

## 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)  $2.38 \times 10^5$  J; c)  $1.00 \times 10^3$  N/m; d) -203 J; e)  $-203 \times 10^{-6}$  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<sup>-1</sup> (Table 2.2);  $w = -3.10$  kJ;  $E = 37.56$  kJ mol<sup>-1</sup>;  $H = q$   
b)  $q = 37.56$  kJ mol<sup>-1</sup>;  $w = 0$ ;  $E = q$ ;  $H = 40.66$  kJ mol<sup>-1</sup>
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  $9.84 \times 10^{-3}$  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<sup>-1</sup> (some friend you've got...)  
b)  $G = -70.48$  kJ mol<sup>-1</sup>  
c)  $G = -1150.15$  kJ mol<sup>-1</sup>
10. a) irreversibly, b) system+surroundings; c) enthalpy change; d) greater than
12. d)  $-4.18$  J K<sup>-1</sup> mol<sup>-1</sup> 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<sup>-1</sup>; b)  $7.5$  J K<sup>-1</sup>; c)  $145.05$  J K<sup>-1</sup>
23. a) decrease; b) zero; c) decrease

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

2. a)  $-48.1 \text{ kJ mol}^{-1}$  b)  $48.1 \text{ kJ mol}^{-1}$
3. a)  $-14.3 \text{ kJ mol}^{-1}$  b) 846 c)  $3.11 \times 10^{-5}$
4. a) 5200 b)  $2.72 \times 10^{-7}$
5. a) 0.22 b)  $-25,200 \text{ J mol}^{-1}$  forward
6. a)  $496 \text{ J mol}^{-1}$  b)  $4596 \text{ J mol}^{-1}$  c) 0.130
7. a)  $-70.9 \text{ kJ mol}^{-1}$  b)  $1.23 \times 10^{12}$
9. a)  $-48.1 \text{ kJ mol}^{-1}$  b)  $48.1 \text{ kJ mol}^{-1}$  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)  $101^\circ\text{C}$
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)  $3.40 \text{ kJ mol}^{-1}$  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 cm<sup>3</sup> g    b) 0.204 s<sup>-1</sup>    c) 4.98x10<sup>-18</sup> cm<sup>3</sup>
11. a) 2.12x10<sup>-8</sup> g s<sup>-1</sup>    b) 6.22x10<sup>-13</sup> 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<sup>-8</sup> s
21. a) 31.8 Å    b) 6.4x10<sup>3</sup> Å<sup>3</sup>    c) -9.3
23. a) 62 Å    b) 60.6 Å    c) Not spherical. A change in shape occurs.
24. 1.76x10<sup>8</sup> g mol<sup>-1</sup>    b) 1.77x10<sup>-16</sup> cm<sup>3</sup>    c) 1.12x10<sup>-6</sup> g s<sup>-1</sup>    d) 5.91x10<sup>-6</sup> cm
25. 0.67 cm<sup>3</sup> g<sup>-1</sup>

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

1. a) I<sub>2</sub> 0      ketone 1      H<sup>+</sup> 1
- b)  $-\frac{dI_2}{dt} = k[ket][H^+]$     k=0.034 M<sup>-1</sup> s<sup>-1</sup>
- c) 0.059 s    faster when doubling ket or H<sup>+</sup>, but not I<sub>2</sub>      Not possible
- d) *ketone + H<sup>+</sup> → H<sup>+</sup> ketone* (slow)
- H<sup>+</sup> ketone + I<sub>2</sub> → iodoketone + H<sup>+</sup>* (fast)
2. a) kinetic order 2    b) 0.10 M<sup>-1</sup> s<sup>-1</sup>    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) 2.91x10<sup>9</sup> atoms
18. a) 1x10<sup>-3</sup> s<sup>-1</sup>    b) 1x10<sup>-3</sup> s<sup>-1</sup>    c) 44.6 kJ mol<sup>-1</sup>
20. 52.9 kJ mol<sup>-1</sup>
21. a) 10<sup>3</sup> M s<sup>-1</sup>    b) 10<sup>-5</sup> M s<sup>-1</sup>    c) 10<sup>-4</sup> s    d) 66.4 kJ mol<sup>-1</sup>
24. a) second order    b) A + A → P    c) 5 M<sup>-1</sup> min<sup>-1</sup>    d) 67 min
25. a) first order    b) A + B → P

- c) 1<sup>st</sup> order in A and 1<sup>st</sup> order in B, but since there is a large excess of B, it appears 0<sup>th</sup> order in B (is pseudo-0<sup>th</sup> 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)  $\text{pH} = 5.1$

### Chapter 8 (recommended: 1-7, 9, 10a-d, 12-14, 16, 18, 19, 21a, 22, 25)

1.  $K_m = 0.42 \text{ M}$ ,  $V = 0.34 \text{ } \mu\text{mol CO}_2 \text{ min}^{-1}$
2. a)  $K_m^F = 10 \text{ mM}$ ;  $k_2^F = 9 \times 10^4 \text{ s}^{-1}$    b)  $K_m^R = 12.5 \text{ mM}$ ;  $k_2^R = 3 \times 10^4 \text{ s}^{-1}$    c)  $K^{eq} = 3 \times 10^{-7}$
3.  $K^{eq} = 4.1$
4. a)  $V = 3 \times 10^{-5} \text{ } \mu\text{mol PP}_i / (\text{s mg - enzyme})$ , b)  $[E]_o = 5.0 \times 10^{-8} \text{ mol sites}$   
 c)  $k_2 = 600 \text{ s}^{-1}$ , d)  $K_m = 5 \times 10^{-6} \text{ M}$
5. a)  $\frac{d[P]}{dt} = \frac{k_2[E]_o}{1 + \frac{K_m}{[S]}} = 10^{-3} \text{ M s}^{-1}$    b)  $E_a = 24.2 \text{ kJ mol}^{-1}$    c)  $K_1^{eq} = 10^4 \text{ M}^{-1}$   
 d)  $H^\circ = -14.16 \text{ kJ mol}^{-1}$
6. As the catalyst lowers the activation energy, the reaction becomes less sensitive to temperature.
7. a)  $E_a = 36.9 \text{ kJ mol}^{-1}$    b)  $S^\ddagger = -68.5 \text{ J K}^{-1} \text{ mol}^{-1}$    c)  $T_2 = 972^\circ \text{ C}$
9. a)  $k_1$  characterizes  $E + F \rightarrow EF$   
 $k_2$  characterizes  $EF + EM$   
 $k_3$  characterizes  $E + M \rightarrow EM$
10. a)  $\frac{[ES]}{[E]_o} = 0.99$    b)  $T = 16 \text{ min}$    c)  $K_m = 5 \times 10^{-5} \text{ M}$
11. a)  $K_m = 44 \text{ mM}$
- 12.

### Chapter 9 (recommended: 2-7, 13, 16, 23a)

2. a)  $\lambda = \frac{h}{mv} = 4.85 \times 10^{-3} \text{ nm}$    b)  $p = \frac{1}{2} \frac{\hbar}{x} = 5.27 \times 10^{-25} \text{ kg m s}^{-1}$
3. a)  $1.8 \times 10^{-6}$  (classical)   b)  $2.9 \times 10^{-6}$  (classical)   c) 179 (quantum mechanical)
4. a)  $E_1 = 6.0 \times 10^{-20} \text{ J}$     $\lambda_{1,2} = 11,000 \text{ } \text{Å}$    b)  $E_1 = 1.5 \times 10^{-20} \text{ J}$     $\lambda_{1,2} = 44,000 \text{ } \text{Å}$   
 c) both electrons in the ground state;  $\lambda_{1,2} = 11,000 \text{ } \text{Å}$
- d) For one electron:  $-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi = E \psi$   
 For two electrons:  $-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi_1 + \frac{d^2}{dx^2} \psi_2 = E_1 \psi_1 + E_2 \psi_2$

If they're independent of each other, the above can be separated into two one electron equations.

- e) If there is interaction, then this must be included in the potential energy side. The calculus gets messier. Electrons will repel, so that each one's energy (and the overall energy) will increase.
5. a) 0.04 b) 0 c) mass doubled, doubles; charge doubled, unchanged; length doubles, increases by  $2^2=4$  fold
7. Skip, but it's quite interesting. a)  $E_{n_x, n_y} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2)$
13.  $E_n = \frac{-Z^2 (1312 \text{ kJ mol}^{-1})}{n^2}$  (see bottom of page 520), equations 9.26 and 9.27  
 $E_1 = -5248 \text{ kJ mol}^{-1}$  Ionization potential =  $+5248 \text{ kJ mol}^{-1}$
16.  $\int_0^R \psi^2(1s) dV = 0.90$  Solve for R. See example 9.5  
 b)  $=1216 \text{ \AA} = 122 \text{ nm}$  (Far UV) c) skip, but see pp 461-3  
 d)  $2 \times 10^{11} \text{ m}$  (VERY long radiowaves)
23. a) Bohr radius:  $-2626 \text{ kJ mol}^{-1}$  H-bond:  $-322 \text{ kJ mol}^{-1}$

**Chapter 10 (recommended: 1, 4-10, 12, 15-17, 19, 21, 23, 30b-c, 35)**

1. a)  $E = \frac{hc}{\lambda} = 2.9 \times 10^{-19} \text{ J} = 1.82 \text{ eV} = 176 \text{ kJ mol}^{-1}$  (an Einstein is a mole of photons, see p. 375)
4. a)  $c=10^{-2} \text{ M}$  b)  $c=2 \times 10^{-2} \text{ M}$  c)  $c=10.3 \text{ M}$   $l=9.8 \times 10^{-4} \text{ cm}$
5. pH=6.7
7. a)  $[C] = 6.67 \times 10^{-5} \text{ M}$  b)  $K = 1.04 \times 10^3 \text{ M}^{-1}$  c) 208 nm
8. a) pH=4 b) skip c)  $\lambda_{excite}^{InH^+} = 400 \text{ nm}$   $\lambda_{excite}^{InH} = 460 \text{ nm}$  for minimal overlap
9. a) 100 c) 530 photons  $s^{-1}$  d)  $9.3 \times 10^8$  photons  $s^{-1}$   
 e) fluorescence is more sensitive because each molecule can emit MANY photons (excite, emit, excite, emit, ...). Radioactive decays occurs only once. But fluorescence background can be a problem.
10. a)  $\tau = 6.9 \text{ ns}$  b)  $k_0 = 1.0 \times 10^8 \text{ s}$  c)  $R = 19 \text{ \AA}$
12. a)  $10^{15}$  photons  $s^{-1}$   
 b) Much less. Fluorescence is in all directions, but the detector only sees a fraction of them.  
 c) Longer. Think about energies  
 d) Getting rid of a "deexcitation" pathway, will allow more decay via fluorescence
15. a)  $-0.50 \text{ M}^{-1} \text{ cm}^{-1}$  b) RNA:  $0.52 \times 10^{-4} \text{ M}$ ; DNA:  $0.11 \times 10^{-4} \text{ M}$   
 c) CD at 260 nm will decrease  
 d) increase e) decrease
16. a) Phe has an asymmetric carbon. b) Phe c) Phe and adenine
17.  $R = 4 \text{ nm}$
19.  $k_0 = 1.96 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$   $=0.2$  Relative fluor intensity = 20
21. a)  $A = 3000$  too big  
 b)  $A = 0.25$  easily measured  
 c) Fluorescence could be measured

d) CD has largest percent change, so is best.

e)  $K = \frac{[U]}{[S]} = \frac{f}{1-f}$     f)  $f = \frac{P(T) - P_s}{P_U - P_s}$  so that  $K = \frac{P(T) - P_s}{P_U - P(T)}$

30. b) NOE depends on inverse 6<sup>th</sup> power of distance between two protons.  
Two protons separated by greater than about 5 Å show little NOE

c) -helix