CHEM1612 Worksheet 9: Complexes

Model 1: The Stability of Complexes

Complexes contain a metal ion bonded to ligands. Most transition metal ions exist in aqueous solution as aqua complexes $[M(OH_2)_m]^{n+}$ The stability of a complex can be measured using the *stability constant* or K_{stab}. This is just an equilibrium constant, like the others you have met, and represents the formation of the complex from the aquo ion and the ligands. For example,

$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq) \qquad K_{stab} = \frac{[Ag(CN)_2{}^-]}{[Ag^+][CN^-]^2} = 1 \times 10^{20}$$

Critical thinking questions

1. The K_{stab} values for $[Zn(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ are 1×10^9 and 1×10^{13} respectively.

   (a) Which complex ion is more stable?

   (b) Excess NH_3 is added to a solution containing equal amounts of $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$. Does the resulting solution contain more uncomplexed $Zn^{2+}(aq)$ or $Cu^{2+}(aq)$?

2. The ligand $EDTA^{4-}$ forms very stable complexes with metal ions such as Ca^{2+}. It is administered as the complex $[Ca(EDTA)]^{2-}$ to treat lead poisoning.

   (a) Is K_{stab} larger for $[Ca(EDTA)]^{2-}$ or $[Pb(EDTA)]^{2-}$?

   (b) Why do you think it is administered as $[Ca(EDTA)]^{2-}$?

We are often interested in working out exactly how much of a metal ion is *not* complexed. Consider a solution prepared by mixing 0.0200 M silver nitrate (10.0 mL) with 1.00 M sodium cyanide (10.0 mL).

3. *Without* performing a calculation, how much free Ag^+ would you expect to be present in this solution once complexation has occurred? (*Hint*: remember that $K_{stab} = 1 \times 10^{20}$ and CN^- is present in excess)

4. After mixing, what are the *initial* concentrations of Ag^+ and CN^-?

   $[Ag^+]_{init}$ = $\qquad$ $[CN^-]_{init}$ =

5. From the chemical equation, each mole of Ag^+ reacts with two moles of CN^-. What is the equilibrium concentration of CN^- ?

   $[CN^-]_{equilibrium}$ =

6. *Virtually* all of the Ag^+ initially present reacts to form the complex $[Ag(CN)_2^-]$, so

   $[Ag(CN)_2^-]_{equilibrium} \approx [Ag^+]_{init}$ =

7. Finally, substitute your values from Q5 and Q6 into the expression for K_{stab} and solve to work out $[Ag^+]$.

8. What do you predict will happen if 1 mL of 1.00 M NH_3 is added to this solution? ($K_{stab} = 1 \times 10^7$ for $[Ag(NH_3)_2]^+$.)

9. What is the concentration of copper(II) ion in a solution made by dissolving copper(II) sulfate (0.100 mole) and ammonia (2.00 mole) in water and making up to 500 mL? ($K_{stab} = 1 \times 10^{13}$ for $[Cu(NH_3)_4]^{2+}$.)

Model 2: Using Complexation to Increase Solubility

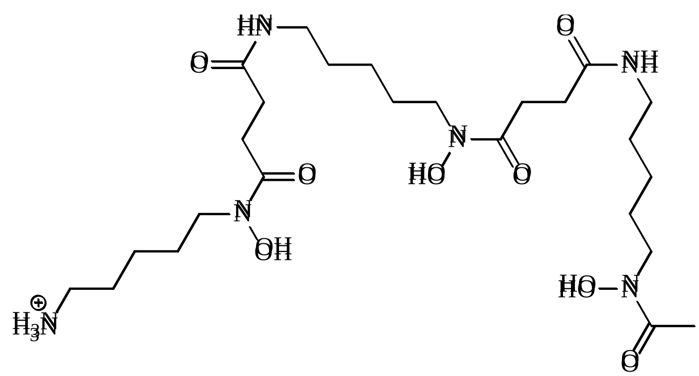
Hemochromatosis or "iron overload" is a potentially fatal disorder in which excess iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide.

It can be treated by administration of desferioxamine B (*Desferal*, drawn opposite), a natural substance isolated from fungi.

Desferal is taken over 8-12 hour periods up to six times per week. The equilibrium below has $K = 10^{30.6}$:

$$Fe^{3+}(aq) + LH_3(aq)^+ \rightleftharpoons FeL^+(aq) + 3H^+(aq)$$

where LH_3^+ = *Desferal*



Critical thinking questions

1. You will recall from week 6 that $[Fe^{3+}(aq)]$ is *very* low. Explain in chemical terms how *Desferal* treatment is able to dissolve insoluble hydrated iron(III) oxide.

2. Circle the atoms on *Desferal* which could form metal-ligand bonds in the FeL^+ complex.

3. Slow addition of sodium iodide to a mercury(II) nitrate solution results initially in the precipitation of red mercury(II) iodide and then the dissolution of this salt as a result of the reaction

$$HgI_2(s) + 2I^- \rightleftharpoons [HgI_4]^{2-}$$

(a) Write down the equilibrium constant for this reaction.

K =

(b) Write down the equilibrium expression corresponding to stability constant of $[HgI_4]^{2-}$ and the solubility product of HgI_2.

K_{stab} = K_{sp} =

(c) Using your answers to (a) and (b), calculate the equilibrium constant for this reaction.
$K_{stab} = 10^{30.28}$ for $[HgI_4]^{2-}$ and $K_{sp} = 10^{-10.37}$ for HgI_2.

(d) 0.030 mol of solid $Hg(NO_3)_2 . ½H_2O$ is added to 1.00 L of 0.200 M sodium iodide solution Calculate the final concentration of free (uncomplexed) mercury(II) ion?

Model 3: The electronic configuration of transition metal cations

The sum of the charges of the metal cation and its ligands adds up to give the charge of the complex ion. If the complex ion is charged, this is balanced by counter ions.

The number of valence electrons on an atom is equal to its group number. In a cation, the oxidation number is equal to the number of these electrons which have been removed. Transition metal cations have a configuration d^z where z is the number of valence electrons *left over after ionisation*:

***z* = number of valence electrons on atom – charge of cation**
= group number – oxidation number

For example:

(a) Ni is in group 10 so Ni^{2+} has (10 – 2) = 8 valence electrons left: it has a d^8 configuration.
(b) Cr is in group 6 so Cr^{3+} has (6 – 3) = 3 valence electrons left: it has a d^3 configuration.

Critical thinking questions

1. Complete the 'oxidation number' column of the table below by working out the oxidation number of each of the transition metal cations.

2. Complete the '*d* configuration' column in the table by working out *z* for each of the transition metal ions.

There are five *d*-orbitals and, as each orbital can accommodate two electrons, there is space for a maximum of ten electrons. To minimize repulsion, electrons occupy orbitals singly before they pair up. This has been done for the complexes in the first three rows of the table.

If this process leads to unpaired electrons, the complex is *paramagnetic* and is attracted towards magnetic field. If there are no unpaired electrons, the complex is *diamagnetic* and is weakly repelled by magnets.

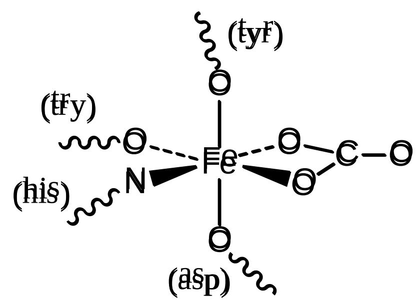
Critical thinking questions

1. Show the electron configuration for the transition metal cation using the box notation in the table.
2. Indicate if the complex is paramagnetic or not in the final column of the table.

Coordination Compound or Complex	Oxidation Number	*d* Configuration	Electron Arrangement	Paramagnetic?
$K_2[NiCl_4]$	+2	d^8	[↑↓] [↑↓] [↑↓] [↑] [↑]	Yes
$[Cr(en)_3]Br_3$	+3	d^3	[↑] [↑] [↑] [ ] [ ]	Yes
$Na[MnO_4]$			[ ] [ ] [ ] [ ] [ ]	
$(NH_4)_2[CoCl_4]$			[ ] [ ] [ ] [ ] [ ]	
$[Cr(NH_3)_5(H_2O)]Cl_3$			[ ] [ ] [ ] [ ] [ ]	
$[Zn(en)_2Cl_2]$			[ ] [ ] [ ] [ ] [ ]	

*en is $NH_2CH_2CH_2NH_2$ and can bond through lone pairs on *both* N atoms.

Model 4: Transferrin



Iron is found in many biological molecules. Typical of its coordination chemistry in fairly recently evolved systems is *transferrin*, which is used to transport iron in the blood. The Fe(III) atom is bonded to O and N atoms through five ligands: 4 amino acids and 1 carbonate anion (CO_3^{2-}).

Critical thinking questions

1. How many unpaired electrons will the Fe(III) atom have?

2. What is the coordination number and approximate coordination geometry of the Fe(III) atom? Describe how this is achieved with 5 ligands.

3. The Fe(III) is released in a cell by a decrease in the pH. Use your knowledge of acid-base chemistry to suggest what the effect of low pH will be on the ligands in the complex.