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Pre-Health Post-Baccalaureate Program
Study Guide and Practice Problems

Course: CHM2046

Textbook Chapter: 19.4 (Silberberg 6e)

Topics Covered: Equilibria of Complex Ions

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1. Definitions and Overarching Concept

A *complex ion* is composed of a “central metal ion covalently bonded to two or more anions or molecules, called *ligands*” (textbook).

Now, how do they form?

When we dissolve a salt in water, we see the formation of a complex ion. The metal cation is in the center, surrounded by covalently-bonded water molecules.

2. Another K

When we have a complex ion with water acting as the ligands, and we add another ligand to the mix, we see that the new ligand “kicks out” the water to take its place. This does not happen all at once, but rather in a stepwise manner.

Believe it or not (and I’m sure, at this point, that you can believe it), we can come up with yet another K value. This value, called the formation constant (K_f), queues us into how much of the new complex ion (same metal cation with new ligand) forms compared to the original complex ion and the new ligand reagent, separately.

$$M(H_2O)_4{}^{2+}{}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons M(NH_3)_4{}^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

$$K_c = \frac{[M(NH_3)_4{}^{2+}][H_2O]^4}{[M(H_2O)_4{}^{2+}][NH_3]^4}$$

$$K_f = \frac{K_c}{[H_2O]^4} = \frac{[M(NH_3)_4{}^{2+}]}{[M(H_2O)_4{}^{2+}][NH_3]^4}$$

3. Complex Ions of Amphoteric Hydroxides

In the case of amphoteric hydroxides, we see very little solubility in water, but much greater solubility in acidic and basic solutions.

In water:

$$Al(OH)_{3\,(s)} \rightleftharpoons Al^{3+}_{(aq)} + 3\,HO^{-}_{(aq)}$$

In acid (solubility due to water formation):

$$Al(OH)_{3\,(s)} + 3\,H_3O^{+}_{(aq)} \longrightarrow Al^{3+}_{(aq)} + 6\,H_2O_{(l)}$$

In base (solubility due to complex ion formation):

$$Al(OH)_{3\,(s)} + HO^{-}_{(aq)} \longrightarrow Al(OH)^{-}_{4\,(aq)}$$

Problems

① If the K_f of $Zn(NH_3)_4^{2+}$ is 7.8×10^8, find the equilibrium concentration of $Zn(H_2O)_4^{2+}$ in the reaction of 50 L of 0.002 M $Zn(H_2O)_4^{2+}$ and 25 L of 0.15 M NH_3.

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	$Zn(H_2O)_4^{2+}$ +	$4NH_3$ ⇌	$Zn(NH_3)_4^{2+}$ + $4H_2O$
I	$\frac{50\,L \times 0.002\,M}{75\,L}$ $= 1.3 \times 10^{-3}$ M	$\frac{25\,L \times 0.15\,M}{75\,L}$ $= 5 \times 10^{-2}$ M	0
C	$\sim(-1.3 \times 10^{-3})$	$-4(1.3 \times 10^{-3})$ $\sim(-5.2 \times 10^{-3})$	$\sim(+1.3 \times 10^{-3})$
E	x	$\sim 4.5 \times 10^{-2}$	$\sim 1.3 \times 10^{-3}$

$$K_f = \frac{[Zn(NH_3)_4^{2+}]}{[Zn(H_2O)_4^{2+}][NH_3]^4} = 7.8 \times 10^8$$

$$\frac{1.3 \times 10^{-3}}{x\,(4.5 \times 10^{-2})} = 7.8 \times 10^8$$

$$x \approx 4.1 \times 10^{-7}\ M$$

(2) If solid FeS is added to water, it is only slightly soluble ($K_{sp} = 8 \times 10^{-16}$). Given that the K_f of $Fe(CN)_6^{4-}$ is 3×10^{35}, explain how we can know that solubility increases when a complex ion is added.

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$$Fe_{(s)} + H_2O_{(l)} \rightleftharpoons Fe^{2+}_{(aq)} + HS^-_{(aq)} + HO^-_{(aq)}$$

$$Fe^{2+}_{(aq)} + 6\,CN^-_{(aq)} \rightleftharpoons Fe(CN)_6^{4-}{}_{(aq)}$$

$$K_{total} = K_{sp} \times K_f$$

$$= (8 \times 10^{-16})(3 \times 10^{35})$$

$$= 2 \times 10^{20} >>> 1$$

We can know from Le Chat's and from K_{total}.