

We now have a weak base problem. To calculate the pH of this solution, we will need to calculate the molar concentration of the base and get the K_b for the base.

To calculate the molar concentration of the base, we take the moles of the base (which we calculated previously) and divide it by the total volume in liters (or mmoles by mL).

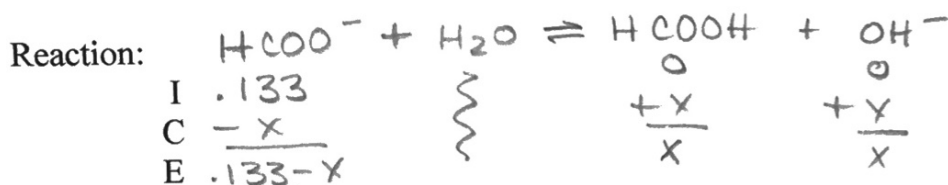
What is the total volume? 75.00 mL

$$\text{Calculate } [\text{HCOO}^-] = \frac{10.0 \text{ mmol}}{75.00 \text{ mL}} = .133 \text{ M HCOO}^-$$

How do we calculate the value for K_b ?

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

Now use the reaction of the formate ion in water and do an equilibrium problem for the weak base.



Calculation for pH:

$$K_b = \frac{x^2}{.133-x}$$

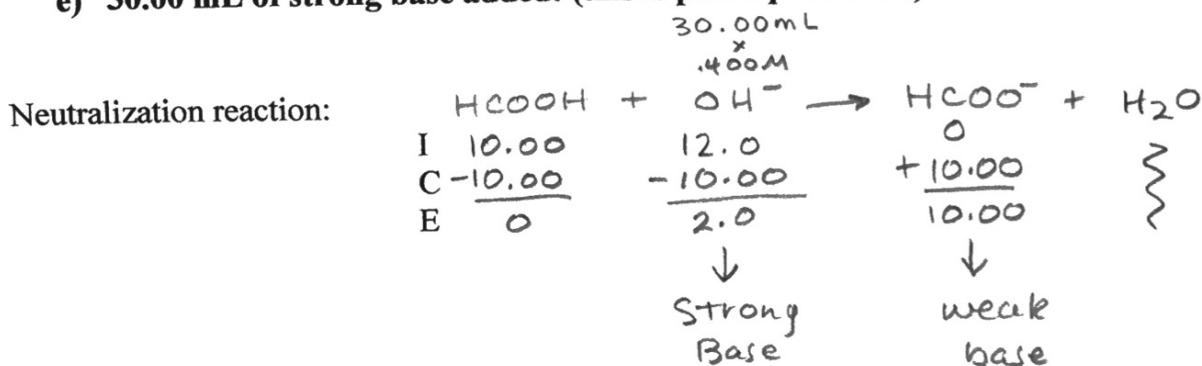
$$5.56 \times 10^{-11} = \frac{x^2}{.133-x}$$

$$x = 2.72 \times 10^{-6} \text{ M OH}^-$$

$\text{pOH} = 5.57$
 $\text{pH} = 8.43$
 basic

Notice that the pH at the equivalence point in the titration of a weak and with a strong base is basic. This is to be expected because at the equivalence point of a titration between a weak acid and strong base the only species left in solution will be a weak base. The same idea applies for a strong acid-weak base titration. In this case the only species left at equivalence will be a weak acid and the pH will be acidic. The only case where the pH at equivalence will be neutral is that involving a strong acid-strong base, because at equivalence we only have water.

e) 30.00 mL of strong base added: (this is post equivalence)

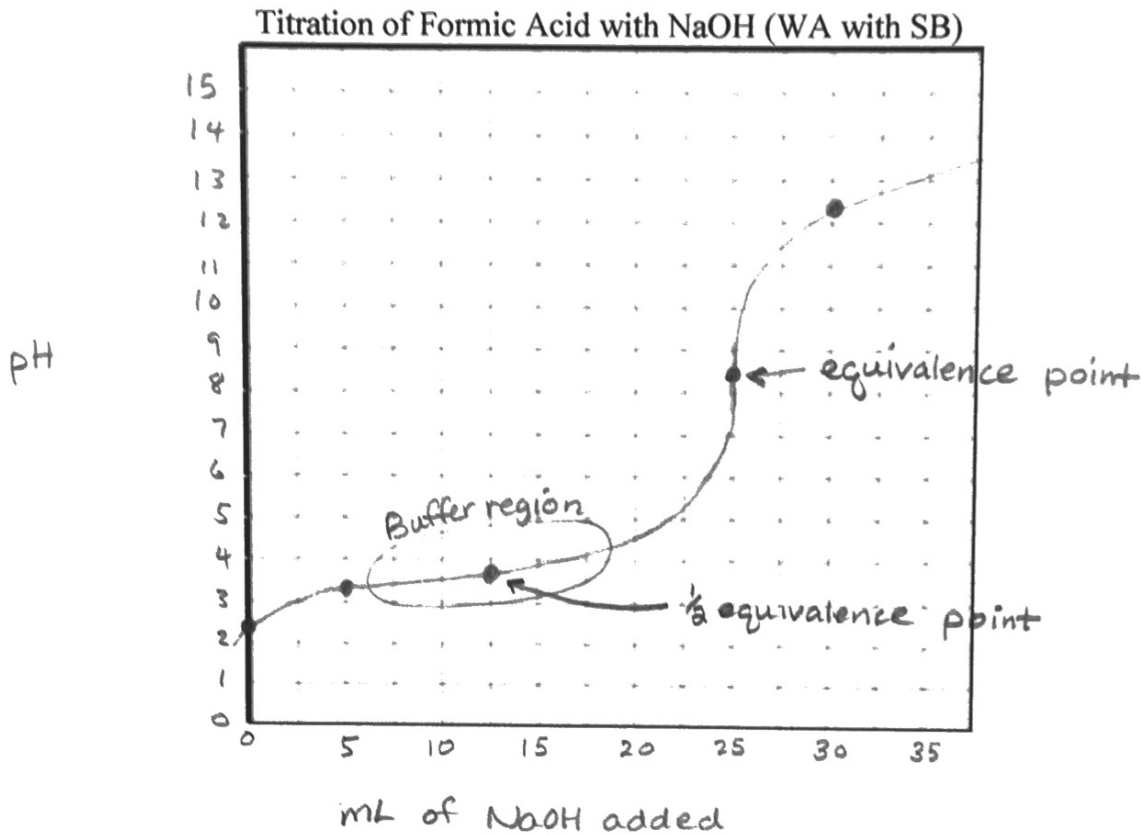


NOTE: we have passed the equivalence point! We now have strong base in excess and the excess strong base dictates the pH. So all we need do is calculate the molar concentration of the excess hydroxide ion and calculate the pH.

$$\text{Excess } [\text{OH}^-] = \frac{2.0 \text{ mmol}}{80.0 \text{ mL}} = .025 \text{ M OH}^-$$

$$\begin{aligned} \text{pOH} &= -\log .025 \\ &= 1.60 \\ \text{pH} &= 12.40 \end{aligned}$$

Use the graph below and the five titration points from above (a - e) to sketch a titration curve. Label both axes, the equivalence point and the half equivalence point. Use the pH values and volumes from your problems. Draw a circle around the buffer region of the graph.



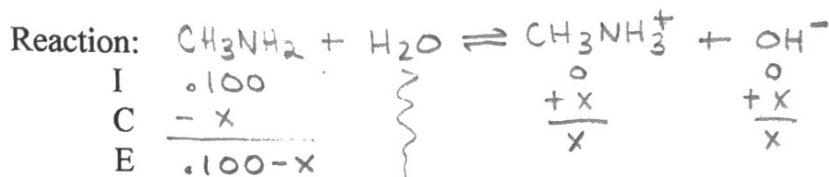
You should also be aware that the slope of the line near equivalence is less vertical compared to a strong acid-strong base titration and the pH at equivalence is basic.

Now let's try a **weak base strong acid titration problem**. These kinds of titrations are handled using the same strategies as those involving weak acids and strong bases. There is a buffer region, equivalence point, and post-equivalence.

Calculate the pH at each of the following points in the titration of 50.00 mL of a 0.100 M methyl amine (CH_3NH_2) solution with 0.100 M HCl solution (K_b for $\text{CH}_3\text{NH}_2 = 4.38 \times 10^{-4}$).

a) **Initially: (before any acid is added, this is just a weak base problem)**

Ionization of methyl amine in water:



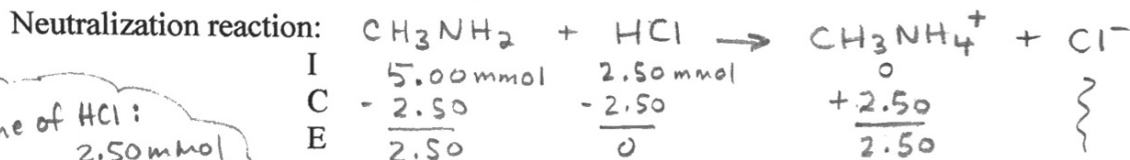
Calculation for pH: $4.38 \times 10^{-4} = \frac{x^2}{.100-x}$

$x = .00640 \text{ M OH}^-$

$\text{pOH} = 2.194 \quad \text{pH} = 11.806$

b) **Midpoint (half-equivalence point):**

How many mmoles of acid will need to be added? Refer to previous titration example for help.



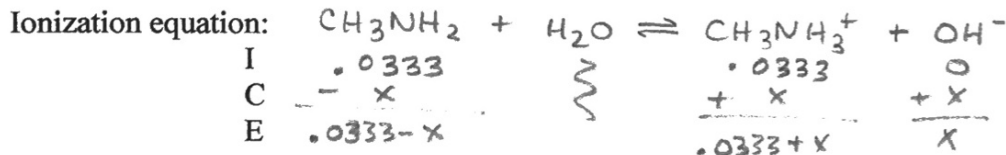
Volume of HCl:
 $.100 \text{ M} = \frac{2.50 \text{ mmol}}{x \text{ mL}}$
 $x = 25.0 \text{ mL}$

$\frac{25.0 \text{ mL}}{50.0 \text{ mL}} + \frac{50.0 \text{ mL}}{75.0 \text{ mL}}$

Let's now calculate the new molar concentrations of both by dividing the moles by the total volume in liters (or mmoles by mL).

$[\text{CH}_3\text{NH}_2] = \frac{2.50 \text{ mL}}{75.0 \text{ mL}} = .0333 \text{ M} \quad [\text{CH}_3\text{NH}_3^+] = \frac{2.50 \text{ mL}}{75.0 \text{ mL}} = .0333 \text{ M}$

Now let's go back to the original equation for the ionization of methyl amine and put in the new concentrations of base and conjugate acid:



Use K_b to calculate new $[\text{H}_3\text{O}^+]$ and pH:

$4.38 \times 10^{-4} = \frac{(.0333+x)(x)}{.0333-x}$

$x = 4.27 \times 10^{-4} \text{ M OH}^-$

$\text{pOH} = 3.370$

$\text{pH} = 10.630$

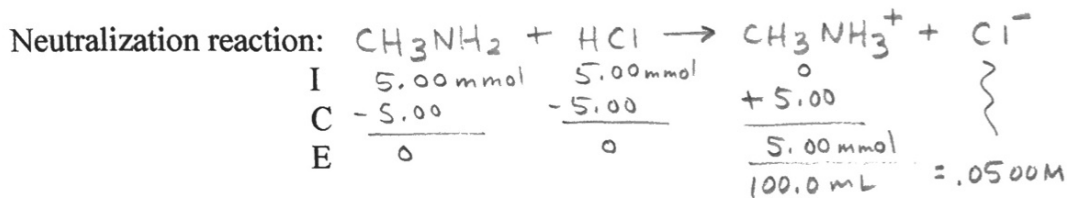
Was there an easier way to determine the pH? That's right! H-H equation! Do that here:

$$pH = pK_a + \log \frac{B}{A}$$

$$pH = -\log \frac{1 \times 10^{-14}}{4.38 \times 10^{-4}} + \log \frac{2.50}{2.50}$$

$$pH = 10.641$$

c) Equivalence point:

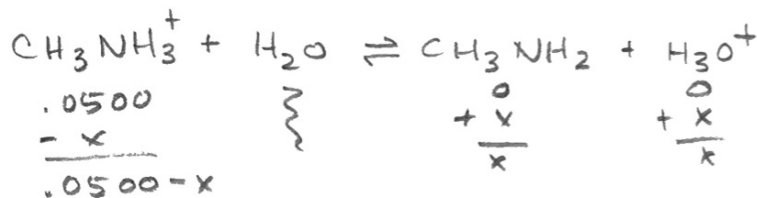


Volume of acid used
 $.100M = \frac{5.00 \text{ mmol}}{x \text{ mL}}$
 $x = 50.0 \text{ mL}$

What species remains? Does it accept or donate a proton. To calculate the pH at the equivalence point you will need to find the molar concentration of this species, calculate the corresponding K value and do an ICE problem calculation. Do that here:

$CH_3NH_3^+$ remains \rightarrow equilibrium reaction

↓
SCA
(proton donor)

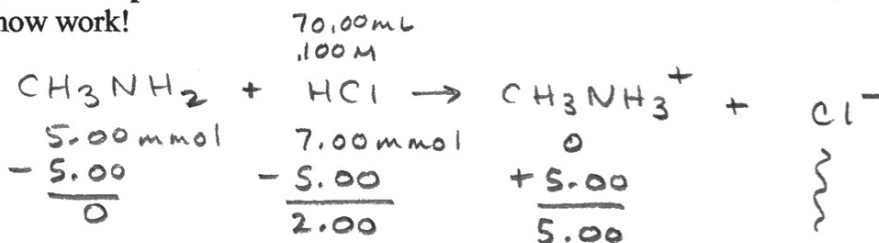


$$\frac{1 \times 10^{-14}}{4.38 \times 10^{-4}} = \frac{x^2}{.0500 - x}$$

$$x = 1.07 \times 10^{-6} \text{ M } H_3O^+$$

$$pH = 5.971$$

d) Calculate the pH after the addition of 70.00 mL of the 0.100 M HCl. Use any method you like! Show work!



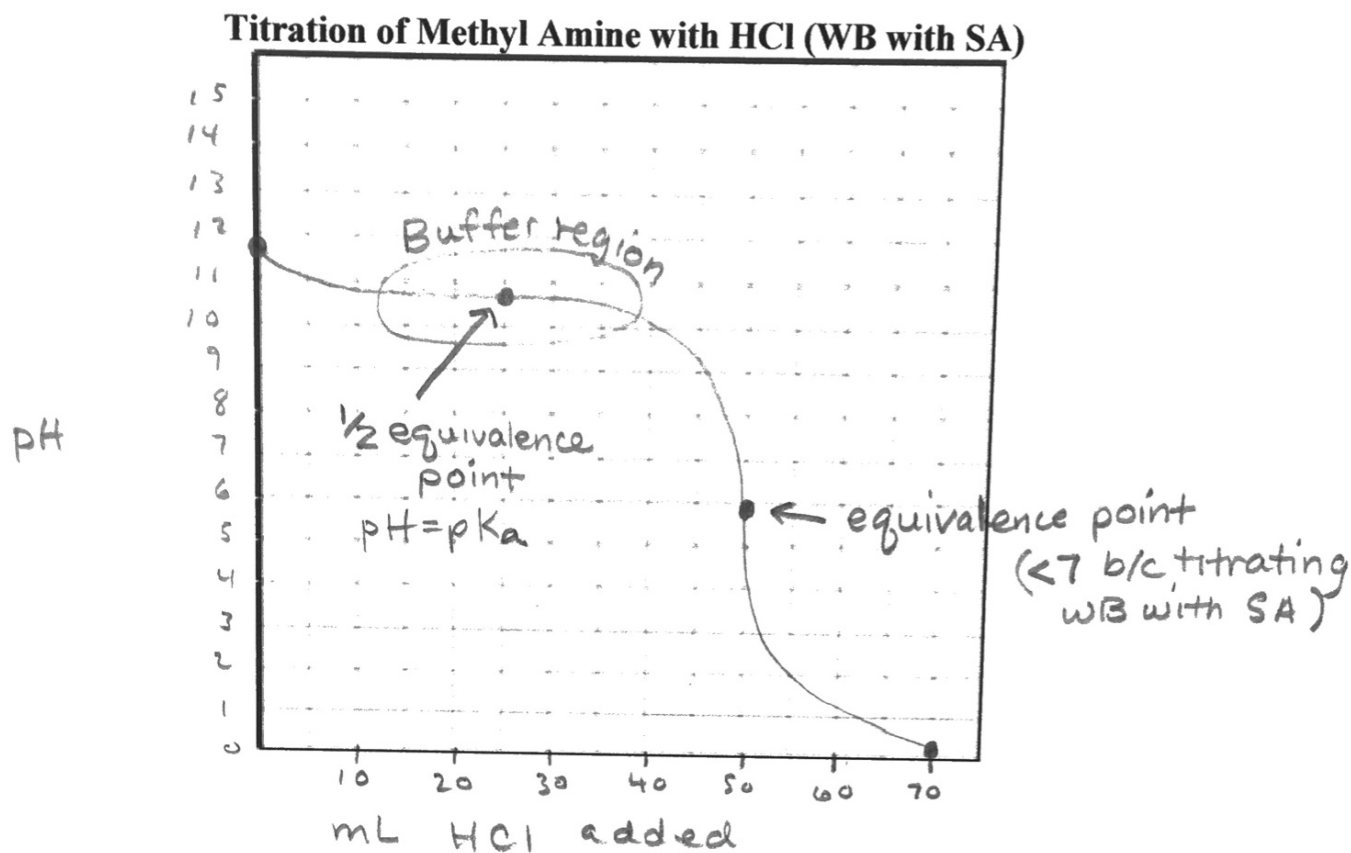
↓
SA
↓
determines
pH

$$pH = -\log[HCl]$$

$$= -\log \frac{2.00 \text{ mmol}}{20.00 \text{ mL}}$$

$$= .234$$

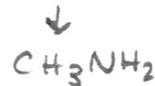
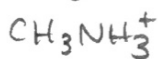
Use the graph below and the three titration points from above (a - d) to sketch a titration curve. Label both axes, the equivalence point and the half equivalence point. Use the pH values and volumes from your problems. Draw a circle around the buffer region of the graph.



Explain how the graph above could be used by itself, to determine the identity of the weak base.

At the $\frac{1}{2}$ equivalence point, the pH is equal to the pK_a of the conjugate to the weak base.

$$pK_b = \frac{K_w}{pK_a}$$



Acid-Base Indicators

The purpose of an indicator is to allow you to know when you have reached the equivalence point in a titration. Acid-base indicators are normally organic acids. Thus, when you add an indicator to a solution and perform a titration, you are titrating the indicator along with your substance of interest. This requires some small extra amount of titrant – negligible!

The volume of titrant at which you visually detect the equivalence point is called the endpoint. The volume at the equivalence point is never exactly equal to the endpoint, but it is usually quite close.

There are two criteria that are used to choose an indicator for a given titration:

- the pK_a of the indicator should be within ± 1 unit of the pH of the solution at the equivalence point.
- the color change at the endpoint should be clearly distinguishable.

Problem: Given three acid-base indicators:

methyl orange - endpoint at pH 4 (this means it changes color at pH 4)

bromthymol blue - endpoint at pH 7

phenolphthalein - endpoint at pH 9

Select the best indicator for each of the following titrations:

a) sulfuric acid with potassium hydroxide

↓
SA

↓
SB

pH = 7 at eq pt
Bromthymol blue

b) ammonia and hydrobromic acid

↓
WB

↓
SA

pH < 7 at eq pt
methyl orange

c) sodium nitrite with hydroiodic acid

salt → NaNO₂

↓
SA

pH > 7 at eq pt
phenolphthalein

SCB → NO₂⁻ → WB

You can calculate the pH at which an indicator will change color, by treating the indicator like a buffer. Humans can detect a change in color when approximately 1/10 of the indicator has converted to the other form. Using H-H equation, $\text{pH} = \text{pK}_a + \log 1/10$. Since $\log 1/10 = -1$, the color change will occur when the **pH = pKa - 1**. Remember the indicator is a weak acid with a corresponding K_a.



Problem: Bromthymol blue is an indicator with a K_a of 5.84×10^{-5} . What percentage of this indicator is in its basic form at a pH of 4.84?

$$\text{pH} = \text{pK}_a + \log \frac{\text{B}}{\text{A}}$$

$$4.84 = 4.23 + \log \frac{\text{B}}{\text{A}}$$

$$.61 = \log \frac{\text{B}}{\text{A}}$$

$$4.07 = \frac{x}{1-x}$$

$$4.07 - 4.07x = x$$

$$4.07 = 5.07x$$

$$x = .802 \Rightarrow 80.2\% \text{ In}^-$$

$$19.8\% \text{ HIn}$$