

7 Acids, bases and ions in aqueous solution

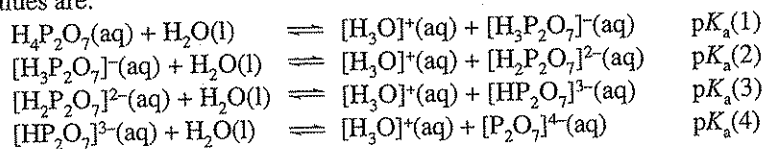
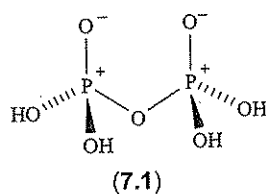
$$7.1 \quad (a) \quad pK_a = -\log K_a \quad \text{or} \quad K_a = 10^{-pK_a}$$

For the first dissociation step: $pK_a(1) = 0.74 \quad \therefore K_a(1) = 10^{-0.74} = 0.18$
 For the second dissociation step: $pK_a(2) = 6.49 \quad \therefore K_a(2) = 10^{-6.49} = 3.24 \times 10^{-7}$

(b)



7.2 The structure of $\text{H}_4\text{P}_2\text{O}_7$ is shown in 7.1. The 4 dissociation steps with associated pK_a values are:



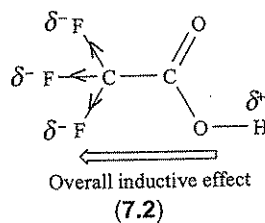
$$pK_a(1) = 1.0 \quad pK_a(2) = 2.0 \quad pK_a(3) = 7.0 \quad pK_a(4) = 9.0$$

These can be assigned on the basis that generally:

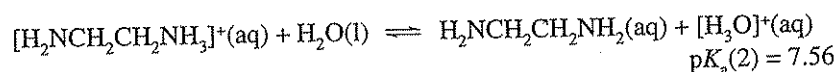
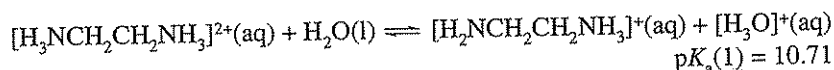
$$K_a(1) > K_a(2) > K_a(3) > K_a(4)$$

removal of H^+ being increasingly more difficult as the negative charge on the anion increases. The larger pK_a , the smaller K_a : e.g. $pK_a(4) = 9.0$ corresponds to $K_a = 1 \times 10^{-9}$, while $pK_a(1) = 1.0$ corresponds to $K_a = 0.1$.

7.3 For $\text{CH}_3\text{CO}_2\text{H}$, $pK_a = 4.75$. For $\text{CF}_3\text{CO}_2\text{H}$, $pK_a = 0.23$. A smaller pK_a corresponds to a larger K_a , since $K_a = 10^{-pK_a}$. The greater acid strength of $\text{CF}_3\text{CO}_2\text{H}$ can be explained in terms of the inductive effect (7.2). A physicochemical interpretation follows from studies of the temperature dependence of pK_a which show that for dissociation of HCO_2H , $\text{CH}_3\text{CO}_2\text{H}$ and $\text{CCl}_3\text{CO}_2\text{H}$, $\Delta H^\circ \approx 0$. The variation in pK_a arises from the variation in entropy of dissociation which becomes less negative along the series $\text{CH}_3\text{CO}_2\text{H}$, HCO_2H , $\text{CCl}_3\text{CO}_2\text{H}$, $\text{CF}_3\text{CO}_2\text{H}$. The withdrawal of electrons away from the CO_2^- group of the anion results in less orientation of surrounding solvent molecules.



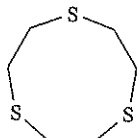
7.4 (a) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ is a Brønsted base. The question asks about pK_a values of the conjugate acid of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, i.e. equilibria involving H^+ loss from the protonated base:



(b) The relationship between pK_b and pK_a , or K_b and K_a is:

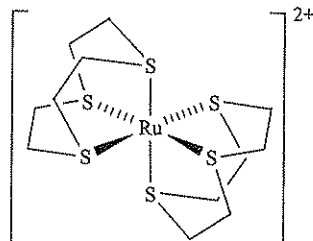
$$pK_a + pK_b = 14.00 \quad \text{or} \quad K_a \times K_b = 10^{-14.00}$$

- 7.31 (a) The Li^+ ion has the highest charge density of the group 1 M^+ ions because it is the smallest metal ion in the group. Therefore the second coordination sphere is heavily solvated; it contains $\approx 20 \text{ H}_2\text{O}$ molecules even though the first coordination sphere contains only 4 H_2O molecules.



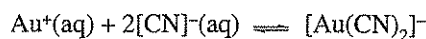
(7.26)

- (b) The ligand in the question is drawn here as ligand 7.26. It is tridentate but the cyclic structure restricts the ligand to binding to an octahedral metal centre in a *fac*-arrangement. Thus, the expected structure for $[\text{Ru}(7.26)_2]^{2+}$ is 7.27. Each coordinated ligand in 7.27 forms 3 chelate rings. Therefore the complex contains 6 chelate rings.



(7.27)

- (c) The stability constant for the formation of $[\text{Au}(\text{CN})_2]^-$ refers to the equilibrium:



$$K \approx 10^{39} \text{ at } 298 \text{ K}$$

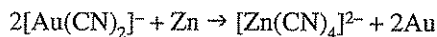
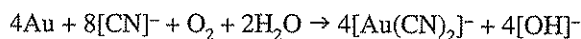
$$\Delta G^\circ = -RT \ln K$$

$$= -(8.314 \times 10^{-3})(298) \ln 10^{39}$$

$$= -222 \text{ kJ mol}^{-1}$$

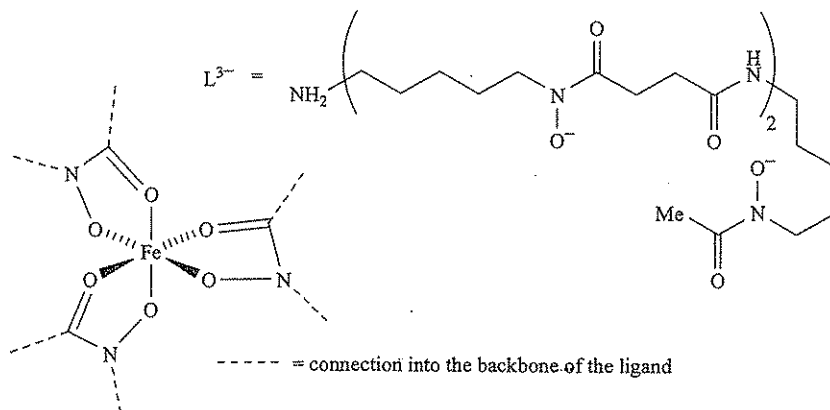
This large, negative value of $\Delta G^\circ(298 \text{ K})$ indicates that the formation of $[\text{Au}(\text{CN})_2]^-$ from Au(I) and cyanide ion is thermodynamically very favourable.

The extraction of Au from its ores takes place using the reactions:

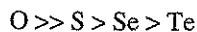
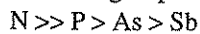


In the first reaction, Au(0) is oxidized to Au(I) and is stabilized in the form of the Au(I) complex $[\text{Au}(\text{CN})_2]^-$. In this form, it is extracted from the ore. In the second reaction, Zn is used to reduce Au(I) to Au(0); Zn is oxidized to Zn(II), the latter as a cyano complex.

- 7.32 Deprotonated desferrioxamine can be represented as L^{3-} and has six hard O-donor sites that are ideally suited to binding hard Fe^{3+} . The ligand has a flexible organic backbone and can wrap around the metal ion forming a complex with three 5-membered chelate rings involving three ONCO-units. This can be represented below and explains the origin of the term *chelation therapy*.



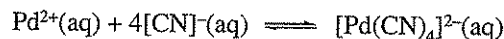
bases' (HSAB) is useful for rationalizing the observed trends in complex stabilities. In aqueous solution, complexes formed between *class (a)*, or *hard*, metal ions (metal ions are Lewis acids) and ligands containing donor atoms from groups 15 and 16 show the following trends in stabilities:



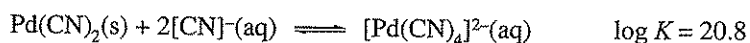
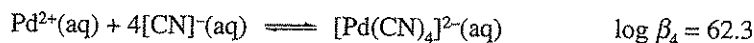
Class (b), or *soft*, metal ions prefer soft donor atoms, e.g. S rather than O, and P rather than N. Of the metal ions given in the question, Gd^{3+} and Fe^{3+} are hard acids while Ag^+ is a soft metal ion. The pattern in values of $\log K$ is consistent with a favourable hard metal ion-hard ligand match, but a less favourable soft metal ion-hard donor atom combination.

- $[DTPA]^{5-}$ is a chelating ligand, and thus is able to form particularly stable complexes with metal ions. The values of $\log K$ of 22.5 and 27.3 are large, and illustrate the 'chelate effect'.

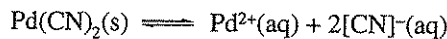
- 7.34 (a) Use of β_n corresponds to an overall stability constant, in contrast to K_n which refers to an individual step. This, $\log \beta_4$ for $[Pd(CN)_4]^{2-}$ refers to the process:



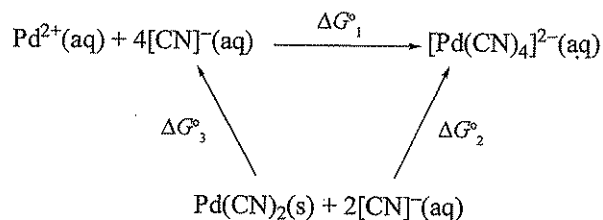
(b) Data available:



The equilibrium that corresponds to K_{sp} is:



Construct a Hess-type cycle that combines these reactions. In the cycle shown below, single arrows rather than equilibrium signs are used to give the cycle a sense of 'direction':



$$\Delta G_3^{\circ} = \Delta G_2^{\circ} - \Delta G_1^{\circ}$$

$$-RT \ln K_3 = -RT \ln K_2 + RT \ln K_1$$

$$\ln K_3 = \ln K_2 - \ln K_1$$

$$\log K_3 = \log K_2 - \log K_1$$

$$\log K_3 = 20.8 - 62.3 = -41.5$$

$$K_3 = K_{sp} = 10^{-41.5}$$