Solutions to problems for Chapter 4

4.1 $\Delta G^0 = \Delta H^0 - T\Delta S^0$, hence $-48.7 = 13.1 - 293\ \Delta S^0$. Thus, $\Delta S^0 = 61.8/293$ kJ K^{-1} mol^{-1} = 211 J K^{-1} mol^{-1}. At first sight the positive value for ΔS^0 is rather surprising. It would appear that two molecules (Mg^{2+} and $EDTA^{4-}$) are combining to form one ($MgEDTA^{2-}$), which should lead to a decrease in randomness, i.e. a negative ΔS^0. However, it should be noted that the reaction involves the release of water of hydration from the charged species (e.g. $6H_2O$ from Mg^{2+}). This release of water leads to a large positive ΔS^0 for the reaction, i.e. the entropy term is dominant in this case.

4.3 Assuming a value of 51.9 kJ mol^{-1} for the ΔG associated with the synthesis or hydrolysis of ATP, the daily requirement would correspond to the turnover of 10 000/51.9 mol ATP, i.e. 193 mol ATP. This amounts to no less than 106 kg ATP, i.e. considerably more than the average body mass. The body has very little capacity for storing ATP (there is less than 100 g in the average adult human male, but has enormous capacity to synthesize and utilize it). This should be borne in mind when we use the term 'energy currency' in connection with ATP.

4.5 A plot of ln (activity remaining) vs time is a straight line, showing that the process is first order. The slope of the line (0.0485 day^{-1}) = $-k$, from which $k = 0.0485$ day^{-1}. The half-life is $\ln 2/k = 0.693/0.0485$ days = 14.3 days.

4.7 Using the equation $-\Delta G^0 = RT \ln K_d$, the ΔG^0_{310} values are: avidin–biotin, -89 kJ mol^{-1}; antigen–antibody, -53.4 to -59.3 kJ mol^{-1}; enzyme–substrate, -23.7 to -35.6 kJ mol^{-1}.

4.9 From any of the appropriate plots (e.g. Lineweaver–Burk), it is seen that in the presence of indole, K_m remains unchanged (3.5 mM), but V_{max} is decreased (from 27 µmol min^{-1} mg^{-1} to 10.8 µmol min^{-1} mg^{-1}). Thus, the inhibition is non-competitive with $K_{EI} = 0.85$ mM.

4.11 Using any of the standard plots (Hughes–Klotz, Scatchard, Hanes–Woolf) the value of K_d is 0.25 mM.

4.13 The V_{max} is 0.0134/60 µmol s^{-1} = 223 pmol s^{-1}. The amount of enzyme added is $1.7 \times 10^{-6}/18\ 000$ mol = 94.4 pmol. Hence, k_{cat} = 223/94.4 pmol $pmol^{-1}$ s^{-1} = 2.4 s^{-1}. The k_{cat}/K_m ratio = 9.6×10^4 M^{-1} s^{-1} (significantly lower than the value for the enzyme from *Streptomyces coelicolor* described in the worked example in section 4.5).

4.15 The half-life of $^{35}S = 7.55 \times 10^6$ s, hence the rate constant for the radioactive decay = $0.693/(7.55 \times 10^6)$ s^{-1} = 9.18×10^{-8} s^{-1}. Hence, the initial rate of decay of 1 mol ^{35}S atoms = $9.18 \times 10^{-8} \times 6.02 \times 10^{23}$ s^{-1}, i.e. 5.52×10^{16} Bq. The percentage of S atoms present as $^{35}S = ((1.9 \times 10^{16})/(5.52 \times 10^{16})) \times 100\% = 34.4\%$. For use as a probe, this sample would be added to a large molar excess of non-radioactive methionine.