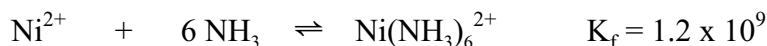


This is a discussion of end-of-chapter exercise 17.65 in the textbook. The question is,

From the value of K_f listed in Table 17.1, calculate the concentration of $\text{Ni}^{2+}(\text{aq})$ and $\text{Ni}(\text{NH}_3)_6^{2+}$ that are present at equilibrium after dissolving 1.25 g NiCl_2 in 100.0 mL of 1.00 M $\text{NH}_3(\text{aq})$. The K_f reaction is the following:



The solutions manual pretty much does it correctly up to a point (with a small mistake in the molar mass of the NiCl_2), until they solve for the free Ni^{2+} conc. I'll go through it completely below.

First, determine how many moles of NiCl_2 (i.e. Ni^{2+}) are added and the moles of NH_3 originally present.

$$? \text{ mol Ni}^{2+} = 1.25 \text{ g NiCl}_2 \times \frac{1 \text{ mol NiCl}_2}{129.599 \text{ g NiCl}_2} \times \frac{1 \text{ mol Ni}^{2+}}{1 \text{ mol NiCl}_2} = 0.009645 \text{ mol Ni}^{2+}$$

$$? \text{ mol NH}_3 = 0.1000 \text{ L soln} \times \frac{1.00 \text{ mol NH}_3}{1 \text{ L soln}} = 0.100 \text{ mol NH}_3$$

What's the limiting reactant?: It would take 0.05787 mol of NH_3 , $6(0.009645 \text{ mol Ni}^{2+})$, to react with all the Ni^{2+} . There's 0.100 mol of NH_3 so the Ni^{2+} is the limiting reactant and it completely reacts, leaving behind excess NH_3 . Then to find the conc. of Ni^{2+} you would reverse the reaction and look at the dissociation of the $\text{Ni}(\text{NH}_3)_6^{2+}$ in the presence of the left over NH_3 .

Initial stoichiometry problem (in moles):

	Ni^{2+}	+	6 NH_3	\rightleftharpoons	$\text{Ni}(\text{NH}_3)_6^{2+}$
I	0.009645		0.100		0
C	- 0.009645		- 0.05787		+ 0.009645
C	0		0.04212		0.009645

We're assuming because K_f is very large ($K_f = 1.2 \times 10^9$) this reaction essentially goes to completion.

This is where the solutions manual takes a shortcut that doesn't always work. They plug the conc. back into K_f and solve for the $[\text{Ni}^{2+}]$. That's technically the correct way to do it and sometimes doesn't work doing it the way they did. You should really reverse the reaction (dissociation of the complex) and see how much of the complex would come apart in the presence of the left over NH_3 .

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Now, we'll treat this as $\text{Ni}(\text{NH}_3)_6^{2+}$ dissociating the presence of the NH_3 . This is done in molarity. So convert the moles above to molarities (0.1000 L of solution) and use the following ICE table for the dissociation of the $\text{Ni}(\text{NH}_3)_6^{2+}$ complex in the presence of the excess NH_3 .

	$\text{Ni}(\text{NH}_3)_6^{2+}$	\rightleftharpoons	Ni^{2+}	+	6NH_3
I	0.09645		0		0.42129
C	- x		+ x		+6x
E	0.09645 - x		x		0.42129 + 6x

$$K_d = \frac{[\text{Ni}^{2+}] [\text{NH}_3]^6}{[\text{Ni}(\text{NH}_3)_6^{2+}]} = 1/K_f = 1/(1.2 \times 10^9) = 8.333 \times 10^{-10}$$

$$\frac{x (0.42129 + x)^6}{(0.09645 - x)} = 8.333 \times 10^{-10}$$

Assume "x" is small (based on the size of K_d),

$$\frac{x (0.42129)^6}{(0.09645)} = 8.333 \times 10^{-10}$$

$$x = [\text{Ni}^{2+}] = 1.437 \times 10^{-8} \text{ M} \quad \text{This is the conc. of free } \text{Ni}^{2+} \text{ in the solution.}$$

$$[\text{Ni}(\text{NH}_3)_6^{2+}] = 0.09645 - 1.437 \times 10^{-8} = 0.09645 \text{ M}$$