Student Solutions Manual to Accompany Atkins' Physical Chemistry

ELEVENTH EDITION

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Numerical solutions to the problems

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Preface

This document is a compilation of the numerical solutions to the (a) *Exercises* and the odd-numbered *Discussion questions* and *Problems* from the 11$^{\text{th}}$ 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`.

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1 The properties of gases

1A The perfect gas

E1A.1(a) 810 Torr 0.962 atm
E1A.2(a) no 24.4 atm
E1A.3(a) 3.42 bar 3.38 atm
E1A.4(a) 30 lb in^{-2}.
E1A.5(a) 0.0427 bar 4.27×10^5 Pa
E1A.6(a) S_8.
E1A.7(a) 6.2 kg
E1A.8(a) $x_{O_2} = 0.240$ $x_{N_2} = 0.760$ $p_{O_2} = 0.237$ bar $p_{N_2} = 0.750$ bar $x_{N_2} = 0.780$ $x_{O_2} = 0.210$ $p_{N_2} = 0.770$ bar $p_{O_2} = 0.207$ bar
E1A.9(a) 0.169 kg mol^{-1}
E1A.10(a) $\theta = -273$ °C
E1A.11(a) $x_{H_2} = \frac{2}{3}$ $x_{N_2} = \frac{1}{3}$ $p_{H_2} = 2.0 \times 10^5$ Pa $p_{N_2} = 1.0 \times 10^5$ Pa $p_{tot} = 3.0 \times 10^5$ Pa
P1A.1 1.15×10^5 Pa 8.315 J K^{-1} mol^{-1}
P1A.3 0.082062 atm dm^3 mol^{-1} K^{-1}
P1A.5 $p = \rho RT/M$ 45.94 g mol^{-1}
P1A.7 24.5 Pa 9.14 kPa 24.5 Pa
P1A.9 between 0.27 km^3 and 0.41 km^3
P1A.11 −2 Pa 0.25 atm
P1A.13 $c_{CCl_3F} = 1.1 \times 10^{-11}$ mol dm^{-3} $c_{CCl_2F_2} = 2.2 \times 10^{-11}$ mol dm^{-3} $c_{CCl_3F} = 8.0 \times 10^{-13}$ mol dm^{-3} $c_{CCl_2F_2} = 1.6 \times 10^{-12}$ mol dm^{-3}

1B The kinetic model

E1B.1(a) 9.975
E1B.2(a) $v_{rms,H_2} = 1.90$ km s^{-1} $v_{rms,O_2} = 478$ m s^{-1}
E1B.3(a) 6.87×10^{-3}
E1B.4(a) 1832 m s^{-1}
E1B.5(a) $v_{mp} = 333$ m s^{-1} $v_{mean} = 376$ m s^{-1} $v_{rel} = 531$ m s^{-1}
E1B.6(a) 1.7×10^{10} s^{-1}
E1B.7(a) 475 m s^{-1} 82.9 nm 8.10×10^9 s^{-1}
E1B.8(a) 0.20 Pa
E1B.9(a) 1.4×10^{-6} m = 1.4 μm
P1B.3 $v_{mean, new} \approx 0.493\, v_{mean}$
P1B.5 3.02×10^{-3} for $n = 3$ 4.89×10^{-6} for $n = 4$
P1B.7 1.12×10^4 m s^{-1} 5.04×10^3 m s^{-1}

P1B.9 0.0722 at 300 K   0.0134 at 1000 K
P1B.11 9.7×10^{10} s^{-1}

1C Real gases

E1C.1(a) 0.99 atm 1.8×10^3 atm
E1C.2(a) $a = 0.0761$ kg m^5 s^{-2} mol^{-2} $b = 2.26 \times 10^{-5}$ m^3 mol^{-1}
E1C.3(a) 0.88   1.2 dm^3 mol^{-1}
E1C.4(a) 140 atm
E1C.5(a) 50.7 atm   35.2 atm   0.695
E1C.6(a) 1.78 atm dm^6 mol^{-2} 0.0362 dm^3 mol^{-1} 153 pm
E1C.7(a) 1.41×10^3 K   175 pm
E1C.8(a) 8.7 atm 3.6×10^3 K   4.5 atm 2.6×10^3 K   0.18 atm   47 K
E1C.9(a) 4.6×10^{-5} m^3 mol^{-1} 0.66
P1C.1 1.62 atm
P1C.3 0.929   0.208 dm^3 mol^{-1}
P1C.5 501.0 K
P1C.7 0.1353 dm^3 mol^{-1} 0.6957   0.5914
P1C.9 0.0594 dm^3 mol^{-1} 5.849 atm dm^6 mol^{-2}.   20.48 atm
P1C.11 0.03464 dm^3 mol^{-1} 1.262 atm dm^6 mol^{-2}
P1C.13 $V_m = 3C/B$ $T = B^2/3CR$ $p = B^3/27C^2$
P1C.15 $B' = 0.0868$ atm^{-1} $B = 2.12$ dm^3 mol^{-1}
P1C.19 $1 + \dfrac{bp}{RT}$ 1.11
P1C.21 −0.01324 dm^3 mol^{-1} 1.063×10^{-3} dm^6 mol^{-2}
P1C.23 $V_m = 13.6$ dm^3 mol^{-1} 2%
I1.1 $v = \left(\dfrac{2RT}{M}\right)^{1/2}$
I1.3 0.071 dm^3 mol^{-1}

2 Internal energy

2A Internal energy

E2A.1(a) 8.7 kJ mol^{-1} 7.4 kJ mol^{-1} 7.4 kJ mol^{-1}
E2A.3(a) −76 J
E2A.4(a) $q = +2.68$ kJ $w = -2.68$ kJ $\Delta U = 0$ $q = +1.62$ kJ $w = -1.62$ kJ $\Delta U = 0$
$q = 0$ $w = 0$ $\Delta U = 0$
E2A.5(a) $p_f = 1.33$ atm $\Delta U = +1.25$ kJ $q = +1.25$ kJ $w = 0$
E2A.6(a) −88 J -1.7×10^2 J
P2A.1 6.2 kJ mol^{-1}
P2A.3 $\frac{1}{2}al^2 - \frac{2}{5}bl^{\frac{5}{2}}$
P2A.7 −1.7 kJ −1.8 kJ −1.5 kJ
P2A.9 −1.5 kJ −1.6 kJ

2B Enthalpy

E2B.1(a) $C_{p,m} = 30$ J K^{-1} mol^{-1} $C_{V,m} = 22$ J K^{-1} mol^{-1}
E2B.2(a) −5.0 kJ mol^{-1}
E2B.3(a) $q_p = +10.7$ kJ $w = -624$ J $\Delta U = +10.1$ kJ $\Delta H = +10.7$ kJ $q_V = +10.1$ kJ
$w = 0$ $\Delta U = +10.1$ kJ $\Delta H = +10.7$ kJ
E2B.4(a) $q_p = \Delta H = +2.2$ kJ $\Delta U = +1.6$ kJ
P2B.1 11 min
P2B.3 62.2 kJ
P2B.5 $w = 0$ $\Delta U = q_V = +2.35$ kJ $\Delta H = 3.0$ kJ

2C Thermochemistry

E2C.1(a) $q = \Delta H = +22.5$ kJ $w = -1.6$ kJ $\Delta U = +21$ kJ
E2C.2(a) -4.57×10^3 kJ mol^{-1}
E2C.3(a) −167 kJ mol^{-1}
E2C.4(a) 1.58 kJ K^{-1} +3.07 K
E2C.5(a) $\Delta_r H^\ominus(3) = -114.40$ kJ mol^{-1} $\Delta_r U^\ominus = -112$ kJ mol^{-1} $\Delta_f H^\ominus(\text{HCl, g}) = -92.31$ kJ mol^{-1}
$\Delta_f H^\ominus(H_2O, g) = -241.82$ kJ mol^{-1}
E2C.6(a) −1368 kJ mol^{-1}
E2C.7(a) $\Delta_r H^\ominus(298\ K) = +131.29$ kJ mol^{-1} $\Delta_r U^\ominus(298\ K) = +128.81$ kJ mol^{-1} $\Delta_r H^\ominus(478\ K) =$
$+134.1$ kJ mol^{-1} $\Delta_r U^\ominus(478\ K) = +130$ kJ mol^{-1}
E2C.8(a) −394 kJ mol^{-1}
P2C.1 37 K 4.1 kg

P2C.3 $+52.98\ \text{kJ mol}^{-1}$ $-32.56\ \text{kJ mol}^{-1}$
P2C.5 $-1.27\times10^{3}\ \text{kJ mol}^{-1}$
P2C.7 $\Delta_c H^\ominus = -25966\ \text{kJ mol}^{-1}$ $\Delta_f H^\ominus = +2355.1\ \text{kJ mol}^{-1}$
P2C.9 $-803\ \text{kJ mol}^{-1}$
P2C.11 $-2.80\times10^{3}\ \text{kJ mol}^{-1}$ $-2.80\times10^{3}\ \text{kJ mol}^{-1}$ $-1.27\times10^{3}\ \text{kJ mol}^{-1}$ $2.69\times10^{3}\ \text{kJ mol}^{-1}$

2D State functions and exact differentials

E2D.1(a) 501 Pa
E2D.2(a) $\Delta U_m = +130\ \text{J mol}^{-1}$ $q = +7.52\ \text{kJ mol}^{-1}$ $w = -7.39\ \text{kJ mol}^{-1}$
E2D.3(a) $+1.3\times10^{-3}\ \text{K}^{-1}$
E2D.4(a) +20 atm
E2D.5(a) $+44.2\ \text{J K}^{-1}\ \text{mol}^{-1}$
P2D.1 0.80 m 1.6 m 2.8 m
P2D.5 $\kappa_T R = \alpha(V_m - b)$
P2D.9 $23\ \text{K MPa}^{-1}$ $14\ \text{K MPa}^{-1}$

2E Adiabatic changes

E2E.1(a) With vibrational contribution $\gamma_{\text{ammonia}} = \frac{10}{9}$ $\gamma_{\text{methane}} = \frac{13}{12}$ Without vibrational contribution $\gamma_{\text{ammonia}} = \gamma_{\text{methane}} = \frac{4}{3}$
E2E.2(a) $1.3\times10^{2}\ \text{K}$
E2E.3(a) $V_f = 8.46\ \text{dm}^3$ 258 K −877 J
E2E.4(a) −194 J
E2E.5(a) 9.7 kPa
P2E.1 $T_f = 194\ \text{K}$ $w_{ad} = -2.79\ \text{kJ}$ $\Delta U = -2.79\ \text{kJ}$

2E Integrated activities

I2.7 −2.6 kJ

3 The second and third laws

3A Entropy

E3A.1(a) not spontaneous
E3A.2(a) +366 J   +309 J
E3A.3(a) $+3.1\ \mathrm{J\,K^{-1}}$
E3A.4(a) $\Delta S = +2.9\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{sur}} = -2.9\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{tot}} = 0$ $\Delta S = +2.9\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{sur}} = 0$ $\Delta S_{\mathrm{tot}} = +2.9\ \mathrm{J\,K^{-1}}$ $\Delta S = \Delta S_{\mathrm{sur}} = \Delta S_{\mathrm{tot}} = 0$
E3A.5(a) 191 K
E3A.6(a) 24.1%
P3A.1 $q = +2.74$ kJ $w = -2.74$ kJ $\Delta U = 0$ $\Delta H = 0$ $\Delta S = +9.13\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{sur}} = -9.13\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{tot}} = 0$ $q = +1.66$ kJ $w = -1.66$ kJ $\Delta U = 0$ $\Delta H = 0$ $\Delta S = +9.13\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{sur}} = -5.54\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{tot}} = +3.59\ \mathrm{J\,K^{-1}}$
P3A.3 $V_{\mathrm{B}} = 2.00\ \mathrm{dm^3}$ $V_{\mathrm{C}} = 3.19\ \mathrm{dm^3}$ $V_{\mathrm{D}} = 1.60\ \mathrm{dm^3}$ $q_1 = +215$ J $q_2 = 0$ $q_3 = -157$ J $q_4 = 0$ $|w| = +58$ J   27%
P3A.5 $|q| \times \left(\frac{T_{\mathrm{h}}}{T_{\mathrm{c}}} - 1\right)$

3B Entropy changes accompanying specific processes

E3B.1(a) $+30\ \mathrm{kJ\,mol^{-1}}$
E3B.2(a) $+87.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $-87.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$
E3B.3(a) $+4.55\ \mathrm{J\,K^{-1}\,mol^{-1}}$
E3B.4(a) $153\ \mathrm{J\,K^{-1}\,mol^{-1}}$
E3B.5(a) $T_{\mathrm{f}} = 298$ K $\Delta S_1 = -31.0\ \mathrm{J\,K^{-1}}$ $\Delta S_2 = +33.7\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{tot}} = +2.7\ \mathrm{J\,K^{-1}}$
E3B.6(a) $-22.1\ \mathrm{J\,K^{-1}}$
E3B.7(a) $+87.3\ \mathrm{J\,K^{-1}}$
P3B.1 $\Delta S = -21.3\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{sur}} = +21.7\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{tot}} = +0.4\ \mathrm{J\,K^{-1}}$ spontaneous $\Delta S = +110\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{sur}} = -111\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{tot}} = -1.5\ \mathrm{J\,K^{-1}}$ not spontaneous
P3B.3 $+10.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$
P3B.5 $\frac{m}{M} C_{p,\mathrm{m}} \ln\left(\frac{(T_{\mathrm{c}} + T_{\mathrm{h}})^2}{4(T_{\mathrm{c}} \times T_{\mathrm{h}})}\right)$ $+22.6\ \mathrm{J\,K^{-1}}$
P3B.7 $\Delta S = +45.4\ \mathrm{J\,K^{-1}}$ $\Delta S = 0\ \mathrm{J\,K^{-1}}$ $\Delta S_{\mathrm{sur}} = +51.2\ \mathrm{J\,K^{-1}}$
P3B.9 $+477\ \mathrm{J\,K^{-1}\,mol^{-1}}$
P3B.11 $+7.5 \times 10^2$ J 6.11×10^3 J   +6.86 kJ   68.6 s

3C The measurement of entropy

E3C.1(a) $4.8 \times 10^{-3}\ \mathrm{J\,K^{-1}\,mol^{-1}}$

E3C.2(a) $-386.1\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $+92.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $-153.1\ \mathrm{J\,K^{-1}\,mol^{-1}}$
E3C.3(a) $-99.38\ \mathrm{J\,K^{-1}}$
P3C.1 $76.04\ \mathrm{J\,K^{-1}\,mol^{-1}}$
P3C.3 $0.93\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $63.9\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $64.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $64.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at 298 K $62.4\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at 273 K
P3C.5 $+42.08\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $+41.16\ \mathrm{kJ\,mol^{-1}}$ at 298 K $+41.15\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $+40.8\ \mathrm{kJ\,mol^{-1}}$ at 398 K
P3C.7 $89.0\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at 100 K $173.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at 200 K $243.9\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at 300 K
P3C.9 $a = 2.569\ \mathrm{JK^{-4}mol^{-1}}$ $b = 2.080\ \mathrm{JK^{-2}mol^{-1}}$ $S_\mathrm{m}(0)+\frac{a}{3}T^3+bT$ $11.01\ \mathrm{J\,K^{-1}\,mol^{-1}}$

3D Concentrating on the system

E3D.1(a) $\Delta_\mathrm{r}H^\ominus = -636.6\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}G^\ominus = -521.5\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}H^\ominus = +53.40\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}G^\ominus = +25.8\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}H^\ominus = -224.3\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}G^\ominus = -178.7\ \mathrm{kJ\,mol^{-1}}$
E3D.2(a) $-480.98\ \mathrm{kJ\,mol^{-1}}$
E3D.3(a) $817.90\ \mathrm{kJ\,mol^{-1}}$
E3D.4(a) $-522.1\ \mathrm{kJ\,mol^{-1}}$ $+25.78\ \mathrm{kJ\,mol^{-1}}$ $-178.6\ \mathrm{kJ\,mol^{-1}}$
E3D.5(a) $-340\ \mathrm{kJ\,mol^{-1}}$
P3D.1 49.9 bar 900 K $+50.7\ \mathrm{J\,K^{-1}}$ $-11.5\ \mathrm{J\,K^{-1}}$ $\Delta U_\mathrm{A} = +24.0\ \mathrm{kJ}$ $\Delta U_\mathrm{B} = 0$ $+3.46 \times 10^3\ \mathrm{J}$ 0
P3D.3 -47 $\mathrm{kJ\,mol^{-1}}$
P3D.5 $\Delta_\mathrm{r}G_1^\ominus = +965\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}G_2^\ominus = -961\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}G^\ominus = +4\ \mathrm{kJ\,mol^{-1}}$

3E Combining the First and Second Laws

E3E.1(a) $-17\ \mathrm{J}$
E3E.2(a) $-36.5\ \mathrm{J\,K^{-1}}$
E3E.3(a) $-85.40\ \mathrm{J}$
E3E.4(a) $+10\ \mathrm{kJ}$ $+1.6\ \mathrm{kJ\,mol^{-1}}$
E3E.5(a) $-1.6 \times 10^2\ \mathrm{J\,mol^{-1}}$
E3E.6(a) $+11\ \mathrm{kJ\,mol^{-1}}$
P3E.1 $\Delta_\mathrm{r}G^\ominus(298\ \mathrm{K}) = -514.38\ \mathrm{kJ\,mol^{-1}}$ $\Delta_\mathrm{r}H^\ominus(298\ \mathrm{K}) = -565.96\ \mathrm{kJ\,mol^{-1}}$ $\Delta G(375\ \mathrm{K}) = -501\ \mathrm{kJ\,mol^{-1}}$
P3E.3 $22\ \mathrm{kJ\,mol^{-1}}$
P3E.5 $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$
P3E.7 $G_\mathrm{m}(p_\mathrm{f}) = G_\mathrm{m}(p_\mathrm{i}) + RT\ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right) + b(p_\mathrm{f} - p_\mathrm{i})$ $V_\mathrm{m} = \frac{RT}{p} - \frac{a}{pRT}$ $G_\mathrm{m}(p_\mathrm{f}) = G_\mathrm{m}(p_\mathrm{i}) + RT\ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right) - \frac{a}{RT}\ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)$

I3.1 −20.8 K   +37.1 J K^{-1} mol^{-1}

I3.3 +19.5 J K^{-1} mol^{-1}

4 Physical transformations of pure substances

4A Phase diagrams of pure substances

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

E4A.2(a) 0.71 J

E4A.3(a) 4

E4A.4(a) area

E4A.5(a) Two phases one phase one phase

4B Thermodynamic aspects of phase transitions

E4B.1(a) $\Delta\mu(\text{liquid}) = -65\ \text{J mol}^{-1}$ $\Delta\mu(\text{solid}) = -43\ \text{J mol}^{-1}$ liquid

E4B.2(a) $-699\ \text{J mol}^{-1}$

E4B.3(a) $+70\ \text{J mol}^{-1}$

E4B.4(a) 2.71 kPa

E4B.5(a) $15.9\ \text{kJ mol}^{-1}$ $45.2\ \text{J K}^{-1}\ \text{mol}^{-1}$

E4B.6(a) 304 K 31.2 °C

E4B.7(a) $20.801\ \text{kJ mol}^{-1}$

E4B.8(a) $34.08\ \text{kJ mol}^{-1}$ 350.4 K 77.30 °C

E4B.9(a) 2.8×10^2 K 8.7 °C

E4B.10(a) 9.6×10^{-5} K

E4B.11(a) $25\ \text{g s}^{-1}$

E4B.12(a) Water 1.7 kg Benzene 31 kg Mercury 1.4 g

E4B.13(a) $49\ \text{kJ mol}^{-1}$ 4.9×10^2 K 2.2×10^2 °C $99\ \text{J K}^{-1}\ \text{mol}^{-1}$

E4B.14(a) 273 K −0.35 °C

P4B.1 $-3.10\ \text{kJ mol}^{-1}$ 7.62 %

P4B.3 9.08 atm 920 kPa

P4B.5 $-22.0\ \text{J K}^{-1}\ \text{mol}^{-1}$ $-109.9\ \text{J K}^{-1}\ \text{mol}^{-1}$ $+110\ \text{J mol}^{-1}$

P4B.7 234.4 K

P4B.9 84 °C $38.0\ \text{kJ mol}^{-1}$

P4B.11 $\text{d}\ln p/\text{d}T = \Delta_{\text{sub}}H/RT^2$ $31.7\ \text{kJ mol}^{-1}$

P4B.13 1.31 kPa

P4B.15 $T = \left(\dfrac{1}{T_0} + \dfrac{R}{\Delta_{\text{vap}}H}\dfrac{a}{H}\right)^{-1}$ 363 K 89.6 °C

I4.1 $(p/\text{kPa}) = 4.80 + (3.18\times10^4)\times[(T/\text{K}) - 278.65]$ $(p/\text{kPa}) = 4.80\times\exp\left[-3.70\times10^3\left(\dfrac{1}{T/\text{K}} - \dfrac{1}{278.65}\right)\right]$

$(p/\text{kPa}) = 4.80\times\exp\left[-4.98\times10^3\left(\dfrac{1}{T/\text{K}} - \dfrac{1}{278.65}\right)\right]$

I4.3 $N = 17$

I4.5 1.60×10^4 bar

5 Simple mixtures

5A The thermodynamic description of mixtures

E5A.1(a) $V_B = \left(35.6774 - 0.91846\,x + 0.051975\,x^2\right)$ cm^3 mol^{-1}
E5A.2(a) V_B = 17.5 cm^3 mol^{-1} V_A = 18.1 cm^3
E5A.3(a) −1.2 J mol^{-1}
E5A.4(a) +1.2 J K^{-1} −3.5 × 10^2 J
E5A.5(a) 6.7 kPa
E5A.6(a) 886.8 cm^3
E5A.7(a) 56.3 cm^3 mol^{-1}
E5A.8(a) 6.4 · 10^3 kPa
E5A.9(a) 3.7 × 10^{-3} mol dm^{-3}
E5A.10(a) 3.4 × 10^{-3} mol kg^{-1} 3.37 × 10^{-2} mol kg^{-1}
E5A.11(a) 0.17 mol dm^{-3}
P5A.3 +4.70 J K^{-1} mol^{-1} +4.711 J K^{-1} mol^{-1} 0.01 J K^{-1} mol^{-1}
P5A.7 4.2934 mol kg^{-1}

5B The properties of solutions

E5B.1(a) 1.3 × 10^2 kPa
E5B.2(a) 84.9 g mol^{-1}
E5B.3(a) 381 g mol^{-1}
E5B.4(a) 273.08 K
E5B.5(a) 273.06 K
E5B.6(a) $\Delta_{mix}G = -3.10 \times 10^3$ J $\Delta_{mix}S = +10.4$ J K^{-1} $\Delta_{mix}H = 0$
E5B.7(a) $\frac{1}{2}$ 0.8600
E5B.8(a) 0.137 mol kg^{-1} 24.3 g
E5B.9(a) p_B = 6.1 Torr p_A = 32 Torr p_{tot} = 38 Torr y_{CCl_4} = 0.84 y_{Br_2} = 0.16
E5B.10(a) $x_{methylbenzene}$ = 0.92 $x_{1,2-dimethylbenzene}$ = 0.08 $y_{methylbenzene}$ = 0.97 $y_{1,2-dimethylbenzene}$ = 0.03
E5B.11(a) x_A = 0.267 x_B = 0.733   58.6 kPa
E5B.12(a) ideal y_A = 0.830 y_B = 0.170
P5B.3 $V_{propionicacid}$ = 75.6 cm^3 mol^{-1} V_{THF} = 99.1 cm^3 mol^{-1}
P5B.5 −4.64 kJ
P5B.7 1.39 × 10^4 g mol^{-1}
P5B.9 1.25 × 10^5 g mol^{-1} B = 1.23 × 10^4 mol^{-1} dm^3
P5B.11 $\frac{1}{2}$
P5B.13 M_J = 1.26 × 10^5 g mol^{-1} B = 4.80 × 10^4 mol^{-1} dm^3

5C Phase diagrams of binary systems: liquids

E5C.1(a) $y_M = 0.354$ $y_M = 0.811$
E5C.3(a) $x_P = 0.150$ $\frac{n_{0.161}}{n_{0.042}} = 9.68$
P5C.1 $y_B = 0.91$ $y_{MB} = 0.085$
P5C.3 6.4 kPa $y_B = 0.77$ $y_{MB} = 0.23$ $p_{tot} = 4.5$ kPa
P5C.5 625 Torr 500 Torr $x_H = 0.5$ $y_H = 0.3$ $x_H = 0.7$ $y_H = 0.5$ $\frac{n_l}{n_v} = 1.1$

5D Phase diagrams of binary systems: solids

E5D.4(a) $x_B \approx 0.25$ $T_2 \approx 190\,°C$
E5D.6(a) 76% $\frac{n_{Ag3Sn}}{n_{Ag}} = 1.11$ $\frac{n_{Ag3Sn}}{n_{Ag}} = 1.46$
P5D.3 (species,phases): b(3,2), d(2,2), e(4,3), f(4,3), g(4,3), k(2,2)
P5D.5 eutectics: $x_{Si} = 0.056$ at 800 °C, $x_{Si} = 0.402$ at 1268 °C, $x_{Si} = 0.694$ at 1030 °C
$\frac{n_{Ca_2Si}}{n_{Ca-richliq}} = 0.7$ $\frac{n_{Si}}{n_{liq}} = 0.53$ $\frac{n_{Si}}{n_{CaSi_2}} = 0.67$
P5D.7 $x_1 = 0.167$ $x_2 = 0.805$ $\frac{n_{x=0.805}}{n_{x=0.167}} = 10.6$ 302.5 °C

5E Phase diagrams of ternary systems

D5E.1 3
E5E.3(a) $x_{CHCl_3} = 0.30$ $x_{CH_3COOH} = 0.20$ $x_{H_2O} = 0.50$ two phase region with phase composition a_2' being approximately 5 times more abundant than the phase with composition a_2''
E5E.5(a) 13 mol dm^{-3} 24 mol dm^{-3}

5F Activities

E5F.1(a) 0.5903
E5F.2(a) $a_A = 0.833$ $a_B = 0.125$ $\gamma_A = 0.926$
E5F.3(a) $a_P = 0.498$ $\gamma_P = 1.24$ $a_M = 0.667$ $\gamma_M = 1.11$
E5F.5(a) 0.9
E5F.6(a) 2.74 g 2.92 g
E5F.7(a) 0.56
E5F.8(a) $B = 1.96$
I5.3 $K_C = 371$ bar
I5.5 56 μg 14 μg 1.7×10^2 μg

6 Chemical equilibrium

6A The equilibrium constant

E6A.1(a) $n_A = 0.90$ mol $n_B = 1.2$ mol
E6A.2(a) −64 kJ mol^{-1}
E6A.3(a) exergonic
E6A.6(a) $K = 3.24 \times 10^{91}$ $K = 3.03 \times 10^{-5}$
E6A.7(a) 1.4×10^{46}
E6A.8(a) −44 kJ mol^{-1} −33 kJ mol^{-1} −27 kJ mol^{-1} −4.4 kJ mol^{-1} +1.3 kJ mol^{-1} 5.84×10^{5} 5.84×10^{5}
E6A.9(a) 2.85×10^{-6}
E6A.10(a) $K = K_c \times (c^{\ominus}RT/p^{\ominus})$
E6A.11(a) $x_A = 0.087$ $x_B = 0.369$ $x_C = 0.195$ $x_D = 0.347$ 0.32 +2.8 kJ mol^{-1}
E6A.12(a) +12 kJ mol^{-1}
E6A.13(a) −14 kJ mol^{-1}
E6A.14(a) -1.1×10^{3} kJ mol^{-1}
P6A.1 +4.48 kJ mol^{-1} 0.101 atm 0.102 bar
P6A.3 $n_{H_2} = 6.67 \times 10^{-3}$ mol $n_{I_2} = 0.107$ mol $n_{HI} = 0.787$ mol

6B The response of equilibria to the conditions

E6B.1(a) 0.141 13.4
E6B.2(a) -68.26 kJ mol^{-1} 9.22×10^{11} 1.27×10^{9}
E6B.3(a) 1.5×10^{3} K
E6B.4(a) +2.77 kJ mol^{-1} −16.5 J K^{-1} mol^{-1}
E6B.5(a) 50%
E6B.6(a) $x_{\text{borneol}} = 0.904$ $x_{\text{isoborneol}} = 0.096$
E6B.7(a) +52.9 kJ mol^{-1} −52.9 kJ mol^{-1}
E6B.8(a) 1109 K
E6B.9(a) 3.07 − 6.48 kJ mol^{-1} 70.2 kJ mol^{-1} 110 J K^{-1} mol^{-1}
P6B.1 −92.2 kJ mol^{-1}
P6B.3 $-\frac{3}{2}R(CT - B)$ +70.5 J K^{-1} mol^{-1}
P6B.5 $K = 2.79 \times 10^{-6}$ $\Delta_r G^{\ominus} = +153$ kJ mol^{-1} $\Delta_r H^{\ominus} = +3.00 \times 10^{2}$ kJ mol^{-1} $\Delta_r S^{\ominus} = +102$ J K^{-1} mol^{-1}
P6B.7 $K = 1.35$ at 437 K $K = 0.175$ at 471 K $\Delta_r H^{\ominus} = -103$ kJ mol^{-1}
P6B.9 1.2×10^{8} 2.7×10^{3}
P6B.11 −225.34 kJ mol^{-1}

6C Electrochemical cells

E6C.1(a) +1.56 V   +0.40 V   −1.10 V
E6C.2(a) +1.10 V   +0.22 V   +1.23 V
E6C.3(a) −0.619 V
E6C.4(a) $-212\ \mathrm{kJ\,mol^{-1}}$
E6C.5(a) +0.030 V
P6C.1 +1.23 V   +1.09 V
P6C.3 2.0

6D Electrode potentials

E6D.1(a) 6.4×10^{9} 1.5×10^{12}
E6D.2(a) 8.445×10^{-17}
E6D.3(a) −0.46 V $\Delta_r G^{\ominus} = +89\ \mathrm{kJ\,mol^{-1}}$ $\Delta_r H^{\ominus} = +146.39\ \mathrm{kJ\,mol^{-1}}$ $\Delta_r G^{\ominus}(308\mathrm{K}) = +87\ \mathrm{kJ\,mol^{-1}}$
E6D.4(a) no
P6D.1 +0.324 V   +0.45 V
P6D.3 −0.6111 V   −0.22 V   +0.4139 V
P6D.5 $-324\ \mathrm{J\,K^{-1}\,mol^{-1}}$ $-571\ \mathrm{kJ\,mol^{-1}}$
I6.1 $-77\ \mathrm{kJ\,mol^{-1}}$
I6.3 $E^{\ominus}_{\mathrm{cell}} = 1.0304$ V $\Delta_r G = -236.81\ \mathrm{kJ\,mol^{-1}}$ $\Delta_r G^{\ominus} = -198.84\ \mathrm{kJ\,mol^{-1}}$ $K = 7.11 \times 10^{34}$ $\gamma_{\pm} = 0.761$ $\gamma_{\pm} = 0.750$ $\Delta_r H = -263\ \mathrm{kJ\,mol^{-1}}$ $\Delta_r S - 87.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$
I6.5 $\gamma_{\pm,1} = 0.501$ $\gamma_{\pm,2} 0.549$
I6.9 41 %   77 %   41 %
I6.11 +0.206 V

7 Quantum theory

7A The origins of quantum mechanics

E7A.1(a) 9.7×10^{-6} m
E7A.2(a) 580 K
E7A.3(a) $(5.49 \times 10^{-2}) \times 3R$
E7A.4(a) 6.6×10^{-19} J 4.0×10^{2} kJ mol^{-1} 6.6×10^{-20} J 40 kJ mol^{-1} 6.6×10^{-34} J 4.0×10^{-13} kJ mol^{-1}
E7A.5(a) 330 zJ 199 kJ mol^{-1} 360 zJ 217 kJ mol^{-1} 496 zJ 298 kJ mol^{-1}
E7A.6(a) 19.9 km s^{-1} 20.8 km s^{-1} 24.4 km s^{-1}
E7A.7(a) 2.77×10^{18} 2.77×10^{20}
E7A.8(a) no electron ejection 3.19×10^{-19} J 837 km s^{-1}
E7A.9(a) 21 m s^{-1}
E7A.10(a) 7.27×10^{6} m s^{-1} 150 V
E7A.11(a) 2.4×10^{-2} m s^{-1}
E7A.12(a) 332 pm
E7A.13(a) 6.6×10^{-29} m 6.6×10^{-36} m 99.8 pm
P7A.1 1.54×10^{-33} J m^{-3} 2.51×10^{-4} J m^{-3}
P7A.5 6.54×10^{-34} J s
P7A.9 500 nm blue-green

7B Wavefunctions

E7B.1(a) $N = (2/L)^{1/2}$
E7B.2(a) $N = (2a/\pi)^{1/4}$
E7B.3(a) can be normalized cannot be normalized
E7B.4(a) 0
E7B.5(a) 1/4
E7B.6(a) length^{-1}
E7B.7(a) cannot be normalized cannot be normalized can be normalized
E7B.8(a) Maxima at $x = L/4, 3L/4$; Node at $x = L/2$
P7B.1 $N = (2\pi)^{-1/2}$ $N = (2\pi)^{-1/2}$
P7B.3 $N = 2/\sqrt{L_x L_y}$ $N = 2/L$
P7B.5 0.0183
P7B.7 2.00×10^{-2} 6.91×10^{-3} 6.58×10^{-6} 0.5
P7B.9 8.95×10^{-6} 1.21×10^{-6}
P7B.11 $x = \pm a$

7C Operators and observables

E7C.6(a) $L/2$
E7C.7(a) 0
E7C.8(a) π π
E7C.9(a) 1.05×10^{-28} m s^{-1} 1.05×10^{-27} m
E7C.10(a) 7.01×10^{-10} m
P7C.1 Yes −1 Yes +1 No
P7C.7 $1/a$
P7C.11 $\langle x \rangle = 0$ $\langle x^2 \rangle = 1/4a$ $\langle p_x \rangle = 0$ $\langle p_x^2 \rangle = \hbar^2 a$ $\Delta x = (4a)^{-1/2}$ $\Delta p_x = \hbar\sqrt{a}$
P7C.13 $-1/x^2$ $2x$

7D Translational motion

E7D.1(a) 3×10^{-25} kg m s^{-1} 5×10^{-20} J
E7D.2(a) $e^{-i(2.7\times10^{33}\ m^{-1})x}$
E7D.3(a) 1.8×10^{-19} J 1.1×10^{2} kJ mol^{-1} 1.1 eV 9.1×10^{3} cm^{-1} 6.6×10^{-19} J 4.0×10^{2} kJ mol^{-1} 4.1 eV 3.3×10^{4} cm^{-1}
E7D.5(a) 0.04 0
E7D.8(a) $\lambda_C/2$
E7D.9(a) $L/6, L/2, 5L/6$ $0, L/3, 2L/3, L$
E7D.10(a) −0.174
E7D.11(a) $n = \dfrac{2mkTL^2}{h^2} - \frac{1}{2}$ 1.24×10^{16}
E7D.12(a) Maxima at (x, y):$(L/4, L/4), (L/4, 3L/4), (3L/4, L/4), (3L/4, 3L/4)$; Nodes at $x = L/2$ and parallel to the y axis, $y = L/2$ and parallel to the x axis
E7D.13(a) $(1, 4)$
E7D.14(a) 3
E7D.15(a) 0.84
P7D.1 6.2×10^{-41} J 2.2×10^{9} 1.8×10^{-30} J
P7D.3 $\langle x \rangle = \frac{L}{2}$ $\langle x^2 \rangle = \frac{L^2}{3} - \frac{1}{2\pi^2}$
P7D.5 3.30×10^{-19} J 4.98×10^{14} Hz lower increases
P7D.11 1.20×10^{6}
P7D.15 $n_1 + n_2 - 2$

7E Vibrational motion

E7E.1(a) 4.30×10^{-21} J
E7E.2(a) 278 N m^{-1}
E7E.3(a) 2.64×10^{-6} m
E7E.5(a) 5.61×10^{-21} J

E7E.6(a) 4.09×10^{-20} J 18.1 pm 1.29×10^{-20} J 32.2 pm
E7E.7(a) 3 4
E7E.8(a) $y = -1, +1$
E7E.9(a) $y = \pm 1$
P7E.1 4.04×10^{14} Hz 5.63×10^{14} Hz
P7E.3 $\nu_{^2H_2} = 93.27$ THz $\nu_{^3H_2} = 76.15$ THz
P7E.5 2.99×10^3 cm^{-1} $k_f = \mu(2\pi\tilde{\nu}c)^2$ 1902 N m^{-1} 2080 cm^{-1}
P7E.7 1420 cm^{-1}
P7E.9 $g = (mk_f)^{1/2}/2\hbar$ $E = \frac{1}{2}\hbar(k_f/m)^{1/2}$
P7E.13 $P = 0.112$
P7E.17 $\upsilon = 0$

7F Rotational motion

E7F.1(a) $2^{1/2}\hbar$ $-\hbar, 0, \hbar$
E7F.3(a) $N = (2\pi)^{-1/2}$
E7F.5(a) 3.32×10^{-22} J
E7F.6(a) 2.11×10^{-22} J
E7F.7(a) 4.22×10^{-22} J
E7F.8(a) 1.49×10^{-34} J s
E7F.10(a) 3 $\theta = \pi/2$, 0.684, 2.46
E7F.11(a) $\phi = \pi/2, 3\pi/2$ *yz* plane $\phi = 0, \pi$ *xz* plane
E7F.12(a) 7
E7F.14(a) $\theta = \pi/4$ $\theta = 0.420$
P7F.1 7.88×10^{-19} J 5.273×10^{-34} J s 5.23×10^{14} Hz
P7F.3 is separable
P7F.5 $E_{0,0} = 0$ $E_{2,-1} = 6\hbar^2/2I$ $E_{3,+3} = 12\hbar^2/2I$ $J_{z(0,0)} = 0$ $J_{z(2,-1)} = -\hbar$ $J_{z(3,+3)} =$ $3\hbar$
I7.1 +74.81 kJ mol^{-1} +80.8... J K^{-1} mol^{-1} $T = 812$ K 2.9×10^{-6} m 1.84×10^{-6}

8 Atomic structure and spectra

8A Hydrogenic Atoms

E8A.1(a) 1 9 25
E8A.2(a) $N = (a_0^3\pi)^{-1/2}$
E8A.3(a) $Z^3/(8\pi a_0^3)$
E8A.4(a) $r = 4a_0/Z$
E8A.5(a) $0.347a_0$
E8A.6(a) $r = (3 \pm \sqrt{3})(3a_0/2Z)$
E8A.7(a) $\theta = \pi/2 \quad \phi = \pi/2$
E8A.8(a) $(3 + \sqrt{5})(a_0/Z)$
E8A.9(a) $4a_0/Z$
E8A.10(a) 3 subshells 9 orbitals
E8A.12(a) 0
P8A.1 $x = 0,\ y = 0,\ z = 2a_0/Z$
P8A.3 $-2.179\,27 \times 10^{-18}$ J
P8A.5 Radial nodes: 3s at $r = (3a_0/2Z)(3 \pm \sqrt{3})$, 3p at $r = 6a_0/Z$, 3d none Anuglar nodes: 3s none, 3p yz plane, 3d xz and yz plane $\langle r\rangle = (27a_0)/(2Z)$
P8A.7 $\sigma = 2.66a_0$
P8A.9 $-\dfrac{Z^2e^4m_e}{32\pi^2\varepsilon_0^2\hbar^2} \times \dfrac{1}{n^2}$
P8A.11 $2a_{0,\mathrm{H}} \quad \frac{1}{2}E_{\mathrm{h,H}}$

8B Many-electron atoms

E8B.2(a) 14
E8B.4(a) [Ar] $3d^8$
E8B.5(a) Li
P8B.1 $a_0/126$

8C Atomic spectra

E8C.1(a) $n_2 = 2 \quad n_2 = \infty$
E8C.2(a) 3.29×10^5 cm^{-1} 30.4 nm 9.87 PHz
E8C.3(a) forbidden allowed allowed
E8C.4(a) $^2P_{1/2}$, $^2P_{3/2}$
E8C.5(a) $j = \frac{5}{2}, \frac{3}{2} \quad j = \frac{7}{2}, \frac{5}{2}$
E8C.6(a) $l = 1$

E8C.7(a) $L = 2 \quad S = 0 \quad J = 2$

E8C.8(a) $S = 1, 0 \quad 3, 1 \quad S = \frac{3}{2}, \frac{1}{2} \quad 4, 1$

E8C.9(a) $M_S = 0 \quad S = 0 \quad M_S = 0, \pm 1 \quad S = 1$

E8C.10(a) ${}^3D_3, {}^3D_2, {}^3D_1, {}^1D_2 \quad {}^3D_1$

E8C.11(a) $J = 0 \quad 1 \quad J = \frac{3}{2}, \frac{1}{2} \quad 4 \quad 2 \quad J = 2, 1, 0 \quad 5, 3, 1$

E8C.12(a) ${}^2S_{1/2} \quad {}^2P_{3/2}, {}^2P_{1/2}$

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

E8C.14(a) allowed forbidden allowed

P8C.1 $n_1 = 6$ for $n_2 = 8, 9$ and 10 $\lambda = 7502.5$ nm, 5908.3 nm and 5128.7 nm

P8C.3 $\tilde{\nu}_{3\to2}({}^4He^+)$=60 956.8 cm^{-1} $\tilde{\nu}_{3\to2}({}^3He^+)$=60 954.1 cm^{-1} $\tilde{\nu}_{2\to1}({}^4He^+)$=329 167 cm^{-1} $\tilde{\nu}_{2\to1}({}^3He^+)$=329 152 cm^{-1}

P8C.5 5.39 eV

P8C.7 $\tilde{A} = 38.5$ cm^{-1}

P8C.9 7 621 cm^{-1} 10 288 cm^{-1} 11 522 cm^{-1} 6.803 eV

P8C.11 $\Delta l = \pm 1, \Delta m_l = \pm 1$

I8.1 ${}^2S_{1/2} \to {}^2P_{1/2} \quad {}^2S_{1/2} \to {}^2P_{3/2}$ 411 289 cm^{-1} 24.313 8 nm $1.233\,01 \times 10^{16}$ Hz $43a_0/4$

I8.3 17.9 T m^{-1}

9 Molecular Structure

9A Valence-bond theory

9B Molecular orbital theory: the hydrogen molecule-ion

E9B.1(a) $N = 1/(1+\lambda^2+2\lambda S)^{1/2}$

E9B.2(a) $\psi_i = 0.163A + 0.947B \quad \psi_j = 1.02A - 0.412B$

E9B.3(a) $R = 2.5\,a_0$ 2.0 eV

P9B.1 1.87×10^6 J mol^{-1} 1.52×10^{-30} J mol^{-1}

9C Molecular orbital theory: homonuclear diatomic molecules

E9C.1(a) 1 0 2

E9C.4(a) In order of increasing atomic number: 1, 0, 1, 2, 3, 2, 1, 0

E9C.6(a) 3.70×10^5 m s^{-1}

P9C.1 $R/a_0 = 8.03$ 0.29

9D Molecular orbital theory: heteronuclear diatomic molecules

E9D.5(a) $\alpha_H = -7.18$ eV $\alpha_{Cl} = -8.29$ eV

E9D.6(a) $E_- = -8.88$ eV $E_+ = -6.59$ eV

E9D.7(a) $E_- = -8.65$ eV $E_+ = -7.05$ eV

9E Molecular orbital theory: polyatomic molecules

E9E.2(a) $7\alpha + 7\beta \quad 5\alpha + 7\beta$

E9E.3(a) $E_{deloc} = 0 \quad E_{bf} = 7\beta \quad E_{deloc} = 2\beta \quad E_{bf} = 7\beta$

E9E.5(a) $14\alpha + 19.3\beta \quad 14\alpha + 19.5\beta$

P9E.7 $\alpha + 2\beta \quad \alpha - \beta$ (doubly degenerate) $E_{tot,H_3^+} = 2\alpha + 4\beta \quad E_{tot,H_3} = 3\alpha + 3\beta \quad E_{tot,H_3^-} = 4\alpha + 2\beta$ -417 kJ mol^{-1} -208 kJ mol^{-1} $E_{tot,H_3^+} = 2\alpha - 834$ kJ mol^{-1} $E_{tot,H_3} = 3\alpha - 625$ kJ mol^{-1} $E_{tot,H_3^-} = 4\alpha - 416$ kJ mol^{-1}

P9E.11 -4.96 eV 1.52β

9E Integrated activities

I9.5 E_{LUMO}/ V in order presented: 0.078, 0.023, −0.067, −0.165, −0.260 −2.99 eV −0.25 V −3.11 eV −0.18 V

10 Molecular symmetry

10A Shape and symmetry

E10A.2(a) D_{2h}
E10A.3(a) R_3 C_{2v} D_{3h} $D_{\infty h}$
E10A.4(a) C_{2v} D_{3h} C_{3v} D_{2h}
E10A.5(a) C_{2v} C_{2h}
P10A.1 D_{3d} Chair: D_{3d} Boat: C_{2v} D_{2h} D_3 D_{4d}
P10A.3 Ethene: D_{2h} Allene: D_{2d} D_{2h} D_{2d} D_2 D_2
P10A.5 D_{2h} C_{2h} C_{2v}

10B Group theory

E10B.1(a) $\boldsymbol{D}(\sigma_h) = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$

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

E10B.5(a) A_2'' E' A_1' E' E'
E10B.6(a) three
E10B.7(a) two
P10B.9 A_1 B_2 B_1 A_1 B_2 B_1 A_2

10C Applications of symmetry

E10C.1(a) zero
E10C.2(a) forbidden
E10C.4(a) 2s $2p_z$ $2p_y$ d_{z^2} $d_{x^2-y^2}$ d_{yz}
E10C.5(a) none of them d_{xy}
E10C.6(a) B_1, B_2, and A_1 x, y and z polarised light respectively
E10C.7(a) $2A_1 + B_1 + E$
E10C.8(a) $A_{1g} + B_{1g} + E_u$
E10C.9(a) A_{2u} or E_{1u} B_{3u}, B_{2u}, or B_{1u}
P10C.1 $A_1 + T_2$ 2s p_x, p_y, and p_z d_{xy}, d_{yz}, and d_{zx}
P10C.3 not necessarily vanish

P10C.5 none

P10C.7 $\psi^{(A_{1g})} = \frac{1}{4}(s_A + s_B + s_C + s_D)$ $\psi^{(B_{2u})} = \frac{1}{4}(s_A + s_B - s_C - s_D)$ $\psi^{(B_{3u})} = \frac{1}{4}(s_A - s_B - s_C + s_D)$ $\psi^{(B_{1g})} = \frac{1}{4}(s_A - s_B + s_C - s_D)$ $\psi^{(B_{1u})} = 0$

11 Molecular Spectroscopy

11A General features of molecular spectroscopy

E11A.1(a) $0.0469\ \mathrm{J\,s\,m^{-3}}$ $1.33 \times 10^{-13}\ \mathrm{J\,s\,m^{-3}}$ $4.50 \times 10^{-16}\ \mathrm{J\,s\,m^{-3}}$
E11A.2(a) 82.9%
E11A.3(a) $5.34 \times 10^{3}\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$
E11A.4(a) 1.09 mM
E11A.5(a) $449\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$
E11A.6(a) $\varepsilon = 1.6 \times 10^{2}\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ $T = 23\%$
E11A.7(a) 0.875 m 2.90 m
E11A.8(a) $1.34 \times 10^{8}\ \mathrm{dm^3\,mol^{-1}\,cm^{-2}}$
E11A.9(a) $0.151\ \mathrm{cm^{-1}}$
E11A.10(a) 680 nm
E11A.11(a) 27 ps 2.7 ps
E11A.12(a) $53\ \mathrm{cm^{-1}}$ $0.53\ \mathrm{cm^{-1}}$
P11A.1 4.4×10^{3}
P11A.5 $1.26 \times 10^{6}\ \mathrm{dm^3\,mol^{-1}\,cm^{-2}}$
P11A.7 $2.42 \times 10^{5}\ \mathrm{dm^3\,mol^{-1}\,cm^{-2}}$ 0.18 $A = 6.35$ $123\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$
P11A.9 $2.301 \times 10^{6}\ \mathrm{m\,s^{-1}}$ 7.15×10^{5} K
P11A.11 $\tau = 1/z$ 0.70 GHz 569 Pa 4.27 Torr

11B Rotational spectroscopy

E11B.1(a) $6.33 \times 10^{-46}\ \mathrm{kg\,m^2}$ $0.442\ \mathrm{cm^{-1}}$
E11B.4(a) $R_{CH} = 0.1062$ nm $R_{CN} = 0.1157$ nm
E11B.5(a) $2.073 \times 10^{-4}\ \mathrm{cm^{-1}}$ 0.25
E11B.6(a) HCl, CH_3Cl and CH_2Cl_2
E11B.7(a) $10.2\ \mathrm{cm^{-1}}$ 307 GHz
E11B.8(a) 125.7 pm
E11B.9(a) $4.4420 \times 10^{-47}\ \mathrm{kg\,m^2}$ 165.9 pm
E11B.10(a) 20 23
E11B.11(a) H_2, HCl, CH_3Cl
E11B.12(a) $20\,475\ \mathrm{cm^{-1}}$
E11B.13(a) 198.9 pm
E11B.14(a) $\frac{5}{3}$
P11B.3 596 GHz $19.9\ \mathrm{cm^{-1}}$
P11B.7 $R_{OC} = 0.1167$ nm $R_{CS} = 0.1565$ nm
P11B.9 $B = 4293.28 \pm 0.03$ MHz $J_{max} = 26$ at 298 K $J_{max} = 15$ at 100 K

P11B.11 $J_{\max} = (kT/2hc\tilde{B})^{1/2} - \frac{1}{2}$ 30 $J_{\max} = (kT/hc\tilde{B})^{1/2} - \frac{1}{2}$ 6

11C Vibrational spectroscopy of diatomic molecules

E11C.1(a) 16 N m^{-1}
E11C.2(a) 1.077%
E11C.3(a) 328.7 N m^{-1}
E11C.4(a) $k_{f,^1H^{19}F} = 967.0\ \text{N m}^{-1}$ $k_{f,^1H^{35}Cl} = 515.6\ \text{N m}^{-1}$ $k_{f,^1H^{81}Br} = 411.7\ \text{N m}^{-1}$ $k_{f,^1H^{127}I} = 314.2\ \text{N m}^{-1}$
E11C.5(a) 0.0670 0.200
E11C.6(a) 1580.4 cm^{-1} 7.65×10^{-3}
E11C.7(a) $4.14 \times 10^4\ \text{cm}^{-1}$ 5.14 eV
E11C.8(a) 2347.2 cm^{-1}
P11C.5 5.15 eV 5.20 eV
P11C.7 $\tilde{\nu} = 1.5\ \text{cm}^{-1}$ $k_f = 2.7 \times 10^{-4}\ \text{N m}^{-1}$ $I = 2.93 \times 10^{-46}\ \text{kg m}^2$ $\tilde{B} = 0.96\ \text{cm}^{-1}$ $\tilde{\nu} = 2.9\ \text{cm}^{-1}$ $x_e = 0.96$
P11C.9 $x_e\tilde{\nu} = 13.7\ \text{cm}^{-1}$ $\tilde{\nu} = 2\,170.7\ \text{cm}^{-1}$
P11C.11 $r_{CC} = 121.0$ pm $r_{CH} = 105.5$ pm
P11C.13 $1/\langle R\rangle^2 = 1/R_e^2$ $\frac{1}{R_e^2}\left(1 - \frac{\langle x^2\rangle}{R_e^2}\right)$ $\frac{1}{R_e^2}\left(1 + \frac{3\langle x^2\rangle}{R_e^2}\right)$
P11C.15 $\tilde{B}_0 = 0.27877\ \text{cm}^{-1}$ $\tilde{B}_1 = 0.27691\ \text{cm}^{-1}$ $\tilde{\nu}_P(3) = 602.292\ \text{cm}^{-1}$ $\tilde{\nu}_R(3) = 606.170\ \text{cm}^{-1}$ $\tilde{D}_= 2.93 \times 10^4\ \text{cm}^{-1} = 3.64$ eV
P11C.17 $\tilde{\nu} = 2143.26\ \text{cm}^{-1}$ 12.82 kJ mol^{-1} 1856 N m^{-1} $\tilde{B} = 1.914\ \text{cm}^{-1}$ 113.3 pm
P11C.19 $\tilde{\nu}_S(J) - \tilde{\nu}_O(J) = 8\tilde{B}_1(J + \frac{1}{2})$ $\tilde{\nu}_S(J-2) - \tilde{\nu}_O(J+2) = 8\tilde{B}_0(J + \frac{1}{2})$

11D Vibrational spectroscopy of polyatomic molecules

E11D.1(a) HCl, CO_2, and H_2O
E11D.2(a) 3 6 12
E11D.3(a) 127
E11D.4(a) $\frac{1}{2}(\tilde{\nu}_1 + \tilde{\nu}_2 + \tilde{\nu}_3)$
E11D.6(a) infrared inactive Raman active
E11D.7(a) does not apply

11E Symmetry analysis of vibrational spectroscopy

E11E.1(a) $4A_1 + A_2 + 2B_1 + 2B_2$
E11E.2(a) all
E11E.3(a) All All
P11E.1 C_{3v} 9 $3A_1 + 3E$ All All

11F Electronic spectra

E11F.1(a) ${}^1\Sigma_g^+$
E11F.2(a) ${}^2\Sigma_g^+$
E11F.3(a) 1 3 u
E11F.5(a) $I^2 = e^{-ax_0^2/2}$
E11F.6(a) $I^2 = (1/32)(3 + 4/\pi)^2$
E11F.7(a) $\dfrac{\tilde{B}' + \tilde{B}}{2(\tilde{B}' - \tilde{B})}$
E11F.8(a) R branch $J = 7$
E11F.9(a) 30 cm^{-1} to 40 cm^{-1} increased
E11F.10(a) $1.43 \times 10^4\ cm^{-1}$ 1.77 eV
E11F.11(a) $\dfrac{3}{8}\left(\dfrac{a^3}{b - a/2}\right)^{1/2}$
E11F.12(a) $a/(4 \times 2^{1/2})$
P11F.1 neither
P11F.3 $4.936 \times 10^4\ cm^{-1}$

11G Decay of excited states

P11G.3 $n \times 150$ MHz 150 MHz
P11G.5 $P_{peak} = 33$ MW $P_{av} = 1.0$ W

11G Integrated activities

I11.1 spherical rotor symmetric rotor linear rotor asymmetric rotor symmetric rotor asymmetric rotor
I11.5 $R_{Hg^{35}Cl_2} = 229$ pm $R_{Hg^{79}Br_2} = 241$ pm $R_{Hg^{127}I_2} = 253$ pm
I11.7 $\Delta\tilde{T}_e = 25\,759.8\ cm^{-1}$ $\tilde{\nu}_0 = 2034.1\ cm^{-1}$ $\tilde{\nu}_1 = 2114.2\ cm^{-1}$ $\tilde{\nu}_1 - \tilde{\nu}_0 = 80.1\ cm^{-1}$ $n_1/n_0 = 0.1$ $T = 1.3 \times 10^3$ K
I11.11 $1.25 \times 10^6\ mol^{-1}\ dm^3\ cm^{-2}$ A_1 B_1 B_2

12 Magnetic resonance

12A General principles

E12A.1(a) $T^{-1}\,s^{-1}$

E12A.2(a) $\sqrt{3}\hbar/2$ $\pm\frac{1}{2}\hbar$ ± 0.9553 rad = $\pm 54.74°$

E12A.3(a) 575 MHz

E12A.4(a) $E_{\pm 3/2} = \mp 2.210 \times 10^{-26}$ J and $E_{\pm 1/2} = \mp 7.365 \times 10^{-27}$ J

E12A.5(a) 165 MHz

E12A.6(a) ^{31}P

E12A.7(a) 1.0×10^{-6} 5.1×10^{-6} 3.4×10^{-5}

E12A.8(a) 5

E12A.9(a) 1.3 T

P12A.1 210 MHz $m_I = -\frac{1}{2}$ 1.65×10^{-5}

P12A.3 6.81% $26.2\, I_{^{13}C}$

12B Features of NMR spectra

E12B.1(a) 5.0

E12B.2(a) 1.5

E12B.3(a) 3040 Hz

E12B.4(a) 1.37

E12B.5(a) 11 μT 110 μT

E12B.9(a) 1:4:6:4:1 quintet

E12B.11(a) 1:2:3:4:5:6:5:4:3:2:1 multiplet

E12B.14(a) $2.6 \times 10^{3}\ s^{-1}$

12C Pulse techniques in NMR

E12C.1(a) 9.40×10^{-4} T 6.25 μs

E12C.2(a) 0.21 s

E12C.3(a) 1.4 s

E12C.5(a) 1.234

P12C.1 $\Delta\tau_{90} = 5.0$ μs 5.00×10^{4} Hz

P12C.7 0.500 s

P12C.9 $M_{xy}(\tau) = M_{xy}(0)e^{-\tau/T_2}$ 50.0 ms

P12C.11 158 pm

12D Electron paramagnetic resonance

E12D.1(a) 2.0022

E12D.2(a) a = 2.3 mT 2.0025

E12D.3(a) 330.2 mT 332.8 mT 332.2 mT 334.8 mT equal intensity

E12D.4(a) 1 : 3 : 3 : 1 1 : 3 : 6 : 7 : 6 : 3 : 1

E12D.5(a) 332.3 mT 1.206 T

E12D.6(a) $I = \frac{3}{2}$

P12D.1 2.8×10^{13} Hz molecular vibrations

P12D.3 $a_{\cdot CD_3}$ = 0.35 mT width $\cdot CD_3$ = 6.9 mT width $\cdot CD_3$ = 2.1 mT

P12D.5 C_1 = 0.122 C_2 = 0.067 C_9 = 0.237

P12D.7 10% 38% 48% 52% λ = 1.95 θ = 105°

I12.3 $k_{1st,60MHz} = 160\ s^{-1}$ $k_{1st,300MHz} = 800\ s^{-1}$ 56 kJ mol^{-1}

13 Statistical thermodynamics

13A The Boltzmann distribution

E13A.1(a) 21 621 600
E13A.2(a) 40 320 5.63×10^3 3.99×10^4
E13A.3(a) 1
E13A.4(a) 524 K
E13A.5(a) 7.43
E13A.6(a) 354 K
P13A.1 $\{N_0,N_1,N_2,N_3,N_4,N_5\} = \{2,2,0,1,0,0\}$ or $\{2,1,2,0,0,0\}$
P13A.3 $\{N_0,N_1,N_2,N_3,N_4,N_5,N_6,N_7,N_8,N_9,N_{10}\}=\{12,6,2,0,0,0,0,0,0,0,0\}$ $T = \varepsilon/(0.795k)$
P13A.5 $T_{\text{electronic}} = 420$ K   not in equilibrium
P13A.7 0.36 for O_2 0.57 for H_2O

13B Partition functions

E13B.1(a) 8.23×10^{-12} m 1.78×10^{27} at 300 K 2.60×10^{-12} m 5.67×10^{28} at 3000 K
E13B.2(a) 0.358
E13B.3(a) 72.1
E13B.4(a) 7.97×10^3 1.12×10^4
E13B.5(a) 18 K
E13B.6(a) 37 K
E13B.7(a) $\sigma = 1$ $\sigma = 2$ $\sigma = 2$ $\sigma = 12$ $\sigma = 3$
E13B.8(a) 660.6
E13B.9(a) 4500 K
E13B.10(a) 2.57
E13B.11(a) 42.1
E13B.12(a) 4.291 $1 : 0.0376 : 0.0353$
P13B.5 5.00   6.262 $\left(\frac{N_0}{N}\right)_{298\text{ K}} = 1.00$ $\left(\frac{N_2}{N}\right)_{298\text{ K}} = 6.54\times10^{-11}$ $\left(\frac{N_0}{N}\right)_{5000\text{ K}} = 0.798$ $\left(\frac{N_2}{N}\right)_{5000\text{ K}} =$ 0.122
P13B.7 1.209 at 298 K   3.003 at 1000 K
P13B.9 4.5 K

13C Molecular energies

E13C.1(a) 8.15×10^{-22} J
E13C.2(a) 19.6 K
E13C.3(a) 26.4 K

E13C.4(a) 4.80×10^3 K
E13C.5(a) 1.10×10^4 K
E13C.6(a) 6.85×10^3 K
E13C.7(a) 4.03×10^{-21} J
P13C.1 4.59 K
P13C.3 2.5 kJ
P13C.5 $-\delta + \dfrac{\delta e^{-\beta\delta} + 2\delta e^{-2\beta\delta}}{1 + e^{-\beta\delta} + e^{-2\beta\delta}}$
P13C.7 $\frac{N_0}{N} = 0.641$ $\frac{N_1}{N} = 0.359$ 8.63×10^{-22} J
P13C.9 $\left(\dfrac{1}{q}\dfrac{d^2q}{d\beta^2}\right)^{1/2}$ $\dfrac{1}{q}\left(q\dfrac{d^2q}{d\beta^2} - \left(\dfrac{dq}{d\beta}\right)^2\right)^{1/2}$ $\dfrac{hc\tilde{\nu}\, e^{-\beta hc\tilde{\nu}/2}}{1 - e^{-\beta hc\tilde{\nu}}}$

13D The canonical ensemble

13E The internal energy and entropy

E13E.1(a) $\frac{7}{2}R$ $3R$ $3R$
E13E.2(a) Without vibrational contribution: $\gamma_{NH_3} = 1.33$ $\gamma_{CH_4} = 1.33$ With vibrational contribution: $\gamma_{NH_3} = 1.11$ $\gamma_{CH_3} = 1.08$
E13E.3(a) 1.96 J K^{-1} mol^{-1} 1.60 J K^{-1} mol^{-1}
E13E.4(a) $C_{V,m} = 14.95$ J K^{-1} mol^{-1} $C_{V,m} = 25.62$ J K^{-1} mol^{-1}
E13E.5(a) 126 J K^{-1} mol^{-1} 169.7 J K^{-1} mol^{-1}
E13E.6(a) 2.42×10^3 K
E13E.7(a) 43.1 43.76 J K^{-1} mol^{-1}
E13E.8(a) 19.14 J K^{-1} mol^{-1}
E13E.9(a) $S_m^V = 4.18$ J K^{-1} mol^{-1} $S_m^V = 14.3$ J K^{-1} mol^{-1}
P13E.3 $q^R = \left(\dfrac{2\pi I}{\beta\hbar^2}\right)^{1/2}$ $C_{V,m}^R = \frac{1}{2}R$ 24.1 J K^{-1} mol^{-1}
P13E.5 28 $31R$
P13E.11 216.1 J K^{-1} mol^{-1}
P13E.15 $R\ln\dfrac{A_m e^2}{\Lambda^2 N_A}$ $R\ln\dfrac{A_m\Lambda}{V_m e^{1/2}}$
P13E.17 9.6×10^{-15} J K^{-1}

13F Derived functions

E13F.1(a) $G_m^R = -13.83$ kJ mol^{-1} $G_m^V = -0.204$ kJ mol^{-1}
E13F.2(a) -5.92 kJ mol^{-1} -11.2 kJ mol^{-1}
E13F.3(a) 3.72×10^{-3}
P13F.3 100 T

P13F.5 $-45.8\ \text{kJ mol}^{-1}$

I13.1 660.6 4.26×10^4

14 Molecular Interactions

14A Electric properties of molecules

E14A.2(a) 1.4 D
E14A.3(a) 37 D 12°
E14A.4(a) 1.2×10^4 V m^{-1}
E14A.5(a) 1.659 D 1.008×10^{-39} C^2 m^2 J^{-1}
E14A.6(a) 4.75
E14A.7(a) 1.42×10^{-39} C^2 m^2 J^{-1}
E14A.8(a) 1.3
E14A.9(a) 17.8
P14A.1 1,2 isomer: 0.7 D 1,3 isomer: 0.4 D 1,4 isomer: 0
P14A.5 1.11 μD
P14A.7 0.79 D 1.3×10^{-23} cm^3
P14A.9 1.582 D 2.197×10^{-24} cm^3 5.73 cm^3 mol^{-1} 1.57 D
P14A.11 $P_m = 8.14$ cm^3 mol^{-1} $\varepsilon_r = 1.75$ $n_r = 1.32$

14B Interactions between molecules

E14B.1(a) 1.77×10^{-18} J 1.07×10^3 kJ mol^{-1}
E14B.2(a) -1.3×10^{-23} J -8.1 J mol^{-1}
E14B.3(a) $\dfrac{6Q^2 l^4}{\pi\varepsilon_0 r^5}$
E14B.4(a) -1.0×10^{-22} J -62 J mol^{-1}
E14B.5(a) -2.1 J mol^{-1}
E14B.6(a) 0.071 J mol^{-1}
P14B.1 -1.2×10^{-20} J -7.5 kJ mol^{-1} -1.6×10^{-22} J -94 J mol^{-1}
P14B.3 2.1 nm
P14B.5 -1.1 kJ mol^{-1}
P14B.7 $-9\alpha_1\alpha_2 \dfrac{I_1 I_2}{I_1 + I_2} \dfrac{1}{r^7}$

14C Liquids

E14C.1(a) 2.6 kPa
E14C.2(a) 72.8 mN m^{-1}
E14C.3(a) 728 kPa
E14C.4(a) 72.0 mN m^{-1}

14D Macromolecules

E14D.1(a) $\overline{M}_{n}=70\ \mathrm{kg\,mol^{-1}}$ $\overline{M}_{W}=71\ \mathrm{kg\,mol^{-1}}$
E14D.2(a) 24 nm
E14D.3(a) $R_c = 3.07\ \mu\mathrm{m}$ $R_{rms} = 30.8\ \mathrm{nm}$
E14D.4(a) 2.2×10^3
E14D.5(a) 0.013
E14D.6(a) 6.4×10^{-3}
E14D.7(a) +40.1% +176%
E14D.8(a) +895% $+(9.84 \times 10^4)$%
E14D.9(a) 0.16 nm
E14D.10(a) 1.8×10^{-14} N
E14D.11(a) $-0.019\ \mathrm{J\,K^{-1}\,mol^{-1}}$
P14D.1 $R_g = (3/5)^{1/2}a$ $R_{g,||} = (2)^{-1/2}a$ $R_{g,\perp} = (a^2/4+l^2/12)^{1/2}$ $R_g = 2.40\ \mathrm{nm}$ $R_{g,||} =$ 0.35 nm $R_{g,\perp} = 46$ nm

14E Self-assembly

E14E.1(a) 4.9
P14E.1 3.5 slope = -1.49 intercept = -1.95 $K_1 = 0.011$
I14.5 $b_0 = 3.59$ $b_1 = 0.957$ $b_2 = 0.362$ -1.72

15 Solids

15A Crystal structure

E15A.1(a) $N = 4$ 4.01 $g\,cm^{-3}$
E15A.2(a) (323) and (110)
E15A.3(a) $d_{112} = 229$ pm $d_{110} = 397$ pm $d_{224} = 115$ pm
E15A.4(a) 220 pm
P15A.1 $3.61 \times 10^5\ g\,mol^{-1}$
P15A.3 $(\sqrt{3}/2)a^2c$
P15A.5 $b = 605.8$ pm $a = 834.2$ pm $c = 870.0$ pm
P15A.7 4
P15A.9 $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

15B Diffraction techniques

E15B.1(a) 70.7 pm
E15B.2(a) 10.1° 14.3° 17.6°
E15B.3(a) 8.17°, 4.82° and 11.8°
E15B.4(a) 2.14°
E15B.5(a) $f(0) = 36$
E15B.6(a) $F_{hkl} = f$
E15B.7(a) for $(h + k)$ odd $F_{hkl} = -f$ for $(h + k)$ even $F_{hkl} = 3f$
E15B.11(a) 6.1 $km\,s^{-1}$
E15B.12(a) 233 pm
P15B.1 118 pm
P15B.3 cubic F lattice 408.55 pm 10.51 $g\,cm^{-3}$

15C Bonding in solids

E15C.1(a) 0.9069
E15C.2(a) 0.5236 0.6802 0.7405
E15C.3(a) 75.0 pm 133 pm
E15C.4(a) expand by 1.6%
E15C.5(a) 3500 $kJ\,mol^{-1}$
P15C.1 0.3401
P15C.3 7.655 $g\,cm^{-3}$

15D The mechanical properties of solids

E15D.1(a) 34.3 MPa
E15D.2(a) 1.6×10^{2} MPa 3.6%
E15D.3(a) 9.3×10^{-4} cm^3

15E The electrical properties of solids

E15E.1(a) 0.269
E15E.2(a) 1.03 eV
E15E.3(a) n-type

15F The magnetic properties of solids

E15F.1(a) three
E15F.2(a) -6.4×10^{-11} $m^3\ mol^{-1}$
E15F.3(a) 4.3
E15F.4(a) 1.59×10^{-8} $m^3\ mol^{-1}$
E15F.5(a) 95 kA m^{-1}
P15F.1 For $S = 2$ $\chi_m = 1.27 \times 10^{-7}$ $m^3\ mol^{-1}$ $S = 3$ $\chi_m = 2.54 \times 10^{-7}$ $m^3\ mol^{-1}$ $S = 4$ $\chi_m = 4.23 \times 10^{-7}$ $m^3\ mol^{-1}$ 2.54×10^{-7} $m^3\ mol^{-1}$

15G The optical properties of solids

E15G.1(a) 3.54 eV
P15G.1 $\mu_{\mathrm{dim},\Psi_+} = (1+S)^{-1/2}\mu_{\mathrm{mon}}$ $\mu_{\mathrm{dim},\Psi_-} = 0$
I15.1 4.811×10^{-5} K^{-1}

16 Molecules in motion

16A Transport properties of a perfect gas

E16A.1(a) 1.9×10^{20}
E16A.2(a) $1.48\ \mathrm{m^2\ s^{-1}}$ $-60.6\ \mathrm{mol\ m^{-2}\ s^{-1}}$ $1.48\times10^{-5}\ \mathrm{m^2\ s^{-1}}$ $-6.06\times10^{-4}\ \mathrm{mol\ m^{-2}\ s^{-1}}$ $1.48\times 10^{-7}\ \mathrm{m^2\ s^{-1}}$ $-6.06\times10^{-6}\ \mathrm{mol\ m^{-2}\ s^{-1}}$
E16A.3(a) $7.6 \times 10^{-3}\ \mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$
E16A.4(a) $0.0795\ \mathrm{nm^2}$
E16A.5(a) $-0.078\ \mathrm{J\,m^{-2}\,s^{-1}}$
E16A.6(a) 103 W
E16A.7(a) $1.79 \times 10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}$ $1.87 \times 10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}$ $3.43 \times 10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}$
E16A.8(a) $0.201\ \mathrm{nm^2}$
E16A.9(a) 104 mg
E16A.10(a) 2.15×10^3 Pa
E16A.11(a) $43.0\ \mathrm{g\,mol^{-1}}$
E16A.12(a) 1.3 days
P16A.1 437 pm $d = 366$ pm
P16A.3 $1.37 \times 10^{17}\ \mathrm{m^2\,s^{-1}}$ $2.84\ \mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$
P16A.5 1.7×10^{14} 1.1×10^{16}

16B Motion in liquids

E16B.1(a) $16.9\ \mathrm{kJ\,mol^{-1}}$
E16B.2(a) $13.87\ \mathrm{mS\,m^2\,mol^{-1}}$
E16B.3(a) $u_{\mathrm{Li^+}} = 4.01 \times 10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$ $u_{\mathrm{Na^+}} = 5.19 \times 10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$ $u_{\mathrm{K^+}} = 7.62 \times 10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$
E16B.4(a) $7.63\ \mathrm{mS\,m^2\,C^{-1}}$
E16B.5(a) $283\ \mathrm{\mu m\,s^{-1}}$
E16B.6(a) $1.90 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$
P16B.1 $10.15\ \mathrm{kJ\,mol^{-1}}$
P16B.3 $\mathcal{K} = 2.53\ \mathrm{mS\,m^2\,(mol\,dm^{-1})^{-3/2}}$ $\Lambda_\mathrm{m}^\circ = 12.7\ \mathrm{mS\,m^2\,mol^{-1}}$
P16B.5 $\mathcal{K} = 6.655\ \mathrm{mS\,m^2\,(mol\,dm^{-1})^{-3/2}}$ $\Lambda_\mathrm{m}^\circ = 12.56\ \mathrm{mS\,m^2\,mol^{-1}}$ $12.02\ \mathrm{mS\,m^2\,mol^{-1}}$ $120\ \mathrm{mS\,m^{-1}}$ $172\ \Omega$
P16B.7 0.83 nm

16C Diffusion

E16C.1(a) 6.2×10^3 s

E16C.2(a) 0.00 mol dm^{-3} 0.0121 mol dm^{-3}

E16C.3(a) at x = 10 cm $\mathcal{F}$ = 25 kN mol^{-1} at x = 15 cm $\mathcal{F}$ = 50 kN mol^{-1}

E16C.4(a) 67.5 kN mol^{-1}

E16C.5(a) 1.3×10^3 s

E16C.6(a) 0.42 nm

E16C.7(a) 27.3 ps

E16C.8(a) $\langle x^2\rangle^{1/2}_{\text{iodine}} = 65\ \mu\text{m}$ $\langle x^2\rangle^{1/2}_{\text{sucrose}} = 32\ \mu\text{m}$

P16C.1 12.4 kN mol^{-1} 2.1×10^{-20} N (molecule)$^{-1}$ 16.5 kN mol^{-1} 2.7×10^{-20} N (molecule)$^{-1}$ 24.8 kN mol^{-1} 4.1×10^{-20} N (molecule)$^{-1}$

P16C.7 $\frac{\langle x^4\rangle^{1/4}}{\langle x^2\rangle^{1/2}} = 3^{1/4}$

P16C.11 E_a = 6.9 kJ mol^{-1}

17 Chemical kinetics

17A The rates of chemical reactions

E17A.1(a) no change
E17A.2(a) 0.12 mmol dm^{-3} s^{-1}
E17A.3(a) $d[A]/dt = -2.7$ mol dm^{-3} s^{-1} $d[B]/dt = -5.4$ mol dm^{-3} s^{-1} $d[C]/dt = +8.1$ mol dm^{-3} s^{-1} $d[D]/dt = +2.7$ mol dm^{-3} s^{-1}
E17A.4(a) $v = 1.4$ mol dm^{-3} s^{-1} $d[A]/dt = -2.70$ mol dm^{-3} s^{-1} $d[B]/dt = -1.35$ mol dm^{-3} s^{-1} $d[D]/dt = +4.05$ mol dm^{-3} s^{-1}
E17A.5(a) dm^3 mol^{-1} s^{-1} $d[C]/dt = 3k_r[A][B]$ $-d[A]/dt = k_r[A][B]$
E17A.6(a) $\frac{1}{2}k_r[A][B][C]$ dm^6 mol^{-2} s^{-1}
E17A.7(a) second-order dm^3 mol^{-1} s^{-1} kPa^{-1} s^{-1} third-order dm^6 mol^{-2} s^{-1} kPa^{-2} s^{-1}
E17A.8(a) under all conditions $k_{r2} \gg k_{r3}[B]^{1/2}$ or $k_{r2} \ll k_{r3}[B]^{1/2}$ $k_{r2} \gg k_{r3}[B]^{1/2}$ or $k_{r2} \ll k_{r3}[B]^{1/2}$
E17A.9(a) 2.00
P17A.1 first order 4.92×10^3 s^{-1}
P17A.3 $v = k_r[ICl][H_2]$ $k_r = 0.16$ dm^3 mol^{-1} s^{-1} 2.1×10^{-6} mol dm^{-3} s^{-1}

17B Integrated rate laws

E17B.1(a) 14 Pa s^{-1} 1.5×10^3 s
E17B.2(a) second-order
E17B.3(a) 1.03×10^4 s   489 Torr   461 Torr
E17B.4(a) 0.0978 mol dm^{-3} 0.0502 mol dm^{-3}
E17B.5(a) 1.1×10^5 s
E17B.6(a) 3.1×10^{-3} dm^3 mol^{-1} s^{-1} $t_{1/2}(A) = 1.8$ hours $t_{1/2}(B) = 1$ hour
P17B.3 second-order $k_r = 9.95 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} 2.9 g
P17B.5 second-order 7.33×10^{-5} dm^3 mol^{-1} s^{-1}
P17B.7 first-order 7.65×10^{-3} min^{-1} 91 min
P17B.9 55.4 %   constant
P17B.11 first-order   0.0168 min^{-1}
P17B.13 first-order 7.1×10^{-4} s^{-1}
P17B.15 $\dfrac{2^{n-1}-1}{(n-1)k_r[A]_0^{n-1}}$ $\dfrac{3^{n-1}-1}{(n-1)k_r[A]_0^{n-1}}$
P17B.17 $\dfrac{1}{2([A]_0-2x)^2} - \dfrac{1}{2[A]_0^2} = k_r t$ $\dfrac{1}{[A]_0([A]_0-2x)} + \dfrac{1}{[A]_0^2}\ln\dfrac{[A]_0-2x}{[A]_0-x} - \dfrac{1}{[A]_0^2} = k_r t$

17C Reactions approaching equilibrium

E17C.1(a) 2.5×10^2
E17C.2(a) $23.8\ \mathrm{ms^{-1}}$
P17C.5 $k_a' = 1.7 \times 10^7\ \mathrm{s^{-1}}$ $k_a = 2.8 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ $K = 1.7 \times 10^{-2}$

17D The Arrhenius equation

E17D.1(a) $3.2 \times 10^{-12}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
E17D.2(a) $108\ \mathrm{kJ\ mol^{-1}}$ $6.62 \times 10^{15}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
E17D.3(a) $35\ \mathrm{kJ\ mol^{-1}}$
E17D.4(a) 0.076 7.6 %
E17D.5(a) $2.6 \times 10^3\ \mathrm{K}$
P17D.3 $180\ \mathrm{kJ\ mol^{-1}}$ $2.11\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
P17D.5 $13.7\ \mathrm{kJ\ mol^{-1}}$ $8.75 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$

17E Reaction mechanisms

E17E.3(a) $-3\ \mathrm{kJ\ mol^{-1}}$
P17E.3 39.1 d
P17E.5 $\dfrac{k_a k_b k_c[\mathrm{A}]}{k_a' k_b' + k_a' k_c + k_b k_c}$
P17E.7 $\dfrac{k_r K_1 K_2}{c^{\ominus 2}}[\mathrm{HCl}]^3[\mathrm{CH_3CH{=}CH_2}]$

17F Examples of reaction mechanisms

E17F.1(a) $1.9 \times 10^{-6}\ \mathrm{Pa^{-1}\ s^{-1}}$ $1.9\ \mathrm{MPa^{-1}\ s^{-1}}$
E17F.2(a) $p = 0.996$ $\langle N \rangle = 251$
E17F.3(a) 0.13
E17F.4(a) $1.50\ \mathrm{mmol\ dm^{-3}\ s^{-1}}$
E17F.5(a) $1.1 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
P17F.3 $(2k_r t[\mathrm{A}]_0^2 + 1)^{1/2}$
P17F.7 $2.3\ \mathrm{\mu mol\ dm^{-3}\ s^{-1}}$ $1.1\ \mathrm{\mu mol\ dm^{-3}}$

17G Photochemistry

E17G.1(a) 3.27×10^{21}
E17G.2(a) $4.3 \times 10^7\ \mathrm{s^{-1}}$
E17G.3(a) $0.56\ \mathrm{mol\ dm^{-3}}$
E17G.4(a) 7.1 nm
P17G.1 1.11

P17G.3 6.9 ns 1.0×10^8 s^{-1}

P17G.5 2.00×10^9 dm^3 mol^{-1} s^{-1}

P17G.7 2.6 nm

I17.3 $\dfrac{k_a k_b[\mathrm{AH}]^2[\mathrm{B}]}{k_a'[\mathrm{BH}^+]}$ $\dfrac{k_a k_b}{k_a'}[\mathrm{HA}][\mathrm{H}^+][\mathrm{B}]$

I17.5 $\dfrac{M_1(p^2+4p+1)}{(1+p)(1-p)}$ $\dfrac{M_1(6\langle N\rangle^2-6\langle N\rangle+1)}{2\langle N\rangle-1}$

18 Reaction dynamics

18A Collision theory

E18A.1(a) $1.12 \times 10^{10}\ s^{-1}$ $1.62 \times 10^{35}\ m^{-3}\ s^{-1}$ 1.6%
E18A.2(a) 1.04×10^{-3} $f = 0.069$ $f = 1.19 \times 10^{-15}$ $f = 1.57 \times 10^{-6}$
E18A.3(a) 21%   3.0%   160%   16%
E18A.4(a) $1.0 \times 10^{-5}\ mol^{-1}\ m^3\ s^{-1}$
E18A.5(a) 1.2×10^{-3}
E18A.6(a) 0.73
E18A.7(a) 5.12×10^{-7}
P18A.1 $0.043\ nm^2$ 0.15
P18A.3 $1.64 \times 10^8\ mol^{-1}\ m^3\ s^{-1}$ 7.5 ns
P18A.5 For C_2H_5 $P = 0.024$ For C_6H_{11} $P = 0.043$

18B Diffusion-controlled reactions

E18B.1(a) $4.5 \times 10^7\ m^3\ mol^{-1}\ s^{-1}$
E18B.2(a) $6.61 \times 10^6\ m^3\ mol^{-1}\ s^{-1}$ $3.0 \times 10^7\ m^3\ mol^{-1}\ s^{-1}$
E18B.3(a) $8.0 \times 10^6\ m^3\ mol^{-1}\ s^{-1}$ 84 ns
E18B.4(a) $1.81 \times 10^{11}\ mol\ m^{-3}\ s^{-1}$ $2.37 \times 10^6\ m^3\ mol^{-1}\ s^{-1}$

18C Transition-state theory

E18C.1(a) $69.7\ kJ\ mol^{-1}$ $-25.3\ J\ K^{-1}\ mol^{-1}$
E18C.2(a) $+71.9\ kJ\ mol^{-1}$
E18C.3(a) $-91.2\ J\ K^{-1}\ mol^{-1}$
E18C.4(a) $-74\ J\ K^{-1}\ mol^{-1}$
E18C.5(a) $\Delta^{\ddagger}H = +5.0\ kJ\ mol^{-1}$ $\Delta^{\ddagger}S = -46\ J\ K^{-1}\ mol^{-1}$ $\Delta^{\ddagger}G = +19\ kJ\ mol^{-1}$
E18C.6(a) $k_r^{\circ} = 20.9\ dm^6\ mol^{-2}\ min^{-1}$
E18C.7(a) 0.073
P18C.1 $\Delta^{\ddagger}H = +60.4\ kJ\ mol^{-1}$ $\Delta^{\ddagger}S = -181\ J\ K^{-1}\ mol^{-1}$ $\Delta^{\ddagger}G = +60.4... \times 10^3\ J\ mol^{-1}$ $\Delta^{\ddagger}U = +62.9\ kJ\ mol^{-1}$
P18C.5 $1.4 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ $1.2 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$
P18C.9 $\lg[k_r/(dm^3\ mol^{-1}\ s^{-1})] = 0.1451 \times I - 0.1815$ $k_r^{\circ} = 0.658\ dm^3\ mol^{-1}\ s^{-1}$ $\lg \gamma_B = 0.145\, I$
P18C.11 $408\ N\ m^{-1}$

18D The dynamics of molecular collisions

E18D.2(a) $\overline{P}kT$

18E Electron transfer in homogeneous systems

E18E.1(a) 0.01%

E18E.2(a) $\Delta E_R = 2\ \text{kJ mol}^{-1}$

E18E.3(a) $12.5\ \text{nm}^{-1}$

P18E.3 $\Delta E_R = 1.05\ \text{eV}$

P18E.5 $\beta = 13\ \text{nm}^{-1}$

19 Processes at solid surfaces

19A An introduction to solid surfaces

E19A.1(a) 1.4×10^{14} cm^{-2} s^{-1} 3.1×10^{13} cm^{-2} s^{-1}
E19A.2(a) 0.13 bar
E19A.3(a) 9.1×10^{-3}
P19A.1 $-0.646\left(\frac{C}{a_0}\right)$ $+0.259\left(\frac{C}{a_0}\right)$ $-0.128\left(\frac{C}{a_0}\right)$ $-0.516\left(\frac{C}{a_0}\right)$ (b) is the more favourable arrangement
P19A.3 $n = 1.61\times10^{15}$ cm^{-2} $f_{H_2}(100\text{ Pa}) = 6.7\times10^{5}$ s^{-1} $f_{H_2}(0.10\ \mu\text{Torr}) = 8.9\times10^{-2}$ s^{-1} $f_{C_3H_8}(100\text{ Pa}) = 1.42\times10^{5}$ s^{-1} $f_{C_3H_8}(0.10\ \mu\text{Torr}) = 1.9\times10^{-2}$ s^{-1} $n = 1.14\times10^{15}$ cm^{-2} $f_{H_2}(100\text{ Pa}) = 9.4\times10^{5}$ s^{-1} $f_{H_2}(0.10\ \mu\text{Torr}) = 0.13$ s^{-1} $f_{C_3H_8}(100\text{ Pa}) = 2.0\times10^{5}$ s^{-1} $f_{C_3H_8}(0.10\ \mu\text{Torr}) = 2.7\times10^{-2}$ s^{-1} $n = 1.86\times10^{15}$ cm^{-2} $f_{H_2}(100\text{ Pa}) = 5.8\times10^{5}$ s^{-1} $f_{H_2}(0.10\ \mu\text{Torr}) = 7.7\times10^{-2}$ s^{-1} $f_{C_3H_8}(100\text{ Pa}) = 1.2\times10^{5}$ s^{-1} $f_{C_3H_8}(0.10\ \mu\text{Torr}) = 1.6\times10^{-2}$ s^{-1}

19B Adsorption and desorption

E19B.1(a) 33.6 cm^3
E19B.2(a) 47 s
E19B.3(a) $\theta_{26.0\text{ Pa}} = 0.83$ $\theta_{3.0\text{ Pa}} = 0.36$
E19B.4(a) 0.24 kPa 25 kPa
E19B.5(a) $p_2 = 15$ kPa
E19B.6(a) -12.4 kJ mol^{-1}
E19B.7(a) 651 kJ mol^{-1} 1.7×10^{97} min 0.17 μs
E19B.8(a) 611 kJ mol^{-1}
E19B.9(a) for $E_{a,des} = 15$ kJ mol^{-1} $t_{1/2}(400\text{ K}) = 9.1$ ps $t_{1/2}(1000\text{ K}) = 0.61$ ps for $E_{a,des} = 150$ kJ mol^{-1} $t_{1/2}(400\text{ K}) = 3.9\times10^{6}$ s $t_{1/2}(1000\text{ K}) = 6.8$ μs
P19B.3 165 13.1 cm^3 263 12.5 cm^3
P19B.5 7.3 mol kg^{-1} 5.1×10^{-3} kPa^{-1}
P19B.7 $\Delta_{ad}H^{\ominus} = -20$ kJ mol^{-1} $\Delta_{ad}G^{\ominus} = -64$ kJ mol^{-1}
P19B.9 $c_2 = 2.22$ $c_1 = 0.16$ g

19C Heterogeneous catalysis

E19C.1(a) 11 m^2
P19C.3 $k_c = 3.7 \times 10^{-3}$ kPa s^{-1}

19D Processes at electrodes

E19D.1(a) 0.14 V

E19D.2(a) 2.8 mA cm^{-2}

E19D.3(a) 49 mA cm^{-2}

E19D.4(a) 1.7×10^{-4} A cm^{-2} 1.7×10^{-4} A cm^{-2}

E19D.5(a) 0.31 mA cm^{-2} 5.4 mA cm^{-2} -1.4×10^{42} mA cm^{-2}

E19D.6(a) for H^+/Pt 4.9×10^{15} s^{-1} 3.9 s^{-1} for Fe^{3+}/Pt 1.6×10^{16} s^{-1} 12 s^{-1} for H^+/Pb 3.1×10^{7} s^{-1} 2.4×10^{-8} s^{-1}

E19D.7(a) 33 Ω 3.3×10^{10} Ω

P19D.1 $\alpha = 0.38$ $j_0 = 0.79$ mA cm^{-2}

P19D.3 $E(Fe^{2+}/Fe) = -0.611$ V $\alpha = 0.365$ $j_0 = 8.91$ nA cm^{-2}

P19D.5 $\alpha = 0.50$ $j_0 = 1.99 \times 10^{-5}$ mA m^{-2}

I19.1 $U = \frac{4}{3}\pi\varepsilon r_0^3\mathcal{N}\left[\frac{1}{15}\left(\frac{r_0}{R}\right)^9 - \frac{1}{2}\left(\frac{r_0}{R}\right)^3\right]$ $R_{eq} = 294$ pm -304 kJ mol^{-1}

I19.3 57.7 pN

I19.5 +1.23 V +1.06 V +1.09 V