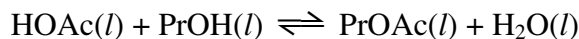CHM 106
Lab 2: Equilibrium

We are studying the esterification of acetic acid with propanol to form propyl acetate and water. I will be abbreviating these compounds accordingly to save space in typing:

$$HOAc(l) + PrOH(l) \rightleftharpoons PrOAc(l) + H_2O(l)$$

We determined the initial concentration of acetic acid, $[HOAc]_0$ by titration last week. Given the volume and concentration of base (0.10 $\underline{M}$ NaOH) and the aliquot volume (0.50 mL) of acetic acid, we can calculate the molarity of acetic acid. Acetic acid has a 1:1 stoichiometry with base in the titration:

$$HOAc(aq) + NaOH(aq) \rightarrow NaOAc(aq) + H_2O(l)$$
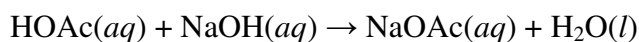
Sometimes when approaching calculations like this it is helpful to plot a solution strategy:

$$\text{volume NaOH} \rightarrow \text{mol NaOH} \rightarrow \text{mol HOAc} \rightarrow \text{conc. HOAc}$$
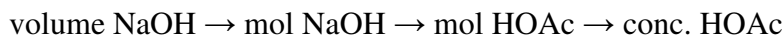
We can then do the appropriate calculations. For this example, assume that 35.0 mL of NaOH were required for the titration. Then,

$$0.0350 \text{ L NaOH} \cdot \frac{0.10 \text{ mol NaOH}}{1 \text{ L NaOH}} \cdot \frac{1 \text{ mol HOAc}}{1 \text{ mol NaOH}} \cdot \frac{1}{0.00050 \text{ L HOAc}} = 7.00 \text{ } \underline{M} = [HOAc]_0$$

Notice that all units cancel out except mol HOAc / L HOAc, which are the units we expect for the concentration of acetic acid. This is no coincidence! It is *imperative* that you use units in chemical calculations because they provide a natural check on the work done. Not including units on routine chemical calculations is one of the leading causes of mistakes.

Now, we need to calculate the initial concentration of PrOH, which should be similar to but probably not identical to the AcOH concentration. Since we know the amounts of acetic acid and propanol we started with in the reaction mixture (You did record those amounts exactly, right?), we can calculate find the solution volume from the concentration and number of moles of acetic acid and then calculate the molarity of propanol initially from that. We'll need densities and molecular weights to do that; for AcOH, $\rho = 1.049$ g / mL and MW = 60.05 g / mol; for PrOH, $\rho = 0.8016$ g / mL and MW = 60.10 g / mol.

Let's assume we used exactly 15.0 mL of AcOH and 20.0 mL of PrOH. We'll also need the molarity of acetic acid determined above. We first calculate solution volume:

$$\text{volume AcOH} \rightarrow \text{mass AcOH} \rightarrow \text{mol AcOH} \rightarrow \text{solution volume}$$
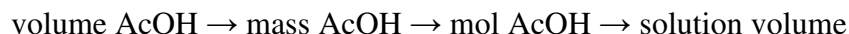
$$15.0 \text{ mL AcOH} \cdot \frac{1.049 \text{ g AcOH}}{1 \text{ mL AcOH}} \cdot \frac{1 \text{ mol AcOH}}{60.05 \text{ g AcOH}} \cdot \frac{1 \text{ L AcOH}}{7.00 \text{ mol AcOH}} = 0.0374 \text{ L}$$

We had to calculate this value because solution volumes are not additive. Next, we calculate the concentration of $[PrOH]_0$ from this:

$$\text{volume PrOH} \rightarrow \text{mass PrOH} \rightarrow \text{mol PrOH} \rightarrow \text{conc. PrOH}$$

$$20.0 \text{ mL PrOH} \cdot \frac{0.8016 \text{ g PrOH}}{1 \text{ mL PrOH}} \cdot \frac{1 \text{ mol PrOH}}{60.10 \text{ g PrOH}} \cdot \frac{1}{0.0374 \text{ L}} = 7.13 \underline{M} = [PrOH]_0$$

Now that we have initial concentrations, we need to calculate the equilibrium concentration of HOAc, as determined by this week's titration. This calculation is much the same as the other titration calculation, although we will need to subtract the volume of base that is consumed by the catalyst, as determined in last week's titrations. Let us suppose that the catalyst required 0.5 mL of base to titrate, and this week's reaction mixture titrations took 15.0 mL of base. Since 0.5 mL of that base was consumed by the acid catalyst, we know the remaining 14.5 mL of base reacted only with acetic acid, and that's the corrected volume we'll use in the calculations.

$$0.0145 \text{ L NaOH} \cdot \frac{0.10 \text{ mol NaOH}}{1 \text{ L NaOH}} \cdot \frac{1 \text{ mol HOAc}}{1 \text{ mol NaOH}} \cdot \frac{1}{0.00050 \text{ L HOAc}} = 2.90 \underline{M} = [HOAc]$$

It should make sense that the acetic acid concentration is lower now than it was last week. Now, let's examine the ICE table for this equilibrium and determine the equilibrium concentrations of the other species:

	HOAc(l)	+	PrOH(l)	$\rightleftharpoons$	PrOAc(l)	+	H$_2$O(l)
Initially:	$[HOAc]_0$		$[PrOH]_0$		0		0
Change:	$-x$		$-x$		$+x$		$+x$
Equilibrium:	$[HOAc]_0 - x$		$[PrOH]_0 - x$		x		x

Recognizing that the concentration of acetic acid at equilibrium $[HOAc] = [HOAc]_0 - x$, and that we have values for both equilibrium and initial concentrations of acetic acid allows us to calculate x and thus all of the equilibrium concentrations. For this example,

$$x = [HOAc]_0 - [HOAc] = 7.00 - 2.90 = 4.10 \underline{M}$$
$$[PrOH] = [PrOH]_0 - x = 7.13 - 4.10 = 3.03 \underline{M}$$
$$[PrOAc] = [H_2O] = x = 4.10 \underline{M}$$

Thus, we can calculate the value of the equilibrium constant.

$$K = \frac{[PrOAc][H_2O]}{[HOAc][PrOH]} = \frac{[4.10][4.10]}{[2.90][3.03]} = 1.91$$

This example's value is perhaps a bit low compared to the rule-of-thumb value of about 4, but we can attribute that to experimental error (or in this case, synthetic data). Keep in mind that you should be calculating concentrations from the titrations three times (once for each trial), and then averaging those concentrations for further calculations.