



# **Instructor Solutions Manual to Accompany Atkins' Physical Chemistry**

ELEVENTH EDITION

Peter Bolgar  
Haydn Lloyd  
Aimee North  
Vladimiras Oleinikovas  
Stephanie Smith  
and  
James Keeler

Department of Chemistry  
University of Cambridge  
UK

**Numerical solutions to the problems**

compiled by Jack Entwistle

Selwyn College and the Department of Chemistry  
University of Cambridge

## Preface

This document is a compilation of the numerical solutions to the (b) *Exercises* and the even-numbered *Discussion questions* and *Problems* from the 11<sup>th</sup> edition of *Atkins' Physical Chemistry*. Where a problem requests the derivation of a result or expression, and provided that expression is not too complex, we have also included such results.

### **Errors and omissions**

In such a complex undertaking some errors will no doubt have crept in, despite the authors' best efforts. Readers who identify any errors or omissions are invited to pass them on to us by email to [pchem@ch.cam.ac.uk](mailto:pchem@ch.cam.ac.uk).

Jack Entwistle  
James Keeler

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# 1 The properties of gases

## 1A The perfect gas

E1A.1(b) 0.222 atm  $1.03 \times 10^5$  Pa

E1A.2(b) no 10.4 bar

E1A.3(b) 1.07 bar 803 Torr

E1A.4(b) 120 kPa

E1A.5(b)  $1.66... \times 10^5$  mol  $2.67 \times 10^3$  kg.

E1A.6(b)  $P_4$ .

E1A.7(b) 2.7 kg

E1A.8(b) 28.2 kPa  $3.14 \text{ dm}^3$

E1A.9(b)  $0.0164 \text{ kg mol}^{-1}$

E1A.10(b)  $\theta = -270^\circ\text{C}$

E1A.11(b)  $x_{\text{H}_2} = \frac{3}{8}$   $x_{\text{N}_2} = \frac{5}{8}$   $p_{\text{H}_2} = 1.5 \times 10^5 \text{ Pa}$   $p_{\text{N}_2} = 2.5 \times 10^5 \text{ Pa}$   $p_{\text{tot}} = 4.0 \times 10^5 \text{ Pa}$

P1A.2  $-233^\circ\text{N}$ .

P1A.4  $-273.96^\circ\text{C}$

P1A.6  $102 \text{ g mol}^{-1}$

P1A.8  $p_{\text{tot}} = 1.69 \times 10^5 \text{ Pa}$   $p_{\text{N}_2} = 0.338 \times 10^5 \text{ Pa}$   $p_{\text{NH}_3} = 1.35 \times 10^5$

P1A.10  $n_{\text{O}_3,250 \text{ DU}} = 1.12 \times 10^{-3} \text{ mol}$   $n_{\text{O}_3,100 \text{ DU}} = 4.46 \times 10^{-4} \text{ mol}$   $c_{\text{O}_3,250 \text{ DU}} = 2.79 \times 10^{-9} \text{ mol dm}^{-3}$   $c_{\text{O}_3,100 \text{ DU}} = 1.12 \times 10^{-9} \text{ mol dm}^{-3}$

P1A.12  $4.6 \times 10^3 \text{ mol}$   $1.3 \times 10^2 \text{ kg}$   $1.2 \times 10^2 \text{ kg}$

P1A.14 51 km 0.0030 atm

## 1B The kinetic model

E1B.1(b) 7.08

E1B.2(b)  $v_{\text{rms,CO}_2} = 408 \text{ m s}^{-1}$   $v_{\text{rms,He}} = 1.35 \text{ km s}^{-1}$

E1B.3(b) 0.0107

E1B.4(b)  $650 \text{ m s}^{-1}$

E1B.5(b)  $v_{\text{mp}} = 1.56 \times 10^3 \text{ m s}^{-1}$   $v_{\text{mean}} = 1.75 \times 10^3 \text{ m s}^{-1}$   $v_{\text{rel}} = 2.48 \times 10^3 \text{ m s}^{-1}$

E1B.6(b)  $6.2 \times 10^9 \text{ s}^{-1}$

E1B.7(b)  $475 \text{ m s}^{-1}$   $6.30 \times 10^4 \text{ m}$   $1.07 \times 10^{-2} \text{ s}^{-1}$

E1B.8(b)  $3.4 \times 10^6 \text{ Pa}$

E1B.9(b)  $5.8 \times 10^{-7} \text{ m} = 0.58 \mu\text{m}$

P1B.2  $f(v) dv = \left(\frac{m}{kT}\right) v e^{-mv^2/2kT}$   $\langle v \rangle = \left(\frac{\pi kT}{2m}\right)^{1/2}$

P1B.4 39% 61% 47% greater than 53% less than

P1B.6  $\langle v^n \rangle^{1/n} = \frac{2^{1/n}}{\pi^{1/2n}} \left(\frac{2RT}{M}\right)^{\frac{1}{2}} \left(\left[\frac{1}{2}(n+1)\right]!\right)^{1/n}$  for odd  $n$   $\langle v^n \rangle^{1/n} = \left(\frac{RT}{M}\right)^{1/2} [(n+1)!!]^{1/n}$  for even  $n$

$$\text{PIB.10 } v_{\max} = \left( \frac{2RT}{M} \right)^{1/2}$$

### 1C Real gases

$$\text{EIC.1(b) } 0.99 \text{ atm } \quad 1.9 \times 10^2 \text{ atm}$$

$$\text{EIC.2(b) } a = 0.134 \text{ kg m}^5 \text{ s}^{-2} \text{ mol}^{-2} \quad b = 4.36 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$\text{EIC.3(b) } 1.12 \quad 2.7 \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{EIC.4(b) } V_m = 0.124 \text{ dm}^3 \text{ mol}^{-1}. \quad V_m = 0.112 \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{EIC.5(b) } 8.7 \text{ cm}^3 \quad -0.15 \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{EIC.6(b) } 4.28 \text{ atm dm}^6 \text{ mol}^{-2} \quad 0.0546 \text{ dm}^3 \text{ mol}^{-1} \quad 176 \text{ pm}$$

$$\text{EIC.7(b) } 1.26 \times 10^3 \text{ K} \quad 163 \text{ pm}$$

$$\text{EIC.8(b) } 6.5 \text{ atm} \quad 1.5 \times 10^3 \text{ K} \quad 2.2 \text{ atm} \quad 7.2 \times 10^2 \text{ K} \quad 1.4 \text{ atm} \quad 3.6 \times 10^2 \text{ K}$$

$$\text{EIC.9(b) } 1.3 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \quad 0.67$$

$$\text{PIC.2 } 12.5 \text{ dm}^3 \text{ mol}^{-1} \quad 12.3 \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{PIC.4 } 0.94 \text{ dm}^3 \text{ mol}^{-1} \quad 2.7 \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{PIC.6 } -0.082\%$$

$$\text{PIC.8 } T_c = (8/3)p_c V_c / R \quad 208 \text{ K} \quad 174 \text{ pm}$$

$$\text{PIC.12 } V_m = 3b \quad T = 8a/27Rb \quad p = a/27b^2$$

$$\text{PIC.14 } B = B'RT \quad C = R^2 T^2 [(B')^2 + C']$$

$$\text{PIC.16 } \left( \frac{\partial V_m}{\partial T} \right)_p = \frac{RV_m + b}{2pV_m - RT}$$

$$\text{PIC.20 } 53.42 \text{ atm} \quad 494.7 \text{ K}$$

$$\text{II.2 } 0.25 \text{ J cm}^{-3}$$

## 2 Internal energy

### 2A Internal energy

E2A.1(b)  $7.4 \text{ kJ mol}^{-1}$   $7.4 \text{ kJ mol}^{-1}$   $7.4 \text{ kJ mol}^{-1}$

E2A.3(b)  $-281 \text{ J}$

E2A.4(b)  $q = +2.68 \text{ kJ}$   $w = -6.3 \text{ kJ}$   $\Delta U = 0$   $q = +3.41 \text{ kJ}$   $w = -3.41 \text{ kJ}$   $\Delta U = 0$   
 $q = 0$   $w = 0$   $\Delta U = 0$

E2A.5(b)  $p_f = 143 \text{ kPa}$   $\Delta U = +3.28 \text{ kJ}$   $q = +3.28 \text{ kJ}$   $w = 0$

E2A.6(b)  $-19 \text{ J}$   $-53 \text{ J}$

P2A.2 0

P2A.4  $9.1 \times 10^{-16} \text{ N}$

P2A.8  $-8.9 \text{ kJ}$

### 2B Enthalpy

E2B.1(b)  $C_{p,m} = 53 \text{ J K}^{-1} \text{ mol}^{-1}$   $C_{v,m} = 44 \text{ J K}^{-1} \text{ mol}^{-1}$

E2B.2(b)  $\Delta H_m = \Delta U_m$

E2B.3(b)  $q_p = +11.6 \text{ kJ}$   $w = -624 \text{ J}$   $\Delta U = +11.0 \text{ kJ}$   $\Delta H = +11.6 \text{ kJ}$   $q_v = +11.0 \text{ kJ}$   
 $w = 0$   $\Delta U = +11.0 \text{ kJ}$   $\Delta H = +11.6 \text{ kJ}$

E2B.4(b)  $q_p = \Delta H = +2.0 \text{ kJ}$   $\Delta U = +1.6 \text{ kJ}$

P2B.2  $6.1 \times 10^2 \text{ s}$

P2B.4  $a = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$   $b = 2.79 \times 10^{-2} \text{ J K}^{-2} \text{ mol}^{-1}$   $c = -1.51 \times 10^5 \text{ J K mol}^{-1}$   
 $\alpha = 24.6 \text{ J K}^{-1} \text{ mol}^{-1}$   $\beta = 3.83 \times 10^{-2} \text{ J K}^{-2} \text{ mol}^{-1}$   $\gamma = -6.58 \times 10^{-6} \text{ J K}^{-3} \text{ mol}^{-1}$

### 2C Thermochemistry

E2C.1(b)  $q = \Delta H = +76.1 \text{ kJ}$   $w = -3.78 \text{ kJ}$   $\Delta U = +72.3 \text{ kJ}$

E2C.2(b)  $-3054 \text{ kJ mol}^{-1}$

E2C.3(b)  $-55 \text{ kJ mol}^{-1}$

E2C.4(b)  $5.09 \times 10^{-2} \text{ kJ K}^{-1}$   $+79.6 \text{ K}$

E2C.5(b)  $\Delta_r H^\circ(3) = -589.56 \text{ kJ mol}^{-1}$   $\Delta_r U^\circ = -582 \text{ kJ mol}^{-1}$   $\Delta_f H^\circ(\text{HCl, g}) = +26.48 \text{ kJ mol}^{-1}$   
 $\Delta_f H^\circ(\text{H}_2\text{O, g}) = -241.82 \text{ kJ mol}^{-1}$

E2C.6(b)  $-760.3 \text{ kJ mol}^{-1}$

E2C.7(b)  $\Delta_r H^\circ(298 \text{ K}) = -174.83 \text{ kJ mol}^{-1}$   $\Delta_r U^\circ(298 \text{ K}) = -172 \text{ kJ mol}^{-1}$   $\Delta_r H^\circ(478 \text{ K}) =$   
 $-179 \text{ kJ mol}^{-1}$

E2C.8(b)  $-53.7 \text{ kJ mol}^{-1}$

P2C.2  $3.4 \times 10^4 \text{ kJ}$

P2C.4  $-1152.4 \text{ kJ mol}^{-1}$

P2C.6  $\Delta_r H^\circ = +18 \text{ kJ mol}^{-1}$      $\Delta_f H^\circ = +116 \text{ kJ mol}^{-1}$

P2C.8  $+239.7 \text{ kJ mol}^{-1}$      $+228.0 \text{ kJ mol}^{-1}$

P2C.10  $1.9 \times 10^3 \text{ kJ mol}^{-1}$

## 2D State functions and exact differentials

E2D.1(b)  $1.12 \times 10^3 \text{ Pa}$

E2D.2(b)  $\Delta U_m = +131 \text{ J mol}^{-1}$      $q = +8.51 \text{ kJ mol}^{-1}$      $w = -8.37 \text{ kJ mol}^{-1}$

E2D.3(b)  $+1.3 \times 10^{-3} \text{ K}^{-1}$

E2D.4(b)  $+4.5 \times 10^2 \text{ atm}$

E2D.5(b)  $+28.4 \text{ J K}^{-1} \text{ mol}^{-1}$

P2D.6  $322 \text{ m s}^{-1}$

## 2E Adiabatic changes

E2E.1(b) With vibrational contribution  $\gamma = \frac{15}{13}$     Without vibrational contribution  $\gamma = \frac{7}{5}$

E2E.2(b)  $200 \text{ K}$

E2E.3(b)  $37 \text{ dm}^3$      $269 \text{ K}$      $-1.7 \text{ kJ}$

E2E.4(b)  $-325 \text{ J}$

E2E.5(b)  $3.6 \text{ Torr}$

P2E.2  $41.397 \text{ J K}^{-1} \text{ mol}^{-1}$

## 2E Integrated activities

I2.2  $n = 0.90$      $k = -73.7 \text{ kJ mol}^{-1} (\text{g mol}^{-1})^{-0.9}$

I2.6  $346 \text{ m s}^{-1}$

## 3 The second and third laws

### 3A Entropy

E3A.1(b) spontaneous

E3A.2(b) +853 J +670 J

E3A.3(b) +0.481 J K<sup>-1</sup>

E3A.4(b)  $\Delta S = +0.81 \text{ J K}^{-1}$   $\Delta S_{\text{sur}} = -0.81 \text{ J K}^{-1}$   $\Delta S_{\text{tot}} = 0$   $\Delta S = +0.81 \text{ J K}^{-1}$   $\Delta S_{\text{sur}} = 0$   $\Delta S_{\text{tot}} = +0.81 \text{ J K}^{-1}$   $\Delta S = \Delta S_{\text{sur}} = \Delta S_{\text{tot}} = 0$

E3A.5(b) 390 K

E3A.6(b) 282 K

P3A.2 2.5 dm<sup>3</sup> -1.2 × 10<sup>2</sup> J +1.2 × 10<sup>2</sup> J +0.16 J K<sup>-1</sup>

P3A.4  $nR(T_h - T_c) \ln(V_B/V_A)$   $nR(T_h - T_c) \ln(V_B/V_A)$

P3A.6 0.09 kW

### 3B Entropy changes accompanying specific processes

E3B.1(b) +30 kJ mol<sup>-1</sup>

E3B.2(b) +104.6 J K<sup>-1</sup> mol<sup>-1</sup> -104.6 J K<sup>-1</sup> mol<sup>-1</sup>

E3B.3(b) -2.55 J K<sup>-1</sup> mol<sup>-1</sup>

E3B.4(b) 153 J K<sup>-1</sup> mol<sup>-1</sup>

E3B.5(b)  $T_f = 336 \text{ K}$   $\Delta S_1 = -476 \text{ J K}^{-1}$   $\Delta S_2 = +532 \text{ J K}^{-1}$   $\Delta S_{\text{tot}} = +56 \text{ J K}^{-1}$

E3B.6(b) -7.3 J K<sup>-1</sup>

E3B.7(b) +130.4 J K<sup>-1</sup>

P3B.2  $\Delta S_{\text{tot}} = -0.4 \text{ J K}^{-1}$  not spontaneous

P3B.4 +198.3 J K<sup>-1</sup> mol<sup>-1</sup> +198.1 J K<sup>-1</sup> mol<sup>-1</sup>

P3B.6  $\ln\left(\frac{T - T_{\text{sur}}}{T_i - T_{\text{sur}}}\right) = -\alpha t$   $S(T_i) + C \ln\left(\frac{T_{\text{sur}} + (T_i - T_{\text{sur}}) \times e^{-\alpha t}}{T_i}\right)$

P3B.8 330 K +43.9 kJ  $\Delta S_{\text{water}} = -118 \text{ J K}^{-1}$   $\Delta S_{\text{copper}} = +146 \text{ J K}^{-1}$   $\Delta S_{\text{tot}} = +28 \text{ J K}^{-1}$

P3B.10  $\eta = 60.2\%$   $\Delta S_1 = \Delta S_{\text{sur},1} = 0$   $\Delta S_2 = +33.5 \text{ J K}^{-1}$   $\Delta S_{\text{sur},2} = -33.5 \text{ J K}^{-1}$

$\Delta S_3 = \Delta S_{\text{sur},3} = 0$   $\Delta S_4 = -33.5 \text{ J K}^{-1}$   $\Delta S_{\text{sur},4} = +35.5 \text{ J K}^{-1}$

P3B.12 +200.71 J K<sup>-1</sup> mol<sup>-1</sup> +232.00 J K<sup>-1</sup> mol<sup>-1</sup>

### 3C The measurement of entropy

E3C.1(b)  $6.5 \times 10^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$

E3C.2(b) -21.0 J K<sup>-1</sup> mol<sup>-1</sup> +512.0 J K<sup>-1</sup> mol<sup>-1</sup>

E3C.3(b) -74.33 J K<sup>-1</sup>

P3C.2 256.0 J K<sup>-1</sup> mol<sup>-1</sup>

**P3C.4**  $297 \text{ J K}^{-1} \text{ mol}^{-1}$  at 200 K  $138 \text{ J K}^{-1} \text{ mol}^{-1}$  at 100 K

**P3C.6**  $-99.38 \text{ J K}^{-1} \text{ mol}^{-1}$   $-46.11 \text{ kJ mol}^{-1}$  at 298 K  $+111.15 \text{ J K}^{-1} \text{ mol}^{-1}$   $-50.70 \text{ kJ mol}^{-1}$   
at 500 K

**P3C.8**  $46.57 \text{ J K}^{-1} \text{ mol}^{-1}$   $46.73 \text{ J K}^{-1} \text{ mol}^{-1}$

**P3C.10** 2.86 K the Debye contribution

### 3D Concentrating on the system

**E3D.1(b)**  $\Delta_r H^\circ = -218.66 \text{ kJ mol}^{-1}$   $\Delta_r G^\circ = -212.40 \text{ kJ mol}^{-1}$   $\Delta_r H^\circ = -5644 \text{ kJ mol}^{-1}$   
 $\Delta_r G^\circ = -5797 \text{ kJ mol}^{-1}$

**E3D.2(b)**  $-72 \text{ kJ mol}^{-1}$

**E3D.3(b)**  $2108.11 \text{ kJ mol}^{-1}$

**E3D.4(b)**  $-212.55 \text{ kJ mol}^{-1}$   $-5798 \text{ kJ mol}^{-1}$

**E3D.5(b)**  $-373 \text{ kJ mol}^{-1}$

**P3D.2**  $+35 \text{ J K}^{-1} \text{ mol}^{-1}$   $12 \text{ W m}^{-3}$   $0.46 \text{ mol}$

**P3D.4**  $\Delta_r G_1^\circ = +718 \text{ kJ mol}^{-1}$   $\Delta_r G_2^\circ = -729 \text{ kJ mol}^{-1}$   $\Delta_r G^\circ = -10 \text{ kJ mol}^{-1}$

**P3D.6**  $\Delta_{\text{solv}} S^\circ = 0$   $\Delta_{\text{solv}} H^\circ = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \times \left(1 - \frac{1}{\epsilon_r}\right)$

### 3E Combining the First and Second Laws

**E3E.1(b)**  $-13 \text{ J}$

**E3E.2(b)**  $-42.8 \text{ J K}^{-1}$

**E3E.3(b)**  $-73.1 \text{ J}$

**E3E.4(b)**  $+40.0 \text{ J}$   $+7.23 \text{ J mol}^{-1}$

**E3E.5(b)**  $+2.5 \times 10^2 \text{ J mol}^{-1}$

**E3E.6(b)**  $+2.88 \text{ kJ mol}^{-1}$

**P3E.2**  $\Delta_r G^\circ(298 \text{ K}) = -32.90 \text{ kJ mol}^{-1}$   $\Delta_r H^\circ(298 \text{ K}) = -92.22 \text{ kJ mol}^{-1}$   $\Delta G(500 \text{ K}) =$   
 $+7.31 \text{ kJ mol}^{-1}$   $\Delta G(1000 \text{ K}) = +107 \text{ kJ mol}^{-1}$

**P3E.4**  $\frac{R}{V_m} \frac{R}{V_m - b} \left(1 + \frac{a}{RT^2 V_m}\right) \frac{R}{V_m - b} e^{-a/(RTV_m)}$

**P3E.6**  $-497 \text{ J}$

**P3E.8**  $\Delta_r G_1^\circ = +57.2 \text{ kJ mol}^{-1}$   $\Delta_r G_2^\circ = +85.6 \text{ kJ mol}^{-1}$   $\Delta_r G_3^\circ = +112.8 \text{ kJ mol}^{-1}$

## 4 Physical transformations of pure substances

### 4A Phase diagrams of pure substances

E4A.1(b) one phase   three phases   three phases   two phases

E4A.2(b)  $-1.2 \text{ J}$

E4A.3(b) 6

E4A.4(b) line

E4A.5(b) one phase   one phase   three phases

### 4B Thermodynamic aspects of phase transitions

E4B.1(b)  $\Delta\mu(\text{liquid}) = +98 \text{ J mol}^{-1}$     $\Delta\mu(\text{solid}) = +65 \text{ J mol}^{-1}$    solid

E4B.2(b)  $-2.7 \times 10^3 \text{ J mol}^{-1}$

E4B.3(b)  $+8.8 \times 10^2 \text{ J mol}^{-1}$

E4B.4(b) 3.42 kPa

E4B.5(b)  $2.4 \text{ kJ mol}^{-1}$     $5.5 \text{ J K}^{-1} \text{ mol}^{-1}$

E4B.6(b) 296 K    $22.9^\circ\text{C}$

E4B.7(b)  $25.249 \text{ kJ mol}^{-1}$

E4B.8(b)  $31.11 \text{ kJ mol}^{-1}$    276.9 K    $3.720^\circ\text{C}$

E4B.9(b) 272 K    $-0.935^\circ\text{C}$

E4B.10(b) 0.37 K

E4B.11(b)  $3.6 \text{ kg s}^{-1}$

E4B.12(b) 0.40 kPa   yes

E4B.13(b)  $29 \text{ kJ mol}^{-1}$    22 kPa at  $25^\circ\text{C}$    77 kPa at  $60^\circ\text{C}$

E4B.14(b) 272 K    $-0.74^\circ\text{C}$

P4B.2 196.00 K   11.079 Torr

P4B.4  $5.56 \text{ kPa K}^{-1}$     $5.42 \text{ kPa K}^{-1}$    2.61 %

P4B.6  $-1.63 \times 10^{-6} \text{ J Pa}^{-1} \text{ mol}^{-1}$     $0.0301 \text{ J Pa}^{-1} \text{ mol}^{-1}$     $610 \text{ J mol}^{-1}$

P4B.8  $22.3^\circ\text{C}$

P4B.10  $227.5^\circ\text{C}$     $53.6 \text{ kJ mol}^{-1}$

P4B.14 0.071 % increase

P4B.16  $(\partial^2 \mu / \partial T^2)_p = -C_{p,m} / T$    liquid line:  $-0.202 \text{ J K}^{-2} \text{ mol}^{-1}$    gas line:  $-0.0900 \text{ J K}^{-2} \text{ mol}^{-1}$

I4.2 178.18 K   383.54 K    $33.0 \text{ kJ mol}^{-1}$

I4.4 112 K    $8.49 \text{ kJ mol}^{-1}$

## 5 Simple mixtures

### 5A The thermodynamic description of mixtures

E5A.1(b)  $V_B = (-22.5749 + 1.13784x + 0.03069x^2 + 0.00936x^3) \text{ cm}^3 \text{ mol}^{-1}$

E5A.2(b)  $V_B = -1.39 \text{ cm}^3 \quad V_A = 18.0 \text{ cm}^3$

E5A.3(b)  $+3.3 \text{ J mol}^{-1}$

E5A.4(b)  $+0.0634 \text{ J K}^{-1} \quad -17.3 \text{ J}$

E5A.5(b)  $19 \text{ kPa} \quad y_{1,2\text{-dimethylbenzene}} = 0.53 \quad y_{1,3\text{-dimethylbenzene}} = 0.47$

E5A.6(b)  $843.5 \text{ cm}^3$

E5A.7(b)  $18.1 \text{ cm}^3 \text{ mol}^{-1}$

E5A.8(b)  $8.4 \cdot 10^3 \text{ kPa}$

E5A.9(b)  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$

E5A.10(b)  $b_{\text{N}_2} = 5.1 \times 10^{-4} \text{ mol kg}^{-1} \quad b_{\text{O}_2} = 2.7 \times 10^{-4} \text{ mol kg}^{-1}$

E5A.11(b)  $0.067 \text{ mol dm}^{-3}$

P5A.2  $73.96 \text{ cm}^3 \text{ mol}^{-1}$

P5A.4  $K_A = 15.6 \text{ kPa} \quad K_B = 47.0 \text{ kPa}$

P5A.6  $4.4 \text{ cm}^3$

### 5B The properties of solutions

E5B.1(b)  $1.5 \times 10^2 \text{ kPa}$

E5B.2(b)  $273 \text{ g mol}^{-1}$

E5B.3(b)  $178 \text{ g mol}^{-1}$

E5B.4(b)  $272.75 \text{ K}$

E5B.5(b)  $273.07 \text{ K}$

E5B.6(b)  $\Delta_{\text{mix}}G = -3.44 \times 10^3 \text{ J} \quad \Delta_{\text{mix}}S = +11.5 \text{ J K}^{-1} \quad \Delta_{\text{mix}}H = 0$

E5B.7(b)  $\frac{1}{2} \quad 0.7358$

E5B.8(b)  $52 \text{ mol kg}^{-1} \quad 11 \text{ kg}$

E5B.9(b)  $p_B = 4.8 \text{ kPa} \quad p_A = 21 \text{ kPa} \quad p_{\text{tot}} = 26 \text{ kPa} \quad y_A = 0.82 \quad y_B = 0.18$

E5B.10(b)  $x_{1,2\text{-dimethylbenzene}} = 0.5 \quad x_{1,3\text{-dimethylbenzene}} = 0.5 \quad y_{1,2\text{-dimethylbenzene}} = 0.53$   
 $y_{1,3\text{-dimethylbenzene}} = 0.47$

E5B.11(b)  $x_A = 0.653 \quad x_B = 0.347 \quad 73.4 \text{ kPa}$

E5B.12(b) not ideal

P5B.2 4

P5B.6  $\mu_A = \mu_A^* + gRTx_B^2 + RT \ln x_A$

P5B.8  $84784 \text{ g cm K}^{-1} \text{ mol}^{-1} \quad M = 1.1 \times 10^5 \text{ g mol}^{-1} \quad B' = 16.4 \text{ g}^{-1} \text{ cm}^3 \quad C' = 241 \text{ g}^{-2} \text{ cm}^6$

$B' = 30.6 \text{ g}^{-1} \text{ cm}^3 \quad C' = 234 \text{ g}^{-2} \text{ cm}^6$

P5B.10  $\frac{1}{2}$

### 5C Phase diagrams of binary systems: liquids

E5C.1(b)  $y_A = 0.81$   $y_A = 0.90$

E5C.3(b)  $x_A = 0.345$   $\frac{n_{0.618}}{n_{0.308}} = 0.135$

P5C.2  $y_{DE} = 0.67$   $y_{DP} = 0.33$

P5C.4 391 K  $x_{\text{Butanol}} = 0.17$   $y_{\text{Butanol}} = 0.37$   $\frac{m}{n_v} = 0.54$

P5C.6 1

### 5D Phase diagrams of binary systems: solids

E5D.4(b)  $x_B \approx 0.58$   $T_2$

E5D.6(b) B is soluble in A in all proportions  $x_B = 0.63$   $\frac{n_{AB_2}}{n_A} = 0.53$

### 5E Phase diagrams of ternary systems

E5E.3(b)  $x_{\text{CHCl}_3} = 0.023$   $x_{\text{CH}_3\text{COOH}} = 0.019$   $x_{\text{H}_2\text{O}} = 0.958$  one-phase region

### 5F Activities

E5F.1(b) 0.8882

E5F.2(b)  $a_A = 0.9701$   $\gamma_A = 0.980$

E5F.3(b)  $a_A = 0.436$   $\gamma_A = 1.98$   $a_B = 0.755$   $\gamma_B = 0.968$

E5F.5(b) 0.320

E5F.6(b) 45.0 g 38.8 g

E5F.7(b) 0.44

E5F.8(b)  $B = 1.53$

P5F.2 0.02

P5F.4  $I = 0.00$  to  $I = 0.18$

I5.6  $K' = 1.17 \times 10^6$   $N = 5.23$

## 6 Chemical equilibrium

### 6A The equilibrium constant

E6A.1(b)  $n_A = 1.15 \text{ mol}$   $n_B = 0.42 \text{ mol}$

E6A.2(b)  $-47 \text{ kJ mol}^{-1}$

E6A.3(b) endergonic

E6A.6(b)  $K = 2.02 \times 10^{31}$   $K = 1.80 \times 10^{37}$

E6A.7(b)  $1.1 \times 10^{40}$

E6A.8(b)  $-10 \text{ kJ mol}^{-1}$   $-4.7 \text{ kJ mol}^{-1}$   $+0.98 \text{ kJ mol}^{-1}$   $+6.7 \text{ kJ mol}^{-1}$  6.75 6.75

E6A.9(b) 0.168

E6A.10(b)  $K = K_c \times (c^\ominus RT/p^\ominus)^{-2}$

E6A.11(b)  $x_A = 0.178$   $x_B = 0.031$   $x_C = 0.116$   $x_D = 0.674$  9.6  $-5.6 \text{ kJ mol}^{-1}$

E6A.12(b)  $-41.0 \text{ kJ mol}^{-1}$

E6A.13(b)  $+12 \text{ kJ mol}^{-1}$

E6A.14(b)  $-1.3 \times 10^2 \text{ kJ mol}^{-1}$

P6A.2  $1.69 \times 10^{-5}$

P6A.4  $+1.5 \text{ kJ mol}^{-1}$   $+2.0 \text{ kJ mol}^{-1}$   $-1.4 \text{ kJ mol}^{-1}$   $-3.5 \text{ kJ mol}^{-1}$   $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$

### 6B The response of equilibria to the conditions

E6B.1(b) 0.24 1.3

E6B.2(b)  $-3.08 \dots \times 10^2 \text{ kJ mol}^{-1}$   $1.3 \times 10^{54}$   $3.6 \times 10^{49}$

E6B.3(b)  $1.4 \times 10^3 \text{ K}$

E6B.4(b)  $7.2 \text{ kJ mol}^{-1}$   $-21 \text{ J K}^{-1} \text{ mol}^{-1}$

E6B.5(b) zero

E6B.6(b) 0.018

E6B.7(b)  $+38.7 \text{ kJ mol}^{-1}$   $-38.7 \text{ kJ mol}^{-1}$

E6B.8(b) 398 K

E6B.9(b) 9.24  $-12.9 \text{ kJ mol}^{-1}$   $+162 \text{ kJ mol}^{-1}$   $+249 \text{ J K}^{-1} \text{ mol}^{-1}$

P6B.2  $1.24 \times 10^{-9}$   $1.30 \times 10^{-8}$   $1.76 \times 10^{-4}$

P6B.4  $-1.9 \times 10^2 \text{ kJ mol}^{-1}$

P6B.6  $\Delta_r G^\ominus / \text{kJ mol}^{-1} = 78 - 0.16(T/\text{K})$

P6B.8  $+156 \text{ kJ mol}^{-1}$

P6B.10  $\text{H}_2: +14.7 \text{ kJ mol}^{-1}$   $\text{CO}: +18.8 \text{ kJ mol}^{-1}$

### 6C Electrochemical cells

E6C.1(b)  $-0.91 \text{ V}$   $-0.26 \text{ V}$   $+0.89 \text{ V}$

**E6C.2(b)** +1.88 V +0.54 V +0.83 V

**E6C.3(b)**  $-89.9 \text{ kJ mol}^{-1}$  +0.223 V

**E6C.4(b)**  $+7.7 \text{ kJ mol}^{-1}$

**E6C.5(b)**  $-0.014 \text{ V}$

**P6C.2**  $-237 \text{ kJ mol}^{-1}$

## 6D Electrode potentials

**E6D.1(b)**  $1.7 \times 10^{16}$   $8.2 \times 10^{-7}$

**E6D.2(b)**  $4.3 \times 10^{-98}$

**E6D.3(b)**  $-6.1 \times 10^2 \text{ kJ mol}^{-1}$

**E6D.4(b)** yes

**P6D.2** right-hand electrode +0.09106 V

**P6D.4** 0.26838 V

**P6D.6**  $\Delta_f G^\ominus(\text{Cl}^-, \text{aq}) = -131.3 \text{ kJ mol}^{-1}$   $\Delta_f H^\ominus(\text{Cl}^-, \text{aq}) = -167.1 \text{ kJ mol}^{-1}$   $S_m^\ominus(\text{Cl}^-, \text{aq}) = 56.8 \text{ J K}^{-1} \text{ mol}^{-1}$

**I6.2**  $I_{\text{CuSO}_4} = 4.00 \times 10^{-3}$   $I_{\text{ZnSO}_4} = 1.20 \times 10^{-2}$   $\gamma_{\pm, \text{CuSO}_4} = 0.743$   $\gamma_{\pm, \text{ZnSO}_4} = 0.598$   $Q =$

2.41  $E_{\text{cell}}^\ominus = +1.102 \text{ V}$   $E_{\text{cell}} = +1.09 \text{ V}$

**I6.4**  $-68.6 \text{ J K}^{-1} \text{ mol}^{-1}$   $+59.6 \text{ kJ mol}^{-1}$

**I6.6**  $B = 2.54$   $C = -0.204$   $\text{p}K_a = 6.74$

**I6.8**  $\Delta_r G = -49 \text{ kJ mol}^{-1}$ ; Under standard biological conditions  $\Delta_r G^\oplus = -31 \text{ kJ mol}^{-1}$ ;  $\Delta_r G^\ominus + 11 \text{ kJ mol}^{-1}$

**I6.10** yes

**I6.12**  $-73.1 \text{ kJ mol}^{-1}$   $-147 \text{ J K}^{-1} \text{ mol}^{-1}$   $+131 \text{ kJ mol}^{-1}$   $307 \text{ J K}^{-1} \text{ mol}^{-1}$

## 7 Quantum theory

### 7A The origins of quantum mechanics

E7A.1(b)  $1.1 \times 10^{-3} \text{ m}$

E7A.2(b)  $2.7 \text{ K}$

E7A.3(b)  $(0.97) \times 3R$

E7A.4(b)  $2.65 \times 10^{-19} \text{ J}$   $160 \text{ kJ mol}^{-1}$   $3.00 \times 10^{-19} \text{ J}$   $181 \text{ kJ mol}^{-1}$   $6.6 \times 10^{-31} \text{ J}$   $3.99 \times 10^{-10} \text{ kJ mol}^{-1}$

E7A.5(b)  $991 \text{ zJ}$   $597 \text{ kJ mol}^{-1}$   $1.32 \text{ pJ}$   $7.96 \times 10^5 \text{ kJ mol}^{-1}$   $19.8 \text{ yJ}$   $1.19 \times 10^{-2} \text{ kJ mol}^{-1}$

E7A.6(b)  $17.3 \text{ km s}^{-1}$   $631 \text{ km s}^{-1}$   $0.0773 \text{ km s}^{-1}$

E7A.7(b)  $3.52 \times 10^{17}$   $3.52 \times 10^{18}$

E7A.8(b) no electron ejection  $6.84 \times 10^{-19} \text{ J}$   $1.23 \text{ Mm s}^{-1}$

E7A.9(b)  $158 \text{ m s}^{-1}$

E7A.10(b)  $7.27 \times 10^6 \text{ m s}^{-1}$   $8.19 \times 10^{-2} \text{ V}$

E7A.11(b)  $1.3 \times 10^{-5} \text{ m s}^{-1}$

E7A.12(b)  $1.89 \times 10^{-27} \text{ kg m s}^{-1}$   $0.566 \text{ m s}^{-1}$

E7A.13(b)  $123 \text{ pm}$   $39 \text{ pm}$   $3.88 \text{ pm}$

P7A.2  $3.96 \times 10^{-8} \text{ J m}^{-3}$   $5.12 \times 10^{-163} \text{ J m}^{-3}$

P7A.4  $2.9 \times 10^{-3} \text{ K m}$

P7A.6  $255 \text{ K}$   $1.14 \times 10^{-5} \text{ m}$

P7A.8  $a = 8\pi hc$   $b = -hc/\lambda$

P7A.10  $\theta_E/T \ll 1$   $3R \times (0.0314)$   $3R \times (0.896)$

### 7B Wavefunctions

E7B.1(b)  $N = (2/L)^{1/2}$

E7B.2(b)  $N = (2a)^{1/2}$

E7B.3(b) cannot be normalized can be normalized

E7B.4(b)  $(2/L)dx$

E7B.5(b)  $1/3$

E7B.7(b) is is is not

E7B.8(b) Maxima at  $x = L/6, L/2, 5L/6$ ; Nodes at  $x = L/3, 2L/3$

P7B.2  $N = (\pi)^{-1/2}$   $N = (\pi)^{-1/2}$

P7B.4  $N = (4ab/\pi^2)^{1/2}$

P7B.6  $0.186$

P7B.8  $1/4$   $0.670$

P7B.10  $N = (\pi a^2)^{-1/4}$   $0.843$

## 7C Operators and observables

E7C.6(b)  $L/2$

E7C.7(b) 0

E7C.8(b)  $\hbar \quad m_1 \hbar$

E7C.9(b)  $100 \text{ pm} \quad 5.79 \times 10^5 \text{ m s}^{-1}$

E7C.10(b)  $5.82 \times 10^{-6} \text{ m}$

P7C.6  $\hbar k \quad 0 \quad 0$

P7C.8  $\cos^2 \chi \quad \sin^2 \chi \quad (\hbar k)^2/2m$

P7C.12  $\hbar/i$

P7C.14  $\hbar$

## 7D Translational motion

E7D.1(b)  $5 \times 10^{-25} \text{ kg m s}^{-1} \quad 2 \times 10^{-19} \text{ J}$

E7D.2(b)  $e^{+i(9.5 \times 10^{31} \text{ m}^{-1})x}$

E7D.3(b)  $1.3 \times 10^{-19} \text{ J} \quad 81 \text{ kJ mol}^{-1} \quad 0.84 \text{ eV} \quad 6.7 \times 10^3 \text{ cm}^{-1} \quad 3.5 \times 10^{-19} \text{ J} \quad 2.1 \times 10^2 \text{ kJ mol}^{-1} \quad 2.2 \text{ eV} \quad 1.8 \times 10^4 \text{ cm}^{-1}$

E7D.5(b) 0.031 0.029

E7D.8(b)  $\sqrt{3/8} \lambda_C$

E7D.9(b)  $L/10, 3L/10, L/2, 7L/10, 9L/10 \quad 0, L/5, 2L/5, 3L/5, 4L/5, L$

E7D.10(b) 0.235

E7D.11(b)  $n = (2L/h)(mkT)^{1/2} \quad 5.0 \times 10^7$

E7D.12(b) Maxima at  $(x, y): (L/2, L/6), (L/2, L/2), (L/2, 5L/6)$ ; Nodes at  $y = L/3$  and parallel to the  $x$ -axis,  $y = 2L/3$  and parallel to the  $x$ -axis

E7D.13(b) (4, 4)

E7D.14(b) 6

E7D.15(b)  $5.7 \times 10^{-14}$

P7D.2  $7.25 \times 10^{10} \quad 1.71 \times 10^{-31} \text{ J} \quad 27.6 \text{ pm}$

P7D.4  $\langle p_x \rangle = 0 \quad \langle p_x^2 \rangle = 4\pi^2 \hbar^2 / L^2$

P7D.6  $L^2(1/3 - 1/2n^2\pi^2)$

P7D.8  $L/2 \quad L^2/3$

P7D.14  $N^2/2\kappa \quad N^2/(2\kappa)^2$

## 7E Vibrational motion

E7E.1(b)  $3.92 \times 10^{-21} \text{ J}$

E7E.2(b)  $260 \text{ N m}^{-1}$

E7E.3(b)  $1.32 \times 10^{-5} \text{ m}$

E7E.5(b)  $2.3422 \times 10^{-20} \text{ J}$

**E7E.6(b)**  $1.23 \times 10^{-19} \text{ J}$  28.5%  $3.88 \times 10^{-20} \text{ J}$  50.7%

**E7E.7(b)** 5 35

**E7E.8(b)**  $y = 0, \pm\sqrt{3}$

**E7E.9(b)**  $y = \pm 0.6021$   $y = \pm 2.034$

**P7E.2**  $3.98 \times 10^{14} \text{ Hz}$  1.5% difference

**P7E.4**  $\nu_{12\text{C}^{16}\text{O}} = 64.3 \text{ THz}$   $\nu_{13\text{C}^{16}\text{O}} = 62.8 \text{ THz}$   $\nu_{12\text{C}^{18}\text{O}} = 62.7 \text{ THz}$   $\nu_{13\text{C}^{18}\text{O}} = 61.3 \text{ THz}$

**P7E.6**  $k_{\text{f}, ^1\text{H}^{35}\text{Cl}} = 512 \text{ N m}^{-1}$   $k_{\text{f}, ^1\text{H}^{81}\text{Br}} = 409 \text{ N m}^{-1}$   $k_{\text{f}, ^1\text{H}^{127}\text{I}} = 312 \text{ N m}^{-1}$   $k_{\text{f}, ^{12}\text{C}^{16}\text{O}} = 1902 \text{ N m}^{-1}$   $k_{\text{f}, ^{14}\text{N}^{16}\text{O}} = 1595 \text{ N m}^{-1}$   $\text{HI} < \text{HBr} < \text{HCl} < \text{NO} < \text{CO}$

**P7E.10**  $\langle y^2 \rangle_{v=0} = \frac{1}{2}$   $\langle y^2 \rangle_{v=1} = \frac{3}{2}$

**P7E.12**  $\langle x^3 \rangle_v = 0$   $\langle x^4 \rangle_v = \alpha^4 \frac{3}{4} [2v^2 + 2v + 1]$

## 7F Rotational motion

**E7F.1(b)**  $6^{1/2}\hbar$   $-2\hbar, -\hbar, 0, \hbar, 2\hbar$

**E7F.3(b)**  $\pi^{-1/2}$

**E7F.5(b)** 2.49

**E7F.6(b)**  $3.62 \times 10^{-22} \text{ J}$

**E7F.7(b)**  $7.25 \times 10^{-22} \text{ J}$

**E7F.8(b)**  $1.49 \times 10^{-34} \text{ J s}$

**E7F.10(b)** 4

**E7F.11(b)**  $\phi = \pi/4, 3\pi/4, 5\pi/4, 7\pi/4$   $\phi = 0, \pi/2, \pi, 3\pi/2$

**E7F.12(b)** 9

**P7F.4**  $E_0 = 0$ ,  $E_1 = 2.64 \times 10^{-22} \text{ J}$ ,  $E_2 = 7.91 \times 10^{-22} \text{ J}$ ,  $E_3 = 1.58 \times 10^{-21} \text{ J}$

**P7F.8**  $\phi = \pi/2, 3\pi/2$   $yz$  plane

## 8 Atomic structure and spectra

### 8A Hydrogenic Atoms

E8A.1(b) 1 64 25

E8A.2(b)  $N = (32\pi a^3)^{-1/2}$

E8A.3(b)  $Z^3/(27\pi a^3)$

E8A.4(b)  $r = (3a_0/2Z)(5 \pm \sqrt{7})$

E8A.5(b)  $0.381a_0$  and  $2.08a_0$   $0.555a_0$  and  $1.64a_0$

E8A.6(b)  $r = (2a_0/Z)(5 \pm \sqrt{5})$

E8A.7(b)  $\phi = 0$   $\phi = \pi/2$

E8A.8(b)  $8.72 \times (3a_0/2Z)$

E8A.9(b)  $8(3a_0/2Z)$

E8A.10(b) 4 subshells 16 orbitals

E8A.12(b) 0

P8A.4 122.3 eV

P8A.8  $Z/a_0$   $Z/4a_0$   $Z/4a_0$

### 8B Many-electron atoms

E8B.2(b) 22

E8B.4(b) [Ar]

E8B.5(b)  $\text{Be}^+$

P8B.4  $\text{Fe}^{2+}$

### 8C Atomic spectra

E8C.1(b)  $n_2 = 6$   $n_2 = \infty$

E8C.2(b)  $2.22 \times 10^5 \text{ cm}^{-1}$  450 nm 666 THz

E8C.3(b) forbidden allowed forbidden

E8C.4(b)  ${}^2F_{7/2}, {}^2F_{5/2}$

E8C.5(b)  $j = \frac{3}{2}, \frac{1}{2}$   $j = \frac{11}{2}, \frac{9}{2}$

E8C.6(b)  $J = 8, 7, 6, 5, 4, 3, 2$

E8C.7(b)  $L = 3$   $S = 1$   $J = 4$

E8C.8(b)  $S = 2, 1, 0$   $5, 3, 0$   $S = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$  6, 4, 2

E8C.9(b)  $S = \frac{3}{2}, \frac{1}{2}$   $M_S = \pm \frac{3}{2}, \pm \frac{1}{2}$   $M_S = \pm \frac{1}{2}$

E8C.10(b)  ${}^3F_4, {}^3F_3, {}^3F_2, {}^3D_3, {}^3D_2, {}^3D_1, {}^3P_2, {}^3P_1, {}^3P_0, {}^1F_3, {}^1D_2, {}^1P_1, {}^3F_2$

E8C.11(b)  $J = 3, 2, 1$  7, 5, 3  $J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$  8, 6, 4, 2  $J = \frac{9}{2}, \frac{7}{2}$  10, 8

E8C.12(b)  ${}^1S_0$   ${}^2P_{3/2}, {}^2P_{1/2}$

**E8C.13(b)**  $+(3/2)hc\tilde{A}$   $-2hc\tilde{A}$

**E8C.14(b)** allowed allowed forbidden

**P8C.2** 397.13 nm  $5.4466 \times 10^{-19}$  J

**P8C.4**  $109\,740\text{ cm}^{-1}$   $137\,175\text{ cm}^{-1}$   $185\,186\text{ cm}^{-1}$  122.45 eV

**P8C.8**  $m_{\text{D}} = 3.345\,19 \times 10^{-27}$  kg 2.014 52  $m_{\text{u}}$  0.999 728

**P8C.10**  $0.94\text{ cm}^{-1}$  very small

**I8.2**  $4.357 \times 10^{-24}$  J 15 000  $a_0$   $2.179 \times 10^{-22}$  J  $510\text{ m s}^{-1}$

## 9 Molecular Structure

### 9A Valence-bond theory

### 9B Molecular orbital theory: the hydrogen molecule-ion

$$\text{E9B.1(b)} \quad N = 1/(1 + \lambda^2 + \lambda'^2 + 2\lambda S + 2\lambda' S)^{1/2}$$

$$\text{E9B.2(b)} \quad \psi_a = 0.960A + 0.190B \quad \psi_j = 0.304A - 0.989B$$

$$\text{P9B.2} \quad 8.7 \times 10^{-7} \quad 8.7 \times 10^{-7} \quad 3.6 \times 10^{-7} \quad 4.9 \times 10^{-7} \quad 1.9 \times 10^{-6} \quad 1.9 \times 10^{-6} \quad 0 \quad 5.5 \times 10^{-7}$$

### 9C Molecular orbital theory: homonuclear diatomic molecules

$$\text{E9C.1(b)} \quad \frac{1}{2} \quad 3 \quad 1$$

$$\text{E9C.4(b)} \quad \text{In order of increasing atomic number } X_2^+: \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \quad X_2^-: \frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}$$

$$\text{E9C.6(b)} \quad 1.78 \times 10^6 \text{ m s}^{-1}$$

$$\text{P9C.2} \quad R = 2.10 a_0$$

$$\text{P9C.4} \quad 10.20 \text{ eV} \quad 12.98 \text{ eV} \quad 5.99 \text{ eV}$$

### 9D Molecular orbital theory: heteronuclear diatomic molecules

$$\text{E9D.5(b)} \quad \alpha_{\text{H}} = -7.18 \text{ eV} \quad \alpha_{\text{Br}} = -7.59 \text{ eV}$$

$$\text{E9D.6(b)} \quad E_- = -8.40 \text{ eV} \quad E_+ = -6.36 \text{ eV}$$

$$\text{E9D.7(b)} \quad E_- = -8.02 \text{ eV} \quad E_+ = -6.95 \text{ eV}$$

$$\text{P9D.2} \quad E_n (c_A, c_B, c_C): E_1 = -10.7 \text{ eV} (0.294, 0.950, 0.102) \quad E_2 = -8.71 \text{ eV} (0.349, -0.206, 0.914)$$

$$E_3 = -6.58 \text{ eV} (0.890, -0.233, -0.392) \quad E_1 = -10.9 \text{ eV} \quad E_2 = -8.86 \text{ eV} \quad E_3 = -6.93 \text{ eV}$$

### 9E Molecular orbital theory: polyatomic molecules

$$\text{E9E.2(b)} \quad 3\alpha + 2.82\beta \quad 3\alpha + 4\beta$$

$$\text{E9E.3(b)} \quad E_{\text{deloc}} = -0.18\beta \quad E_{\text{bf}} = 2.82\beta \quad E_{\text{deloc}} = \beta \quad E_{\text{bf}} = 4\beta$$

$$\text{E9E.5(b)} \quad 10\alpha + 13.4\beta \quad 12\alpha + 16.6\beta$$

$$\text{P9E.2} \quad \text{benzene: } E_0 = \alpha + 2\beta, E_{\pm 1} = \alpha + \beta, E_{\pm 2} = \alpha - \beta, E_{+3} = \alpha - 2\beta \quad E_{\pi} = 6\alpha + 8\beta$$

$$E_{\text{deloc}} = 2\beta \quad \text{cyclooctatetraene: } E_0 = \alpha + 2\beta, E_{\pm 1} = \alpha + 1.41\beta, E_{\pm 2} = \alpha, E_{\pm 3} = \alpha - 1.41\beta,$$

$$E_{+4} = \alpha - 2\beta \quad \text{hexatriene: } E_{\pi} 6\alpha + 6.98\beta \quad E_{\text{deloc}} = 0.99\beta \quad \text{octatetraene: } E_{\pi} = 8\alpha + (9.51)\beta$$

$$E_{\text{deloc}} = 1.52\beta$$

### 9E Integrated activities

$$\mathbf{19.6} \quad 3.09 \times 10^4 \text{ cm}^{-1}$$

# 10 Molecular symmetry

## 10A Shape and symmetry

E10A.2(b)  $C_{2h}$

E10A.3(b)  $C_{\infty v}$   $D_{2h}$   $C_s$   $D_{3h}$   $D_3$

E10A.4(b)  $C_{2v}$   $C_{2v}$   $C_3$

E10A.5(b)  $C_{\infty v}$   $C_{5h}$   $C_{2v}$   $D_{3h}$   $O_h$   $T_d$

P10A.2 SF<sub>6</sub>:  $O_h$  SF<sub>5</sub>Cl:  $C_{4v}$  *trans*-SF<sub>4</sub>Cl<sub>2</sub>:  $D_{4h}$  *cis*-SF<sub>4</sub>Cl<sub>2</sub>:  $C_{2v}$  *fac*-SF<sub>3</sub>Cl<sub>3</sub>:  $C_{3v}$  *mer*-SF<sub>3</sub>Cl<sub>3</sub>:  $C_{2v}$

P10A.4 All *trans*:  $D_{2h}$  A, B or C *trans*:  $C_{2v}$  All *cis*:  $C_1$

P10A.6  $D_{2d}$

## 10B Group theory

$$\text{E10B.1(b)} \quad D(C_3) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\text{E10B.2(b)} \quad D(C_3)D(\sigma_h) = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix} \quad S_3 \text{ operation}$$

E10B.5(b)  $A_{1g}$   $A_{2u}$   $E_u$   $A_{1g}$   $B_{1g}$   $B_{2g}$   $E_g$

E10B.6(b) five

E10B.7(b) one

## 10C Applications of symmetry

E10C.1(b) zero

E10C.2(b) forbidden

E10C.4(b)  $B_2$   $A_1$   $2s$   $2p_z$   $2p_y$

E10C.5(b)  $p_z$   $d_{yz}$  and  $d_{zx}$

E10C.6(b)  $A_2$

E10C.7(b)  $A_1 + B_1 + 2B_2 + 2B_3$

E10C.8(b)  $A_{1g} + E_g + T_{1u}$

E10C.9(b)  $B_{3u}$ ,  $B_{2u}$ , or  $B_{1u}$   $A_{2u}$  or  $E_{1u}$

P10C.2 yes yes

P10C.4 not allowed  $T_1$  are allowed G are not

**P10C.6** is allowed

$$\begin{aligned}
 \text{P10C.8 } \psi^{(B_{2g})} &= \frac{1}{4}(p_A - p_B - p_C + p_D) & \psi^{(B_{3g})} &= \frac{1}{4}(p_A + p_B - p_C - p_D) & \psi^{(A_u)} &= \frac{1}{4}(p_A - p_B + \\
 p_C - p_D) & \psi^{(B_{1u})} &= \frac{1}{4}(p_A - p_B + p_C - p_D) & A_g + B_{1g} + B_{2u} + B_{3u} & \psi^{(A_g)} &= \frac{1}{4}(p_A - p_B - p_C + p_D) \\
 \psi^{(B_{1g})} &= \frac{1}{4}(p_A + p_B - p_C - p_D) & \psi^{(B_{2u})} &= \frac{1}{4}(p_A - p_B + p_C - p_D) & \psi^{(B_{3u})} &= \frac{1}{4}(p_A + p_B + p_C + p_D)
 \end{aligned}$$

# 11 Molecular Spectroscopy

## 11A General features of molecular spectroscopy

E11A.1(b)  $7.73 \times 10^{-32} \text{ J s m}^{-3}$   $6.2 \times 10^{-28} \text{ J s m}^{-3}$

E11A.2(b) 23.2%

E11A.3(b)  $\epsilon = 1.18 \times 10^6 \text{ cm}^2 \text{ mol}^{-1}$

E11A.4(b) 1.04 mM

E11A.6(b)  $\epsilon = 58 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$   $T = 54\%$

E11A.7(b) 1.0 cm 3.3 cm

E11A.8(b)  $4.44 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

E11A.9(b)  $2.92 \times 10^{-3} \text{ cm}^{-1}$

E11A.10(b)  $7.31 \times 10^7 \text{ m s}^{-1}$

E11A.11(b) 796 ps 2.17 ps

E11A.12(b) 0.16 GHz 16 MHz

P11A.6  $\mathcal{A} = 4.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$   $\mathcal{A} = 4.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$

P11A.8 receding  $3.38 \times 10^5 \text{ m s}^{-1}$

## 11B Rotational spectroscopy

E11B.1(b)  $7.16 \times 10^{-47} \text{ kg m}^2$   $3.91 \text{ cm}^{-1}$

E11B.4(b)  $R_{\text{OC}} = 0.1161 \text{ nm}$   $R_{\text{CS}} = 0.1561 \text{ nm}$

E11B.5(b)  $2.028 \times 10^{-8} \text{ cm}^{-1}$  0.98

E11B.6(b) All

E11B.7(b)  $7.729 \text{ cm}^{-1}$  231.7 GHz

E11B.8(b) 141.4 pm

E11B.9(b)  $5.420 \times 10^{-46} \text{ kg m}^2$  162.8 pm

E11B.10(b) 35 40

E11B.11(b)  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CH}_3$  and  $\text{N}_2\text{O}$

E11B.12(b)  $20\,603 \text{ cm}^{-1}$

E11B.13(b) 141.79 pm

P11B.4  $2.6832 \times 10^{-47} \text{ kg m}^2$  128.4 pm

P11B.6  $B = 3013.8 \text{ MHz}$  219 pm

P11B.8  $\tilde{B} = 1.922\,529 \text{ cm}^{-1}$   $\tilde{D}_J = 6.128 \times 10^{-6} \text{ cm}^{-1}$

P11B.10  $\tilde{\nu}(J, K) = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3 - 2\tilde{D}_{JK}(J+1)K^2$   $D_{JK} = 0.45 \text{ MHz}$   $D_J = 0.042 \text{ MHz}$   $B = 25.536 \text{ GHz}$

P11B.14  $R_{\text{CC}} = 139.7 \text{ pm}$   $R_{\text{CH}} = 108.4 \text{ pm}$

## 11C Vibrational spectroscopy of diatomic molecules

**E11C.1(b)**  $3.95 \text{ N m}^{-1}$

**E11C.2(b)** 28.38%

**E11C.3(b)**  $245.9 \text{ N m}^{-1}$

**E11C.4(b)**  $\tilde{\nu}_{\text{f}, 2\text{H}^{19}\text{F}} = 3002.3 \text{ cm}^{-1}$   $\tilde{\nu}_{\text{f}, 2\text{H}^{35}\text{Cl}} = 2143.7 \text{ cm}^{-1}$   $\tilde{\nu}_{\text{f}, 2\text{H}^{81}\text{Br}} = 1885.8 \text{ cm}^{-1}$

$\tilde{\nu}_{\text{f}, 2\text{H}^{127}\text{I}} = 1640.1 \text{ cm}^{-1}$

**E11C.5(b)** 0.212 0.561

**E11C.6(b)**  $2358.5 \text{ cm}^{-1}$   $6.07 \times 10^{-3}$

**E11C.7(b)**  $3.24 \times 10^4 \text{ cm}^{-1}$  4.02 eV

**E11C.8(b)**  $2615.1 \text{ cm}^{-1}$

**P11C.2**  $2hc\tilde{D}_e a^2$

**P11C.4**  $k_{\text{f}} = 93.8 \text{ N m}^{-1}$   $\tilde{G}(0) = 142.81 \text{ cm}^{-1}$   $\tilde{D}_0 = 2.71 \times 10^4 \text{ cm}^{-1}$

**P11C.8**  $v_{\text{max}} = 1/2x_e - \frac{1}{2}$

**P11C.10** 112.8 pm 123.5 pm

**P11C.12**  $\tilde{B}_1 = 10.11 \text{ cm}^{-1}$   $\tilde{B}_0 = 10.42 \text{ cm}^{-1}$

**P11C.18**  $\tilde{B}_1 = 1.905 \text{ cm}^{-1}$   $\tilde{B}_0 = 1.923 \text{ cm}^{-1}$

## 11D Vibrational spectroscopy of polyatomic molecules

**E11D.1(b)**  $\text{CH}_3\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$

**E11D.2(b)** 30 39 13

**E11D.3(b)** 103

**E11D.4(b)**  $\frac{1}{2}(\tilde{\nu}_1 + \tilde{\nu}_2 + \tilde{\nu}_3)$

**E11D.5(b)** infrared active not Raman active

**E11D.6(b)** infrared active not Raman active

**E11D.7(b)** does apply

## 11E Symmetry analysis of vibrational spectroscopy

**E11E.1(b)**  $A_{1g} + A_{1u} + E_{1u}$

**E11E.2(b)**  $A_{1u}$  and  $E_{1u}$  infrared active  $A_{1g}$  Raman active

**E11E.3(b)** All All

**P11E.2** 7  $C_{2h}$   $C_{2v}$   $C_2$

## 11F Electronic spectra

**E11F.1(b)**  $\sigma_g^1 \pi_u^1$

**E11F.2(b)**  $^2\Pi_g$

**E11F.3(b)** 5 3 0 g

**E11F.5(b)**  $I^2 = (ax_0^2/2)e^{-ax_0^2/2}$

**E11F.6(b)**  $I^2 = 1/\pi^2$

$$\text{E11F.7(b)} \frac{\tilde{B} - 3\tilde{B}'}{2(\tilde{B}' - \tilde{B})}$$

**E11F.8(b)** P branch  $J = 64$

**E11F.9(b)**  $5.65 \text{ cm}^{-1}$  to  $5.66 \text{ cm}^{-1}$  decreased

**E11F.10(b)**  $3.28 \times 10^4 \text{ cm}^{-1}$  4.07 eV

$$\text{E11F.11(b)} \frac{1 - c^2}{(1 - c)^{1/2}} \frac{a}{2}$$

**E11F.12(b)** zero

**P11F.2**  ${}^2\Sigma_g^+$   ${}^2\Pi_g$

**P11F.4**  $\tilde{D}'_0 = 6815 \text{ cm}^{-1} = 0.8450 \text{ eV}$   $4.10 \times 10^4 \text{ cm}^{-1} = 5.08 \text{ eV}$

**P11F.8** increases

## 11G Decay of excited states

**P11G.4**  $l_C = 0.10 \text{ m}$   $\Delta\lambda \rightarrow 0$

**P11G.6** 0.41 ns

## 11G Integrated activities

**11I.2** 87.64 pm or 89.87 pm  $\tilde{B} = 43.87 \text{ cm}^{-1}$   $\tilde{C} = 21.94 \text{ cm}^{-1}$   $\tilde{\nu}_D = 1783.8 \text{ cm}^{-1}$

$\tilde{B}_D = 21.79 \text{ cm}^{-1}$   $\tilde{C}_D = 10.36 \text{ cm}^{-1}$

**11I.4**  $796 \text{ cm}^{-1}$   $\text{Fe}_2^{3+}\text{O}_2^{2-}$

## 12 Magnetic resonance

### 12A General principles

E12A.1(b)  $\text{A s kg}^{-1}$

E12A.2(b)  $\sqrt{2}\hbar \quad 0, \pm\hbar \quad 0, \pm 0.7854 \text{ rad (or } 0^\circ, \pm 45.00^\circ)$

E12A.3(b) 685 MHz

E12A.4(b)  $E_0 = 0$  and  $E_{\pm 1} = \mp 2.14 \times 10^{-26} \text{ J}$

E12A.5(b) 44.2 MHz

E12A.6(b)  $\Delta E(^{14}\text{N}) = 2.87 \times 10^{-26} \text{ J}$     $\Delta E(e) = 5.57 \times 10^{-24} \text{ J}$

E12A.7(b)  $4.3 \times 10^{-7} \quad 2.2 \times 10^{-6} \quad 1.34 \times 10^{-5}$

E12A.8(b) 0.2

E12A.9(b) 0.33 GHz

P12A.4  $I \propto 2 \sin [\cos^{-1} (z/r)]$

### 12B Features of NMR spectra

E12B.1(b) 150

E12B.2(b) -14.98

E12B.3(b) 2450 Hz

E12B.4(b) 125

E12B.5(b)  $4.2 \mu\text{T} \quad 36.3 \mu\text{T}$

E12B.9(b) 1:2:3:2:1 multiplet

E12B.11(b) 1:3:6:10:15:21:25:27:27:25:21:15:10:6:3:1 multiplet

E12B.14(b)  $1.0 \times 10^3 \text{ s}^{-1}$

P12B.6  $580 - 78.9 \cos \phi + 394 \cos 2\phi$  trans

### 12C Pulse techniques in NMR

E12C.1(b)  $1.2 \text{ mT} \quad 10 \mu\text{s}$

E12C.2(b) 0.027 s

E12C.3(b) 0.035 s

E12C.5(b) 0.5313

P12C.8 0.72 s

P12C.12 -0.578 mT

### 12D Electron paramagnetic resonance

E12D.1(b) 2.0022

**E12D.2(b)**  $a = 2.2 \text{ mT}$  1.9921

**E12D.3(b)** 328.865, 330.975, 331.735, 331.755, 333.845, 333.865, 334.625 and 336.735 mT equal intensity

**E12D.5(b)** 339.0 mT 1.241 T

**E12D.6(b)**  $I = 1$

**P12D.2** parallel: 1.992 bisector: 2.002

**I12.4**  $[I]_0 = \frac{\Delta\nu}{\delta\nu} [E]_0 - K_I$

## 13 Statistical thermodynamics

### 13A The Boltzmann distribution

E13A.1(b)  $2.05 \times 10^{12}$

E13A.2(b) 3 628 800  $4.54 \times 10^5$   $3.60 \times 10^6$

E13A.3(b) 0

E13A.4(b) 623 K

E13A.5(b) 81.7

E13A.6(b) 213 K

P13A.2  $\{N_0, N_1, N_2, N_3, N_4, N_5, N_6, N_7, N_8, N_9\} = \{4, 2, 2, 1, 0, 0, 0, 0, 0, 0\}$

P13A.4 0.092

### 13B Partition functions

E13B.1(b)  $2.244 \times 10^{-11}$  m  $8.85 \times 10^{25}$  at 300 K  $7.095 \times 10^{-12}$  m  $2.80 \times 10^{27}$  at 3000 K

E13B.2(b) 2.785

E13B.3(b) 52.2

E13B.4(b) 43.1 60.4

E13B.5(b) 61 K

E13B.6(b) 0.4 K

E13B.7(b)  $\sigma = 2$   $\sigma = 2$   $\sigma = 3 \times 2 = 6$   $\sigma = 24$   $\sigma = 4$

E13B.8(b)  $4.26 \times 10^4$

E13B.9(b) 3000 K

E13B.10(b) 2.25

E13B.11(b)  $3.43 \times 10^3$

E13B.12(b) 5.809 1 : 0.181 : 0.755

P13B.4 0.030 K 9.57

P13B.6  $\frac{N(^3F_2)}{N} = 0.257$   $\frac{N(^3F_3)}{N} = 0.336$   $\frac{N(^3F_4)}{N} = 0.396$   $\frac{N(^5F_1)}{N} = 0.0109$

P13B.8  $q^R = 19.90$

P13B.10 at 100 K  $q^V = 1.05$   $\frac{N_0}{N} = 0.955$   $\frac{N_1}{N} = 4.31 \times 10^{-2}$   $\frac{N_2}{N} = 2.10 \times 10^{-3}$  at 298 K  
 $q^V = 1.54$   $\frac{N_0}{N} = 0.647$   $\frac{N_1}{N} = 0.229$   $\frac{N_2}{N} = 8.30 \times 10^{-2}$

### 13C Molecular energies

E13C.1(b)  $1.23 \times 10^{-21}$  J

E13C.2(b) 66.2 K

E13C.3(b) 0.29 K

E13C.4(b)  $3.19 \times 10^3$  K

- E13C.5(b)**  $2.52 \times 10^4$  K  
**E13C.6(b)**  $3.92 \times 10^3$  K  
**E13C.7(b)**  $1.01 \times 10^{-20}$  J  
**P13C.2**  $\varepsilon \left( \frac{e^{\beta\varepsilon} + 2}{e^{2\beta\varepsilon} + e^{\beta\varepsilon} + 1} \right)$   
**P13C.4**  $(36.4 \text{ K cm}) \times \tilde{\nu}$   
**P13C.8**  $1.0 \times 10^2$  K  $a + 1$

## 13D The canonical ensemble

### 13E The internal energy and entropy

- E13E.1(b)**  $3R$   $3R$   $\frac{5}{2}R$   
**E13E.2(b)** Without vibrational contribution:  $\gamma = 1.40$  With vibrational contribution:  $\gamma = 1.15$   
**E13E.3(b)**  $1.92 \times 10^{-9} \text{ J K}^{-1} \text{ mol}^{-1}$   
**E13E.4(b)**  $S_m^V = 5.88 \text{ J K}^{-1} \text{ mol}^{-1}$   $S_m^V = 16.5 \text{ J K}^{-1} \text{ mol}^{-1}$   
**E13E.5(b)**  $144.9 \text{ J K}^{-1} \text{ mol}^{-1}$   $156.0 \text{ J K}^{-1} \text{ mol}^{-1}$   
**E13E.6(b)** 174 K  
**E13E.7(b)** 5837  $84.57 \text{ J K}^{-1} \text{ mol}^{-1}$   
**E13E.8(b)**  $14.89 \text{ J K}^{-1} \text{ mol}^{-1}$   
**E13E.9(b)**  $S_m^V = 5.88 \text{ J K}^{-1} \text{ mol}^{-1}$   $S_m^V = 16.5 \text{ J K}^{-1} \text{ mol}^{-1}$   
**P13E.2** At 50 K:  $C_{V,m}/R = 4.49 \times 10^{-3}$  0.15% At 298 K:  $C_{V,m}/R = 1.27 \times 10^{-4}$   $4.2 \times 10^{-3}$  %  
**P13E.8**  $5.41 \text{ J K}^{-1} \text{ mol}^{-1}$   
**P13E.10**  $191.5 \text{ J K}^{-1} \text{ mol}^{-1}$   
**P13E.16**  $c_s = (1.40RT/M)^{1/2}$   $c_s = (1.40RT/M)^{1/2}$   $c_s = (3RT/4M)^{1/2}$   $346 \text{ m s}^{-1}$   
**P13E.18**  $kT/\varepsilon = 0.417$

### 13F Derived functions

- E13F.1(b)**  $G_m^R = -20.11 \text{ kJ mol}^{-1}$   $G_m^V = -0.112 \text{ kJ mol}^{-1}$   
**E13F.2(b)**  $-3.65 \text{ kJ mol}^{-1}$   
**E13F.3(b)** 0.250  
**P13F.2**  $K = 3.90$   $K = 2.42$   
**P13F.4**  $-512 \text{ kJ mol}^{-1}$   
**P13F.6**  $G_m^\circ(10.00) - G_m^\circ(0) = -798 \text{ J mol}^{-1}$   $G_m^\circ(100.0) - G_m^\circ(0) = -15.7 \text{ kJ mol}^{-1}$

## 14 Molecular Interactions

### 14A Electric properties of molecules

E14A.2(b) 2.3 D

E14A.3(b) 28 D 14°

E14A.4(b)  $7.1 \times 10^3 \text{ V m}^{-1}$

E14A.5(b) 0.9690 D  $2.552 \times 10^{-39} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$

E14A.6(b) 8.97

E14A.7(b)  $3.40 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$

E14A.8(b) 1.1

E14A.9(b) 15

P14A.4 Nitrogen  $-0.123e$  Carbon  $+0.123e$

P14A.6 196 pm

P14A.10 1.85 D  $1.30 \times 10^{-24} \text{ cm}^3$

### 14B Interactions between molecules

E14B.1(b)  $2.31 \times 10^{-19} \text{ J}$   $139 \text{ kJ mol}^{-1}$

E14B.2(b)  $-2.6 \times 10^{-24} \text{ J}$   $-1.6 \text{ J mol}^{-1}$

E14B.3(b)  $\frac{9Q^2l^4}{4\pi\epsilon_0r^5}$

E14B.4(b)  $-6.9 \times 10^{-23} \text{ J}$   $-41 \text{ J mol}^{-1}$

E14B.5(b)  $-2.1 \text{ J mol}^{-1}$

E14B.6(b)  $3.1 \text{ J mol}^{-1}$

P14B.2 In a vacuum  $4.8 \times 10^{-19} \text{ J}$   $2.9 \times 10^2 \text{ kJ mol}^{-1}$  In water  $6.0 \times 10^{-21} \text{ J}$   $3.6 \text{ kJ mol}^{-1}$

P14B.4  $-1.1 \times 10^8 \text{ V m}^{-1}$   $-4.1 \times 10^9 \text{ V m}^{-1}$   $-4.1 \times 10^3 \text{ V m}^{-1}$

P14B.6  $-9.6 \text{ kJ mol}^{-1}$   $-\frac{9\alpha'^2I}{2r^7}$

### 14C Liquids

E14C.1(b) 5.9 kPa

E14C.2(b)  $71.2 \text{ mN m}^{-1}$

E14C.3(b) 204 kPa

E14C.4(b)  $139.7 \text{ mN m}^{-1}$

P14C.2  $4.1 \times 10^{-7} \text{ mol m}^{-2}$

### 14D Macromolecules

**E14D.1(b)**  $\overline{M}_n = 68 \text{ kg mol}^{-1}$   $\overline{M}_w = 69 \text{ kg mol}^{-1}$

**E14D.2(b)** 38.97 nm

**E14D.3(b)**  $R_c = 1.27 \text{ }\mu\text{m}$   $R_{\text{rms}} = 19.8 \text{ nm}$

**E14D.4(b)**  $1.8 \times 10^3$

**E14D.5(b)**  $9.8 \times 10^{-3}$

**E14D.6(b)**  $6.3 \times 10^{-3}$

**E14D.7(b)** +73.2% +420%

**E14D.8(b)** +600%  $+(3.42 \times 10^4)\%$

**E14D.9(b)** 0.19 nm

**E14D.10(b)**  $2.9 \times 10^{-14} \text{ N}$

**E14D.11(b)**  $-0.058 \text{ J K}^{-1} \text{ mol}^{-1}$

**P14D.2**  $R_{\text{rms}} = N^{1/2}l$   $\langle r \rangle = \left(\frac{8N}{3\pi}\right)l$   $r_{\text{mp}} = \left(\frac{2N}{3}\right)^{1/2}l$   $R_{\text{rms}} = 9.74 \text{ nm}$   $\langle r \rangle = 8.97 \text{ nm}$   
 $r_{\text{mp}} = 7.95 \text{ nm}$

**P14D.8**  $\frac{1}{2\pi l} \left(\frac{RT}{M}\right)^{1/2}$  3.2 GHz

## 14E Self-assembly

**E14E.1(b)** 4.0

**I14.2**  $1.51 \times 10^{-23} \text{ J}$  265 pm

**I14.4**  $\mu = 3.695 \text{ D}$

**I14.8**  $0.39 \text{ m}^3 \text{ mol}^{-1}$   $1.1 \text{ m}^3 \text{ mol}^{-1}$

## 15 Solids

### 15A Crystal structure

E15A.1(b)  $N = 5$   $2.90 \text{ g cm}^{-3}$

E15A.2(b)  $(\bar{2}1\bar{2})$  and  $(\bar{4}1\bar{1})$

E15A.3(b)  $d_{123} = 190 \text{ pm}$   $d_{222} = 206 \text{ pm}$   $d_{246} = 95.1 \text{ pm}$

E15A.4(b)  $200 \text{ pm}$

P15A.2  $abc \sin \beta$

P15A.4  $3.96 \times 10^{-28} \text{ m}^3$

P15A.6  $1.01 \text{ g cm}^{-3}$

P15A.8  $1.99 \text{ g cm}^{-3}$   $2.19 \text{ g cm}^{-3}$

### 15B Diffraction techniques

E15B.1(b)  $67.1 \text{ pm}$

E15B.2(b)  $15.9^\circ$   $18.5^\circ$   $26.6^\circ$

E15B.3(b)  $4.166^\circ$ ,  $3.001^\circ$  and  $7.057^\circ$

E15B.4(b)  $1.61^\circ$

E15B.5(b)  $f(0) = 10$

E15B.6(b) for  $(h+k+l)$  even  $F_{hkl} = 2f$  for  $(h+k+l)$  odd  $F_{hkl} = 0$

E15B.7(b) for  $(h+k+l)$  odd  $F_{hkl} = -f$  for  $(h+k+l)$  even  $F_{hkl} = 3f$

E15B.11(b)  $6.93 \times 10^3 \text{ km s}^{-1}$

E15B.12(b)  $9.58 \text{ nm}$

P15B.2 cubic P  $a = 344 \text{ pm}$

P15B.4  $629 \text{ pm}$

P15B.6 0

P15B.8 Neutrons  $\theta_{\max} = 0$   $\theta_{\min} = 14.0^\circ$  Electrons  $\theta_{\max} = 0$   $\theta_{\min} = 0.72^\circ$   $R_{\text{CCl}} = 178 \text{ pm}$

### 15C Bonding in solids

E15C.1(b)  $\frac{2}{3}$

E15C.2(b)  $0.3702$

E15C.3(b)  $61.7 \text{ pm}$   $109 \text{ pm}$

E15C.4(b) contract by 1.2%

E15C.5(b)  $2421 \text{ kJ mol}^{-1}$

P15C.2  $0.907$

P15C.8  $\Delta H_{\text{L}} = 685 \text{ kJ mol}^{-1}$   $\Delta_{\text{f}}H^\circ = -146 \text{ kJ mol}^{-1}$

**P15C.10**  $A = 4 \ln 2 = 2.773$

### 15D The mechanical properties of solids

**E15D.1(b)**  $0.97 \text{ cm}^3$

**E15D.2(b)**  $17 \text{ N}$

**E15D.3(b)**  $3.3 \times 10^{-3} \text{ dm}^3$

**P15D.2**  $7.7 \text{ kJ mol}^{-1}$

### 15E The electrical properties of solids

**E15E.1(b)**  $0.731$

**E15E.2(b)**  $2.06 \text{ eV}$

**E15E.3(b)** p-type

**P15E.2**  $3.2 \text{ eV}$

**P15E.4**  $0.736 \text{ eV}$

**P15E.6**  $0.406$

### 15F The magnetic properties of solids

**E15F.1(b)** four

**E15F.2(b)**  $-8.2 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$

**E15F.3(b)**  $2.5$

**E15F.4(b)**  $1.85 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$

**E15F.5(b)**  $2.1 \text{ K}$

### 15G The optical properties of solids

**E15G.1(b)**  $1.11 \text{ } \mu\text{m}$

**P15G.2** For  $N = 5$ ,  $\tilde{\nu}_{\min} = 2.277 \times 10^4 \text{ cm}^{-1}$  For  $N = 10$ ,  $\tilde{\nu}_{\min} = 2.253 \times 10^4 \text{ cm}^{-1}$  For  $N = 15$ ,  $\tilde{\nu}_{\min} = 2.247 \times 10^4 \text{ cm}^{-1}$  For large  $N$ ,  $\tilde{\nu}_{\min} = 2.242 \times 10^4 \text{ cm}^{-1}$  independent of chain size

## 16 Molecules in motion

### 16A Transport properties of a perfect gas

**E16A.1(b)**  $5.3 \times 10^{22}$

**E16A.2(b)**  $1.48 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$   $-0.73 \text{ mol m}^{-2} \text{ s}^{-1}$   $1.48 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$   $-7.3 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$   $7.38 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$   $-3.6 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$

**E16A.3(b)**  $1.3 \times 10^{-2} \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$

**E16A.4(b)**  $0.218 \text{ nm}^2$

**E16A.5(b)**  $-0.11 \text{ J m}^{-2} \text{ s}^{-1}$

**E16A.6(b)**  $67 \text{ W}$

**E16A.7(b)**  $1.34 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$   $1.40 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$   $2.56 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$

**E16A.8(b)**  $0.424 \text{ nm}^2$

**E16A.9(b)**  $489 \text{ mg}$

**E16A.10(b)**  $1.09 \times 10^3 \text{ Pa}$

**E16A.11(b)**  $555 \text{ g mol}^{-1}$

**E16A.12(b)**  $41.4 \text{ days}$

**P16A.2**  $9.13$

**P16A.4**  $7.28 \times 10^{-3} \text{ Pa}$

**P16A.6**  $p = p_0 e^{-\alpha t}$   $\alpha = \frac{A_0}{V} \left( \frac{RT}{2\pi M} \right)^{1/2}$  or  $p = p_0 e^{-t/\tau}$   $\tau = \frac{V}{A_0} \left( \frac{2\pi M}{RT} \right)^{1/2}$   $t_{1/2} = \frac{V \ln 2}{A_0} \left( \frac{2\pi M}{RT} \right)^{1/2}$

### 16B Motion in liquids

**E16B.1(b)**  $2.64 \text{ kJ mol}^{-1}$

**E16B.2(b)**  $21.68 \text{ mS m}^2 \text{ mol}^{-1}$

**E16B.3(b)**  $u_{\text{Li}^+} = 4.01 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$   $u_{\text{Na}^+} = 5.19 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$   $u_{\text{K}^+} = 7.62 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$

**E16B.4(b)**  $4.09 \text{ mS m}^2 \text{ C}^{-1}$

**E16B.5(b)**  $192 \text{ } \mu\text{m s}^{-1}$

**E16B.6(b)**  $1.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

**P16B.2**  $14.3 \text{ kJ mol}^{-1}$

**P16B.4**  $6.13 \text{ S cm}^2 \text{ mol}^{-1}$

**P16B.6**  $s_{\text{Li}^+} = 80.2 \text{ } \mu\text{m s}^{-1}$   $t_{\text{Li}^+} = 623 \text{ s}$   $s_{\text{Na}^+} = 104 \text{ } \mu\text{m s}^{-1}$   $t_{\text{Na}^+} = 481 \text{ s}$   $s_{\text{K}^+} = 152 \text{ } \mu\text{m s}^{-1}$   $t_{\text{K}^+} = 329 \text{ s}$   $d(\text{Li}^+) = 12.8 \text{ nm} = 43 \text{ solvent diameters}$   $d(\text{Na}^+) = 16.5 \text{ nm} = 55 \text{ solvent diameters}$   $d(\text{K}^+) = 24.3 \text{ nm} = 81 \text{ solvent diameters}$

**P16B.8**  $D_{\text{Li}^+} = 1.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$   $a_{\text{Li}^+} = 238 \text{ pm}$   $D_{\text{Na}^+} = 1.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$   $a_{\text{Na}^+} = 184 \text{ pm}$   $D_{\text{K}^+} = 1.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$   $a_{\text{K}^+} = 125 \text{ pm}$   $D_{\text{Rb}^+} = 2.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$   $a_{\text{Rb}^+} =$

120 pm  $N_w(\text{Li}^+) = 4$   $N_w(\text{Na}^+) = 1$  to 2

### 16C Diffusion

**E16C.1(b)**  $7.4 \times 10^3$  s

**E16C.2(b)**  $0.00 \text{ mol dm}^{-3}$   $0.199 \text{ mol dm}^{-3}$

**E16C.3(b)** at  $x = 8 \text{ cm}$   $\mathcal{F} = 5.4 \text{ kN mol}^{-1}$  at  $x = 16 \text{ cm}$   $\mathcal{F} = 7.3 \text{ kN mol}^{-1}$

**E16C.4(b)**  $33.5 \text{ kN mol}^{-1}$

**E16C.5(b)**  $4.1 \times 10^3$  s

**E16C.6(b)**  $0.207 \text{ nm}$

**E16C.7(b)**  $20.1 \text{ ps}$

**E16C.8(b)** Benzene  $t(1.0 \text{ mm}) = 78 \text{ s}$   $t(1.0 \text{ cm}) = 2.2 \text{ h}$  Sucrose  $t(1.0 \text{ mm}) = 320 \text{ s}$   $t(1.0 \text{ cm}) = 8.9 \text{ h}$

**P16C.2**  $(5.0 \text{ MN mol}^{-1}) \times (x/\text{m})$   $(8.2 \times 10^{-18} \text{ N molecule}^{-1}) \times (x/\text{m})$

**P16C.4**  $0.00 \text{ mol dm}^{-3}$   $4.25 \times 10^{-5} \text{ mol dm}^{-3}$

**P16C.8** 0 0.0156 0.0537

**P16C.10**  $1.7 \times 10^{-2} \text{ s}$

## 17 Chemical kinetics

### 17A The rates of chemical reactions

E17A.2(b)  $+0.6 \text{ mol dm}^{-3} \text{ s}^{-1}$

E17A.3(b)  $d[A]/dt = -2.7 \text{ mol dm}^{-3} \text{ s}^{-1}$   $d[B]/dt = -8.1 \text{ mol dm}^{-3} \text{ s}^{-1}$   $d[C]/dt = +2.7 \text{ mol dm}^{-3} \text{ s}^{-1}$   
 $d[D]/dt = +5.4 \text{ mol dm}^{-3} \text{ s}^{-1}$

E17A.4(b)  $v = 0.90 \text{ mol dm}^{-3} \text{ s}^{-1}$   $d[A]/dt = -0.90 \text{ mol dm}^{-3} \text{ s}^{-1}$   $d[C]/dt = +0.90 \text{ mol dm}^{-3} \text{ s}^{-1}$   
 $d[D]/dt = +1.8 \text{ mol dm}^{-3} \text{ s}^{-1}$

E17A.5(b)  $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$   $d[C]/dt = k_r[A][B]^2$   $-d[A]/dt = k_r[A][B]^2$

E17A.6(b)  $k_r[A][B][C]^{-1} \text{ s}^{-1}$

E17A.7(b) second-order  $\text{m}^3 \text{ molecules}^{-1} \text{ s}^{-1}$   $\text{Pa}^{-1} \text{ s}^{-1}$  third-order  $\text{m}^6 \text{ molecules}^{-2} \text{ s}^{-1}$   $\text{Pa}^{-2} \text{ s}^{-1}$

E17A.9(b) 1.00

P17A.21 second-order  $2.1 \times 10^9 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

### 17B Integrated rate laws

E17B.1(b)  $1.12 \times 10^{-4} \text{ s}^{-1}$

E17B.2(b) zeroth-order

E17B.3(b)  $9.74 \times 10^5 \text{ s}$   $33.0 \text{ kPa}$   $33.0 \text{ kPa}$

E17B.4(b)  $0.014 \text{ mol dm}^{-3}$   $0.027 \text{ mol dm}^{-3}$

E17B.5(b)  $1.6 \times 10^6 \text{ s}$

E17B.6(b)  $3.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   $t_{1/2}(\text{A}) = \text{infinite}$   $t_{1/2}(\text{B}) = 2.2 \times 10^3 \text{ s}$

P17B.4 first-order  $5.42 \times 10^{-2} \text{ h}^{-1}$   $0.97 \times 10^{-2} \text{ mol dm}^{-3}$

P17B.6  $5.7 \times 10^{-14} \text{ mol dm}^{-3} \text{ s}^{-1}$   $4.4 \times 10^8 \text{ s}$

P17B.8 first-order  $k_r = 0.175 \text{ min}^{-1}$   $k_r = 0.175 \text{ min}^{-1}$

P17B.10  $k_r = 3.670 \times 10^{-3} \text{ min}^{-1}$   $189 \text{ min}$

P17B.12  $1.18 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   $4.97 \text{ ms}$

P17B.14 first-order in propene third-order in HCL

P17B.16 
$$\frac{1}{2[B]_0 - 3[A]_0} \ln \frac{([B]_0 - 3x)[A]_0}{([A]_0 - 2x)[B]_0} = k_r t$$

P17B.18 
$$\frac{2^{n-1} - 1}{\left(\frac{4}{3}\right)^{n-1} - 1}$$

### 17C Reactions approaching equilibrium

E17C.1(b)  $7.5 \times 10^5 \text{ s}^{-1}$

E17C.2(b) 21 ms

P17C.4  $\frac{k_a}{k'_a} \times \frac{k_b}{k'_b} \times \frac{k_c}{k'_c} \times \dots$

**P17C.6**  $8.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   $1.7 \times 10^{-7} \text{ s}^{-1}$

### 17D The Arrhenius equation

**E17D.1(b)**  $5.6 \times 10^{30} \text{ s}$   $74 \text{ s}$

**E17D.2(b)**  $56.3 \text{ kJ mol}^{-1}$   $1.21 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

**E17D.3(b)**  $53 \text{ kJ mol}^{-1}$

**E17D.4(b)**  $298.9 \text{ K}$   $25.7 \text{ }^\circ\text{C}$

**E17D.5(b)**  $4.4 \times 10^{-9}$

**P17D.2**  $97.0 \text{ kJ mol}^{-1}$

**P17D.4**  $16.7 \text{ kJ mol}^{-1}$   $1.13 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

**P17D.6**  $2.5 \times 10^{-16} \text{ mol dm}^{-3} \text{ s}^{-1}$   $5.1 \times 10^{11} \text{ kg}$

### 17E Reaction mechanisms

**E17E.3(b)**  $+7 \text{ kJ mol}^{-1}$

**P17E.10**  $\frac{k_2 k'_1}{k'_2 k_1} = \frac{K_2}{K_1}$

### 17F Examples of reaction mechanisms

**E17F.1(b)**  $9.9 \times 10^{-6} \text{ Pa}^{-1} \text{ s}^{-1}$   $9.9 \text{ MPa}^{-1} \text{ s}^{-1}$

**E17F.2(b)**  $p = 0.981$   $\langle N \rangle = 51$

**E17F.3(b)**  $15.8$

**E17F.4(b)**  $0.212 \text{ mmol dm}^{-3} \text{ s}^{-1}$

**E17F.5(b)**  $3.7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

**P17F.2**  $k_r[M][\text{In}]^{-1/2}$

**P17F.4**  $\frac{k_b[E]_0}{1 + k'_a/k_a[S]_0}$

**P17F.8**  $0.0249 \text{ mol dm}^{-3}$   $4.80 \text{ mol dm}^{-3} \text{ s}^{-1}$

### 17G Photochemistry

**E17G.1(b)**  $8.88 \times 10^{21}$

**E17G.2(b)**  $7.4 \times 10^7 \text{ s}^{-1}$

**E17G.3(b)**  $0.038 \text{ mol dm}^{-3}$

**E17G.4(b)**  $2.9 \text{ nm}$

**P17G.2**  $5.9 \times 10^{-13} \text{ mol dm}^{-3} \text{ s}^{-1}$

**P17G.4**  $5.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

**P17G.6**  $3.5 \text{ nm}$

**I17.2**  $S \rightarrow I$  spreads if  $a/r < S$  Dies out if  $a/r > S$

$$\text{II7.4 } \frac{M_1 p^{1/2}}{1-p} M_1 \{k_r t[\text{A}]_0 (1 + k_r t[\text{A}]_0)\}^{1/2}$$

$$\text{II7.6 } \left(\frac{I_a}{k_r}\right)^{1/2}$$

## 18 Reaction dynamics

### 18A Collision theory

- E18A.1(b)  $7.90 \times 10^9 \text{ s}^{-1}$   $1.13 \times 10^{35} \text{ m}^{-3} \text{ s}^{-1}$  1.6%  
 E18A.2(b)  $2.45 \times 10^{-3}$   $f = 0.105$   $f = 7.64 \times 10^{-27}$   $f = 1.61 \times 10^{-10}$   
 E18A.3(b) 21% 2.8% 596% 32%  
 E18A.4(b)  $1.7 \times 10^{-15} \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}$   
 E18A.5(b)  $1.4 \times 10^{-3}$   
 E18A.6(b) 0.46  
 E18A.7(b)  $4.19 \times 10^{-5}$   
 P18A.2  $0.0039 \text{ nm}^2$  0.0065

### 18B Diffusion-controlled reactions

- E18B.1(b)  $3.1 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 E18B.2(b)  $1.97 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$   $2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 E18B.3(b)  $1.18 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$  42 ns  
 E18B.4(b)  $1.71 \times 10^{11} \text{ mol m}^{-3} \text{ s}^{-1}$   $4.81 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 P18B.4  $6.23 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$  0.4 nm

### 18C Transition-state theory

- E18C.1(b)  $46.8 \text{ kJ mol}^{-1}$   $-34.1 \text{ J K}^{-1} \text{ mol}^{-1}$   
 E18C.2(b)  $+44.1 \text{ kJ mol}^{-1}$   
 E18C.3(b)  $-124 \text{ J K}^{-1} \text{ mol}^{-1}$   
 E18C.4(b)  $-79 \text{ J K}^{-1} \text{ mol}^{-1}$   
 E18C.5(b)  $\Delta^\ddagger H = +25 \text{ kJ mol}^{-1}$   $\Delta^\ddagger S = -32 \text{ J K}^{-1} \text{ mol}^{-1}$   $\Delta^\ddagger G = +35 \text{ kJ mol}^{-1}$   
 E18C.6(b)  $k_r^\circ = 1.08 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$   
 E18C.7(b) 0.86  
 P18C.2  $E_a = +86.3 \text{ kJ mol}^{-1}$   $\Delta^\ddagger H = +84.2 \text{ kJ mol}^{-1}$   $\Delta^\ddagger S = +19.7 \text{ J K}^{-1} \text{ mol}^{-1}$   $\Delta^\ddagger G = +79.2 \text{ kJ mol}^{-1}$   
 P18C.8 +2 or +3

### 18D The dynamics of molecular collisions

- E18D.2(b)  $kT(1 - e^{-V/kT})$   
 P18D.2  $\sigma_{\text{CH}_2\text{F}_2}/\sigma_{\text{Ar}} = 4.8$

**18E Electron transfer in homogeneous systems**

**E18E.1(b)** 13 orders

**E18E.2(b)**  $\Delta E_{\text{R}} = 1.53 \text{ eV}$   $H_{\text{et}}(d) = 9.47 \times 10^{-24} \text{ J}$

**E18E.3(b)**  $498 \text{ s}^{-1}$

**P18E.2**  $5.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

**P18E.4**  $\Delta E_{\text{R}} = 1.2 \text{ eV}$

## 19 Processes at solid surfaces

### 19A An introduction to solid surfaces

**E19A.1(b)** For  $\text{N}_2$   $Z_w(10.0 \text{ Pa}) = 2.88 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$      $Z_w(0.150 \text{ } \mu\text{Torr}) = 5.76 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$

For  $\text{CH}_4$   $Z_w(10.0 \text{ Pa}) = 3.81 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$      $Z_w(0.150 \text{ } \mu\text{Torr}) = 7.62 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$

**E19A.2(b)**  $7.3 \times 10^2 \text{ Pa}$

**E19A.3(b)** 0.1

**P19A.2**  $2.69 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}$      $2.69 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$      $1.79 \times 10^8$      $1.79 \times 10^3$

### 19B Adsorption and desorption

**E19B.1(b)**  $27.4 \text{ cm}^3$

**E19B.2(b)**  $1.6 \times 10^2 \text{ s}$

**E19B.3(b)**  $\theta_{36.0 \text{ Pa}} = 0.75$      $\theta_{4.0 \text{ Pa}} = 0.25$

**E19B.4(b)**  $0.46 \text{ kPa}$      $5.5 \text{ kPa}$

**E19B.5(b)**  $p_2 = 12.1 \text{ kPa}$

**E19B.6(b)**  $-6.40 \text{ kJ mol}^{-1}$

**E19B.7(b)**  $285 \text{ kJ mol}^{-1}$      $1.5 \times 10^{36} \text{ s}$      $0.14 \text{ ms}$

**E19B.8(b)**  $5.4 \text{ kJ mol}^{-1}$

**E19B.9(b)** for  $E_{a,\text{des}} = 20 \text{ kJ mol}^{-1}$   $t_{1/2}(298 \text{ K}) = 3.8 \times 10^2 \text{ ps}$      $t_{1/2}(800 \text{ K}) = 2.4 \text{ ps}$     for

$E_{a,\text{des}} = 200 \text{ kJ mol}^{-1}$   $t_{1/2}(298 \text{ K}) = 1.4 \times 10^{22} \text{ s}$      $t_{1/2}(800 \text{ K}) = 1.4 \text{ s}$

**P19B.2**  $V_\infty = 0.47 \text{ cm}^3$      $\alpha = 3.9 \times 10^{-3} \text{ Pa}^{-1}$

**P19B.4**  $1.44 \text{ cm}^3$      $1.3 \text{ m}^2$

**P19B.6**  $3.99$      $75.3 \text{ cm}^3$

**P19B.8**  $0.0247$

**P19B.10**  $0.54$      $K = 0.078 \text{ mg g}^{-1}$

### 19C Heterogeneous catalysis

**E19C.1(b)**  $11 \text{ m}^2$

### 19D Processes at electrodes

**E19D.1(b)**  $0.17 \text{ V}$

**E19D.2(b)**  $1.6 \text{ mA cm}^{-2}$

**E19D.3(b)**  $8.5 \text{ mA cm}^{-2}$

**E19D.4(b)**  $0.34 \text{ A cm}^{-2}$      $0.34 \text{ A cm}^{-2}$

**E19D.5(b)**  $j = (2.5 \text{ mA cm}^{-2}) \times (e^{0.5f[E-(0.77 \text{ V})]} - e^{-0.5f[E-(0.77 \text{ V})]})$

**E19D.6(b)** for  $\text{H}^+/\text{Cu}$   $6.2 \times 10^{12} \text{ s}^{-1}$   $4.2 \times 10^{-3} \text{ s}^{-1}$  for  $\text{Ce}^{4+}/\text{Pt}$   $2.5 \times 10^{14} \text{ s}^{-1}$   $0.17 \text{ s}^{-1}$

**E19D.7(b)**  $5.1 \times 10^9 \Omega$   $10 \Omega$

**P19D.2**  $a_{\text{Sn}^{2+}}/a_{\text{Pb}^{2+}} = 2.18$

**P19D.4**  $\alpha = 0.49$   $j_0 = 0.150 \text{ A m}^{-2}$   $-0.0402 \text{ A m}^{-2}$

**P19D.6**  $j_0 f^2 \eta_0^2 \frac{1}{2} (\frac{1}{2} - \alpha)$   $7.2 \mu\text{A cm}^{-2}$

**I19.2**  $\lambda_{\text{non-rel}} = 5.48 \text{ pm}$   $\lambda_{\text{rel}} = 5.36 \text{ pm}$

**I19.4** 0.235