1 \text{ J K}^{-1} \text{ mol}^{-1}$

### Topic 64

E64.1a (a)  $-521.5 \text{ kJ mol}^{-1}$  (b)  $+25.8 \text{ kJ mol}^{-1}$  (c)  $-178.7 \text{ kJ mol}^{-1}$

E64.2a  $-480.98 \text{ kJ mol}^{-1}$

E64.3a  $817.90 \text{ kJ mol}^{-1}$

E64.4a  $-13.8 \text{ kJ mol}^{-1}$ ,  $-0.20 \text{ kJ mol}^{-1}$

E64.5a (a)  $-6.42 \text{ kJ mol}^{-1}$  (b)  $-14.0 \text{ kJ mol}^{-1}$

### Topic 65

E65.1a (a)  $-522.1 \text{ kJ mol}^{-1}$  (b)  $+25.78 \text{ kJ mol}^{-1}$  (c)  $-178.6 \text{ kJ mol}^{-1}$

E65.2a  $-340 \text{ kJ mol}^{-1}$

### Topic 66

E66.1a  $-17 \text{ J}$

E66.2a  $-36.5 \text{ J K}^{-1}$

E66.3a  $+10 \text{ kJ}$ ,  $1.6 \text{ kJ mol}^{-1}$

E66.4a  $+11 \text{ kJ mol}^{-1}$

E66.5a  $12 \text{ kJ}$

### Topic 67

E67.1a  $P = 1$ ,  $P = 3$

### Topic 69

E69.1a  $\mu_{\text{W}}(\text{s}) = \mu_{\text{W}}(\text{l}), \mu_{\text{E}}(\text{s}) = \mu_{\text{E}}(\text{l})$

E69.2a  $-0.38 \text{ J mol}^{-1}$

E69.3a  $-3 \times 10^2 \text{ J mol}^{-1}$

E69.4a  $1.79 \times 10^5 \text{ J mol}^{-1}$

E69.5a  $+45 \text{ J K}^{-1} \text{ mol}^{-1}, +1.59 \times 10^4 \text{ J mol}^{-1} = +15.9 \text{ kJ mol}^{-1}$

E69.6a  $+12487 \text{ J mol}^{-1} = +12.487 \text{ kJ mol}^{-1}$

E69.7a  $37^\circ\text{C}$

E69.8a (a)  $2.97 \times 10^4 \text{ J mol}^{-1} = 29.7 \text{ kJ mol}^{-1}$  (b)  $0.169 \text{ bar}, 0.82 \text{ bar}$

E69.9a  $-0.35^\circ\text{C}, 272.80 \text{ K}$

### Topic 70

E70.1a (a)  $1.1 \times 10^3 \text{ g} = 1.1 \text{ kg}$  (b)  $2.0 \times 10^4 \text{ g}, 20. \text{ kg}$

E70.2a  $-1.04 \text{ kJ}, +3.5 \text{ J K}^{-1}$

E70.3a  $-1.37 \times 10^3 \text{ J mol}^{-1} = -1.37 \text{ kJ mol}^{-1}$

E70.4a  $\frac{1}{2}, 0.4624, 0.5376$

E70.5a  $6.4 \times 10^3 \text{ kPa}$

E70.6a  $0.268, 0.732, 58.6 \text{ kPa}$

E70.7a  $2.0 \times 10^2 \text{ kPa}$

E70.8a  $85 \text{ g mol}^{-1}$

E70.9a (a)  $3.4 \times 10^{-3} \text{ mol kg}^{-1}$  (b)  $3.4 \times 10^{-2} \text{ mol kg}^{-1}$

### Topic 71

E71.1a  $88.2 \text{ kg mol}^{-1}$

E71.2a (a)  $18 \text{ kg mol}^{-1}$  (b)  $20 \text{ kg mol}^{-1}$  (c)  $1.1$

**Topic 72**

E72.1a 2.8, phase separation does occur

E72.2a 0.833,  $0.9\bar{3}$ , 0.125,  $1.2\bar{5}$ ,  $2.\bar{8}$ ,  $1.2\bar{5}$ 

E72.3a 0.498, 0.667, 1.24, 1.11

E72.4a 0.694

E72.5a 1.55

E72.6a (a) 8.75 g (b) 9.35 g

E72.7a 0.0190, 0.72, 0.85

E72.8a 2.01

**Topic 73**

$$\text{E73.1a (a) (i) } K = \frac{a_{\text{COCl(g)}} a_{\text{Cl(g)}}}{a_{\text{CO(g)}} a_{\text{Cl}_2\text{(g)}} \quad \text{(ii) } K = \frac{p_{\text{COCl}} p_{\text{Cl}}}{p_{\text{CO}} p_{\text{Cl}_2}}$$

$$\text{(b) (i) } K = \frac{a_{\text{SO}_3\text{(g)}}^2}{a_{\text{SO}_2\text{(g)}}^2 a_{\text{O}_2\text{(g)}} \quad \text{(ii) } K = \frac{p_{\text{SO}_3}^2 p^\ominus}{p_{\text{SO}_2}^2 p_{\text{O}_2}}$$

$$\text{(c) (i) } K = \frac{a_{\text{FeSO}_4\text{(aq)}}}{a_{\text{PbSO}_4\text{(aq)}} \quad \text{(ii) } K = \frac{\gamma_{\text{FeSO}_4}}{\gamma_{\text{PbSO}_4}} \times \frac{b_{\text{FeSO}_4}}{b_{\text{PbSO}_4}}$$

$$\text{(d) (i) } K = \frac{a_{\text{HCl(aq)}}^2}{a_{\text{H}_2\text{(g)}} \quad \text{(ii) } K = \frac{\gamma_{\text{HCl(aq)}}^2 b_{\text{HCl(aq)}}^2}{p_{\text{H}_2\text{(g)}}} \times \frac{p^\ominus}{(b^\ominus)^2}$$

$$\text{(e) (i) } K = \frac{a_{\text{CuCl}_2\text{(aq)}}}{a_{\text{CuCl(aq)}}^2 \quad \text{(ii) } K = \frac{\gamma_{\text{CuCl}_2}}{\gamma_{\text{CuCl}}^2} \times \frac{b_{\text{CuCl}_2} b^\ominus}{b_{\text{CuCl}}^2}$$

E73.2a  $\nu_{\text{Hg}_2\text{Cl}_2} = -1$ ,  $\nu_{\text{H}_2} = -1$ ,  $\nu_{\text{HCl}} = 2$ ,  $\nu_{\text{Hg}} = 2$ E73.3a  $+12.3 \text{ kJ mol}^{-1}$ E73.4a  $-11.20 \text{ kJ mol}^{-1}$ E73.5a  $-1108 \text{ kJ mol}^{-1}$ E73.6a (a) 0.087, 0.370, 0.196, 0.348, 1.001 (b) 0.33 (c) 0.33 (d)  $+2.8 \text{ kJ mol}^{-1}$ E73.7a  $-30 \text{ kJ mol}^{-1}$



**Topic 74**

74.1a 0.003 725

**Topic 75**E75.1a  $K_x$  is reduced by 67 per centE75.2a 0.045,  $1500\text{ K}$ E75.3a  $+3.47\text{ kJ mol}^{-1}$ ,  $-14.8\text{ J K}^{-1}\text{ mol}^{-1}$ E75.4a (a)  $+53\text{ kJ mol}^{-1}$  (b)  $-53\text{ kJ mol}^{-1}$ E75.5a  $1110\text{ K}$ E75.6a (a)  $-68.26\text{ kJ mol}^{-1}$ ,  $9.2 \times 10^{11}$  (b)  $-63.99\text{ kJ mol}^{-1}$ ,  $1.3 \times 10^9$ ,  $-69.7\text{ kJ mol}^{-1}$ **Topic 76**E76.1a (a)  $+0.80\text{ V}$ ,  $-0.76\text{ V}$ ,  $+1.56\text{ V}$  (b)  $0$ ,  $-0.40\text{ V}$ ,  $+0.40\text{ V}$  (c)  $-0.74\text{ V}$ ,  $+0.36\text{ V}$ ,  $-1.10\text{ V}$  (d)  $+0.15\text{ V}$ ,  $+0.77\text{ V}$ ,  $-0.62\text{ V}$ **Topic 77**E77.1a  $-1.46\text{ V}$ 

E77.2a Elemental mercury cannot spontaneously displace the zinc(II) cation from solution under standard conditions.

E77.3a (a)  $9.2 \times 10^{-9}\text{ M}$  (b)  $8.3 \times 10^{-17}$ E77.4a  $-52\text{ kJ mol}^{-1}$ ,  $-58\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $-69\text{ kJ mol}^{-1}$ 

E77.5a

|     | $\nu$ | $E_R^\ominus/\text{V}$ | $E_L^\ominus/\text{V}$ | $E_{\text{cell}}^\ominus/\text{V}$ | $\Delta_r G_{\text{cell}}^\ominus/(\text{kJ mol}^{-1})$ |
|-----|-------|------------------------|------------------------|------------------------------------|---------------------------------------------------------|
| (a) | 2     | +0.80                  | -0.76                  | +1.56                              | -301                                                    |
| (b) | 2     | 0.00                   | -0.40                  | +0.40                              | -77                                                     |
| (c) | 3     | -0.74                  | +0.36                  | -1.10                              | +318                                                    |
| (d) | 2     | +0.15                  | +0.77                  | -0.62                              | +120                                                    |

E77.6a (a)  $-0.13\text{ V}$ ,  $-0.44\text{ V}$ ,  $+0.31\text{ V}$  (b)  $+0.27\text{ V}$ ,  $0$ ,  $+0.27\text{ V}$  (c)  $+1.23\text{ V}$ ,  $0$ ,  $+1.23\text{ V}$

E77.7a (a)  $\text{Cd}^{2+}(\text{aq}) + 2\text{Br}^{-}(\text{aq}) + 2\text{Ag}(\text{s}) \rightarrow \text{Cd}(\text{s}) + 2\text{AgBr}(\text{s})$  (c)  $-0.62\text{ V}$

E77.8a (a)  $6.4 \times 10^9$  (b)  $8.9 \times 10^{43}$

### Topic 78

E78.1a (a)  $9.975$  (b)  $1$

E78.2a  $1904\text{ m s}^{-1}$ ,  $478\text{ m s}^{-1}$

E78.3a  $0.69\text{ per cent}$

E78.4a  $333\text{ m s}^{-1}$ ,  $375\text{ m s}^{-1}$ ,  $530\text{ m s}^{-1}$

E78.5a (a)  $475\text{ m s}^{-1}$  (b)  $82.9\text{ nm}$  (c)  $8.10 \times 10^9\text{ s}^{-1}$

E78.6a  $0.195\text{ Pa}$

E78.7a  $1.38 \times 10^{-6}\text{ m}$

E78.8a (a)  $5.3 \times 10^{10}\text{ s}^{-1}$  (b)  $5.3 \times 10^9\text{ s}^{-1}$  (c)  $5.3 \times 10^3\text{ s}^{-1}$

E78.9a  $1.2 \times 10^{21}$

E78.10a  $537\text{ s}$

E78.11a  $16\text{ mg}$

E78.12a  $319\text{ g mol}^{-1}$

E78.13a  $1.3\text{ days}$

### Topic 79

E79.1a  $7.6 \times 10^{-3}\text{ J K}^{-1}\text{ m}^{-1}\text{ s}^{-1}$

E79.2a (a)  $D = 1.5\text{ m}^2\text{ s}^{-1}$ ,  $J_z/N_A = -61\text{ mol m}^{-2}\text{ s}^{-1}$  (b)  $D = 1.5 \times 10^{-5}\text{ m}^2\text{ s}^{-1}$ ,  $J_z/N_A = -6.1 \times 10^{-4}\text{ mol m}^{-2}\text{ s}^{-1}$  (c)  $D = 1.5 \times 10^{-7}\text{ m}^2\text{ s}^{-1}$ ,  $J_z/N_A = -6.1 \times 10^{-6}\text{ mol m}^{-2}\text{ s}^{-1}$

E79.3a  $-0.078\text{ J m}^{-2}\text{ s}^{-1}$

E79.4a  $0.0795\text{ nm}^2$

E79.5a  $103\text{ W}$

E79.6a  $0.201\text{ nm}^2$

E79.7a (a)  $\eta = 178 \mu\text{P}$  (b)  $\eta = 186 \mu\text{P}$  (c)  $\eta = 342 \mu\text{P}$

### Topic 80

E80.1a  $16.8 \text{ J mol}^{-1}$

E80.2a  $7.63 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

E80.3a  $283 \mu\text{m s}^{-1}$

E80.4a  $13.87 \text{ mS m}^2 \text{ mol}^{-1}$

E80.5a  $4.01 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $5.19 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $7.62 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$

E80.6a  $420 \text{ pm}$

### Topic 81

81.1a  $6.2 \times 10^3 \text{ s}$

81.2a (a)  $0.00 \text{ mol dm}^{-3}$  (b)  $0.0121 \text{ mol dm}^{-3}$

### Topic 82

E82.1a No change in pressure

E82.2a  $8.1 \text{ mol dm}^{-3} \text{ s}^{-1}$ ,  $2.7 \text{ mol dm}^{-3} \text{ s}^{-1}$ ,  $2.7 \text{ mol dm}^{-3} \text{ s}^{-1}$ ,  $5.4 \text{ mol dm}^{-3} \text{ s}^{-1}$

E82.3a  $1.35 \text{ mol dm}^{-3} \text{ s}^{-1}$ ,  $4.05 \text{ mol dm}^{-3} \text{ s}^{-1}$ ,  $2.7 \text{ mol dm}^{-3} \text{ s}^{-1}$ ,  $1.35 \text{ mol dm}^{-3} \text{ s}^{-1}$

E82.4a  $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (a)  $k_r[\text{A}][\text{B}]$  (b)  $3k_r[\text{A}][\text{B}]$

E82.5a  $\frac{1}{2}k_r[\text{A}][\text{B}][\text{C}]$ ,  $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

E82.6a (a)  $[k_r] = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $[k_r] = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  (b)  $[k_r] = \text{kPa}^{-1} \text{ s}^{-1}$ ,  $[k_r] = \text{kPa}^{-2} \text{ s}^{-1}$

### Topic 83

E83.1a  $n = 2$

E83.2a  $1.03 \times 10^4 \text{ s}$  (a)  $498 \text{ Torr}$  (b)  $461 \text{ Torr}$

E83.3a (a)  $0.098 \text{ mol dm}^{-3}$  (b)  $0.050 \text{ mol dm}^{-3}$

E83.4a  $1.11 \times 10^5 \text{ s} = 1.28 \text{ days}$

### Topic 84

E84.1a  $4.0 \times 10^{10} \text{ dm}^3 \text{ mol s}^{-1}$ ,  $7.1 \times 10^5 \text{ s}^{-1}$ ,  $1.28 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

### Topic 85

E85.1a  $1.08 \times 10^5 \text{ J mol}^{-1} = 108 \text{ kJ mol}^{-1}$ ,  $6.50 \times 10^{15} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $6.50 \times 10^{15} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

E85.2a  $3.49 \times 10^4 \text{ J mol}^{-1} = 34.9 \text{ kJ mol}^{-1}$

### Topic 86

E86.1a (i)  $k_2 K^{1/2} [A_2]^{1/2} [B]$  (ii)  $\frac{k_2^2 [B]^2}{4k_1'} \left\{ \left( 1 + \frac{16k_1' k_1 [A_2]}{k_2^2 [B]^2} \right)^{1/2} - 1 \right\}$ ,  $k_2 K^{1/2} [A_2]^{1/2} [B]$ ,  $2k_1 [A_2]$

E86.2a  $-3 \text{ kJ mol}^{-1}$

### Topic 87

E87.1a  $1.13 \times 10^{10} \text{ s}^{-1}$ ,  $1.62 \times 10^{35} \text{ s}^{-1} \text{ m}^{-3}$ , 1.7 per cent

E87.2a (a) (i)  $1.04 \times 10^{-3}$  (ii) 0.069 (b) (i)  $1.19 \times 10^{-15}$  (ii)  $1.57 \times 10^{-6}$

E87.3a (a) (i) 22 per cent (ii) 3 per cent (b) (i) 170 per cent (ii) 16 per cent

E87.4a  $1.03 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 1.03 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

E87.5a  $0.79 \text{ nm}^2$ ,  $1.16 \times 10^{-3}$

### Topic 88

E88.1a  $4.5 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 4.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

E88.2a (a)  $6.61 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 6.61 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (b)  $3.0 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 3.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

E88.3a  $8.0 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 8.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $4.2 \times 10^{-8} \text{ s}$

E88.4a  $1.81 \times 10^8 \text{ mol dm}^{-3} \text{ s}^{-1}$

### Topic 89

E89.1a  $+69.7 \text{ kJ mol}^{-1}$ ,  $-25 \text{ J K}^{-1} \text{ mol}^{-1}$

E89.2a  $+73.4 \text{ kJ mol}^{-1}$ ,  $+71.9 \text{ kJ mol}^{-1}$

E89.3a  $-91 \text{ J K}^{-1} \text{ mol}^{-1}$

E89.4a  $-74 \text{ J K}^{-1} \text{ mol}^{-1}$

E89.5a (a)  $-46 \text{ J K}^{-1} \text{ mol}^{-1}$  (b)  $+5.0 \text{ kJ mol}^{-1}$  (c)  $+18.7 \text{ kJ mol}^{-1}$

E89.6a  $7.1 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$

### Topic 90

E90.1a Reactant is high in translational energy and low in vibrational energy. Product is high in vibrational energy and relatively lower in translational energy.

### Topic 91

E91.1a  $1.9 \times 10^{-6} \text{ Pa}^{-1} \text{ s}^{-1}$  or  $1.9 \text{ MPa}^{-1} \text{ s}^{-1}$

E91.2a 0.73

E91.3a  $5.1 \times 10^{-7}$

### Topic 92

E92.1a  $\frac{k_b K [\text{AH}]^2 [\text{B}]}{[\text{BH}^+]}$

E92.2a  $1.50 \text{ mmol dm}^{-3} \text{ s}^{-1}$

E92.3a  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$

### Topic 93

E93.1a  $3.3 \times 10^{18}$

E93.2a  $0.56 \text{ mol dm}^{-3}$

### Topic 94

E94.1a  $4 \times 10^{-21} \text{ J}$  or  $2 \text{ kJ mol}^{-1}$

E94.2a  $12.5 \text{ nm}^{-1}$

### Topic 95

E95.1a (i)  $1.4 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$  (ii)  $3.1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$

E95.2a  $0.13 \text{ bar}$

### Topic 96

E96.1a  $33.6 \text{ cm}^3$

E96.2a Chemisorption,  $50 \text{ s}$

E96.3a  $0.83, 0.36$

E96.4a (a)  $0.24 \text{ kPa}$  (b)  $25 \text{ kPa}$

E96.5a  $15 \text{ kPa}$

E96.6a  $-12.4 \text{ kJ mol}^{-1}$

E96.7a  $65.1 \text{ kJ mol}^{-1}$  (a)  $1.6 \times 10^{97} \text{ min}$  (b)  $2.8 \times 10^{-6} \text{ min}$

E96.8a  $61.1 \text{ kJ mol}^{-1}$

E96.9a (a)  $9.1 \text{ ps}, 0.60 \text{ ps}$  (b)  $4.1 \times 10^6 \text{ s}, 6.6 \mu\text{s}$

E96.10a (a) zeroth-order (b) first-order

### Topic 97

E97.1a  $12 \text{ m}^2$