CHEM1612 Worksheet 9 – Answers to Critical Thinking Questions

The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

Model 1: The Stability of Complexes

1. (a) \([\text{Cu(NH}_3\text{)}_4]^2^+\)
   (b) \(\text{Zn}^{2+}(\text{aq})\)

2. (a) \([\text{Pb(EDTA)}]^2^-\). If it were not, then the therapy would not work.
   (b) EDTA\(^4-\) forms strongly bonded complexes with Ca\(^{2+}\) and it would strip them from the bones.

3. Very little.

4. \([\text{Ag}^+]_{\text{init}} = 0.0100 \text{ M}\) \([\text{CN}^-]_{\text{init}} = 0.50 \text{ M}\)

5. \([\text{CN}^-]_{\text{equilibrium}} = (0.50 - 2 \times 0.0100) \text{ M} = 0.48 \text{ M}\)

6. \([\text{Ag(CN)}_2^-]_{\text{equilibrium}} \approx [\text{Ag}^+]_{\text{init}} = 0.0100 \text{ M}\)

7. \(K_{\text{stab}} = \frac{[\text{Ag(CN)}_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = \frac{(0.0100)}{(0.48)^2} = 1 \times 10^{20} \text{ so } [\text{Ag}^+] = 4 \times 10^{-22} \text{ M}\)

8. Nothing as \([\text{Ag(CN)}_2^-]\) is more stable than \([\text{Ag(NH}_3\text{)}_2]^+\).

9. \([\text{Cu}^{2+}(\text{aq})] = 2 \times 10^{-16} \text{ M}.\)

   \(Hint: \ K_{\text{stab}} = \frac{[\text{Cu(NH}_3\text{)}_4]^2^+}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{(0.200)}{(3.20)^4} = 10^{19.91}\)

Model 2: Using Complexation to Increase Solubility

1. The solubility of \(\text{Fe}_2\text{O}_3\) is very small – the equilibrium for the reaction below lies far to the left:

   \(\text{Fe}_2\text{O}_3(\text{s}) + \text{excess } \text{H}_2\text{O} \rightleftharpoons 2\text{Fe}^{3+}(\text{aq}) + 6\text{OH}^- (\text{aq})\)

   Complexation of Fe\(^{3+}\) ions with \text{Desferal} is very favourable – the equilibrium for the complexation reaction far to the right (as \(K\) for this reaction is \(10^{30.6}\)). The Desferal complexes all free Fe\(^{3+}\)(aq) ions, so more \text{Fe}_2\text{O}_3 must dissolve to re-establish the first equilibrium (Le Chatelier's principle). Eventually all the \text{Fe}_2\text{O}_3 will dissolve.

2. All of the O atoms could potentially form metal-ligand bonds. The N atoms are either in amide groups or are protonated. These are not basic also cannot act as Lewis bases to a metal ion.

3. (a) \(K = \frac{[\text{Hgl}_4^{2-}]}{[\text{I}^-]^2}\)

   (b) \(K_{\text{stab}} = \frac{[\text{Hgl}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}\) \(K_{\text{sp}} = [\text{Hg}^{2+}][\text{I}^-]^2\)

   (c) \(K = K_{\text{stab}} \times K_{\text{sp}}\) \(\text{as } \frac{[\text{Hgl}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4} \times [\text{Hg}^{2+}][\text{I}^-]^2 = \frac{[\text{Hgl}_4^{2-}]}{[\text{I}^-]^2}\)

\(K = 10^{30.28} \times 10^{-10.37} = 10^{19.91}\)
(d) The reaction is $\text{Hg}^{2+} (\text{aq}) + 4\text{I}^- (\text{aq}) \rightleftharpoons \text{HgI}_4^{2-} (\text{aq})$, which corresponds to $K_{\text{stab}}$. The calculation is the same as in Model 1.

\[
\left[\text{Hg}^{2+}\right]_{\text{init}} = 0.030 \ \text{M} \quad \left[\text{I}^-\right]_{\text{init}} = 0.200 \ \text{M}
\]

\[
\left[\text{I}^-\right]_{\text{equilibrium}} = (0.200 - 4 \times 0.030) \ \text{M} = 0.080 \ \text{M}
\]

\[
\left[\text{HgI}_4^{2-}\right]_{\text{equilibrium}} \approx \left[\text{Hg}^{2+}\right]_{\text{init}} = 0.030 \ \text{M}
\]

\[
K_{\text{stab}} = \frac{\left[\text{HgI}_4^{2-}\right]}{\left[\text{Hg}^{2+}\right]^4\left[\text{I}^-\right]^4} = \frac{(0.030)}{[\text{Hg}^{2+}(0.080)]^4} = 10^{30.28} \quad \text{so} \quad \left[\text{Hg}^{2+}\right] = 3.8 \times 10^{-28} \ \text{M}
\]

Model 3: The electronic configuration of transition metal cations

1 – 2. See table below.

<table>
<thead>
<tr>
<th>Coordination Compound or Complex</th>
<th>Oxidation Number</th>
<th>$d$ Configuration</th>
<th>Electron Arrangement</th>
<th>Paramagnetic?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na[MnO$_4$]</td>
<td>+7</td>
<td>$d^0$</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2[\text{CoCl}_4]$</td>
<td>+2</td>
<td>$d^7$</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>[Cr(NH$_3)_5$(H$_2$O)]Cl$_3$</td>
<td>+3</td>
<td>$d^3$</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>[Zn(en)$_2$Cl$_2$]</td>
<td>+2</td>
<td>$d^{10}$</td>
<td></td>
<td>No</td>
</tr>
</tbody>
</table>

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. Five unpaired electrons.
2. Coordination number is 6 and coordination geometry is approximately octahedral. CO$_3^{2-}$ bonds through 2 O atoms (it is bidentate).
3. CO$_3^{2-}$ is a weak base and will become protonated at low pH. This will lead to it detaching from the iron.