

Answers to selected problems (see also answers in the Appendix!):

- Note: 1) An answer is not correct without the correct units
2) Please try to work through the problems as you would on an exam. When that fails, you can go to the answer and try to work backwards. But in the end, be certain that were you to get the same (or a similar) problem again, with different numbers, you could work it through without knowing the answer.

Chapter 2 (recommended: 1, 3, 4, 6-20, 23)

- 1.
3. a) 981 J; b) 2.38×10^5 J; c) 1.00×10^3 N/m; d) -203 J; e) -203×10^{-6} J; f) -111 J
6. a) 41.9 kJ; b) -33.3 kJ; c) 226 kJ
7. a) -2.49 kJ; b) $E = 6.24$ kJ, $H = 8.73$ kJ; c) 8.73 kJ
8. a) 5.74 kJ; b) $T_2 = 192$ K, $E = -1.347$ kJ, $H = -2.245$ kJ
9. a) $q_T = 2.23$ kJ; b) $q = 1.559$ kJ, $H = 2.182$ kJ; c) 1.252 atm; d) $T_2 < T_1$
11. a) $q = 40.66$ kJ mol⁻¹ (Table 2.2); $w = -3.10$ kJ; $E = 37.56$ kJ mol⁻¹; $H = q$
b) $q = 37.56$ kJ mol⁻¹; $w = 0$; $E = q$; $H = 40.66$ kJ mol⁻¹
13. a) $T_f = 113.1$ °C; $V = -0.98$ L
b) $T_f = 94.7$ °C; $V = 18.75$ mL
c) $T_f = 100$ °C; $V = -0.30$ L; phase change of 9.84×10^{-3} mol of water
d) (a), (+)
15. a) $q = 0$; $w = 0$; $E = 0$; $H = 0$; $V = 0$
b) $q = 0$; $w > 0$; $E > 0$; $H > 0$; $(PV) = 0$
c) $q = 0$; $w = 0$; $E = 0$; $H = 0$; ideal gases
18. Heat loss = 180 kJ/day (1.5% of food energy)
19. a) $w = 750$ kJ/24 hr; b) 765 kg (about 0.85 tons)

Chapter 3 (recommended: 1, 4, 5, 9, 10, 12a+d, 14-17, 20-24, 25a)

1. a) $w = -1247.1$ J; $q = -415.7$ J
b) $w = -415.7$ J; $q = -831.4$ J
9. a) $G = +129.66$ kJ mol⁻¹ (some friend you've got...)
b) $G = -70.48$ kJ mol⁻¹
c) $G = -1150.15$ kJ mol⁻¹
10. a) irreversibly, b) system+surroundings; c) enthalpy change; d) greater than
12. d) -4.18 J K⁻¹ mol⁻¹ conversion will be even less favorable (why?)
16. a) $w = -P_m(\Delta V_m)$; $E = q_m + w$ $H = q_m$ $S = \frac{q_m}{T_m}$ $G = 0$
b) $H = q_m + (C_{p,\beta} - C_{p,\alpha})(T^* - T_m)$ $S = \frac{q_m}{T_m} + (C_{p,\beta} - C_{p,\alpha}) \ln \frac{T^*}{T_m}$
21. a) -3.53 J K⁻¹; b) 7.5 J K⁻¹; c) 145.05 J K⁻¹
23. a) decrease; b) zero; c) decrease

Chapter 4 (recommended: 1-17, 30, 32a)

2. a) $-48.1 \text{ kJ mol}^{-1}$ b) 48.1 kJ mol^{-1}
3. a) $-14.3 \text{ kJ mol}^{-1}$ b) 846 c) 3.11×10^{-5}
4. a) 5200 b) 2.72×10^{-7}
5. a) 0.22 b) $-25,200 \text{ J mol}^{-1}$ forward
6. a) 496 J mol^{-1} b) 4596 J mol^{-1} c) 0.130
7. a) $-70.9 \text{ kJ mol}^{-1}$ b) 1.23×10^{12}
9. a) $-48.1 \text{ kJ mol}^{-1}$ b) 48.1 kJ mol^{-1} c) $G' = -200 \text{ J mol}^{-1}$
32. a) $K = \frac{f}{(1-f)C_p}$

Chapter 5 (recommended: 1-11, 16-21, 24-32)

2. a) P_1 b) P_1 c) 101, 0.0101
3. b) $1.35 \times 10^{-3} \text{ M}$ c) $>$
4. 9.4
6. a) $\bar{G} = RT \ln \frac{a_{\text{outside}}}{a_{\text{inside}}}$ b) 3573 J c) 10719 J d) 0 e) 0 f) 0.30 M g) $1.67 \times 10^6 \text{ M}$
7. Identical, independent sites; 5 sites per molecule; $K = 1.0 \times 10^{-5} \text{ M}^{-1}$
9. $H^\circ = 38 \text{ kJ mol}^{-1}$ $G^\circ (293\text{K}) = -22.4 \text{ kJ mol}^{-1}$ $S^\circ = 182 \text{ J K}^{-1}$
10. a) $(2.6/4.8/17) \times 10^{-4} \text{ M}$ ($\text{O}_2/\text{N}_2/\text{CO}_2$) b) 23.755 torr
11. a) 101°C
17. a) 0.0942 torr b) 1.000 c) 7.1/7.2 atm
19. 957 mL
24. 69200
27. a) 24.4/0.367 atm c) 43.8 J d) the lake
32. a) 0.980 b) 4.51 torr c) 271 K

Chapter 6 (recommended: 1, 2, 4-7, 9-13, 21-26, 29)

1. a) $1.838 \times 10^3 \text{ m s}^{-1}$ b) 3.40 kJ mol^{-1} c) $2.689 \times 10^{10} \text{ cm}^{-3}$ d) $1.34 \times 10^{-5} \text{ cm}$
e) $1.264 \times 10^{10} \text{ s}^{-1}$ f) $1.699 \times 10^{29} \text{ cm}^{-3} \text{ s}^{-1}$
4. Measure D provides frictional coefficient, from which you can calculate the radius of an *assumed* spherical protein. Changes in shape will alter f .
Measure sedimentation velocity. With f above, can calculate M (molecular weight)
Measure sedimentation equilibrium. This depends on molecular weight only (ideally).
Electrophoresis depends on net charge and on f . Electrophoresis in SDS depends only on molecular weight (ideally, not so good for membrane proteins).
DNA is a polyanion, so electrophoresis depends substantially on the number of monomer units.
6. a) $5.05 \times 10^7 \text{ g mol}^{-1}$ b) $2.58 \times 10^7 \text{ g mol}^{-1}$ (large fraction is DNA!)

7. $\frac{s_2}{s_1} = \frac{M_2 f_1}{M_1 f_2} = \frac{M_2 r_1}{M_1 r_2}$ but $V = \frac{M_1}{N_0} \bar{v} = \frac{4}{3} \pi r^3$ so $r = \sqrt[3]{\frac{3}{4\pi} \frac{M}{N_0}}$
- $\frac{s_2}{s_1} = \frac{M_2}{M_1} \frac{M_1}{M_2} = \frac{M_1}{M_2}$ $\frac{D_2}{D_1} = \frac{f_1}{f_2} = \frac{M_1}{M_2}$
9. a) 0.8889 cm³ g b) 0.204 s⁻¹ c) 4.98x10⁻¹⁸ cm³
11. a) 2.12x10⁻⁸ g s⁻¹ b) 6.22x10⁻¹³ s
12. a) 4.64 b) 0.5 cm c) 0.18 cm and 0.26 cm (diffusion not a problem) d) No
13. a) 7.3x10⁻⁸ s
21. a) 31.8 Å b) 6.4x10³ Å³ c) -9.3
23. a) 62 Å b) 60.6 Å c) Not spherical. A change in shape occurs.
24. 1.76x10⁸ g mol⁻¹ b) 1.77x10⁻¹⁶ cm³ c) 1.12x10⁻⁶ g s⁻¹ d) 5.91x10⁻⁶ cm
25. 0.67 cm³ g⁻¹

Chapter 7 (recommended: 1-18, 20-27, 29-31)

1. a) I₂ 0 ketone 1 H⁺ 1
 b) $-\frac{dI_2}{dt} = k[ket][H^+]$ k=0.034 M⁻¹ s⁻¹
 c) 0.059 s faster when doubling ket or H⁺, but not I₂ Not possible
 d) *ketone + H⁺ H⁺ ketone* (slow)
H⁺ ketone + I₂ iodoketone + H⁺ (fast)
2. a) kinetic order 2 b) 0.10 M⁻¹ s⁻¹ c) 2000 s / 3000 s
 d) Any of $v = k[OH^-]^a [CH_3XOOX_2H_5]^b$ where $a + b = 2$
4. a) $-\frac{d[A]}{dt} = k_1[A]$
 b) $-\frac{d[B]}{dt} = k_1[A] - k_2[B][C]$
 c) $-\frac{d[D]}{dt} = k_2[B][C]$
 d) $[A] = [A]_0 e^{-k_1 t}$
7. a) $\frac{d[D]}{dt} = \frac{k_3 k_1 [A][C]}{k_2 + k_3 [C]}$ b) $\frac{d[D]}{dt} = kK[A][B][C]$
10. a) 0.010 b) 0.0526 c) will reach 0 before 2 hrs d) 0.0353
11. a) 0.010 b) 0.182 c) 0 d) 0.156
12. a) $\frac{d[P]}{dt} = k_3 K_1 K_2 [A]^3 [B]$
14. a) 14 days b) 2.91x10⁹ atoms
18. a) 1x10⁻³ s⁻¹ b) 1x10⁻³ s⁻¹ c) 44.6 kJ mol⁻¹
20. 52.9 kJ mol⁻¹
21. a) 10³ M s⁻¹ b) 10⁻⁵ M s⁻¹ c) 10⁻⁴ s d) 66.4 kJ mol⁻¹
24. a) second order b) A + A P c) 5 M⁻¹ min⁻¹ d) 67 min
25. a) first order b) A + B P

c) 1st order in A and 1st order in B, but since there is a large excess of B, it appears 0th order in B (is pseudo-0th order in B).

30. a) $k_{-1} = 30.3 \text{ s}^{-1}$ $k_1 = 303 \text{ s}^{-1}$ b) 28°C

c) Doubling should have no effect on k_1 or k_{-1}

31. a) $k_{-1} = 8.2 \times 10^6 \text{ s}^{-1}$ $k_1 = 6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ b) $K = 780 \text{ M}^{-1}$ c) $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$

32. b) $k_{-1} = 2.0 \times 10^6 \text{ s}^{-1}$ $k_1 = 8.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ c) $-15.0 \text{ kJ mol}^{-1}$

33. a) $t = 0.39 \text{ } \mu\text{s}$ b) $\text{pH} = 5.1$