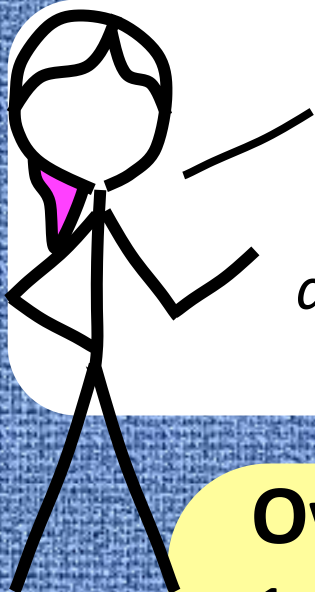
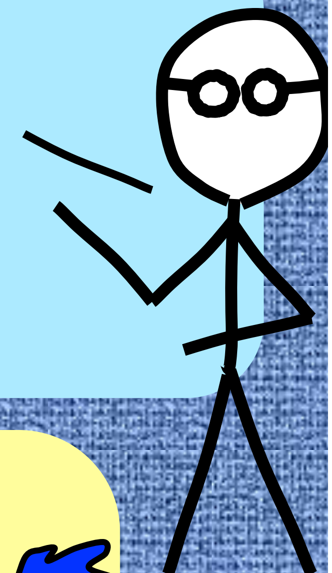
Experiment 4
20 February 2020
Equilibrium

Objectives: To study a reaction at equilibrium and determine the equilibrium constant, K_c.



Today we will study a reaction at equilibrium. We will be able to determine the equilibrium constant as well.

The reaction is extremely fast – instantaneous – so we don't have to worry about kinetics.



Overview:

1. The equilibrium
2. Deriving the equation we will use
3. The experiment
4. Procedure: What we will do today
5. Your lab report

1. The equilibrium

So here is our equilibrium. It features bromothymol blue which is yellow or blue or a little of each – making it look green!

Yellow ⇄ Blue

"HBB" + H_2O ⇄ "BB^-" + H_3O^+

Bromothymol blue has the formula $C_{27}H_{28}Br_2O_5S$ – so that is why we just call it HBB for short. HBB is yellow as shown here in the left test tube.

Info for Introduction

1. The equilibrium

Yellow $\rightleftharpoons$ **Blue**

"HBB" + H_2O $\rightleftharpoons$ **"BB^-" + H_3O^+**

*These solutions all contain mixtures of yellow **HBB** and blue **BB^-**. This particular test tube contains a lot more **BB^-** than **HBB**, so it looks blue.*

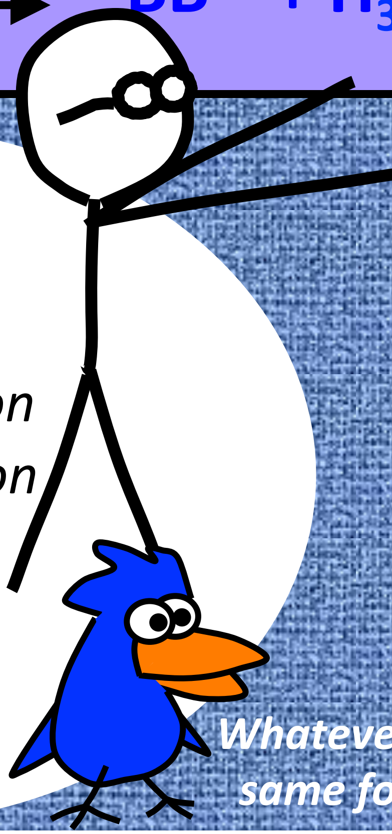
*The test tubes in the middle have both yellow **HBB** and blue **BB^-**, so they look green!*

Info for Introduction

1. The equilibrium

$$\text{Yellow} \rightleftharpoons \text{Blue} \qquad K_c = \frac{[\text{Blue}]}{[\text{Yellow}]}$$

$$\text{“HBB”} + H_2O \rightleftharpoons \text{“BB}^-\text{”} + H_3O^+ \qquad K_c = \frac{[BB^-][H_3O^+]}{[HBB]}$$



Here are the equilibrium expressions – stuff on the right over stuff on the left, omitting water.

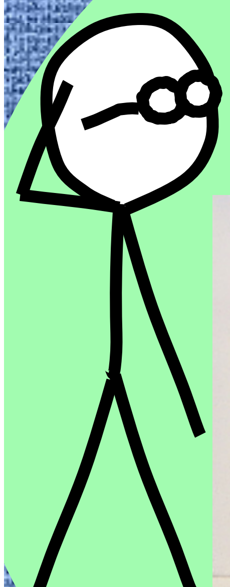
Whatever the value of K_c turns out to be, it is the same for all of these various colored solutions.

Info for Introduction

1. The equilibrium

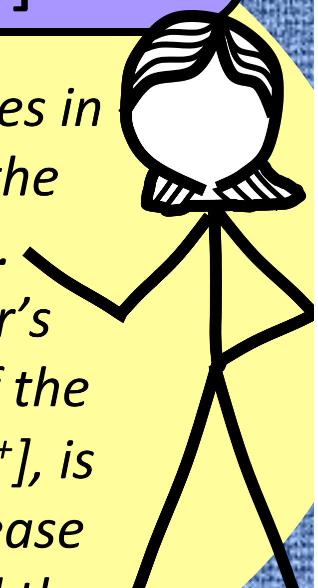
Yellow ⇆ Blue $\qquad K_c = \dfrac{[Blue]}{[Yellow]}$

"HBB" + H_2O ⇆ "BB^-" + H_3O^+ $\qquad K_c = \dfrac{[BB^-][H_3O^+]}{[HBB]}$



So… tell me again how all of these solutions can have the same K_c value...

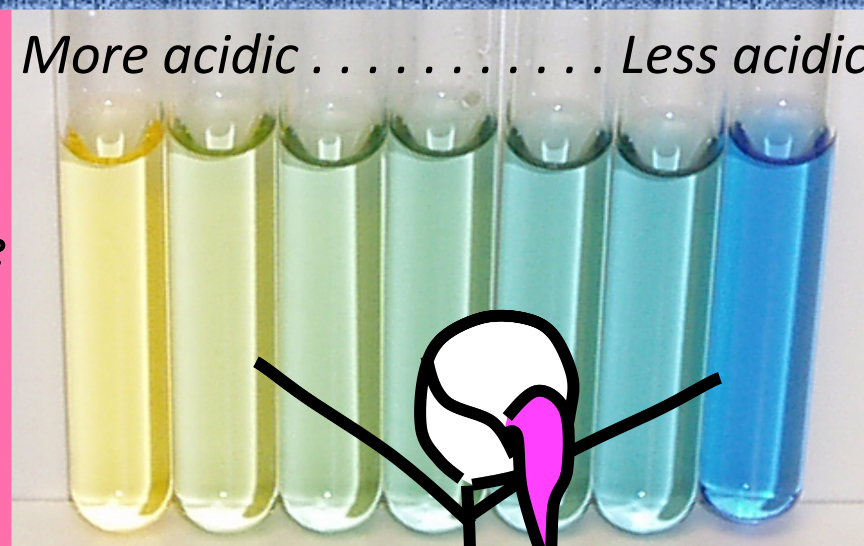
Well, remember only changes in temperature will change the equilibrium constant, K_c. Otherwise, it's LeChâtelier's principle that explains it. If the concentration of acid, $[H_3O^+]$, is increased, $[BB^-]$ must decrease and [HBB] will increase and the solution will appear yellow.

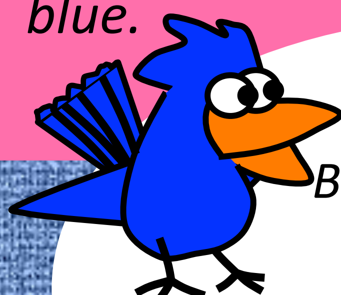


1. The equilibrium

"HBB" + H_2O ⇆ "BB⁻" + H_3O^+ $\quad K_c = \frac{[BB^-][H_3O^+]}{[HBB]}$

*So if the solution is acidic, that means **[H_3O^+]** is a bit larger, and the solution will be yellow because blue **[BB^-]** will be rather small and yellow **[HBB]** will be rather large. But if **[H_3O^+]** is smaller, the solution is less acidic and will be blue.*

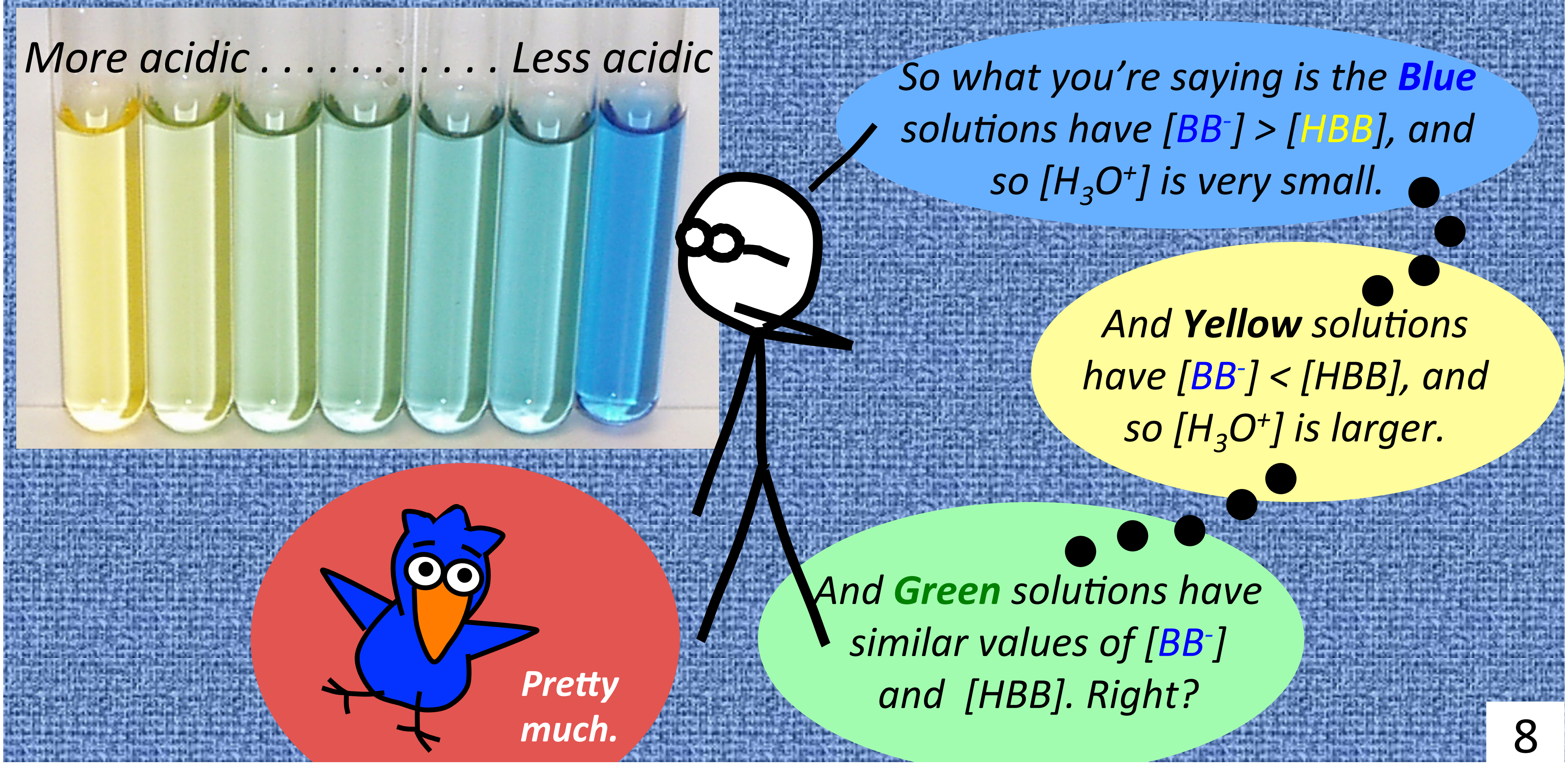




But no matter what, K_c is always the same constant.

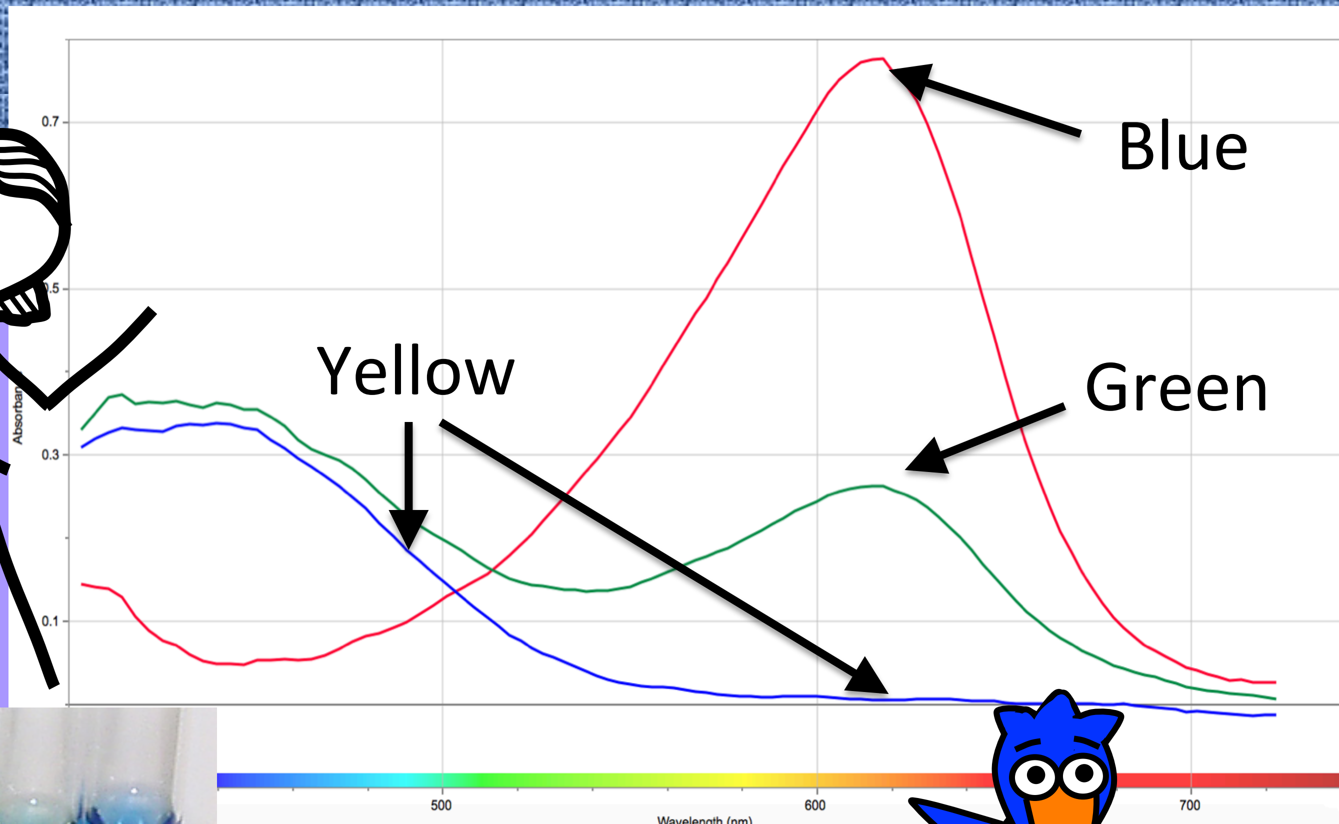
1. The equilibrium

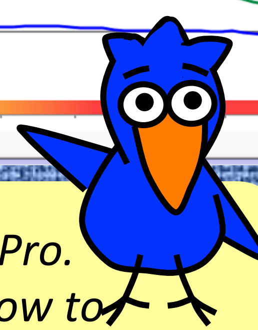
$$\text{"HBB"} + H_2O \rightleftharpoons \text{"BB}^-\text{"} + H_3O^+ \qquad K_c = \frac{[BB^-][H_3O^+]}{[HBB]}$$



1. The equilibrium

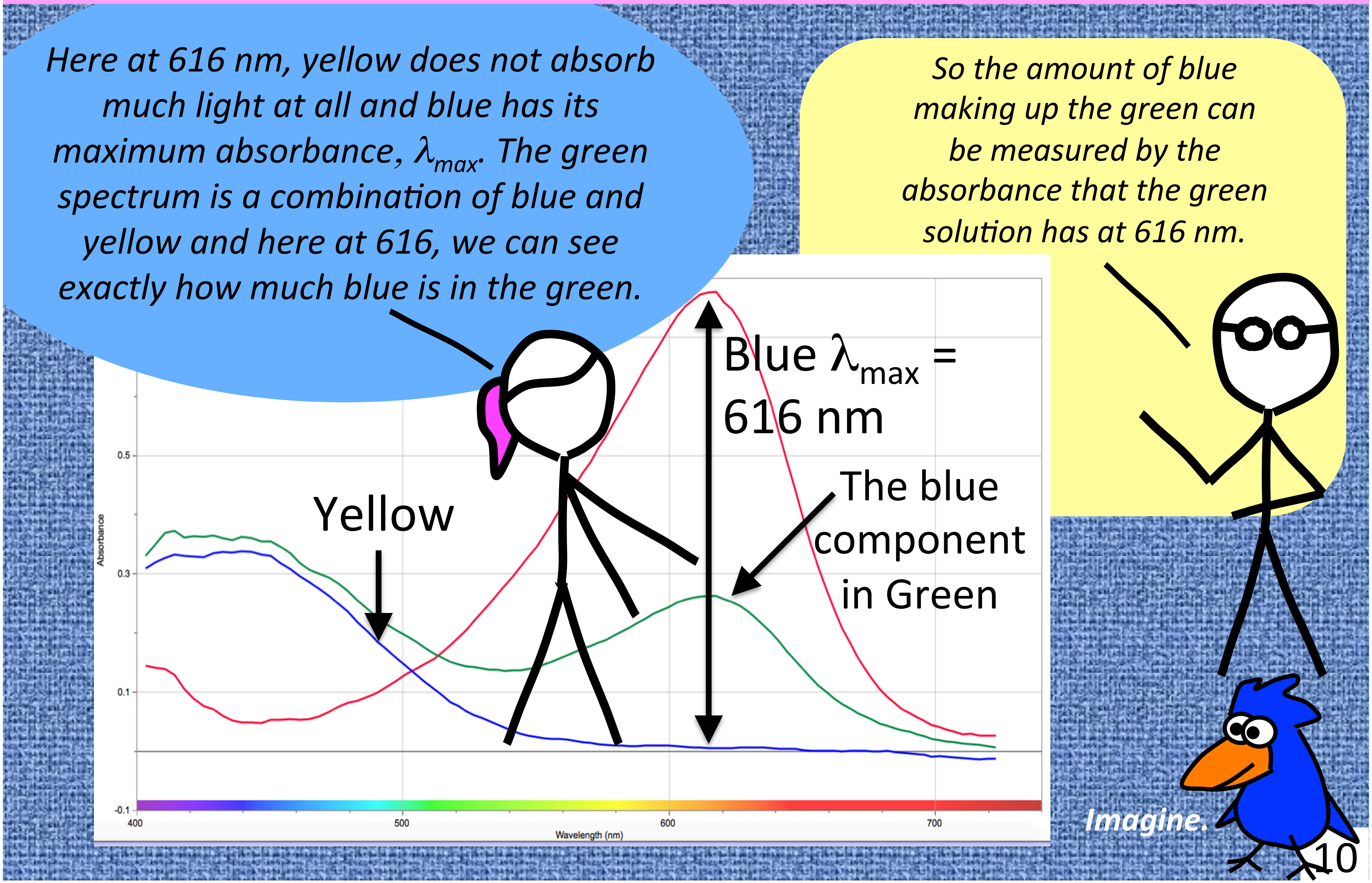
We will create a plot like this as part of our lab report. It is actually three separate spectra plotted on the same graph.



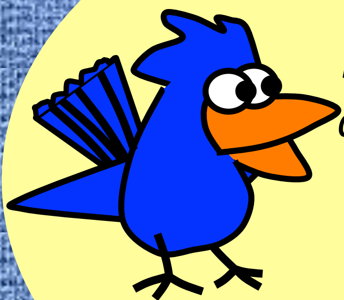


This graph is made in LoggerPro. (Remember how we learned how to display the ROYGBIV ribbon along the bottom in Experiment 2 – Beer's law.)

1. The equilibrium



2. Deriving the equation we will use



This is a crazy important slide – and so is the next one. Both are about the ***Green solution****.*

$$X_{blue} = \frac{n_{blue}}{n_{blue} + n_{yellow}}$$

The mole fraction of Blue ranges from…

0 . . . . to 1

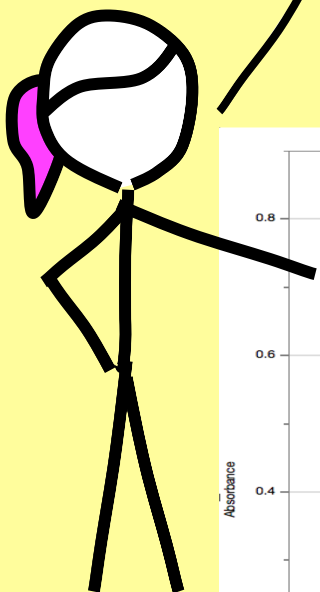
Down at this end, the mole fraction of Blue is small and the Green solution is yellowish green in color.

But down here, the mole fraction of Blue gets closer to 1 and the Green solution is more blue in color.

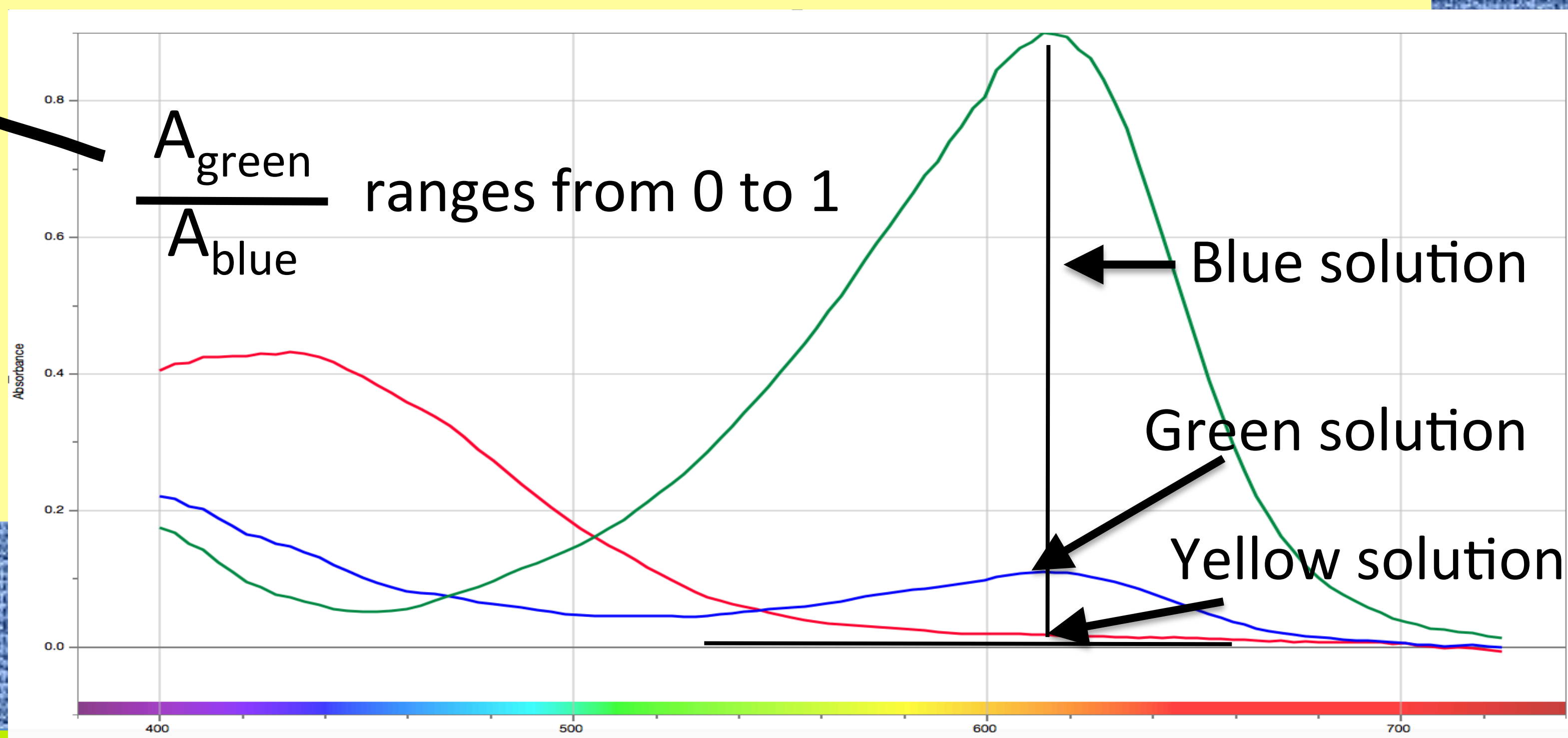
0 0.2 0.4 0.5 0.6 0.8 1.0

X_{blue} (mole fraction of blue)

2. Deriving the equation we will use



So here we notice that the Absorbance of Green at 616 nm divided by the Absorbance of Blue at 616 nm, is exactly the same as the mole fraction of Blue! Both range from 0 to 1.



X_{blue} (mole fraction of blue) is the same as A_{green}/A_{blue}

0 1

0 0.2 0.4 0.5 0.6 0.8 1.0

2. Deriving the equation we will use

"HBB" + H_2O ⇆ "BB^-" + H_3O^+

$$K_c = \frac{[BB^-][H_3O^+]}{[HBB]}$$

HBB — X_{BB^-} — BB^-

0 1

$$\frac{A_{green}}{A_{blue}}$$

Ok, the mole fraction of Blue is the same as the Absorbance of Green divided by the Absorbance of Blue, both at 616 nm.

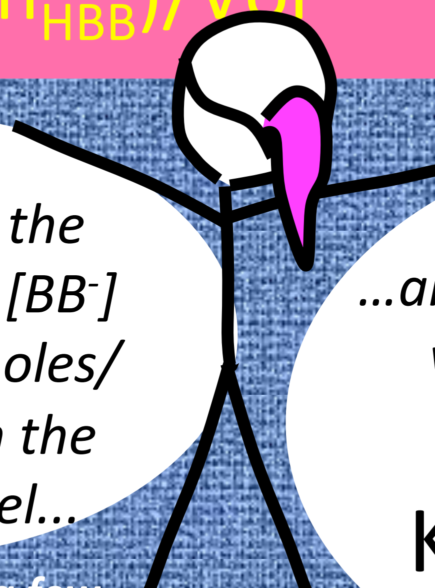
Are we good with this? This is important and will come back on Slide 17.

$$X_{BB^-} = \frac{A_{green}}{A_{blue}}$$

2. Deriving the equation we will use

"HBB" + H_2O ⇆ "BB^-" + H_3O^+ $K_c = \frac{[BB^-][H_3O^+]}{[HBB]}$

$$K_c = \frac{[BB^-][H_3O^+]}{[HBB]} = \frac{(n_{BB^-})/Vol \times [H_3O^+]}{(n_{HBB})/Vol} = \frac{(n_{BB^-}) \times [H_3O^+]}{(n_{HBB})}$$



First we write the concentrations $[BB^-]$ and [HBB] as moles/ volume. Then the volumes cancel...

...and we go on to the next slide with this equation for K_c...

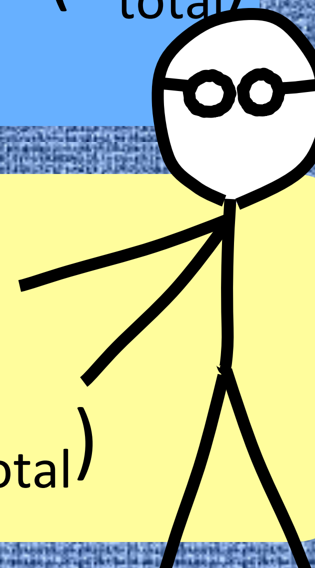
$$K_c = \frac{(n_{BB^-}) \times [H_3O^+]}{(n_{HBB})}$$

2. Deriving the equation we will use

In this blue box, we see the definition for the mole fraction of BB⁻, which is the blue stuff. In the second equation we've rearranged for the moles of BB⁻.

$$X_{BB^-} = n_{BB^-}/n_{total}$$

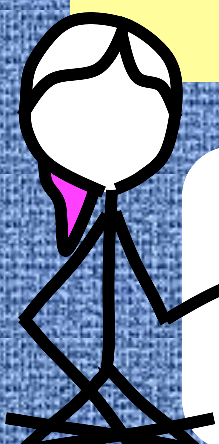
$$n_{BB^-} = (X_{BB^-})x(n_{total})$$



And here we've done the same for the mole fraction of HBB and then the moles of HBB – the yellow stuff.

$$X_{HBB} = n_{HBB}/n_{total}$$

$$n_{HBB} = (X_{HBB}) \times (n_{total})$$



Next we will substitute in for moles into the equation from the previous slide.

$$K_c = \frac{(X_{BB^-}) \times (n_{total}) \times [H_3O^+]}{(X_{HBB}) \times (n_{total})}$$

2. Deriving the equation we will use

And… Poof! Just like that total moles cancel!

$$K_c = \frac{(X_{BB^-}) \times [H_3O^+]}{(X_{HBB})}$$

Remember how mole fractions work? The fractions add up to 1.

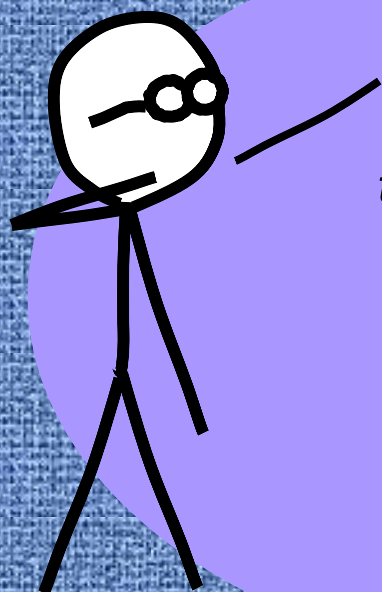
$$X_{BB^-} + X_{HBB} = 1$$

$$X_{HBB} = 1 - X_{BB^-}$$

$$K_c = \frac{(X_{BB^-}) \times [H_3O^+]}{(1 - X_{BB^-})}$$

This lets us sub in for X_{HBB} and reduce the number of variables.

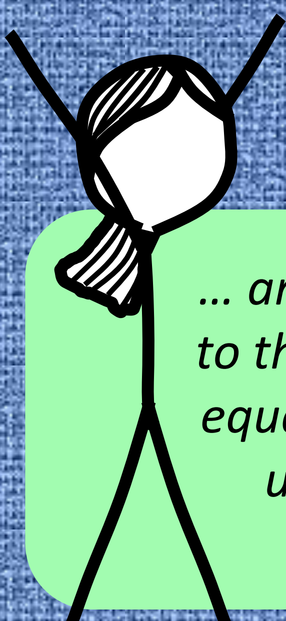
2. Deriving the equation we will use



From Slide 13 we saw this interesting relationship for the mole fraction of the blue stuff – we can use this for one final substitution…

$$X_{BB^-} = \frac{A_{green}}{A_{blue}}$$

Prizes are good.

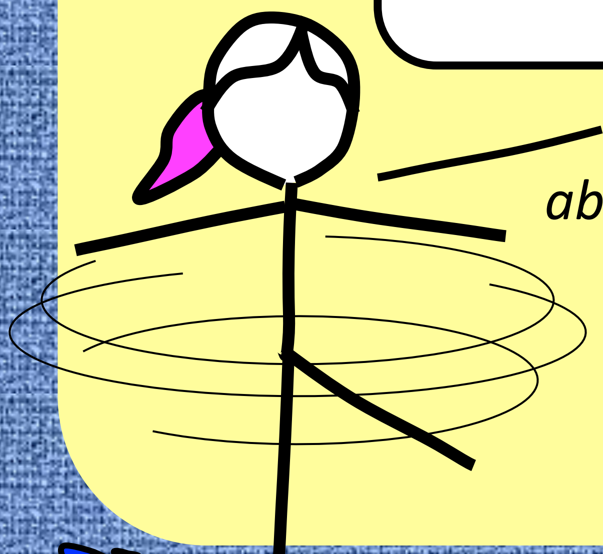


… and that leads to the prize! The equation we will use today!

$$K_c = \frac{(A_{green}/A_{blue}) \times [H_3O^+]}{(1 - A_{green}/A_{blue})}$$

3. The experiment

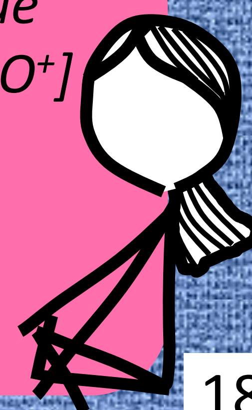
$$K_c = \frac{(A_{green}/A_{blue}) \times [H_3O^+]}{(1 - A_{green}/A_{blue})}$$



All we need is two absorbance values and $[H_3O^+]$ and we will have K_c!

You will be provided with a pH value and from there we can calculate $[H_3O^+]$ with is equation:

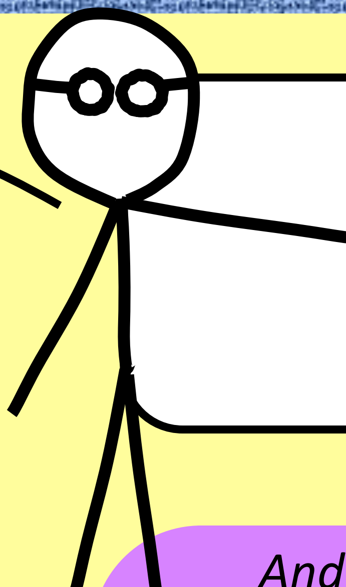
$$[H_3O^+] = 10^{-pH}$$



Our $[H_3O^+]$ will have two only significant figures

3. The experiment

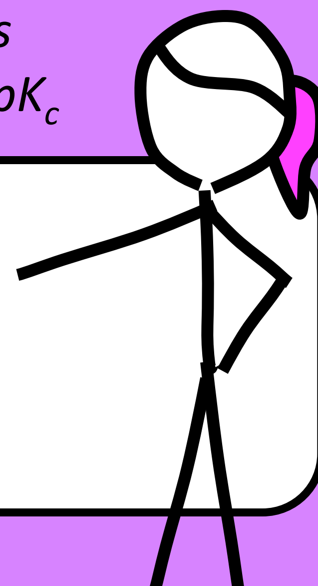
This is how we go from pH to $[H_3O]^+$ and back. We will use this a lot in the coming weeks.



$$[H_3O^+] = 10^{-pH}$$

$$pH = -\log_{10}[H_3O^+]$$

And these analogous equations relate K_c to pK_c

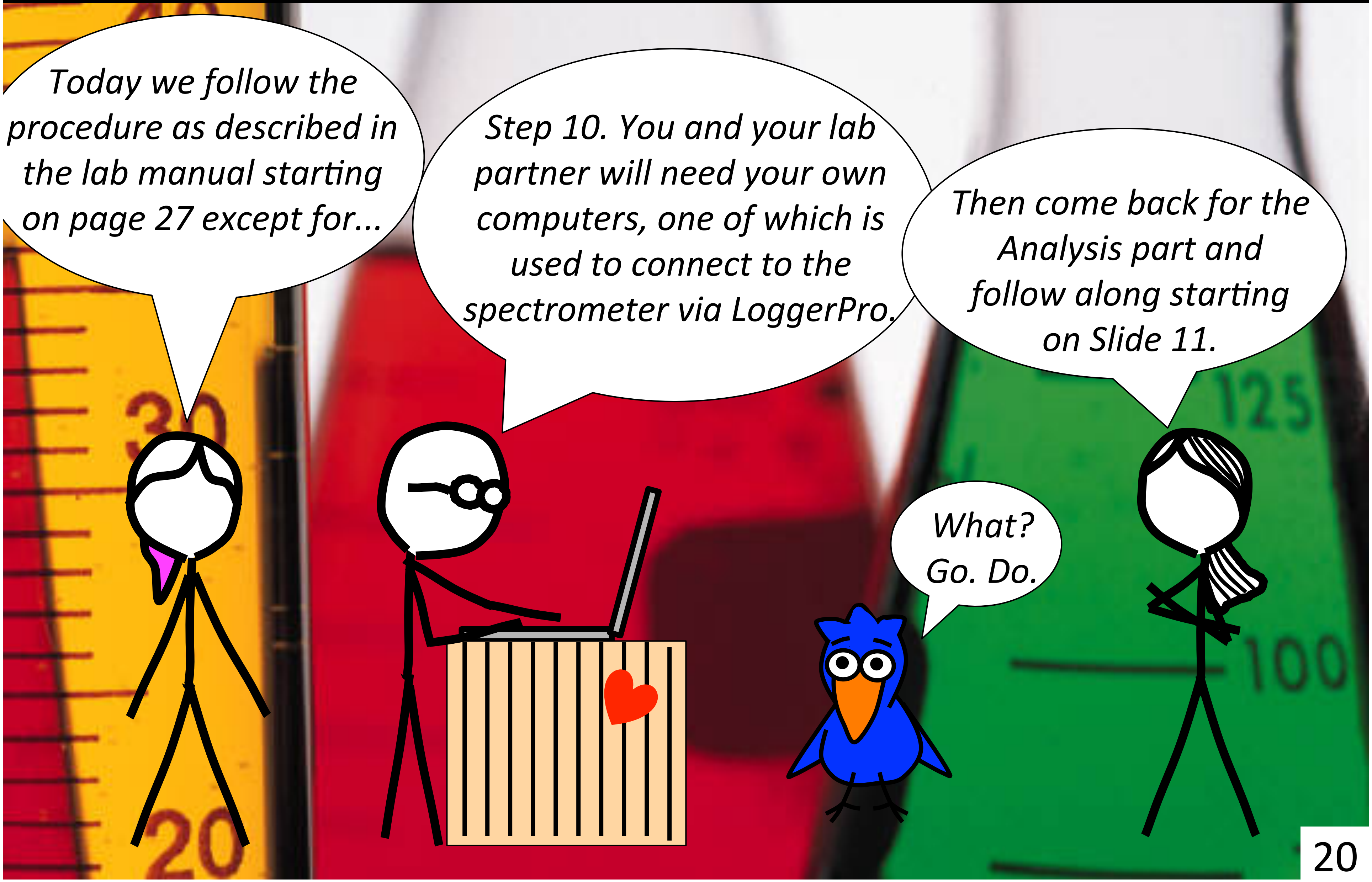


$$K_c = 10^{-pK_c}$$

$$pK_c = -\log_{10}K_c$$

I like fancy equations… and shiny things.

4. Procedure: What we will do today



4. Procedure: What we will do today

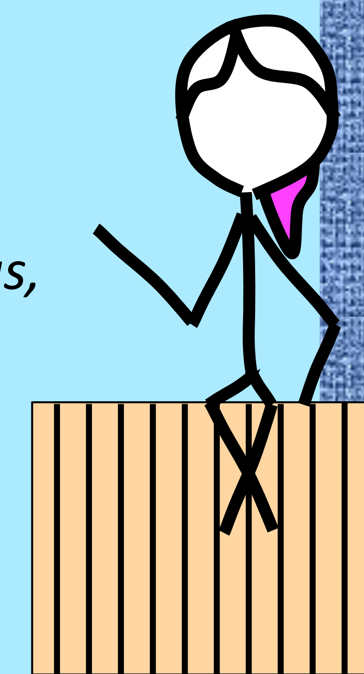
① *Wearing your safety glasses is necessary today. Also, dress for a mess as we are using acid and base.*

② *Take time writing an introduction in your own words before lab. Include Objectives from Slide 2 and equations from Slides 3 – 5. You should also copy the derivation from Part 2 and make sure you understand it.*

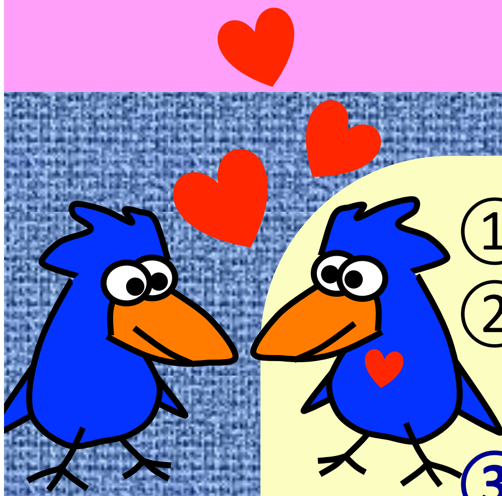
③ *Record observations and details as carefully as possible. Show your calculations with formulas, units, and significant figures!*

④ *Show your work when determining K_c.*

⑤ *Submit on-line data before you leave today.*



5. Your lab report



① First, the cover page with TA initials.

② Next, the trimmed copy pages from your lab notebook.

③ **On-line results** due at the end of class today. Remember the required format for exponentials: **8.00E-6** (and no spaces). Late submissions are not graded – see the syllabus.

④ **Attachments:** Your spectra of Blue, Green, and Yellow (preferably all on one page). Staple entire report together.

⑤ Turn in lab report ***before*** the start of class tomorrow. Late labs may not be graded – see the syllabus.

Stick people inspired by xkcd cartoons by Randall Munroe (www.xkcd.com)