SCH 4U – GRADE 12 CHEMISTRY, UNIVERSITY PREPARATION

EQUILIBRIUM UNIT – Choice of Indicators for Acid-Base Titrations

Acid base indicators are themselves weak acids (or weak bases) with the general formula HIn

In solution they undergo a dissociation   HIn (colour A) + $H_2O \leftrightarrow H_3O^+$ + In^- (colour B)

As the titration proceeds, the pH and $[H_3O^+]$ changes which affects the extent of the dissociation of the indicator molecules according to le Chatelier's Principle. In low pH (high $[H_3O^+]$, the reaction does not proceed forward to any great extent and the colour A of the undissociated molecule predominates. At higher pH, the reaction does proceed forward and the colour B of the In^- is visible.

The goal of the titration is to identify the exact moment when the same number of moles of H_3O^+ and OH^- have reacted and the result is water and a salt (the equivalence point).

Ka for the indicator is given by $k_a = \frac{[H_3O^+][In^{-1}]}{[HIn]}$ let [HIn] = $[In^-]$ $Ka = \frac{[H_3O^+][In^{-1}]}{[HIn]}$ $pH = pKa$

If   [HIn] = $[In^-]$ the indicator colour will be a blend of the two colours and any slight change in pH will cause one or other of the colours to predominate. The ideal indicator is the one that has a pKa equal to the pH of the solution at the equivalence point so the change in colour occurs at the equivalence point and the titration can be stopped. Not all salt solutions formed as a result of a titration are neutral, pH=7, so it is essential to choose the proper indicator for individual cases.

Textbooks typically show examples that allow students to calculate the pH at the equivalence point (using the Kb of the conjugate base or Ka of the conjugate acid contained in the salt) as well just before and just after the equivalence point so a titration curve can be plotted. (See Nelson Chemistry 12 p.596-607)

The relationship between the pH changes, location of the equivalence point, and colour of indicator can be demonstrated using a couple of on-line titration simulations.

The first is http://chem-ilp.net/labTechniques/AcidBaseIdicatorSimulation.htm . This shows hypothetical strong/weak - acid/base combinations and allows the choice of indicator (none, phenolphthalein, bromothymol blue, or methyl orange). As the titration proceeds, the colour of the indicator in the flask can be observed and the titration curve is plotted. Students should be asked to watch the indicator in the flask and note whether or not the change occurs at the equivalence point. After several different titrations, it should become obvious that not all indicators are suitable in all cases.

The second is http://faculty.concordia.ca/bird/java/Titration/Titration_demo.html This simulation has several weak bases to be titrated against HCl and several weak acids to be titrated against NaOH. There are several indicators with different pH ranges available. The burette can be filled with either acid or base, concentrations of acid and base can be altered, and the titration can be stopped and restarted at any time. The titration curve is plotted continuously and the colour of the indicator is visible in the flask as well as above the curve. In addition, the drop rate can be adjusted as the titration proceeds to make it easier to stop exactly at the correct time. If this is used as part of an interactive whiteboard lesson or projected on the screen using an LCD/laptop computer combination, students could be asked to choose an appropriate indicator for a given acid-base combination and then carry out the simulated titration, stopping at the endpoint indicated by the indicator. They could see how close they come to the actual equivalence point and if necessary repeat the same titration with a different indicator.

Use of on-line titration simulations with interactive white board or LCD projector

Open web site http://chem-ilp.net/labTechniques/AcidBaseIdicatorSimulation.htm Select strong acid-strong base titration with no indicator

Discuss with students likely pH changes as a titration of strong base with strong acid proceeds.

- What is approximate pH of a strong acid before it is titrated? (low 1-2)
- What will happen as base is added? (pH will increase)
- What will pH be when the titration is finished – at endpoint or equivalence point? (pH = 7)
- What would happen to pH if the endpoint was missed and more base was added? (continue to increase)

Start the simulation and watch the changes in pH as the base is added. It should match the predictions. Have students note the very dramatic change in pH close to the equivalence point.

Discuss purpose of indicator in titration (change colour to signal end of titration). Have students choose an indicator.

Reset, and select the indicator. Start the simulation.
Have students monitor colour of indicator, especially at equivalence point. Ask if the colour change would allow them to stop the titration at the appropriate time.
Reset and repeat the titration with the other indicators. Are they equally suitable for use in this type of titration? (yes, many indicators are suitable for strong acid-strong base titrations)

Illustrate the suitability by reversing to strong base-strong acid combination and repeating the simulations.

Discuss likely pH changes for weak acid-strong base titration.

- What is approximate pH of weak acid at beginning (slightly higher 3-5)
- What will happen as base is added? (pH will increase)
- What will pH be when the titration is finished – at endpoint or equivalence point? (students may say pH = 7 or they may recognize hydrolysis of salt will produce higher pH)
- What would happen to pH if the endpoint was missed and more base was added? (continue to increase)

If students predict pH=7 at equivalence point, start simulation of weak acid-stong base with no indicator and have students watch for pH at equivalence point. (somewhat higher than 7)

Discuss reason for higher pH – hydrolysis of salt, anion reacts with water to form weak acid and release OH^{1-} ion

Ask students to choose an appropriate indicator, based on observations of earlier behaviour (probably phenolphthalein or bromothymol blue)

Reset and start titration with chosen indicator. Evaluate appropriateness of choice – did the colour change correctly signal the equivalence point?
Reset and start titration with other indicators. Have students identify why methyl orange is an inappropriate choice.

Repeat simulations with other acid/base combinations and justify choice of indicators.

Include weak acid-weak base combination and note why titrations are **not** typically done with this choice (nearly impossible to select indicator due to lack of rapid pH change)

Open web site http://faculty.concordia.ca/bird/java/Titration/Titration_demo.html

Click on the *start* button to open the simulation window. Click and drag it to one side of the screen so the instructions are visible.

Use hydrochloric acid in the buret and sodium hydroxide solution in the flask. The simulation is set up to use 25 mL in the flask. Set the concentrations for some value between 0.15 and 0.25 for the acid in the buret and between 0.05 and 0.15 for the base in the flask. (Note: you **must** push enter after selecting a concentration for each or the simulation will continue to use the default values)

Select a suitable indicator, bromothymol blue for example.

Have one student volunteer to monitor the simulation. All other students should calculate the volume of acid needed to completely neutralize the base.

The volunteer student should ensure that the buret volume reads 0.00. Set the drop rate moderately high and begin the simulation. As the student monitors the colour in the flask and the pH changes, the drop rate should be slowed. The student should click on the buret valve to stop the titration when the indicator changes colour.

Compare the volume of acid used by the student volunteer to the volume calculated by the class.

Discuss the titration of a weak acid (acetic acid, Ka = 1.8 x 10^{-5}) with a strong acid (NaOH). Assume 0.10 M concentrations for both acid and base so equal volumes would be needed to complete the titration. Since the concentrations are equal, the final concentration of the salt solution will be half the initial concentration of the acid. Calculate the pH at the equivalence point of the titration.

$$\mathrm{CH_3COO^-} + \mathrm{H_2O} \leftrightarrow \mathrm{CH_3COOH} + \mathrm{OH^-}$$

$$\mathrm{k}_b = \frac{k_w}{k_a} = \frac{1\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

$$\mathrm{k}_b = \frac{[\mathrm{CH_3COOH}][\mathrm{OH^-}]}{[\mathrm{CH_3COO^-}]} = \frac{x^2}{0.05} = 5.56\times10^{-10}$$

$$[\mathrm{OH^-}] = x = \sqrt{(5.56\times10^{-10})(.05)} = 5.27\times10^{-6}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = 5.28 \qquad \mathrm{pH} = 14 - \mathrm{pOH} = 8.72$$

Choose an indicator based on the predicted pH (phenolphthalein)

Set up the simulation with acetic acid in the flask and NaOH solution in the buret. Set the concentrations to some convenient value. Have students complete the calculation to determine the stoichiometric equivalence point.

Have a student conduct the simulation and stop the titration when the indicator changes colour. Compare the simulated volume with the calculated volume. Discuss the suitability of the indicator choice.

Repeat the exercise using a weak base (ethylamine Kb = 4.3×10^{-4}, pH = 5.97 at equivalence) Bromothymol blue would be a good indicator. Some students may wish to try erichrome black T – try the simulation and note that there is more than one colour change and students must pick the proper one to reach the correct endpoint.

Repeat as needed with other acid-base combinations, concentrations, and indicators.