
Answers to problems

Detailed solutions for selected problems (indicated with an asterisk) can be found in the *Student's Solutions Manual for Physical Chemistry*, sixth edition, by P.W. Atkins, C.A. Trapp, M. Cady, and C. Giunta.

- 1.1* 0.50 m³.
1.2 1.5 kPa.
1.3* -233°N.
1.4 3.2×10^{-2} atm.
1.5* $p = \rho RT/M$, 46.0 g mol⁻¹.
1.6 -272.95°C.
1.7* (a) 4.6 kmol; (b) 130 kg; (c) 120 kg.
1.8 102 g mol⁻¹, CH₂FCF₃ or CHF₂CHF₂.
1.9* (a) 0.184 Torr; (b) 68.6 Torr; (c) 0.184 Torr.
1.10 0.33 atm (N₂), 0 (H₂), 1.33 atm (NH₃), 1.66 atm.
1.11*
1.12* (a) 2.8 km h⁻¹ E; (b) 86 km h⁻¹; (c) 86 km h⁻¹.
1.13 (a) 1.89 m; (b) 1.89 m.
1.14* $v = (2gR)^{1/2}$.
1.15 (a) 12.5 L mol⁻¹; (b) 12.3 L mol⁻¹.
1.16* 0.927, 0.208 L.
1.17* (a) 0.939 L mol⁻¹; (b) 439 K.
1.18* (a) 0.1353 L mol⁻¹; (b) 0.6957; (c) 0.58 (from expansion in $1/V_m$), 0.71 (from expansion in p).
1.19 210 K, 0.28 nm.
1.20 5.649 L² atm mol⁻¹, 59.4 cm³ mol⁻¹, 21 atm.
1.22* $c^* = (2kT/m)^{1/2}$.
1.23* $c_{\text{mean}} = (\pi ki/2m)^{1/2}$.

- 1.24 $v = 0.47v_{\text{initial}}$.
- 1.25* (a) 0.39; (b) 0.61; (c) 0.47, 0.53.
- 1.26 3.02×10^{-3} , 4.9×10^{-6} .
- 1.27*
- 1.28 $B = b - a/RT$, $C = b^2$, $1.26 \text{ L}^2 \text{ atm mol}^{-2}$, $34.6 \text{ cm}^3 \text{ mol}^{-1}$.
- 1.29* $V_c = 3C/B$, $T_c = B^2/3RC$, $p_c = B^3/27C^2$, $\frac{1}{3}$.
- 1.30* $B' = B/RT$, $C' = (C - B^2)/R^2T^2$.
- 1.31 -0.18 atm^{-1} , -4.4 L mol^{-1} .
- 1.32 $(dV_m/dT)_p = (RV_m + b)/(2pV_m + RT)$.
- 1.33* no.
- 1.34 1.11.
- 1.35* $(p - p_0)/p_0 = (a) 0.00$; (b) 0.05.
- 1.36* 8.54, 15.1.
- 1.37 0.011.
- 1.38* (a) $B = -1.32 \times 10^{-2} \text{ L mol}^{-1}$; (b) $B = -1.51 \times 10^{-2} \text{ L mol}^{-1}$, $C = 1.07 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2}$.
- 1.39 (a) $1.12 \times 10^{-3} \text{ mol}$, $2.8 \times 10^{-9} \text{ mol L}^{-1}$; (b) $4.46 \times 10^{-4} \text{ mol}$, $1.1 \times 10^{-9} \text{ mol L}^{-1}$.
- 1.40* (a) $1.1 \times 10^{-11} \text{ mol L}^{-1}$, $2.2 \times 10^{-11} \text{ mol L}^{-1}$; (b) $8.0 \times 10^{-13} \text{ mol L}^{-1}$, $1.6 \times 10^{-12} \text{ mol L}^{-1}$.
- 1.41* (a) $7.1 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1}$; on that basis alone, perfect gas law should apply, but other forces may be significant; (b) $1.6 \times 10^7 \text{ K}$; (c) no, $T_{\text{perfect}} \approx T_{\text{van der Waals}}$.
- 1.43* 51.5 km, $3.0 \times 10^{-3} \text{ bar}$.
- 1.44 $Z = 0.611$ for all gases; the experimental value from Fig. 1.27 is close to 0.55.
- 2.1* $q = \Delta H = \Delta U = 2.6 \text{ MJ}$.
- 2.2 +37 K, 4.09 kg.
- 2.3* (a) -3.46 kJ; (b) 0; (c) -3.46 kJ; (d) +24.0 kJ; (e) +27.5 kJ.
- 2.4* $T_2 = 546 \text{ K}$, $T_3 = 273 \text{ K}$; Step 1→2: $w = -2.27 \text{ kJ}$, $q = +5.67 \text{ kJ}$, $\Delta U = +3.40 \text{ kJ}$, $\Delta H = +5.67 \text{ kJ}$; Step 2→3: $w = 0$, $q = -3.40 \text{ kJ}$, $\Delta U = -3.40 \text{ kJ}$, $\Delta H = -5.67 \text{ kJ}$; Step 3→1: $w = +1.57 \text{ kJ}$, $q = -1.57 \text{ kJ}$, $\Delta U = 0$, $\Delta H = 0$; Cycle: $w = -0.70 \text{ kJ}$, $q = +0.70 \text{ kJ}$, $\Delta U = 0$, $\Delta H = 0$.
- 2.5 (a) -0.27 kJ; (b) -0.94 kJ.
- 2.6 -8.9 kJ, -8.9 kJ.
- 2.7* +98.7 kJ mol⁻¹, +95.8 kJ mol⁻¹.
- 2.8 36.5 L.
- 2.9* -87.33 kJ mol⁻¹.
- 2.10* -2.13 MJ mol⁻¹, -1.267 MJ mol⁻¹.
- 2.11 +17.7 kJ mol⁻¹, +116.0 kJ mol⁻¹.
- 2.12* more exothermic by 5376 kJ mol⁻¹.
- 2.13 (a) 0.39 mol, 0.50 L, 0.50 L; (b) +19 kJ; (c) -3.0 kJ; (d) $\Delta U = 0$, for all 3 paths; path ACB: $q = -9.5 \times 10^2 \text{ J}$; path ADB: $q = -1.9 \times 10^4 \text{ J}$; path AB: $q = -3.0 \times 10^3 \text{ J}$.
- 2.14* (a) 60 kJ; (b) -70 J; (c) +10 J, +50 J.
- 2.15* $\Delta H = nC_{p,m}(T_f - T_i)$.
- 2.16 $w_r = 3bw/a$; $w_r = -\frac{8}{9}nT_r \ln\{(V_{r,2} - \frac{1}{3})/(V_{r,1} - \frac{1}{3})\} - n(1/V_{r,2} - 1/V_{r,1})$; $w_r/n = -\frac{8}{9} \ln\{\frac{1}{2}(3x - 1)\} - 1/x + 1$.
- 2.17* -25968 kJ mol⁻¹, +2357 kJ mol⁻¹.
- 2.18 -994.30 kJ mol⁻¹.
- 2.19* (a) +16.2 kJ mol⁻¹; (b) +114.6 kJ mol⁻¹; (c) +122.0 kJ mol⁻¹.
- 2.20 (a) 120.3 kJ mol⁻¹; (b) +68.9 kJ mol⁻¹; (c) +48.1 kJ mol⁻¹.
- 2.21* (a) +240 kJ mol⁻¹; (b) +228 kJ mol⁻¹.
- 2.22 (a) -101.8 kJ mol⁻¹; (b) -344.2 kJ mol⁻¹; (c) +44.0 kJ mol⁻¹.
- 2.23* (a) (1) isochoric step: $n = \infty$; isobaric step: $n = 0$; (2) adiabatic step: $n = \nu$; isochoric step: $n = \infty$; (b) (1) isochoric step: $w = 0$, $\Delta U = q = 55.8 \text{ kJ}$, $\Delta H = 78.1 \text{ kJ}$; isobaric step: $w = 22.3 \text{ kJ}$, $\Delta U = -55.8 \text{ kJ}$, $\Delta H = q = -78.1 \text{ kJ}$; overall: $w = -q = 22.3 \text{ kJ}$, $\Delta U = \Delta H = 0$; (2) adiabatic step: $q = 0$, $\Delta U = w = 9.37 \text{ kJ}$, $\Delta H = 13.1 \text{ kJ}$; isochoric step: $w = 0$, $\Delta U = q = -9.37 \text{ kJ}$, $\Delta H = -13.1 \text{ kJ}$; overall: $w = -q = 9.37 \text{ kJ}$, $\Delta U = \Delta H = 0$.
- 2.25* $k = -66.51$, $n = 0.9277$, $R = 0.99958$ (a good fit). Predicted $\Delta_c H^\ominus$ (decane) = -6612.4 kJ mol⁻¹; experimental value, -6772.5 kJ mol⁻¹; error, 2.36 per cent.
- 2.26* (a) no, as a plot of $\ln p$ against $\ln V$ does not yield a straight line; (b) numerical integration yields $w = 685 \text{ J}$; (c) fitting the data to the van der Waals equation yields $T = 350 \text{ K}$.
- 3.1 $2.18 \times 10^{-11} \text{ Pa}^{-1}$, -0.220 cm^3 , 997.2 cm^3 .
- 3.2* (a) +0.75 kJ mol⁻¹; (b) +0.75 kJ mol⁻¹.
- 3.3* 41.40 J K⁻¹ mol⁻¹.
- 3.4* -30.5 J mol⁻¹.
- 3.5 1.67.
- 3.6* not exact.
- 3.7* not exact; dq/T is exact.
- 3.8 $dw = (y + z) dx + (x + z) dy + (x + y) dz$.
- 3.10 $(\partial H/\partial p)_T = -\mu C_p$.
- 3.11* $C_{p,m} - C_{v,m} = R$.
- 3.12* 3.14*
- 3.15 $dp = \{R/(V_m - b)\}dT + \{2a/V_m^3 - RT/(V_m - b)^2\}dV_m$, $(\partial V/\partial T)_p = RV^3(V - b)/(RTV^3 - 2a(V - b)^2)$.
- 3.16* +3.80 kJ.
- 3.17 $dp = \{a(V_m - 2b)/V_m^3 - p\}dV_m/(V_m - b) + (p + a/V_m^2)dT/T$.
- 3.18 $T = p(V - nb)/nR + na(V - nb)/RV^2$, $(\partial T/\partial p)_V = (V_m - b)/R$.
- 3.19* $\alpha = RT^2(V - nb)/\{RTV^3 - 2na(V - nb)^2\}$, $\kappa_T = V^2(V - nb)^2/\{RTV^3 - 2na(V - nb)^2\}$.
- 3.20 $\mu C_p = (1 - b\zeta/V_m)V/(\zeta - 1)$, $\zeta = RTV_m^3/2a(V_m - b)^2$, 1.46 K atm^{-1} , $T_1 = (\frac{27}{4})T_c(1 - b/V_m)^2$, 2021 K .

- 3.21*
 3.22 9.2 J K⁻¹ mol⁻¹.
 3.23* 322 ms⁻¹.
 3.24* 0.80 m, 1.6 m, 2.8 m.
 3.25 (a) 29.9 K MPa⁻¹; (b) -2.99 K.
 3.26* (a) 23.5 K MPa⁻¹; (b) 14.0 K MPa⁻¹.
 3.27* $T_1 = 842 \text{ K}$, $T_2 = T_3 = 348 \text{ K}$; $p_1 = p_2 = p_3 = 1.72 \text{ bar}$;
 $V_1 = 40.7 \text{ L}$, $V_2 = V_3 = 16.8 \text{ L}$; $\Delta U_1 = 11.3 \text{ kJ}$,
 $\Delta U_2 = \Delta U_3 = 1.04 \text{ kJ}$; $\Delta U(\text{total}) = 13.4 \text{ kJ}$.
 3.28 Same answers as for problem 3.27. It does not matter
 whether the piston between chambers 2 and 3 is diathermic
 or adiabatic.
 3.29* increase.
 3.30 (a) $\mu = \alpha T^2/C_p$; (b) $C_V = C_p - R(1 + 2\alpha pT/R)^2$.
- 4.1 (a) -21.3 J K⁻¹ mol⁻¹, +21.7 J K⁻¹ mol⁻¹;
 (b) -111.2 J K⁻¹ mol⁻¹, -1.5 J K⁻¹ mol⁻¹.
 4.2 +11 J K⁻¹.
 4.3* (a) 57.0°C, -43.9 kJ, +146 J K⁻¹, +28 J K⁻¹; (b) 49.9°C.
 4.4* (a) +50.74 J K⁻¹, -11.5 J K⁻¹; (b) ΔA_A is indeterminate,
 $\Delta A_B = +3.46 \text{ kJ}$; (c) ΔG_A is indeterminate,
 $\Delta G_B = +3.46 \text{ kJ}$; (d) +39.2 J K⁻¹, -39.2 J K⁻¹.
 4.5* Step 1→2: $w = -11.5 \text{ kJ}$, $q = +11.5 \text{ kJ}$, $\Delta U = 0$,
 $\Delta H = 0$, $\Delta S = +19.1 \text{ J K}^{-1}$, $\Delta S_{\text{tot}} = 0$; Step 2→3:
 $w = -3.74 \text{ kJ}$, $q = 0$, $\Delta U = -3.74 \text{ kJ}$, $\Delta H = -6.23 \text{ kJ}$,
 $\Delta S = 0$, $\Delta S_{\text{sur}} = 0$; Step 3→4: $w = +5.74 \text{ kJ}$,
 $q = -5.74 \text{ kJ}$, $\Delta U = 0$, $\Delta H = 0$, $\Delta S = +19.1 \text{ J K}^{-1}$,
 $\Delta S_{\text{tot}} = 0$; Step 4→1: $w = +3.74 \text{ kJ}$, $q = 0$,
 $\Delta U = +3.74 \text{ kJ}$, $\Delta H = +6.23 \text{ kJ}$, $\Delta S = 0$, $\Delta S_{\text{tot}} = 0$;
 Cycle: $w = -5.8 \text{ kJ}$, $q = +5.8 \text{ kJ}$, $\Delta U = 0$, $\Delta H = 0$,
 $\Delta S = 0$, $\Delta S_{\text{tot}} = 0$.
 4.6* Path (a): $w = -2.74 \text{ kJ}$, $q = +2.74 \text{ kJ}$, $\Delta U = 0$, $\Delta H = 0$,
 $\Delta S = +9.13 \text{ J K}^{-1}$, $\Delta S_{\text{sur}} = -9.13 \text{ J K}^{-1}$, $\Delta S_{\text{tot}} = 0$; Path
 (b): $w = -1.66 \text{ kJ}$, $q = +1.66 \text{ kJ}$, $\Delta U = 0$, $\Delta H = 0$,
 $\Delta S = +9.13 \text{ J K}^{-1}$, $\Delta S_{\text{sur}} = -5.53 \text{ J K}^{-1}$,
 $\Delta S_{\text{tot}} = +3.60 \text{ J K}^{-1}$.
 4.7* Path (a): $q = 0$, $w = -9.1 \times 10^2 \text{ J}$, $\Delta H = -1.5 \text{ kJ}$, $\Delta S = 0$,
 $\Delta S_{\text{sur}} = 0$, $\Delta S_{\text{tot}} = 0$; Path (b): $q = 0$, $w = -7.5 \text{ kJ}$,
 $\Delta H = -1.2 \text{ kJ}$, $\Delta S = +1.12 \text{ J K}^{-1}$, $\Delta S_{\text{sur}} = 0$,
 $\Delta S_{\text{tot}} = +1.12 \text{ J K}^{-1}$.
 4.8 Process (a): $\Delta S = +5.8 \text{ J K}^{-1}$, $\Delta S_{\text{sur}} = -5.8 \text{ J K}^{-1}$,
 $\Delta H = 0$, $\Delta T = 0$, $\Delta A = -1.7 \text{ kJ}$, $\Delta G = -1.7 \text{ kJ}$; Process
 (b): $\Delta S = +5.8 \text{ J K}^{-1}$, $\Delta S_{\text{sur}} = -1.7 \text{ J K}^{-1}$, $\Delta H = 0$,
 $\Delta T = 0$, $\Delta A = -1.7 \text{ kJ}$, $\Delta G = -1.7 \text{ kJ}$; Process
 (c): $\Delta S = +3.9 \text{ J K}^{-1}$, $\Delta S_{\text{sur}} = 0$, $\Delta H = -0.84 \text{ kJ}$,
 $\Delta T = -41 \text{ K}$, ΔA and ΔG indeterminate.
 4.9 (a) 200.7 J K⁻¹ mol⁻¹; (b) 232.0 J K⁻¹ mol⁻¹.
 4.10 +45.4 J K⁻¹, +51.2 J K⁻¹.
 4.11* -160.07 kJ mol⁻¹.
 4.12 (a) +17.0 J K⁻¹; (b) +36 J K⁻¹.
 4.13* (a) 0.11 kJ mol⁻¹; (b) 0.11 kJ mol⁻¹.
 4.14* (a) 63.88 J K⁻¹ mol⁻¹; (b) 66.08 J K⁻¹ mol⁻¹.
 4.15 7.8 km.
 4.16 at 298 K: +41.16 kJ mol⁻¹, +42.08 J K⁻¹ mol⁻¹; at
 398 K: +40.84 kJ mol⁻¹, +41.08 J K⁻¹ mol⁻¹.
 4.17* (a) +76.9 J K⁻¹ mol⁻¹; (b) +96.864 J K⁻¹ mol⁻¹.
 4.18 at 200 K: 32.00 kJ mol⁻¹, 293.5 J K⁻¹ mol⁻¹.
 4.19* +34.4 kJ mol⁻¹, 243 J K⁻¹ mol⁻¹ at 298 K.
 4.21*
 4.23 $\Delta S = nC_{p,m} \ln(T_f/T_h) + nC_{p,m} \ln(T_f/T_c)$, +22.6 J K⁻¹.
 4.24* -21 K, +35.9 J K⁻¹ mol⁻¹.
 4.25* Step 1: $\Delta S = 0$, $\Delta S_{\text{sur}} = 0$; Step 2: $\Delta S = +33 \text{ J K}^{-1}$,
 $\Delta S_{\text{sur}} = -33 \text{ J K}^{-1}$; Step 3: $\Delta S = 0$, $\Delta S_{\text{sur}} = 0$; Step 4:
 $\Delta S = -33 \text{ J K}^{-1}$, $\Delta S_{\text{sur}} = +33 \text{ J K}^{-1}$.
 4.26*
 4.28* +247.8 J K⁻¹ mol⁻¹, +336.6 J K⁻¹ mol⁻¹,
 +314.7 J K⁻¹ mol⁻¹.
 4.29 (a) +0.8 kJ mol⁻¹; (b) +11.9 kJ mol⁻¹;
 (c) +15.0 kJ mol⁻¹.
 4.30* 46.60 J K⁻¹ mol⁻¹, 46.73 J K⁻¹ mol⁻¹.
 4.31 $\frac{4}{3}$.
 4.32*
 5.1* -501 kJ mol⁻¹.
 5.2 (a) +7 kJ mol⁻¹; (b) +107 kJ mol⁻¹.
 5.3 -27 kJ mol⁻¹.
 5.4* 73 atm.
 5.6*
 5.7* $(\partial S/\partial V)_T = \alpha/\kappa_T$ and $(\partial V/\partial S)_p = \alpha TV/C_p$.
 5.8 $(\partial p/\partial S)_V = \alpha T/\kappa_T C_V$.
 5.9*
 5.10 (a) $(\partial H/\partial p)_T = 0$; (b)
 $(\partial H/\partial p)_T = \{nb - (2na/RT)\lambda^2\}/\{1 - (2na/RTV)\lambda^2\}$,
 $\lambda = 1 - b/V_m \approx -8.3 \text{ J atm}^{-1}$, -8 J.
 5.11*
 5.12 (a) $3.0 \times 10^{-3} \text{ atm}$; (b) 0.30 atm.
 5.13 $(\partial C_V/\partial V)_T = (RT/V_m^2)(\partial^2(BT)/\partial T^2)_V$.
 5.14*
 5.15 $\pi_T = ap/RTV_m$.
 5.16 0.02 per cent.
 5.17* (a) $\Delta_r G' = \tau \Delta_r G + (1 - \tau)\Delta_r H$;
 (b) $\Delta_r G' = \tau \Delta_r G + (1 - \tau)(\Delta_r H - T\Delta_r C_p) - T' \Delta C_p \ln \tau$,
 $\tau = T'/T$.
 5.19* $q_{\text{rev}} = nRT \ln\{(V_f - nb)/(V_i - nb)\}$.
 5.20 -0.50 kJ.
 5.21* $G' = G + p^*V_0(1 - e^{-p/p^*})$, expansion.
 5.22* $\ln \phi = Bp/RT + (C - B^2)p^2/2R^2T^2 + \dots$, 0.999 atm.
 5.23 $\phi = 2e^{\lambda^{1/2}-1}/(1 + \lambda^{1/2})$, $\lambda = 1 + 4p q/R$.
 5.24* 13 per cent.
 5.25 +57.2 kJ mol⁻¹, +85.6 kJ mol⁻¹, +112.8 kJ mol⁻¹.

- 5.26* (a) 0.750; (b) 0.372.
- 5.28* The second option leads to $p = RT/(V - b) + \text{constant}$.
- 5.29* As pressure increases, entropy increases, remains constant, and decreases, respectively.
- 6.1* 196.0 K, 11.1 Torr.
- 6.2* 9 atm.
- 6.3 (a) +5.56 kPa K⁻¹; (b) 2.5 per cent.
- 6.4* (a) -22.0 J K⁻¹ mol⁻¹; (b) -109.0 J K⁻¹ mol⁻¹; (c) +110 J mol⁻¹.
- 6.5 (a) -1.63 cm³ mol⁻¹; (b) +30.1 L mol⁻¹, 0.6 kJ mol⁻¹.
- 6.6* 234.4 K.
- 6.7 22°C.
- 6.8* (a) 357 K (84°C); (b) +37.8 kJ mol⁻¹.
- 6.9 (a) 227.5°C; (b) +55 kJ mol⁻¹.
- 6.10* 6.12*
- 6.13 9.8 Torr.
- 6.14 $1/T_b = 1/T_c + Mgh/TA\Delta_{\text{vap}}H$, 363 K (90°C).
- 6.15* $(\partial^2\mu/\partial T^2)_p = -C_{p,m}/T$.
- 6.16*
- 6.18* (b) 112 K; (c) +8.07 kJ mol⁻¹.
- 6.19 (b) 178.18 K; (c) 383.6 K; (d) +33.0 kJ mol⁻¹.
- 6.20 +31.6 kJ mol⁻¹.
- 6.21* 1.60×10^4 bar.
- 7.1* $K_A = 15.58$ kPa, $K_B = 47.03$ kPa.
- 7.2* 17.5 cm³ mol⁻¹ (NaCl), 18.07 cm³ mol⁻¹ (H₂O).
- 7.3 -1.4 cm³ mol⁻¹ (MgSO₄), 18.04 cm³ mol⁻¹ (H₂O).
- 7.4* 12.0 cm³ mol⁻¹.
- 7.5 57.9 mL ethanol, 45.8 mL water, 0.96 cm³.
- 7.6* (b) $K_A = 450$ Torr, $K_1 = 465$ Torr.
- 7.7 -4.6 kJ.
- 7.8* $\mu_A = \mu_A^* - RT \ln x_A + gRTx_B^2$.
- 7.10* $V_B(x_A, x_B) = V_B(0, 1) - \int_{V_A(0)}^{V_A(x_A)} \{x_A dV_A/(1 - x_A)\}$.
- 7.12*
- 7.14* $V_{\text{cyclo}} = 109.0$ cm³ mol⁻¹, $V_{\text{polymer}} = 279.3$ cm³ mol⁻¹.
- 7.15 (a) $V_1 = V_{m,1} + a_0x_2^2 + a_1(3x_1 - x_2)x_2^2$,
 $V_2 = V_{m,2} + a_0x_1^2 + a_1(x_1 - 3x_2)x_1^2$;
 (b) $V_1 = 75.63$ cm³ mol⁻¹, $V_2 = 99.06$ cm³ mol⁻¹.
- 7.16* For $x_T = 0.228, 0.511, 0.810$, $\gamma_T = 0.490, 0.723, 0.966$, and $\gamma_E = 1.031, 0.920, 0.497$.
- 7.17 $K_H = 371$ bar; at $p = 60.0$ bar, $\gamma_{\text{CO}_2} = 0.98$.
- 7.18* $S_0 = 19.89$ mol L⁻¹, $\tau = 165$ K; fits well, $R = 0.99978$.
- 8.2* (a) 2150°C; (b) $x(\text{MgO}) = 0.35$, $y(\text{MgO}) = 0.18$, ratio 0.4; (c) 2640°C.
- 8.3 (a) $n(l)/n(s) = 5$; (b) no liquid.
- 8.4*
- 8.5* A compound with probable formula A₃B exists. It melts incongruently at 700°C. The proportions of A and B in the product are dependent upon the overall composition and the temperature. A eutectic exists at 400°C and $x_B \approx 0.83$.
- 8.6 The number of distinct chemical species (as opposed to components) and phases present at the indicated points are, respectively $b(3, 2)$, $d(2, 2)$, $e(4, 3)$, $f(4, 3)$, $g(4, 3)$, $k(2, 2)$.
- 8.7* $T_{\text{uc}} = 122^\circ\text{C}$, $T_{\text{ic}} = 8^\circ\text{C}$.
- 8.8 MgCu₂: 16 per cent Mg by mass; Mg₂Cu: 43 per cent Mg by mass.
- 8.9* No phases are in equilibrium as the system cools. The phases through which the system passes upon cooling are: liquid, liquid + solid K₂FeCl₄, solid K₂FeCl₄ + solid KFeCl₃.
- 8.11*
- 8.12* (b) 391.0 K; (c) $n_{\text{liq}}/n_{\text{vap}} = 0.532$.
- 8.13 (b) $n_{\text{liq}}/n_{\text{vap}} = 10.85$.
- 8.14 (b) $n_{\text{left}}/n_{\text{right}} = 0.093$; 302.5 K at $x = 0.750$.
- 8.15* Temperature (y): 78 K (0.9); 80 K (1.08); 82 K (1.04); 84 K (1.00); 86 K (0.99); 88 K (0.99); 90.2 K (0.99). To within experimental uncertainties the solution appears ideal.
- 9.1* (a) +4.48 kJ mol⁻¹; (b) 0.101 atm.
- 9.2 (a) 1.24×10^{-9} ; (b) 1.29×10^{-8} ; (c) 1.8×10^{-4} ; (d) as pressure increases, α decreases; as temperature increases, α increases.
- 9.3 $\Delta_r H^\ominus = -(2.196 \times 10^4 \text{ K} - 8.84T)R$, 8.48R.
- 9.4* $\Delta_r H^\ominus = +3.00 \times 10^5$ J mol⁻¹ and $\Delta_r S^\ominus = +102$ J K⁻¹ mol⁻¹ throughout this temperature range; at 1395 K: $K = 1.22 \times 10^{-6}$, $\Delta_r G^\ominus = +158$ kJ mol⁻¹; at 1443 K: $K = 2.80 \times 10^{-6}$, $\Delta_r G^\ominus = +153$ kJ mol⁻¹; at 1498 K: $K = 7.23 \times 10^{-6}$, $\Delta_r G^\ominus = +147$ kJ mol⁻¹.
- 9.5 $\Delta_r G^\ominus(T)/(\text{kJ mol}^{-1}) = 78 - 0.161(T/\text{K})$.
- 9.6* 1.69×10^{-5} .
- 9.7 5.71, -103 kJ mol⁻¹.
- 9.8* 14.7 kJ mol⁻¹, +18.8 kJ mol⁻¹.
- 9.9 1.800×10^{-3} (at 973 K), 1.109×10^{-2} (at 1073 K), 4.848×10^{-2} (at 1173 K), +158 kJ mol⁻¹.
- 9.10*
- 9.11* $\xi = 1 - 1/(1 + ap/p^\ominus)^{1/2}$. 9.12 0.140.
- 9.13* $\Delta_r G' = \Delta_r G + (T - T')\Delta_r S + \alpha\Delta a + \beta\Delta b + \gamma\Delta c$,
 $\alpha = T' - T - T' \ln(T'/T)$, $\beta = \frac{1}{2}(T'^2 - T^2) - T'(T' - T)$,
 $\gamma = 1/T - 1/T' + \frac{1}{2}T'(1/T'^2 - 1/T^2)$; -225.31 kJ mol⁻¹.
- 9.14* +76.8 kJ mol⁻¹.
- 9.15 (a) -72.4 kJ mol⁻¹, -144 J K⁻¹ mol⁻¹; (b) +131.2 kJ mol⁻¹, +309.2 J K⁻¹ mol⁻¹.
- 9.16* now: 5.64; then: 5.70.
- 9.17 (a) 1.2×10^8 ; (b) 2.7×10^3 .
- 9.18 the trihydrate.
- 9.19* 0.23, 0.46, 0.30.

- 10.1 $\text{Pb(s)}|\text{PbSO}_4\text{(s)}||\text{PbSO}_4\text{(aq)}||\text{Hg}_2\text{SO}_4\text{(aq)}||\text{Hg}_2\text{SO}_4\text{(s)}|\text{Hg(l)}$, +1.03 V.
- 10.2* (a) 4.0×10^{-3} , 1.2×10^{-2} ; (b) 0.74, 0.60; (c) 5.9; (d) +1.102 V; (e) +1.079 V.
- 10.3* 2.0.
- 10.4 (a) +1.23 V; (b) +1.09 V.
- 10.5* (a) $E = E^\ominus - (38.54 \text{ mV}) \times \{\ln(4^{1/3}h) + \ln \gamma_{\pm}\}$; (b) 1.0304 V; (c) 6.84×10^{34} ; (d) 0.763; (e) 0.75; (f) $-87.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $-262.4 \text{ kJ mol}^{-1}$.
- 10.6* +0.268 38 V.
- 10.7 14.23 at 20.0°C, +74.9 kJ mol⁻¹, +80.0 kJ mol⁻¹, -17.1 J K⁻¹ mol⁻¹.
- 10.8 0.533.
- 10.9* (a) +0.2223 V, +0.2223 V; (b) 1.10, 0.796.
- 10.10*
- 10.11 -131.25 kJ mol⁻¹, +56.7 J K⁻¹ mol⁻¹, -167.10 kJ mol⁻¹.
- 10.12*
- 10.13 (a) $E = E^\ominus + (2.303RT/F)\text{pOH}$; (b) $E = E^\ominus + (2.303RT/F) \times (\text{p}K_w - \text{pH})$; (c) -37.6 mV.
- 10.14 -1.2 V.
- 10.15* 10.18*
- 10.19* (a) $-1.991 \text{ V} > E^\ominus > -2.19 \text{ V}$, scandium; (b) 1.4×10^{10} .
- 10.20 $b(\text{H}_2\text{VO}_4^-) = 0.0048 \text{ mol kg}^{-1}$, $b(\text{V}_4\text{O}_{17}^{4-}) = 0.0013 \text{ mol kg}^{-1}$.
- 10.21 (a) $(\partial E/\partial p)_{T,n} = -(\Delta_r V/\nu F)$; (b) $2.84 \times 10^{-6} \text{ V atm}^{-1}$ from fit, $2.98 \times 10^{-6} \text{ V atm}^{-1}$ from $\Delta_r V$; (c) $E_{30^\circ\text{C}}/V = 0.00856 + 2.84 \times 10^{-6} p/(\text{atm})$: A second-order polynomial fit is slightly better; (d) $\kappa_T = -3.2 \times 10^{-7} \text{ atm}^{-1}$.
- 10.22* (a) $\Delta E = -(RT/\nu F) \ln p/(\text{atm})$; fits well below 100 atm, but deviates above that pressure; (b) $\Delta E = (RT/\nu F) \{\ln p/(\text{atm}) + Cp\}$, $(\partial E/\partial p)_T = (RT/\nu F) \{1/p + C\}$, $C = 6.665 \times 10^{-4} \text{ atm}^{-1}$, $R = 0.99940$; (c) From empirical virial equation: $\Delta E = (RT/\nu F) \ln p/(\text{atm}) + 0.000537(p-1)/(\text{atm}) + 1.75 \times 10^{-8}(p^2-1)/(\text{atm}^2)$; (d) p , $\phi/\phi_{1 \text{ atm}}$: 1.00 atm, 1.00; 10 atm, 0.994; 38 atm, 1.02; 51 atm, 1.04; 108 atm, 1.07; 210 atm, 1.03; 380 atm, 1.23; 430 atm, 1.38; 560 atm, 1.44; 720 atm, 1.64; 900 atm, 1.81; 1020 atm, 2.02.
- 11.1* (a) $1.6 \times 10^{-33} \text{ J m}^{-3}$; (b) $2.5 \times 10^{-4} \text{ J m}^{-3}$.
- 11.2* $6.29 \times 10^{-34} \text{ J s}$.
- 11.3 (a) $7.47 \times 10^{-29} \text{ J m}^{-3}$; (b) $4.59 \times 10^{-14} \text{ J m}^{-3}$; (c) $3.49 \times 10^{-11} \text{ J m}^{-3}$; classical values: (a) 0.807 J m⁻³; (b) 1.67 J m⁻³; (c) 2.10 J m⁻³.
- 11.4 (a) 2231 K, 0.031R; (b) 343 K, 0.897R.
- 11.5* (a) 0.020; (b) 0.007; (c) 7×10^{-6} ; (d) 0.5; (e) 0.61.
- 11.6 (a) 9.0×10^{-6} ; (b) 1.2×10^{-6} .
- 11.7 $\lambda_{\text{max}} T = hc/5k$.
- 11.8* (a) $N = (2/L)^{1/2}$; (b) $1/c(2L)^{1/2}$; (c) $1/(\pi a^3)^{1/2}$; (d) $1/(32\pi a^5)^{1/2}$.
- 11.9 (a) $N = 1/(32\pi a_0^3)^{1/2}$; (b) $N = 1/(32\pi a_0^5)^{1/2}$.
- 11.10* (a) ik ; (c) 0.
- 11.11 (a) -1; (b) -1.
- 11.12* (a) $-k^2$; (b) $-k^2$; (c) 0; (d) 0.
- 11.13* (a) $\cos^2 \chi$; (b) $\sin^2 \chi$; (c) $0.95e^{ikx} \pm 0.32e^{-ikx}$.
- 11.14 $\hbar^2 k^2/2m$.
- 11.15 (a) kh ; (b) 0; (c) 0.
- 11.16* (a) $6a_0$, $42a_0^2$; (b) $5a_0$, $30a_0^2$.
- 11.17* (a) $-e^2/4\pi\epsilon_0 a_0$; (b) $\hbar^2/m_e a_0^2$.
- 11.19* (a) 1; (b) 2x; (c) \hbar .
- 11.21* 500 nm, blue green.
- 11.22* 255 K, 11.3 μm .
- 11.23* (a) Assuming $\Delta_r C_p \approx \text{constant}$, methane becomes unstable above $\approx 825 \text{ K}$; the authors' statement is confirmed; (b) $\lambda_{\text{max}}(1000 \text{ K}) = 2880 \text{ nm}$; (c) $\rho(\text{brown dwarf})/\rho(\text{Sun}) = 8.8 \times 10^{-3}$ at $\lambda_{\text{max}}(\text{brown dwarf})$, $M(\text{brown dwarf})/M(\text{Sun}) = 7.7 \times 10^{-4}$; (d) 2.31×10^{-7} , it hardly shines.
- 11.24 $k = 1.382 \times 10^{-23} \text{ J K}^{-1}$, $h = 6.69 \times 10^{-34} \text{ J s}$.
- 12.1* $1.24 \times 10^{-39} \text{ J}$, 2.2×10^9 , $1.8 \times 10^{-30} \text{ J}$.
- 12.2 (a) $1.60 \times 10^{-19} \text{ J}$; (b) $2.42 \times 10^{14} \text{ Hz}$; (c) total number of electrons = 1.12262.
- 12.3* CO (1900 N m⁻¹) > NO (1600 N m⁻¹) > HCl (516 N m⁻¹) > HBr (412 N m⁻¹) > HI (314 N m⁻¹).
- 12.4* $1.30 \times 10^{-22} \text{ J}$, $\pm \hbar$.
- 12.5 $E/(10^{-22} \text{ J}) = 0, 2.62, 7.86, 15.72$.
- 12.6 $E = (\hbar^2/8m) \times (\pi^2/L_1^2 + \pi^2/L_2^2 + \pi^2/L_3^2)$.
- 12.7* (a) $N^2/2\kappa$; (b) $N^2/4\kappa^2$.
- 12.8 $g = \frac{1}{2}(mk/\hbar^2)^{1/2}$.
- 12.9* $\langle T \rangle = \frac{1}{2}(v + \frac{1}{2})\hbar\omega$.
- 12.10 $0, \frac{3}{4}(2v^2 + 2v + 1)\alpha^4$.
- 12.11* (a) $L((1/12) - (1/2\pi^2 n^2))^{1/2}$, $nh/2L$; (b) $\{(v\frac{1}{2})\hbar/\omega m\}^{1/2}$, $\{(v + \frac{1}{2})\hbar\omega m\}^{1/2}$.
- 12.12* $\mu_{v+1,v} = \alpha\{(v+1)/2\}^{1/2}$, $\mu_{v-1,v} = \alpha(v/2)^{1/2}$.
- 12.13 $\langle T \rangle = -\frac{1}{2}\langle V \rangle$.
- 12.14 (a) $+h$, $\hbar^2/2I$; (b) $-2h$, $2\hbar^2/I$; (c) 0, $\hbar^2/2I$; (d) $\hbar \cos 2\chi$, $\hbar^2/2I$.
- 12.15* (a) 0, 0; (b) $3\hbar^2/I$, $6^{1/2}\hbar$; (c) $6\hbar^2/I$, $2(3^{1/2})\hbar$.
- 12.17* $\cos \theta = m_l / \{(l+1)\}^{1/2}$, $54^\circ 44'$.
- 12.18 $-(a^2 + b^2 + c^2)$.
- 12.19* $l_x = (\hbar/i)(y\partial/\partial z - z\partial/\partial y)$ and cyclic permutations, $[l_x, l_y] = i\hbar l_z$.
- 12.20*
- 12.21* 0.49.
- 12.22 (b) $\langle v^2 \rangle_n^{1/2} = [L^2/3 - \frac{1}{4}(n\pi/L)^2]^{1/2}$; as $n \rightarrow \infty$, $\langle v^2 \rangle_n^{1/2} \rightarrow L/\sqrt{3}$.

- 13.1* $n_2 \rightarrow 6, 7503, 5908, 5129, \dots, 3908 \text{ nm}$.
- 13.2 397.13 nm, 3.40 eV.
- 13.3* 987 663 cm^{-1} , 137 175 cm^{-1} , 185 187 cm^{-1} , 122.5 eV.
- 13.4 5.39 eV.
- 13.5* $A = 38.50 \text{ cm}^{-1}$.
- 13.6 $3.3429 \times 10^{-27} \text{ kg}$, $I_D/I_H = 1.000 272$.
- 13.7* 7621 cm^{-1} , 10 228 cm^{-1} , 11 552 cm^{-1} , 6.80 eV.
- 13.8 0.420 pm.
- 13.9* 2s.
- 13.10 106 pm.
- 13.12* $p_x \pm ip_y$.
- 13.13*
- 13.14* $2.66a_0$.
- 13.15 $E = -(Z^2 e^4 m_e / 32\pi^2 \epsilon_0^2 \hbar^2) (1/n^2)$.
- 13.17* $a_{\text{Ps}} = 2a_0$, $E_{1,\text{Ps}} = \frac{1}{2} E_{1,\text{H}}$.
- 13.18* $d_{\text{H}} \approx 0.314 \text{ nm}$, $d_{\text{U}} \approx 0.301 \text{ nm}$.
- 13.19* $v = 2.19 \times 10^6 \text{ m s}^{-1}$, $\mathcal{E} = 5.14 \times 10^{11} \text{ V m}^{-1}$, $\mathcal{H} = 9.98 \times 10^6 \text{ A m}^{-1}$.
- 13.20 $E_{2x} = E_{2y} = -(1/4)(Z^2 \hbar^2 / 2\mu a_0^2)$.
- 13.21* (b) 1663 (from wavelength data), 1840 (from Rydberg constants).
- 13.22* $\Delta E = 4.29 \times 10^{-24} \text{ J} = 0.216 \text{ cm}^{-1}$, $\langle r \rangle_{100} = 529 \text{ nm}$, $I_{100} = 10.9677 \text{ cm}^{-1}$; yes, thermal energy is 207 cm^{-1} and is sufficient, $v_{\text{min}} = 511 \text{ m s}^{-1}$.
- 13.23 (1) ${}^2P_{1/2}$ (lower) and ${}^2P_{3/2}$, (2) ${}^2D_{3/2}$ (lower) and ${}^2D_{5/2}$; simple estimate suggests ${}^2D_{3/2}$ is the ground state.
- 13.24 (b) 23.8 T m^{-1} .
- 14.2*
- 14.3* $R_{\text{max}} = 2.1a_0$.
- 14.6 (a) 8.6×10^{-7} , 2.0×10^{-6} ; (b) 8.6×10^{-7} , 2.0×10^{-6} ; (c) 3.7×10^{-7} , 0; (d) 4.9×10^{-7} , 5.5×10^{-7} .
- 14.7* 1.9 eV, 130 pm.
- 14.8*
- 14.9* $\Delta E = 2.7 \text{ eV}$, $\lambda = 460 \text{ nm}$, orange.
- 14.11*
- 14.13* (a) nonplanar; (b) planar.
- 14.14 (a) $E = -hcR_{\text{H}}$; (b) $-(8/3\pi)hcR_{\text{H}}$.
- 14.16* Thermal motion would cause the molecule to break apart; it is not likely to exist for more than one vibrational period.
- 14.17 $E = \alpha_0$ (twice), $\frac{1}{2} \{(\alpha_0 + \alpha_N) \pm [(\alpha_0 - \alpha_N)^2 + 12\beta^2]^{1/2}\}$; $E(\text{delocalization}) = [(\alpha_0 - \alpha_N)^2 + 12\beta^2]^{1/2} - [(\alpha_0 - \alpha_N)^3 + 4\beta^2]^{1/2}$.
- 14.18* (a) $E = (\alpha - \beta)$ (twice), $\alpha + 2\beta$; binding energies: $\alpha + 2\beta$, $2\alpha + 4\beta$, $3\alpha + 3\beta$, $4\alpha + 2\beta$, respectively; (b) $\Delta_r H = -413 \text{ kJ mol}^{-1}$, slightly less than binding energy of H_2 ($435.94 \text{ kJ mol}^{-1}$); (c) $\beta = (-849 \text{ kJ mol}^{-1} - 2\alpha)/4$; H_2^+ : -425 kJ mol^{-1} ; H_3^+ : -849 kJ mol^{-1} ; H_3 : $3(\alpha/2 - 212 \text{ kJ mol}^{-1})$; H_3^- : $3\alpha - 425 \text{ kJ mol}^{-1}$.
- 14.19*
- 15.1* (a) D_{3d} ; (b) D_{3d} , C_{2v} ; (c) D_{2h} ; (d) D_3 ; (e) D_{4d} .
- 15.2* *trans*-CHCl=CHCl.
- 15.3 $C_2\sigma_{\text{h}} = i$.
- 15.4* 15.5*
- 15.6 representation 1: $\mathbf{D}(\sigma_v) = \mathbf{D}(\sigma_d) = +1$ or -1 ; representation 2: $\mathbf{D}(\sigma_v) = -\mathbf{D}(\sigma_d) = +1$ or -1 .
- 15.7* the matrices do not form a group.
- 15.8 $A_1 + T_2$, s and p , (d_{xy} , d_{yz} , d_{zx}) span T_2 .
- 15.9 (a) all five d orbitals; (b) all except $d_{xy}(A_2)$.
- 15.10* (a) $2A_1 + A_2 + 2B_1 + 2B_2$; (b) $A_1 + 3E$; (c) $A_1 + T_1 + T_2$; (d) $A_{2u} + T_{1u} + T_{2u}$.
- 15.11 (a) yes; (b) no; (c) yes.
- 15.12* irreducible representations: $3A_1 + 2A_2 + 2B_1 + 3B_2$.
- 15.13 irreducible representations: $4A_1 + 2B_1 + 3B_2 + A_2$.
- 15.15 group: S_4 ; operations: S_4, C_2 .
- 15.16* (a) D_{2h} ; (b) (i) C_{2h} , (ii) C_{2v} .
- 15.17 (a) D_{2d} , A_1 ; (b) C_{4v} , A_1 .
- 15.18* neither transition allowed; with vibration transition to T_{1g} becomes allowed, to G_g remains forbidden.
- 15.19* (a) symmetry elements: $E, 2C_3, 3C_2, \sigma_{\text{h}}, 2S_3, 3\sigma_v$; point group: D_{3h} ; (i) reduces to $A'_1 + E'$.
- 15.20 reduces to $A_{1g} + B_{1g} + E_u$.
- 16.1* (a) 2.1×10^{-6} , 1.3 MHz, 0.0063 cm^{-1} ; (b) 9.7×10^{-7} , 6.6 kHz, 0.0004 cm^{-1} .
- 16.2 700 MHz, 1 Torr.
- 16.3* 596 GHz, 19.9 cm^{-1} , 0.503 mm , $B = 9.941 \text{ cm}^{-1}$.
- 16.4 From 112.83 pm to 123.52 pm.
- 16.5* $R(\text{CC}) = 139.6 \text{ pm}$, $R(\text{CH}) = R(\text{CD}) = 108.5 \text{ pm}$.
- 16.6 $k = 93.8 \text{ N m}^{-1}$, 142.81 cm^{-1} , 3.36 eV .
- 16.7* linear, $\tilde{\nu}_1$: 1400 cm^{-1} ; $\tilde{\nu}_2$ (bend): 540 cm^{-1} , $\tilde{\nu}_3$: 2360 cm^{-1} combination band, $\tilde{\nu}_1 + \tilde{\nu}_3$: 3735 cm^{-1} .
- 16.8* $2.728 \times 10^{-47} \text{ kg m}^2$, 129.5 pm ; DCl lines at 10.56, 21.11, 31.67, ... cm^{-1} .
- 16.9 HCl: 128.393 pm , DCl: 128.13 pm .
- 16.10* $R(\text{CO}) = 116.28 \text{ pm}$, $R(\text{CS}) = 155.97 \text{ pm}$.
- 16.11 (a) 5.15 eV; (b) 5.20 eV.
- 16.12*
- 16.14* $J_{\text{max}} = (kT/2hcB)^{1/2} - \frac{1}{2}$, 30, $J_{\text{max}} = (kT/hcB)^{1/2} - \frac{1}{2}$, 6.
- 16.15 230 pm, 240 pm, 250 pm.
- 16.16* $R = 360.71 \text{ pm} = 21.84 \text{ cm}^{-1}$, $k = 0.3746 \text{ N m}^{-1}$.
- 16.17 46.07 cm^{-1} , $1.769 \times 10^8 \text{ cm}^{-1}$.
- 16.18* (a) 152 m^{-1} , $2.72 \times 10^{-4} \text{ kg s}^{-2}$, $2.93 \times 10^{-46} \text{ kg m}^2$, 95.5 m^{-1} ; (b) 293 m^{-1} , 0.96.
- 16.19 14.35 m^{-1} , 26, 15.
- 16.20* 2.35 K.

- 16.21 (b) 87.61 pm (from B), 89.83 pm (from C), 88.7 pm (average); (c) $B = 43.84 \text{ cm}^{-1}$, $C = 21.92 \text{ cm}^{-1}$; (d) $\tilde{\nu}_2(D_3) = 1783.0 \text{ cm}^{-1}$.
- 17.1* 49364 cm^{-1} .
 17.2* 5.1147 eV.
 17.3 14660 cm^{-1} .
 17.4* $4.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-2}$.
 17.5 $1.1 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-2}$.
 17.6* 0.2 ms.
 17.8*
 17.10* (a) allowed; (b) forbidden.
 17.12*
 17.13 lengthen; to blue.
 17.15* $f = (RS/a_0)^2 f_0$.
 17.16* 65 MW.
 17.17* $2\Sigma_g^+$, $2\Pi_g^-$.
 17.18 28 kJ mol^{-1} greater, consistent.
 17.19* (a) $2.42 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-2}$; (b) 0.185; (c) 6.97, 135 $\text{L mol}^{-1} \text{ cm}^{-1}$.
 17.20 6.37, 2.12.
 17.21 $1.24 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-2}$.
 17.22* $V_1 - V_0 = 3.1938 \text{ eV}$, $\tilde{\nu}_1 - \tilde{\nu}_0 = 79.538 \text{ cm}^{-1}$, $\tilde{\nu}_1 = 2113.8 \text{ cm}^{-1}$, $\tilde{\nu}_0 = 2034.3 \text{ cm}^{-1}$, relative populations = 10, $T_{\text{eff}} = 1.3 \times 10^3 \text{ K}$.
- 18.1* 10.3 T, 2.42×10^{-5} , β .
 18.2 57 kJ mol^{-1} .
 18.3* 1.992, 2.002.
 18.4 6.9 mT, 2.1 mT.
 18.5* 1:2:3:2:1 quintet of 1:4:6:4:1 quintets.
 18.6 (7) $\rho(3) = \rho(6) = 0.005$, $\rho(4) = \rho(5) = 0.076$;
 (8) $\rho(2) = \rho(4) = 0.200$, $\rho(3) = 0.048$, $\rho(6) = 0.121$;
 (9) all $\rho = 0.050$.
 18.7* 158 pm.
 18.8* -0.89 mT.
 18.9 $\mathcal{I} = \frac{1}{2} A\tau / \{1 + (\omega_0 - \omega)^2 \tau^2\}$.
 18.10*
 18.11* $300 \times 10^6 \text{ Hz} \pm 10 \text{ Hz}$, 0.29 s.
 18.12* $4 \times 10^2 \text{ s}^{-1}$, 3.7 kJ mol^{-1} , 16 kJ mol^{-1} .
 18.13 both fit data equally well.
 18.14* (a) yes; (b) ${}^3J_{\text{SnSn}}/\text{Hz} = 580 - 79 \cos \phi + 395 \cos 2\phi$;
 (c) a staggered conformation with the two SnMe_3 groups at 180° to each other relative to the C—C bond.
 18.15 (a) $R_\nu(\text{nuclide})/R_\nu(\text{proton})$: 0.409, 0.251, 0.193, 0.941, 0.405; $R_B(\text{nuclide})/R_B(\text{proton})$: 0.00965, 0.01590, 0.00101, 0.83350, 0.06654.
- 19.1 no.
 19.2* 3.5 fK, 7.41.
 19.3* (a) 5.00, 6.26; (b) 1.00 at 298 K, 0.80 at 5000 K; 6.5×10^{-11} at 298 K and 0.12 at 5000 K; (c) 13.38 $\text{JK}^{-1} \text{ mol}^{-1}$, 18.07 $\text{JK}^{-1} \text{ mol}^{-1}$.
 19.4 0.257, 0.336, 0.396, 0.011.
 19.5* (a) 0.64, 0.36; (b) 0.52 kJ mol^{-1} .
 19.6 (a) 1.049, 123 J mol^{-1} , 1.65 $\text{JK}^{-1} \text{ mol}^{-1}$; (b) 1.55, 1.348 kJ mol^{-1} , 8.17 $\text{JK}^{-1} \text{ mol}^{-1}$; proportions are: $p_0 =$ (a) 0.953, (b) 0.645; $p_1 =$ (a) 0.044, (b) 0.230; $p_2 =$ (a) 0.002, (b) 0.083.
 19.7* (a) 1; (b) {2, 2, 0, 1, 0, 0} and {2, 1, 2, 0, 0, 0}.
 19.8 {4, 2, 2, 1, 0, 0, 0, 0, 0}.
 19.9 (a) 160 K.
 19.10* (a) $q = 1 + 3e^{-\epsilon/kT}$, 2.104; (b) 0.5245RT, 2.074 $\text{JK}^{-1} \text{ mol}^{-1}$, 10.55 $\text{JK}^{-1} \text{ mol}^{-1}$.
 19.11* (a) 104 K; (b) $q = 1 + a$; (c) $2Nk \ln 2$.
 19.12 if the separations $\epsilon_2 - \epsilon_1$ and $\epsilon_1 - \epsilon_0$ are equal.
 19.13 (a) no difference; (b) no measurable difference.
 19.14* $W = 2 \times 10^{40}$, $S = 1.282 \times 10^{21} \text{ JK}^{-1}$, $S_1 = 0.637 \times 10^{21} \text{ JK}^{-1}$, $S_2 = 0.645 \times 10^{21} \text{ JK}^{-1}$. Entropy is an extensive property.
 19.15* ${}^4\text{He}$: 7.69 $\times 10^5$, 9, 3; ${}^3\text{He}$: 1.18 $\times 10^6$, 13, 5.
 19.17* $\Delta W/W \approx 2.4 \times 10^{25}$.
 19.18 $\Delta W/W \approx 4.8 \times 10^{21}$.
 19.19* (a) $10^{5.44 \times 10^{23}}$; (b) $10^{5.69 \times 10^{23}}$, the heat capacity is temperature-dependent; (c) $\Delta S = +3.34 \text{ JK}^{-1}$; therefore this is a spontaneous process, $\Delta S_{U,V} > 0$.
 19.20 O_2 : 0.36, H_2O : 0.57.
 19.21*
 19.22 (c) $k = 1.36 \times 10^{-23} \text{ JK}^{-1}$; $N_A = 6.11 \times 10^{23} \text{ mol}^{-1}$.
 19.23 1.209, 3.004.
- 20.1* (a) 0.351R; (b) 0.079R; (c) 0.029R.
 20.2 (a) 0.1 per cent; (b) 4×10^{-3} per cent.
 20.3* 4.2, 15 $\text{JK}^{-1} \text{ mol}^{-1}$.
 20.5* 19.89.
 20.7* (a) 3.89; (b) 2.41.
 20.8* $S_m = R \ln(2\pi e^2 m \sigma_m / h^2 N_A \beta)$, $\sigma_m = \sigma/n$;
 $\Delta S_m = R \ln\{(\sigma_m/V_m)(h^2 \beta / 2\pi m e)^{1/2}\}$.
 20.9 $U - U(0) = H - H(0) = (N\hbar\omega)/(e^x - 1)$,
 $\epsilon'_V = kN\{x^2 e^x / (e^x - 1)^2\}$,
 $S = Nk\{x/(e^x - 1) - \ln(1 - e^{-x})\}$,
 $A - A(0) = G - G(0) = NkT \ln(1 - e^{-x})$.
 20.10* (b) 5.41 $\text{JK}^{-1} \text{ mol}^{-1}$.
 20.11 100 T.
 20.12* 350 ms^{-1} .
 20.13 (a) $\theta_R = 87.55 \text{ K}$, $\theta_V = 6330 \text{ K}$;
 (b) $C_{V,m}(\text{equil. mixt.}) = 2\alpha C_{V,m}(\text{H}) + (1 - \alpha) C_{V,m}(\text{H}_2)$.

$$\alpha = [K/(K+4)]^{1/2}, C_{V,m}(H) = 3R/2,$$

$$C_{V,m}(H_2) = \frac{5}{2}R + \left\{ \frac{(\theta_V/T) [e^{-(\theta_V/2T)} / (1 - e^{-(\theta_V/T)})] \right\}^2 R,$$

$$K = \left\{ kT A^3 (H_2) / p q^R (H_2) q^V (H_2) A^6 (H) \right\} e^{-(D_0/RT)}.$$

- 20.14* 199.4 J K⁻¹ mol⁻¹.
 20.15 513.5 kJ mol⁻¹.
 20.16* 28, 258 J K⁻¹ mol⁻¹.
 20.17 0.6608 kJ mol⁻¹, 241.5 kJ mol⁻¹.
 20.18* 45.76 kJ mol⁻¹.
 20.19 (c) $T \approx 374$ K.
- 21.1 118 pm.
 21.2* P, 342 pm.
 21.3* yes.
 21.4 (a) bcc, 315 pm, 136 pm; (b) fcc, 364 pm, 129 pm.
 21.5* 10.51 g cm⁻³.
 21.7* 628 pm, yes.
 21.8 834 pm, 606 pm, 870 pm.
 21.9* $\alpha_{\text{volume}} = 4.8 \times 10^{-5}$ K⁻¹, $\alpha_{\text{linear}} = 1.6 \times 10^{-5}$ K⁻¹.
 21.10 177 pm.
 21.11*
 21.13* (a) 0.5236; (b) 0.6802; (c) 0.7405.
 21.14*
 21.15 (a) no absences; (b) alternation ($h+k+l$ odd or even); (c) $h+k+l$ odd missing.
 21.16 4.
 21.17* 1.385 g cm⁻³, 1.578 g cm⁻³.
 21.18 0.41.
 21.19* $f = [1 + \frac{1}{4}(ka_0/Z)^2]^{-2}$.
 21.20 $F_{hkl} = f \{ [1 + (-1)^{h+k+l}] + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l} + [(-1)^{h+k+l}]^{1/2} [(-1)^h + (-1)^k + (-1)^l + (-1)^{h+k+l}] \}$.
 21.21* $F_{100} = f(\text{Cs}^+) - f(\text{Cl}^-) = 54 - 18 = 36$;
 $F_{110} = f(\text{Cs}^+) + f(\text{Cl}^-) = 54 + 18 = 72$;
 $F_{200} = f(\text{Cs}^+) + f(\text{Cl}^-) = 54 + 18 = 72$.
- 22.1* (a) 0.11 GV m⁻¹; (b) 4 GV m⁻¹; (c) 4 kV m⁻¹.
 22.2 2.4 nm.
 22.3* 1.2×10^{-23} cm³, 0.86 D.
 22.4 1.38×10^{-23} cm³, 0.34 D.
 22.5* 2.24×10^{-24} cm³, 1.58 D.
 22.6 1.85 D, 1.36×10^{-24} cm³.
 22.7* (a) $6Q_1Q_2/\pi\epsilon_0 r^5$; (b) $9Q_1Q_2/4\pi\epsilon_0 r^5$.
 22.8* $n_r = 1 + p(2\pi\alpha'/kT)$.
 22.10* the relative permittivity should decrease.
 22.11* $\alpha = 2\pi N_A^2 C_6 / 3d^3$.
 22.12 when $A = \sigma = 1$, a minimum occurs at $r = 1.63$
 22.14*
 22.16* $\xi = -e^2 a_0^2 / 2m_e$, $\chi_m = -N_A \mu_0 e^2 a_0^2 / 2m_e$.
- 22.17 the susceptibility varies as $d = 1 - \{1/[(4p/K) + 1]\}^{1/2}$, where d = degree of dimerization.
 22.18 $\chi_m = (25.2 \text{ cm}^3 \text{ mol}^{-1}) / \{(T/K) \times [1 + e^{174(T/K)}]\}$.
 22.19 $4.80 \times 10^{-40} \text{ J}^{-1} \text{ C m}^2$, $0.26 \times 10^{-40} \text{ J}^{-1} \text{ C m}^2$.
 22.20* (a) $1.51 \times 10^{-21} \text{ J}$, 265 pm.
 22.21* $0.127 \text{ cm}^3 \text{ mol}^{-1}$ ($S = 2$), $0.254 \text{ cm}^3 \text{ mol}^{-1}$ ($S = 3$), $0.423 \text{ cm}^3 \text{ mol}^{-1}$ ($S = 4$), $0.254 \text{ cm}^3 \text{ mol}^{-1}$.
 22.22 0.123.
 22.23 $8.14 \text{ cm}^3 \text{ mol}^{-1}$, 1.76, 1.33.
- 23.1* 23.1 kg mol⁻¹, 1.02 m³ mol⁻¹.
 23.2 155 kg mol⁻¹, 13.7 m³ mol⁻¹.
 23.3* 0.0716 L g⁻¹.
 23.4* 5.0 Sv.
 23.5 65.6 kg mol⁻¹.
 23.6 3500 r.p.m.
 23.7* -29 mV.
 23.8* 5 m³ mol⁻¹.
 23.9 69 kg mol⁻¹, 3.4 nm.
 23.10* 0.21 Mg mol⁻¹.
 23.11 5.14 Sv, 60.1 kg mol⁻¹.
 23.12* 158 kg mol⁻¹.
 23.13 (a) $(\frac{2}{3})^{1/2} a$; (b) $l/2(3)^{1/2}$, 2.40 nm, 46 nm.
 23.14* serum albumin and bushy stunt virus resemble spheres; DNA does not.
 23.15 PBLG is rod-like; polystyrene is a random coil.
 23.16* 1.01 g cm⁻³.
 23.17 $M_n = \bar{M} + (2\gamma/\pi)^{1/2}$.
 23.18* $dG = -SdT - ldr$, $dA = -SdT + rdl$.
 23.19 $t = -T(\partial S/\partial l)_T$.
 23.21* (a) $lN^{1/2}$, 9.74 nm; (b) $(8N/3\pi)^{1/2} l$, 8.97 nm; (c) $(2N/3)^{1/2} l$, 7.95 nm.
 23.22* $K = 2.73 \text{ cm}^3 \text{ g}^{-1} \text{ kg}^{-1/2} \text{ mol}^{1/2}$, $a = 0.500$, $M = 1.34 \times 10^3 \text{ kg mol}^{-1}$.
 23.23 (a) g cm mol⁻¹ K⁻¹, (b) $1.1 \times 10^5 \text{ g mol}^{-1}$, (c) 'good', (d) $B' = 21.4 \text{ cm}^3 \text{ g}^{-1}$, $C' = 211 \text{ cm}^6 \text{ g}^{-2}$, (e) $(\pi/c)^{1/2} = (RT/\bar{M}_n)^{1/2} \times (1 + \frac{1}{2}B'c)$; $B' = 28.0 \text{ cm}^3 \text{ g}^{-1}$, $C' = 196 \text{ cm}^6 \text{ g}^{-2}$; yes.
 23.24 (a) toluene: 0.086 L g⁻¹, 0.37; cyclohexane: 0.042 L g⁻¹, 0.35; (b) toluene: $2.4 \times 10^5 \text{ g mol}^{-1}$; cyclohexane: $2.6 \times 10^5 \text{ g mol}^{-1}$; (c) toluene: 42 nm; cyclohexane: 34 nm; (d) toluene: 2.3×10^3 ; cyclohexane: 2.5×10^3 ; (e) toluene: 5.8×10^2 nm; cyclohexane: 6.2×10^2 nm; (f) toluene: 2.1×10^2 nm, 7.4 nm; cyclohexane: 2.2×10^2 nm, 7.7 nm; (g) no reason for them to agree; the manufacturer's claim's valid.
 23.25* $1.26 \times 10^5 \text{ g mol}^{-1}$, $1.23 \times 10^4 \text{ L mol}^{-1}$.
 23.26* (a) $K = 0.0117 \text{ cm}^3 \text{ g}^{-1}$, $a = 0.717$, (b) THF is polar. The constants depend upon both solute and solvent and their interactions.

- 23.27 $K = 2.38 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$, $a = 0.955$; the constants are considerably different and indicate that the conducting polymer exists in a linear chain form.
- 23.28 $M_w = 1.23 \times 10^6 \text{ g mol}^{-1}$, $B' = 3.72 \times 10^{-2} \text{ cm}^3 \text{ mg}^{-1}$. The average molar masses are different and there is no reason for them to be the same; different preparations of the same polymer can lead to much different average molar masses.
- 24.1* 100 Ms.
- 24.2 9.1.
- 24.3* 7.3 mPa.
- 24.4 (a) $Z_w = 2.69 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}$, $Z_{\text{atom}} = 2.0 \times 10^8$;
(b) $1.6 \times 10^3 \text{ s}^{-1}$.
- 24.5* (a) 100 Pa; (b) 24 Pa.
- 24.6 (a) $2 \times 10^{14} \text{ s}^{-1}$; (b) $1 \times 10^{20} \text{ s}^{-1}$.
- 24.7* $5.3 \text{ S cm}^2 \text{ mol}^{-1}$.
- 24.8* (a) $11.96 \text{ mS m}^2 \text{ mol}^{-1}$; (b) 119.6 mS m^{-1} ; (c) 172.5Ω .
- 24.9 $1.36 \times 10^{-5} \text{ mol L}^{-1}$.
- 24.10* $40 \mu\text{m s}^{-1}$, $52 \mu\text{m s}^{-1}$, $76 \mu\text{m s}^{-1}$; 250 s, 190 s, 130 s;
(a) 13 nm, 17 nm, 24 nm. (b) 43, 55, 81.
- 24.11 0.82, 0.0028.
- 24.12* 0.48 , $7.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, $72 \text{ S cm}^2 \text{ mol}^{-1}$.
- 24.13 0.278, 0.278.
- 24.14* (a) 12 kN mol^{-1} , $2.1 \times 10^{-20} \text{ N molecule}^{-1}$;
(b) 17 kN mol^{-1} , $2.8 \times 10^{-20} \text{ N molecule}^{-1}$;
(c) 25 kN mol^{-1} , $4.1 \times 10^{-20} \text{ N molecule}^{-1}$.
- 24.15* Li^+ : 4 water molecules; Na^+ : 1 to 2 water molecules.
- 24.16 $E_a = 9.3 \text{ kJ mol}^{-1}$.
- 24.17* (a) ≈ 0 ; (b) 63 mmol L^{-1} .
- 24.18 $t'/t'' = c'u'z'/c''u''z''$.
- 24.20* (a) 0; (b) 0.016; (c) 0.054.
- 24.21 $n > 60$.
- 24.22* $\Lambda_m^\circ(\text{NaI}) = 60.7 \text{ S cm}^2 \text{ mol}^{-1}$,
 $\Lambda_m^\circ(\text{KI}) = 58.9 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda^\circ(\text{Na}^+) - \lambda^\circ(\text{K}^+) =$
 $1.8 \text{ S cm}^2 \text{ mol}^{-1}$; the analogous quantities in water are,
respectively, 126.9, 150.3, and $-23.4 \text{ S cm}^2 \text{ mol}^{-1}$.
- 24.23 (a) 368 pm, (b) 307 pm.
- 24.24* $1.6 \times 10^{16} \text{ m}^2 \text{ s}^{-1}$, $0.34 \text{ JK}^{-1} \text{ m}^{-1} \text{ s}^{-1}$.
- 24.25 830 pm.
- 25.1* $2, 59 \text{ mL mol}^{-1} \text{ min}^{-1}$, 2.94 g .
- 25.2 $1, 1.51 \times 10^{-5} \text{ s}^{-1}$, 9.82 mmol L^{-1} .
- 25.3* $1, 1.2 \times 10^{-4} \text{ s}^{-1}$.
- 25.4 $1, 5.84 \times 10^{-3} \text{ s}^{-1}$, 1.98 min .
- 25.5* 97.0 kJ mol^{-1} .
- 25.6* 55.4 per cent.
- 25.7 $1, 2.8 \times 10^{-4} \text{ s}^{-1}$.
- 25.8* $3.65 \times 10^{-3} \text{ min}^{-1}$, 274 min .
- 25.9 $2.37 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.
- 25.10* $1, 7.2 \times 10^{-4} \text{ s}^{-1}$.
- 25.11* propene: 1; HCl: 3.
- 25.12* rate = $kK_2K_1[\text{HCl}]^3[\text{CH}_3\text{CH}=\text{CH}_2]$.
- 25.13 -18 kJ mol^{-1} , $+10 \text{ kJ mol}^{-1}$.
- 25.14* $1.14 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$, 16.7 kJ mol^{-1} .
- 25.15 deviates from theory at low pressures.
- 25.16* 10 mmol L^{-1} .
- 25.17* $[\text{B}]_\infty/[\text{A}]_\infty = k/k'$.
- 25.19*
- 25.20 equivalent when B is a reactive intermediate.
- 25.21 $t_{1/2}/t_{3/4} = (2^{n-1} - 1)/\{(\frac{4}{3})^{n-1} - 1\}$.
- 25.22*
- 25.24* $E_a = 105 \text{ kJ mol}^{-1}$, $\Delta G = -26.6 \text{ kJ mol}^{-1}$,
 $\Delta H = -34.3 \text{ kJ mol}^{-1}$; still favourable under prebiotic
conditions.
- 25.25 $v_{\text{max}} = k([A]_0 - [\text{B}]_0)/2$ for $[\text{B}]_0 \leq [\text{A}]_0$,
 $(x/[\text{A}]_0) \leq 1$ corresponds to reality.
- 25.26* 2.01 min, 1 min, 0.693 min.
- 25.27 $x = \{[\text{B}]_0 - [\text{A}]_0 f(t)\}/(1 - f(t))$;
 $f(t) = \exp\{-([\text{A}]_0 - [\text{B}]_0)kt\}$.
- 25.28* $1.03 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, 13.9 kJ mol^{-1} .
- 25.29 $9 \times 10^{-10} \text{ mol L}^{-1} \text{ s}^{-1}$, $3 \times 10^5 \text{ s}$.
- 25.30* (a) $2.1 \times 10^{-15} \text{ mol L}^{-1} \text{ s}^{-1}$; (b) $1.6 \times 10^{-15} \text{ mol L}^{-1} \text{ s}^{-1}$.
- 25.31 (a) $1.1 \times 10^{-16} \text{ mol L}^{-1} \text{ s}^{-1}$; (b) $2.2 \times 10^{11} \text{ kg}$ or 220 Tg .
- 25.32* $121.2 \text{ kJ mol}^{-1}$, $247.0 \text{ JK}^{-1} \text{ mol}^{-1}$.
- 26.1* $1.9 \times 10^{20} \text{ s}^{-1}$, $3.1 \times 10^{-4} \text{ einstein s}^{-1}$.
- 26.2 $5.1 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$.
- 26.3*
- 26.4 $5.0 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.
- 26.5* $N(t) = N_0 e^{(b-d)t}$; fits data with $R^2 = 0.983$.
- 26.6* $([\text{A}]_0 + [\text{P}]_0)^2 k t_{\text{max}} = \frac{1}{2} - p - \ln 2p$.
- 26.7 $([\text{A}]_0 + [\text{P}]_0)^2 k t_{\text{max}} = (2 - p)/2p + \ln(2/p)$.
- 26.9* $f = k_2 k_4 [\text{CO}]/\{k_2 [\text{CO}] + k_3 [\text{M}]\}$.
- 26.11* $\delta M = M\{kt[\text{A}]_0(1 + kt[\text{A}]_0)\}^{1/2}$.
- 26.12 (a) $M(1 + 4p + p^2)/(1 - p^2)$; (b) $(6\langle n \rangle^2 - 6\langle n \rangle + 1)\langle n \rangle$.
- 26.13* ratio = $M(1 + 4p + p^2)/(1 - p^2)$.
- 26.15 $[\text{B}] = (\mathcal{I}_0/k)^{1/2} \propto [\text{A}]^{1/2}$.
- 26.16* $[\text{X}] = k_c/k_b$, $[\text{Y}] = k_a[\text{A}]/k_b$.
- 26.18* Step 1 is autocatalytic. $a/r < S_0$: infection spreads;
 $a/r > S_0$: infection dies out.
- 26.19*
- 26.20 $5.9 \times 10^{-13} \text{ mol L}^{-1} \text{ s}^{-1}$.
- 26.21* (a) For both $\text{X} = \text{H}$ and $\text{X} = \text{Cl}$, the fit of the data to the
second-order integrated rate expression is superior to the
fit to the first-order rate expressions as evidenced by
comparing correlation coefficients and standard deviations
of the slopes and intercepts.
(b) rate = $-k_2 k_1 [(\text{ClRh}(\text{CO})_2)_2][\text{ArHgCl}]/[\text{HgCl}_2]$.

- 26.22* (a) initiation, propagation, propagation, termination, initiation; (b) $d[\text{NO}]/dt = -2k_b(k_{-d}/k_d)^{1/2}[\text{O}_2]^{1/2}[\text{NO}]$; (c) $E_{a,\text{eff}} = E_b + \frac{1}{2}E_{-d} - \frac{1}{2}E_d$; (d) $E_{a,\text{eff}} = 381 \text{ kJ mol}^{-1}$, consistent with high end of range; (e) $d[\text{NO}]/dt = -2k_b(k_c/2k_d[\text{M}])^{1/2}[\text{NO}]^2$; (f) $d[\text{NO}]/dt = -2k_b(k_c/2k_d[\text{M}])^{1/2}[\text{O}]^{1/2}[\text{NO}]^{3/2}$, where k_c is the rate constant for $\text{NO} + \text{O}_2 \rightarrow \text{O} + \text{NO}_2$; $E_{a,\text{eff}} = 253 \text{ kJ mol}^{-1}$, consistent with low end of range.
- 26.24* When step (b) is rate-determining and step (a) is a rapid equilibrium so that $[\text{I}]$ is in a steady state.
- 27.1 (a) 0.044 nm^2 ; (b) 0.15.
- 27.2* 0.007, 0.0040 nm^2 .
- 27.3 $1.7 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$, 3.6 ns.
- 27.4* $+83.8 \text{ kJ mol}^{-1}$, $+19.1 \text{ J K}^{-1} \text{ mol}^{-1}$, 85.9 kJ mol^{-1} , $+79.0 \text{ kJ mol}^{-1}$.
- 27.5* 2-.
- 27.6 $0.658 \text{ L mol}^{-1} \text{ min}^{-1}$.
- 27.8*
- 27.10 $P = 5.2 \times 10^{-6}$.
- 27.11* $\log v \propto t^{1/2}$.
- 27.12* $1.4 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$.
- 27.13* $1.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$.
- 27.15* (a) $2.7 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$; (b) $1.1 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$.
- 27.16 $2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ if $v^\ddagger = v$; $9 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ if $v^\ddagger = \frac{1}{2}v$.
- 27.17*
- 27.18 5.
- 27.19* $k_1 = 3.82 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_2 = 5.1 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_3 = 4.17 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_2/k_1 = 0.13$.
- 27.20 1.6×10^{-3} , 1.8×10^{-3} .
- 27.21* A complex of two univalent ions of the same sign.
- 27.22 $6.23 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, 0.37 nm.
- 27.23* $k = k_1 k_2 / k_d$, $k' = k_1$;
(b) $D(\text{FO}-\text{F}) \approx E_{a1} = 140.6 \text{ kJ mol}^{-1}$, $D(\text{O}-\text{F}) = 244.7 \text{ kJ mol}^{-1}$, $E_{a2} = 20.3 \text{ kJ mol}^{-1}$.
- 27.24 $k_2(\text{atoms})/k_2(\text{molecules}) \approx 3 \times 10^7$.
- 27.25 $-148 \text{ J K}^{-1} \text{ mol}^{-1}$, $60.44 \text{ kJ mol}^{-1}$, 62.9 kJ mol^{-1} , $104.8 \text{ kJ mol}^{-1}$, respectively.
- 27.26* $\ln k$ fits the Arrhenius equation with $A = 3.12 \times 10^{14} \text{ L mol}^{-1} \text{ s}^{-1}$, $E_a = 193 \text{ kJ mol}^{-1}$, $R = 0.99976$; $\ln k'$ fits with $A' = 7.29 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$, $E'_a = 175 \text{ kJ mol}^{-1}$, $R = 0.99848$.
- 28.1 (a) $1.61 \times 10^{15} \text{ cm}^{-2}$; (b) $1.14 \times 10^{15} \text{ cm}^{-2}$;
(c) $1.86 \times 10^{15} \text{ cm}^{-2}$.
- 28.2* 0.37 Torr⁻¹.
- 28.3 (a) 164, 13.1 cm^3 ; (b) 264, 12.5 cm^3 .
- 28.4* 1.4 mL, 5.9 m^2 .
- 28.5 BET better; 75.4 cm^3 , 3.98.
- 28.6* 2.4, 0.16.
- 28.7 0.02 Torr s⁻¹.
- 28.9* $U \propto C_6/R^3$, 294 pm.
- 28.10*
- 28.11*
- 28.12 $d\mu' = (RTV_\infty/\sigma) d \ln(1 - \theta)$.
- 28.13* (a) $v = gkT/p$; (b) $R = 0.959$ for the linear equation which yields $g = 1.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$. $z(t)$ is seen to be nonlinear; $z(t) = a(e^{bt} - 1)$, with $a = 5.71 \text{ cm}$, $b = 0.35 \text{ s}^{-1}$, $R = 0.994$.
- 28.14 $K = 0.138 \text{ mg g}^{-1}$, $n = 0.58$, amount corresponding to monolayer coverage must be known.
- 28.15* $-20.1 \text{ kJ mol}^{-1}$, $-63.6 \text{ kJ mol}^{-1}$.
- 28.16 $n = 5.78 \text{ mol kg}^{-1}$, $K = 7.02 \text{ Pa}^{-1}$.
- 28.17* 40.4.
- 28.18 Regression analysis provides the following coefficients of correlation: $R(\text{Langmuir}) = 0.973$; $R(\text{Freundlich}) = 0.99994$; $R(\text{Temkin}) = 0.9590$. The fit to the Freundlich isotherm is best.
- 28.19* (a) R values range from 0.975 to 0.998; the fit is good at all temperatures. (b) $k_a = 3.68 \times 10^{-3}$, $k_b = 2.62 \times 10^{-5} \text{ ppm}^{-1}$, $\Delta_{\text{ad}}H = -8.67 \text{ kJ mol}^{-1}$, $\Delta_{\text{b}}H = -15.7 \text{ kJ mol}^{-1}$.
- 28.20* (a) $k = 0.2289$ and $n = 0.6180$; $R = 0.9995$.
(c) $k = 0.5227$, $n = 0.7273$; $R = 0.996$.
- 28.21 (a) $K[(\text{mg L}^{-1})^{-1}]$, $K_F[(\text{mg L}^{-1})^{-1/n}]$, $K_L[(\text{mg L}^{-1})^{-1}]$;
(b) $R(\text{linear}) = 0.9612$, $R(\text{Freundlich}) = 0.9682$, $R(\text{Langmuir}) = 0.9690$; on that basis alone the fits are equally satisfactory, but not good. The Langmuir isotherm can be eliminated, as it gives a negative value for K_L ; the fit to the Freundlich isotherm has a large standard deviation. Hence, the linear isotherm seems best, but the Freundlich isotherm is preferred for this kind of system.
(c) $q_{\text{rubber}}/q_{\text{charcoal}} = 0.164c_{\text{eq}}^{-0.46}$; hence much worse.
- 29.1* 0.38, 0.78 mA cm⁻².
- 29.2 $a(\text{Sn}^{2+}) \approx 2.2a(\text{Pb}^{2+})$.
- 29.3* 0.25 mm.
- 29.4 45 per cent, 45 per cent.
- 29.5* 87 mA.
- 29.6*
- 29.7 6 μA .
- 29.8* 0.28 mg cm⁻² d⁻¹.
- 29.9* 7.2 μA .
- 29.11* $j/j_L = 1 - \exp(F\eta_c/RT)$.
- 29.12* (a) $E_0 = -0.618 \text{ V}$, $\eta/\text{mV} = -84, -109, -134, -194$;
(b) $j_c/(\mu\text{A cm}^{-2}) = 0.0324, 0.0469, 0.0663, 0.154$;
(c) $j_0 = 0.00997 \mu\text{A cm}^{-2}$, $\alpha = 0.363$; excellent fit, $R = 0.99994$.
- 29.14 0.50, 0.150 A m^{-2} , -0.038 A m .
- 29.15* (a) No linear region exists; the Tafel equation cannot be used to calculate j_0 and α .
- 29.16* $j_0 = 2.00 \times 10^{-5} \text{ mA m}^{-2}$, $\alpha = 0.498$; $R = 0.9990$. There are no significant deviations.