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 Ni^{2+} (aq) and $Ni(NH_3)_6^{2+}$ that are present at equilibrium after dissolving 1.25 g $NiCl_2$ in 100.0 mL of 0.20 M NH_3(aq).

The solutions manual doesn't really solve this in the way one would expect to based on the way the problem is stated. They did it as Sample Exercise 17.15 was done, with the conc of NH_3 being 0.20 M at equilibrium. However, the problems states $NiCl_2$ is added to 100.0 mL of 0.20 M NH_3(aq), implying there's a beaker with 100.0 mL of 0.20 M NH_3(aq) to which the solid $NiCl_2$ is added. Thus, one really needs to do a stoichiometry problem to determine which is the limiting reactant first and then complete the problem based on that.

Turns out, with the way this problem is worded the NH_3 is the limiting reactant, which is quite unusual in these types of problems but certainly not out of the question (although this is not the way the solution's manual treats it).

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

$$? \text{ mol } Ni^{2+} = 1.25 \text{ g } NiCl_2 \times \frac{1 \text{ mol } NiCl_2}{129.599 \text{ g } NiCl_2} \times \frac{1 \text{ mol } Ni^{2+}}{1 \text{ mol } NiCl_2} = 0.0096\underline{\mathbf{4}}5 \text{ mol } Ni^{2+}$$

$$? \text{ mol } NH_3 = 0.1000 \text{ L soln} \times \frac{0.20 \text{ mol } NH_3}{1 \text{ L soln}} = 0.020 \text{ mol } NH_3$$

What's the limiting reactant?: It would take 0.05787 mol of NH_3, 6(0.0096**4**5 mol Ni^{2+}), to react with all the Ni^{2+}. There's only 0.020 mol of NH_3. It would take 0.00333 mol of Ni^{2+}, 1/6(0.020 mol NH_3) to react with all the NH_3.

Initial stoichiometry problem (in moles):

	Ni^{2+}	+	$6\ NH_3$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}$
I	0.0096**4**5		0.020		0
C	- 0.003**3**33		- 0.020		+ 0.003**3**33
C	0.006**3**11		0.000		0.003**3**33

We're then essentially done at this point because K is quite large ($K_f = 1.2 \times 10^9$) which means this reaction essentially goes to completion. We could see how much of the complex would come apart in the presence of the left over Ni^{2+} to see more accurately how much NH_3 remains.

Now, we'll treat this as $Ni(NH_3)_6^{2+}$ dissociating the presence of the Ni^{2+}. This is done in molarity.

	$Ni(NH_3)_6^{2+}$	$\rightleftharpoons$	Ni^{2+}	+	$6\ NH_3$
I	0.03**3**33		0.06**3**11		0
C	- x		+ x		+6x
E	0.03**3**33 - x		0.06**3**11 + x		6x

$$K_d = \frac{[Ni^{2+}]\,[NH_3]^6}{[Ni(NH_3)_6^{\,2+}]} = 1/K_f = 1/(1.2 \times 10^9) = 8.333 \times 10^{-10}$$

$$\frac{(0.06\underline{3}11 + x)\,(6x)^6}{(0.03\underline{3}33 - x)} = 8.333 \times 10^{-10}$$

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

$$\frac{(0.06\underline{3}11)\,(6x)^6}{(0.03\underline{3}33)} = 8.333 \times 10^{-10}$$

x = 0.0045966 M

This is a 13.8% error compare to 0.03333 M so technically it can’t be ignored. If one does the method of successive approximations you can get a better “x”.

$x = 0.004\underline{4}379$ M

$[Ni(NH_3)_6^{\,2+}] = 0.03\underline{3}33 - 0.004\underline{4}379 = 0.02\underline{8}89$ M
$[Ni^{2+}] = 0.06\underline{3}11 + 0.004\underline{4}379 = 0.06\underline{7}555$ M
$[NH_3] = 6(0.004\underline{4}379) = 0.02\underline{6}627$ M

So, there’s still some NH_3 remaining even as big as K_f. The reaction didn’t go completely and use up all the NH_3.

Plug these back into the K_f to make sure it gives the correct value for K_f.

$$K_f = \frac{[Ni(NH_3)_6^{\,2+}]}{[Ni^{2+}]\,[NH_3]^6} = \frac{(0.02\underline{8}89)}{(0.06\underline{7}555)\,(0.02\underline{6}627)^6} = 1\underline{1}999 \times 10^9 = 1.2 \times 10^9$$

The solutions manual does this as if the **equilibrium conc**. of **NH_3** is 0.20 M and all the Ni^{2+} is in the form of the complex and then solves for the conc. of “free” Ni^{2+} by simply using the K_f.

$$K_f = \frac{[Ni(NH_3)_6^{\,2+}]}{[Ni^{2+}]\,[NH_3]^6} = \frac{(0.096\underline{4}5)}{x\,(0.20)^6} = 1.2 \times 10^9$$

$x = [Ni^{2+}] = 1.\underline{2}6 \times 10^{-6}$ M $\qquad [Ni(NH_3)_6^{\,2+}] = 0.096\underline{4}48$ M

However, this is NOT how the problem was worded.

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Here's how the problem might be presented in different way, as the example I did in class.

From the value of K_f listed in Table 17.1, calculate the concentration of Ni^{2+} (aq) and $Ni(NH_3)_6^{2+}$ that are present at equilibrium after dissolving 1.25 g $NiCl_2$ in 1.00 L of 0.20 M NH_3(aq).

In this case the Ni^{2+} will be the limiting reactant and completely react, 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 $Ni(NH_3)_6^{2+}$ in the presence of NH_3.

Initial stoichiometry problem (in moles):

	Ni^{2+}	+	$6\ NH_3$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}$
I	$0.0096\underline{4}5$		0.20		0
C	$-\ 0.0096\underline{4}5$		$-\ 6(0.0096\underline{4}5)$		$+\ 0.0096\underline{4}5$
C	0		$0.1\underline{4}2129$		$0.0096\underline{4}5$

Now, we'll treat this as $Ni(NH_3)_6^{2+}$ dissociating the presence of the NH_3. This is done in molarity.

	$Ni(NH_3)_6^{2+}$	$\rightleftharpoons$	Ni^{2+}	+	$6\ NH_3$
I	$0.0096\underline{4}5$		0		$0.1\underline{4}2129$
C	$-\ x$		$+\ x$		$+6x$
E	$0.0096\underline{4}5 - x$		x		$0.1\underline{4}2129 + 6x$

$$K_d = \frac{[Ni^{2+}]\,[NH_3]^6}{[Ni(NH_3)_6^{2+}]} = 1/K_f = 1/(1.2 \times 10^9) = 8.333 \times 10^{-10}$$

$$\frac{x\,(0.1\underline{4}2129 + x)^6}{(0.0096\underline{4}5 - x)} = 8.333 \times 10^{-10}$$

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

$$\frac{x\,(0.1\underline{4}2129)^6}{(0.0096\underline{4}5)} = 8.\underline{3}33 \times 10^{-10}$$

$x = [Ni^{2+}] = 9.\underline{7}50 \times 10^{-7}$ M This is the conc. of free Ni^{2+} in the solution.

$[Ni(NH_3)_6^{2+}] = 0.0096\underline{4}5 - 9.\underline{7}50 \times 10^{-7} = 0.0096\underline{4}4$ M