In class we discussed Common-Ion problems. I used an example adding 0.020 moles of NH_4Cl to 100.0 mL of a 0.15 M NH_3 solution. I briefly showed one way to approach the problem (the hard) way and then showed the easy way (the way it should be approached, by assuming you are putting both things into solution at the same time). I always receive several questions about the whole process. I'm including the following in hopes it may answer any questions that may remain.

1) First look at the problem as it actually occurs physically. We have a beaker with a solution of 0.15 M NH_3. We can first do a weak base calculation to determine the concentrations of everything in the beaker.

	NH_3	$+$	H_2O	$\rightleftharpoons$	NH_4^+	$+$	OH^-
I	0.15				0		0
C	- x				+ x		+ x
E	0.15 - x				x		x

$$K_b = \frac{x^2}{0.15 - x} = 1.8 \times 10^{-5}$$

Assume "x" is small and $0.15 - x \approx 0.15$

$$K_b = \frac{x^2}{0.15} = 1.8 \times 10^{-5}$$

$x = [NH_4^+] = [OH^-] = 1.\underline{\mathbf{6}}43 \times 10^{-3}$ M (1.1 % error, that's okay)

$[NH_3] = 0.15 - 1.\underline{\mathbf{6}}43 \times 10^{-3} = 0.1\underline{\mathbf{4}}83$ M

pH = 11.22

To the beaker we add 0.020 moles of NH_4Cl. This dissociates into 0.020 moles of NH_4^+ and 0.020 moles of Cl^-. The Cl^- ion does not react with H_2O (it doesn't hydrolyze and is neutral) or anything in the above equilibrium. The NH_4^+ is an ion involved in the above equilibrium. This is a common-ion problem.

When we add the 0.020 moles NH_4^+ ions to 100.0 mL of solution we get 0.20 M NH_4^+. This adds to what we already have in the beaker,

NH_3	$+$	H_2O	$\rightleftharpoons$	NH_4^+	$+$	OH^-
0.1483 M				0.00164 M		0.00164 M
				+ 0.20 M		
0.1483 M				0.20164 M		0.00164 M

This is no longer at equilibrium. There's too much NH_4^+ to be at equilibrium. We've added some product and the reaction SHIFTS to the LEFT. We don't need to calculate Q to determine this will go to the left (in the reverse direction) because we added a product to a system at equilibrium. We need to do this ICE table calculation to determine the new concentrations after adding the NH_4^+. This table will be going right to left.

	NH_3	+	H_2O	⇌	NH_4^+	+	OH^-
I	0.1483				0.20164		0.00164
C	+ y				- y		- y
E	0.1483 + y				0.20164 - y		0.00164 - y

$$K_b = \frac{(0.20164 - y)\,(0.00164 - y)}{0.1483 + y} = 1.8 \times 10^{-5}$$

The rxn would proceed right to left (in reverse direction). The K in the forward direction is small meaning it doesn't go far to the right (mostly reactants at equil.). Since this is going in the reverse direction we would expect it to go far to the left toward reactant. Even so, we'll assume the "y" is relatively small compared to 0.1483 and 0.20164 so 0.1483 + y ≈ 0.1483 and (0.20164 - y)≈ 0.20164. However, we probably can't safely do this with the 0.00164 since it's pretty small.

$$K_b = \frac{(0.20164)\,(0.00164 - y)}{0.1483} = 1.8 \times 10^{-5}$$

$0.00164 - y = 1.3238 \times 10^{-5}$

$y = 1.6299 \times 10^{-3}$ M (1.1 % error when we look at it compared to 0.1483 and that's okay. If the quadratic eqn is solved the answer is 1.626×10^{-3} M.)

So the new equilibrium conc. will be,

$[NH_4^+] = 0.20164 - 1.6299 \times 10^{-3} = 0.20001$ M
$[OH^-] = 1.64 \times 10^{-3}$ M $- 1.6299 \times 10^{-3}$ M $= 1.324 \times 10^{-5}$
$[NH_3] = 0.1483 + 1.6299 \times 10^{-3} = 0.14998$ M

pH = 9.12 (solving the quadratic gives a pH of 9.13)

***** see the next page for the easier way of approaching this *****

2) Instead of doing the problem the way I've outlined above (which is what is actually physically occurring) we can think of adding the NH_3 and NH_4^+ simultaneously (at the same time) to 100.0 mL of water. This will have the same affect as adding the right amount of NH_3 first to make the solution 0.15 M in NH_3 and then adding the NH_4^+ to make the solution 0.20 M in NH_4^+. Years ago someone in my office hours likened it to making Kool-Aid. You could add the Kool-Aid to the water first and then the sugar. You could add the Kool-Aid and sugar at the same time (simultaneously). You will wind up with the same mixture in the end. So lets write our ICE table doing it this way.

	NH_3	$+$	H_2O	$\rightleftharpoons$	NH_4^+	$+$	OH^-
I	0.15				0.20		0
C	- z				+ z		+ z
E	0.15 - z				0.20 + z		z

$$K_b = \frac{(0.20 + z)\ (z)}{(0.15 - z)} = 1.8 \times 10^{-5}$$

Assume "z" is small and 0.15 - x ≈ 0.15 and 0.20 + z ≈ 0.20

$$K_b = \frac{(0.20)\ (z)}{(0.15)} = 1.8 \times 10^{-5}$$

$z = 1.35 \times 10^{-5}$ (0.009 % error compared to 0.15 so the assumption that "x" is small is good)

So the equilibrium conc. will be,

$[NH_4^+] = 0.20 + 1.35 \times 10^{-5} = 0.2000135\ M = 0.20\ M$
$[OH^-] = 1.35 \times 10^{-5}\ M$
$[NH_3] = 0.15 - 1.35 \times 10^{-5} = 0.1\underline{\mathbf{4}}998\ M = 0.15\ M$

pH = 9.13

This is essentially the same as what I got in (1) above, doing it the "hard" way (slight differences because I didn't use a quadratic). It should be the same. We are just treating it in two different but equivalent ways. This way is a whole lot easier.

Just picture this as starting the reaction with the reactant (NH_3) and one of the products (NH_4^+ in this example) rather than just starting with the reactant. So we started the reaction with NH_3 and NH_4^+ and no OH^-. Since one of the products is still missing the reaction has to go to the right (in the forward direction). Also, since we started with one of the products the reaction will not go as far in the forward direction as it would if we started w/o any products. That's why less OH^- is produced from the reaction of NH_3 with H_2O in the presence of the common ion, NH_4^+. The pH winds up lower than it would be with just 0.15 M NH_3 (pH=9.13 compared to a pH of 11.22 with only the NH_3). It should makes sense the pH went down since a weak acid, NH_4^+, was added. You also can get a common-ion problem by adding OH^-.

Thus, a common-ion problem boils down to starting a rxn. with not just a reactant but also one of the products.

I hope this all made sense and makes it easier to understand why we do it this way.