8.4 Acid-Base Titration

- In an acid-base titration, the concentration of an acid or base solution of unknown concentration is determined by the delivery (from a buret) of a measured volume of a solution of known concentration (the titrant). If the sample in the flask is an acid, the titrant used is a base, and vice versa.
- Titration: the precise addition of a solution in a buret into a measured volume of a sample solution.
- Titrant: the solution in a buret during the titration.
- Sample: the solution being analyzed in a titration.
- Accuracy is essential. The titrant needs to be standardized. Primary standards are used to measure a titrant's concentration. Sodium carbonate ($Na_2CO_{3(s)}$) is a base used to standardize acids. Potassium hydrogen phthalate ($KHC_7H_4O_{4(s)}$) is an acid used to standardize bases.
- Primary Standard: a chemical available in a pure and stable form, for which an accurate concentration can be prepared; the solution is then used to determine precisely, by means of titrating, the concentration of the titrant.
- Equivalence point: in a titration, the measured quantity of titrant recorded at the point at which chemically equivalent amounts have reacted.
- Endpoint: the point in a titration at which a sharp change in a measurable and characteristic property occurs; e.g. a colour change in an acid-base indicator.
- How to perform a basic titration where the titrant is a dilute strong base and the sample is a dilute strong base.
  - Create your stock titrant solution following good lab practices to minimize errors.
  - Rinse the buret with the stock solution and allow it to flow through the wide-open nozzle to knock out any air bubbles.
  - Fill the buret, keeping in mind that you can waste a great deal of time trying to get it to zero, therefore don't. Just fill to near the top and record your starting volume.
  - Standardize your titrant by accurately measuring and creating a primary standard solution of known concentration.
  - Add an indicator that will change colour at the equivalence point. The endpoint of the indicator should be close the equivalence point.

o Carefully add the titrant to the primary standard until you reach the endpoint. Record the volume. Repeat until results are consistent (±0.2 mL).
o Calculate the amount of titrant delivered.
o Calculate the concentration of the titrant.
o Perform the titration on the unknown and repeat until results are consistent.
o Calculate the concentration of the unknown.

Titrating a Strong Acid with a Strong Base
- Consider the neutralization of HCl with NaOH:
  o $HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)}$ molecular equation
  o $H_3O^+ + OH^- \rightarrow 2H_2O_{(l)}$ net ionic equation
  o $H^+_{(aq)} + OH^- \rightarrow H_2O_{(l)}$ abbreviated net ionic eq.
- E.g. In a titration, 20.00 mL of 0.300 mol/L $HCl_{(aq)}$ is titrated with standardized 0.300 mol/L $NaOH_{(aq)}$. What is the amount of unreacted $HCl_{(aq)}$ and the pH of the solution after the following volumes of $NaOH_{(aq)}$ have been added?
  (a) 0 mL
  (b) 10.0 mL
  (c) 20.0 mL

Strong acid and strong base, therefore, the ions of interest are H^+, OH^-, and H_2O. We can use the abbreviated net ionic equation to represent the reaction. $H^+_{(aq)} + OH^- \rightarrow H_2O_{(l)}$

(a) No NaOH has been added therefore we are only concerned with HCl. Since it is a strong acid it will completely ionize and we know we will have 0.300 mol/L of H^+ and 0.300 mol/L of Cl^-

$[H^+] = 0.300$ mol/L
$pH = -\log[H^+] = -\log[0.300] = 0.5$

$n = v \times C = 0.020$ ml $\times 0.300$ mol/L $= 0.006$ mol

Before we add any titrant the pH is 0.5 and we have 0.006 moles of HCl (but since it completely disassociates we have 0.006 mol of H^+ and 0.006 mol of Cl^-).

(b)   By adding 10 mL of 0.300 mol/L $NaOH_{(aq)}$ to 20.00 mL of 0.300 mol/L $HCl_{(aq)}$ we can deduce that the reaction has reached the halfway point. We need to figure out how much of the acid was neutralized.

NaOH
n = v × C = 0.010 ml × 0.300 mol/L = 0.003 mol
Therefore we have 0.003 mol of NaOH but since it completely disassociates we have 0.003 mol of Na^+ and 0.003 mol of OH^-. Using the equation, $H^+_{(aq)} + OH^- \rightarrow H_2O_{(l)}$, we know we started with 0.006 mol of H^+ and we added 0.003 mol of OH^-. Therefore the H^+ will combine with OH^- using up all the OH^- and leaving behind 0.003 mol of H^+.

We must also take into consideration the new volume: 20 mL + 10 mL = 30 mL

$[H^+]$ = 0.003 mol/0.03L = 0.100 mol/L
pH = – log $[H^+]$ = – log [0.100] = 1.0

We have 0.003 mol of H^+ after adding 10 mL of NaOH and it will have a pH of 1.0.

(c) By adding 20 mL of 0.300 mol/L $NaOH_{(aq)}$ to 20 mL of 0.300 mol/L $HCl_{(aq)}$ we can deduce that the reaction has reached the endpoint. All the OH^- and H^+ will have combined to form water and since Na^+ and Cl^- do not have an influence on pH we can determine that $[H^+] = 1.0$ x 10^{-7} (from the auto-ionization of water) and pH = 7.

- Look at Figure 2 on page 599 to see the titration curve for this question.
- The midpoint will have a rapid change in pH.

Titrating a Weak Acid with a Strong Base

- These are the most challenging type of questions. Since we are also working with a weak acid we have to determine how equilibrium will exert itself after the base is added.
- E.g. In a titration of 20.00 mL of 0.300 mol/L $HC_2H_3O_{2(aq)}$ (acetic acid) with standardized 0.300 mol/L $NaOH_{(aq)}$, what is the amount of unreacted $HC_2H_3O_{2(aq)}$ and the pH of the solution:
  (a) before titration begins
  (b) after 10.00 mL of NaOH is added
  (c) after 20 mL of NaOH is added.

We need to remember that this is a weak acid and will not disassociate easily and equilibrium will re-exert itself.

(a) Before the titration only $HC_2H_3O_{2(aq)}$ has to be considered which makes it a simple equilibrium problem.

	$HC_2H_3O_{2(aq)}$	$\leftrightarrow$	$H^+_{(aq)}+$	$C_2H_3O_2^-{}_{(aq)}$
Initial	0.300		0	0
Change	–x		+x	+x
Equilibrium	0.300–x		x	x

$$K_a = 1.8 \times 10^{-5} = \frac{\left[H^+_{(aq)}\right]\left[C_2H_3O_2^-{}_{2(aq)}\right]}{\left[HC_2H_3O_{2(aq)}\right]} = \frac{(x)(x)}{0.300 - x}$$

We can use the hundred rule and assume that 0.300-x = 0.300

$$\frac{x^2}{0.300} \cong 1.8 \times 10^{-5}$$

$$x^2 \cong 5.4 \times 10^{-6}$$

$$x \cong 2.3 \times 10^{-3}$$

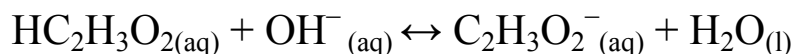$[H^+] = 2.3 \times 10^{-3}$ mol/L

$pH = -\log[H^+] = -\log[2.3 \times 10^{-3}] = 2.62$

$n = v \times C = 0.020$ ml $\times 0.300$ mol/L $= 0.006$ mol

The staring pH is 2.62 and the starting amount is 0.006 mol.

(b)   After adding 10 mL of NaOH.

Perform the stoichiometric calculations first.
The $OH^-_{(aq)}$ will react with $HC_2H_3O_{2(aq)}$ to form acetate and water.

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \leftrightarrow C_2H_3O_2^-_{(aq)} + H_2O_{(l)}$$

How much OH^- reacts with the acid (assume that NaOH disassociates completely)?
$n = V \times C = 0.01\ L \times 0.300\ mol/L = 0.003\ mol$

We have already calculated that we have 0.006 moles of $HC_2H_3O_{2(aq)}$, therefore 0.003 moles of $HC_2H_3O_{2(aq)}$ will be neutralized by the $OH^-_{(aq)}$.

$0.006\ mol - 0.003\ mol = 0.003\ mol$ *(All the $OH^-_{(aq)}$ is consumed and 0.300 mol of $HC_2H_3O_{2(aq)}$ remain.)*
$20\ mL + 10\ mL = 30\ mL$ *(the new volume)*

Perform equilibrium calculations
Before equilibrium exerts itself we know a few things. We have 0.003 mol of $HC_2H_3O_{2(aq)}$ and 0.003 mol of $C_2H_3O_2^-_{(aq)}$ in 0.03 L to give 0.100 mol/L of each. We now need to figure out how equilibrium will exert itself.

	$HC_2H_3O_{2(aq)}$	$\leftrightarrow$	$H^+_{(aq)} +$	$C_2H_3O_2^-_{(aq)}$
Initial	0.100		0	0.100
Change	−x		+x	+x
Equilibrium	0.100–x		x	0.100+x

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+_{(aq)}][C_2H_3O_2^-_{2(aq)}]}{[HC_2H_3O_{2(aq)}]} = \frac{(x)(0.100x)}{0.100 - x}$$

We can use the hundred rule and assume that 0.100-x = 0.100 and 0.100+x = 0.100

$$\frac{(x)(0.100)}{0.100} \cong 1.8 \times 10^{-5}$$

$$x \cong 1.8 \times 10^{-5}$$

$[H^+] = 1.8 \times 10^{-5}$ mol/L
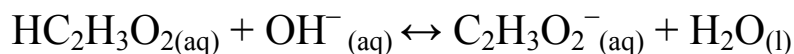$pH = -\log [H^+] = -\log [1.8 \times 10^{-5}] = 4.74$

After 10 mL of NaOH, the pH is 4.74 and the amount of acid is 0.003 mol.

(c)After adding 20 mL of NaOH at the equivalence point.

Perform the stoichiometric calculations first.
The $OH^-_{(aq)}$ will react with $HC_2H_3O_{2(aq)}$ to form acetate and water.

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \leftrightarrow C_2H_3O_2^-_{(aq)} + H_2O_{(l)}$$

How much OH^- reacts with the acid (assume that NaOH disassociates completely)?
n = V × C = 0.02 L × 0.300 mol/L = 0.006 mol

We have already calculated that we have 0.006 moles of $HC_2H_3O_{2(aq)}$, therefore all of $HC_2H_3O_{2(aq)}$ will be neutralized by the $OH^-_{(aq)}$.

0.006 mol – 0.006 mol = 0 mol *(All the $OH^-_{(aq)}$ is consumed and none of the $HC_2H_3O_{2(aq)}$ remain.)*
20 mL + 20 mL = 40 mL *(the new volume)However, we will have all the $HC_2H_3O_{2(aq)}$ converted into $C_2H_3O_2^-_{(aq)}$.*

Perform equilibrium calculations
Before equilibrium exerts itself we know a few things. We have 0.006 mol of $C_2H_3O_2^-_{(aq)}$ in 0.04 L to give 0.150 mol/L. We now need to

figure out how equilibrium will exert itself. But the reaction now changes. We have 100% acetate and we have to figure out the equilibrium for it.

$$C_2H_3O_2^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HC_2H_3O_{2\,(aq)} + OH^-{}_{(aq)}$$

Initial	0.150	*	0	0
Change	−x	*	+x	+x
Equilibrium	0.150–x	*	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b = 5.6 \times 10^{-10} = \frac{[HC_2H_3O_{2(aq)}][OH^-_{(aq)}]}{[C_2H_3O^-_{(aq)}]} = \frac{(x)(x)}{0.150 - x}$$

We can use the hundred rule and assume that 0.150-x = 0.150

$$\frac{x^2}{0.150} \cong 5.6 \times 10^{-10}$$

$$x \cong 9.2 \times 10^{-6}$$

$[OH^-] = 9.2 \times 10^{-6}$ mol/L

$pOH = -\log[OH^-] = -\log[9.2 \times 10^{-6}] = 5.03$

$pH = 14 - 5.03 = 8.97$

After 20 mL of NaOH, the pH is 8.97 and the amount of acid is 0 mol.

Titrating a Weak Base with a Strong Acid
- The questions are similar to the one above.

Acid-Base Indicators
- Indicators will change colour at a specific pH.
- Transition Point: the pH at which an indicator changes colour
- $$K_{In} = \frac{[In^-_{(aq)}][H_3O^+_{(aq)}]}{HIn_{(aq)}}$$

- See table 7 on page 609 for information about the indicators.
- You can calculate which indicator will be the best to use by calculating the pH at a reactions equivalence point.

Polyprotic Acid Titrations
- These titrations are the same as monoprotic titrations except there are multiple endpoints.

Homework
- Practice 1,2,3,4,5,6,10
- Questions 1,2,3,4,5,6,7,8,9,10