

## 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

- $[\text{Cu}(\text{NH}_3)_4]^{2+}$
  - $\text{Zn}^{2+}(\text{aq})$
- $[\text{Pb}(\text{EDTA})]^{2-}$ . If it were not, then the therapy would not work.
  - $\text{EDTA}^{4-}$  forms strongly bonded complexes with  $\text{Ca}^{2+}$  and it would strip them from the bones.
- Very little.
- $[\text{Ag}^+]_{\text{init}} = 0.0100 \text{ M}$                        $[\text{CN}^-]_{\text{init}} = 0.50 \text{ M}$
- $[\text{CN}^-]_{\text{equilibrium}} = (0.50 - 2 \times 0.0100) \text{ M} = 0.48 \text{ M}$
- $[\text{Ag}(\text{CN})_2^-]_{\text{equilibrium}} \approx [\text{Ag}^+]_{\text{init}} = 0.0100 \text{ M}$
- $K_{\text{stab}} = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = \frac{(0.0100)}{[\text{Ag}^+](0.48)^2} = 1 \times 10^{20}$  so  $[\text{Ag}^+] = 4 \times 10^{-22} \text{ M}$
- Nothing as  $[\text{Ag}(\text{CN})_2^-]$  is more stable than  $[\text{Ag}(\text{NH}_3)_2]^+$ .
- $[\text{Cu}^{2+}(\text{aq})] = 2 \times 10^{-16} \text{ M}$ .

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

### Model 2: Using Complexation to Increase Solubility

- The solubility of  $\text{Fe}_2\text{O}_3$  is very small - the equilibrium for the reaction below lies far to the left:  
$$\text{Fe}_2\text{O}_3(\text{s}) + \text{excess H}_2\text{O} \rightleftharpoons 2\text{Fe}^{3+}(\text{aq}) + 6\text{OH}^-(\text{aq})$$
Complexation of  $\text{Fe}^{3+}$  ions with *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  $\text{Fe}^{3+}(\text{aq})$  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.
- 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.
- $K = \frac{[\text{HgI}_4^{2-}]}{[\text{I}^-]^2}$
  - $K_{\text{stab}} = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}$                        $K_{\text{sp}} = [\text{Hg}^{2+}][\text{I}^-]^2$
  - $K = K_{\text{stab}} \times K_{\text{sp}}$                       as  $\frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4} \times [\text{Hg}^{2+}][\text{I}^-]^2 = \frac{[\text{HgI}_4^{2-}]}{[\text{I}^-]^2}$   
 $K = 10^{30.28} \times 10^{-10.37} = 10^{19.91}$

- (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.

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

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

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

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

### Model 3: The electronic configuration of transition metal cations

1 – 2. See table below.

Coordination Compound or Complex	Oxidation Number	<i>d</i> Configuration	Electron Arrangement	Paramagnetic?					
Na[MnO <sub>4</sub> ]	+7	<i>d</i> <sup>0</sup>	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td style="width: 20px; height: 20px;"></td><td style="width: 20px; height: 20px;"></td><td style="width: 20px; height: 20px;"></td><td style="width: 20px; height: 20px;"></td><td style="width: 20px; height: 20px;"></td></tr></table>						No
(NH <sub>4</sub> ) <sub>2</sub> [CoCl <sub>4</sub> ]	+2	<i>d</i> <sup>7</sup>	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td style="width: 20px; height: 20px; text-align: center;">↑↓</td><td style="width: 20px; height: 20px; text-align: center;">↑↓</td><td style="width: 20px; height: 20px; text-align: center;">↑</td><td style="width: 20px; height: 20px; text-align: center;">↑</td><td style="width: 20px; height: 20px; text-align: center;">↑</td></tr></table>	↑↓	↑↓	↑	↑	↑	Yes
↑↓	↑↓	↑	↑	↑					
[Cr(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O)]Cl <sub>3</sub>	+3	<i>d</i> <sup>3</sup>	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td style="width: 20px; height: 20px; text-align: center;">↑</td><td style="width: 20px; height: 20px; text-align: center;">↑</td><td style="width: 20px; height: 20px; text-align: center;">↑</td><td style="width: 20px; height: 20px;"></td><td style="width: 20px; height: 20px;"></td></tr></table>	↑	↑	↑			Yes
↑	↑	↑							
[Zn(en) <sub>2</sub> Cl <sub>2</sub> ]	+2	<i>d</i> <sup>10</sup>	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td style="width: 20px; height: 20px; text-align: center;">↑↓</td><td style="width: 20px; height: 20px; text-align: center;">↑↓</td></tr></table>	↑↓	↑↓	↑↓	↑↓	↑↓	No
↑↓	↑↓	↑↓	↑↓	↑↓					

### 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<sub>3</sub><sup>2-</sup>).

#### Critical thinking questions

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