PRACTICAL NUMBER 8
TITRATION CURVES

INTRODUCTION

In this exercise you will titrate various bases with acid (or *vice versa*) and monitor the pH of the solution in the conical flask (the *titrand*) using a pH meter or acid/base indicators. Unlike a normal titration you will not stop when you reach the end-point. You will continue until a large excess of titrant has been added from the burette. You will plot graphs of your results, and in some cases draw in curves calculated by applying the various theoretical equations governing the behaviour of weak acids and bases in solution. Note that these equations do not apply to very dilute solutions ($<10^{-5}$ M), or very weak acids or bases (pK>13).

For a Brønsted-Lowry acid in solution:

$$\underset{\text{acid}}{HA(aq)} + H_2O(l) \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{base}}}{A^-(aq)} + H_3O^+(aq) \qquad (7.1)$$

For a strong acid the equilibrium lies well over to the right (virtually no intact HA molecules remain) but for a weak acid the equilibrium lies to the left (virtually all HA molecules remain intact). This is the situation in the conical flask before any titrant has been added. The pH may be calculated using equations (7.2) or (7.3), as appropriate. In these equations C_a represents the *analytical* concentration of the acid, the concentration which would be determined by titration, or in other words the concentration assuming no dissociation of the acid.

Table 8.1 – Equations for calculating pH

The solution contains	*pH given by*	*Equation number*
a strong acid, whether together with its conjugate base or not	$pH = -\lg C_a$	(7.2)
a weak acid, in the absence of its conjugate base and strong acid	$pH = ½pK_a - ½\lg C_a$	(7.3)
a weak acid in the presence of its conjugate base and in the absence of strong base	$pH = pK_a + \lg(C_b/C_a)$	(8.1)
a strong base, whether together with its conjugate acid or not	$pH = pK_w + \lg C_b$	(8.2)
a weak base in the absence of its conjugate acid.	$pH = ½pK_w + ½pK_a + ½\mathrm{Lg}\ C_b$ or $pH = pK_w - ½pK_b + ½\mathrm{Lg}\ C_b$[8]	(8.3)

The titrant (from the burette), in the first two parts of this experiment, is a solution of a strong base (sodium hydroxide). When it is added to the conical flask the hydroxide ions react with any H_3O^+ present and converts it back to H_2O.

$$OH^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l) \qquad (8.4)$$

Two case now arise:

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[8] derived from the first equation by substituting for pK_a from $pK_w = pK_a + pK_b$.

1) HA is a strong acid

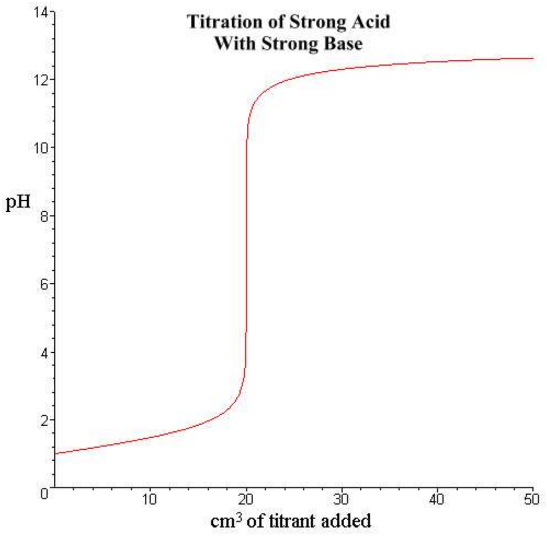
The only effect of adding the sodium hydroxide solution is a decrease in the concentration of H_3O^+, according to equation (8.4) since virtually no HA molecules are present, and so cannot dissociate to replace the H_3O^+ lost. Equation (7.2) may still be used to calculate the pH so long as the acid remains in excess, but C_a must be calculated by employing equation (7.1) to determine how many moles of H_3O^+ remain and taking into account the increase in volume resulting from addition of titrant.

When sufficient titrant has been added to neutralise all the acid, the situation is described as the *equivalence point*. The H_3O^+ has been used up completely and so, in principle, the solution should be neutral. (Neither Na^+ nor A^- have appreciable acidic or basic properties.)

If more titrant is added after the equivalence point has been reached, the solution becomes alkaline due to the excess OH^- present. The pH is now calculated using equation (8.2). C_b represents the concentration of the excess OH^-.

The variation in pH is shown in figure 8.1.

Figure 8.1



2) HA is a weak acid

If HA is weak, H_3O^+ still reacts with OH^- according to (8.4) but now some of the HA dissociates to replace the H_3O^+ used up, in accordance with Le Chatelier's principle, and at the same time more A^- is produced. Both the parent acid (HA) and its conjugate base (A^-) are present in comparable concentration. The appropriate equation for calculating the pH, up to but not including the equivalence point, is now (8.2). C_a and C_b must be calculated by firstly treating the reaction between titrand and titrant as simply

$$HA(aq) + OH^-(aq) \rightarrow H_2O(l) + A^-(aq) \qquad (8.5)$$

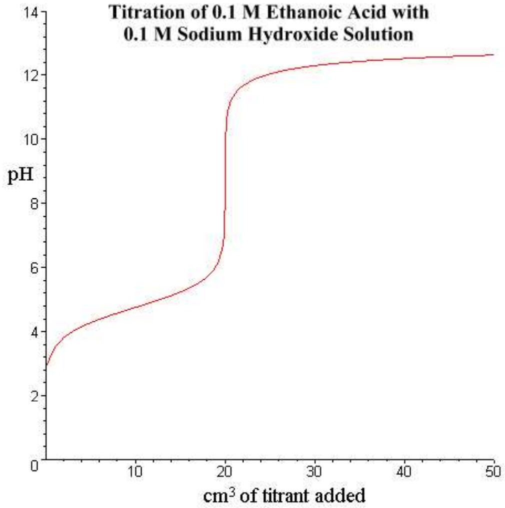
and secondly taking into account the fact that adding titrant increases the total volume of the solution and so decreases the concentrations of HA and A^- proportionately.

Once sufficient OH^- has been added to exactly use up all the HA in equation 8.5, we have reached the equivalence point. Now all the HA has been converted to A^-, a weak base. Consequently the solution is basic and its pH is calculated using equation (8.3). The number of moles of A^- is the same as the original number of moles of HA, but the solution is more dilute because of the increase in volume due to added titrant.

After the equivalence point, further addition of titrant introduces the strong base, OH^-, in excess. This completely overwhelms the effect of the weak base, A^-, which is still present. Once again equation (8.2) is used.

The variation in pH is shown in figure 8.2.

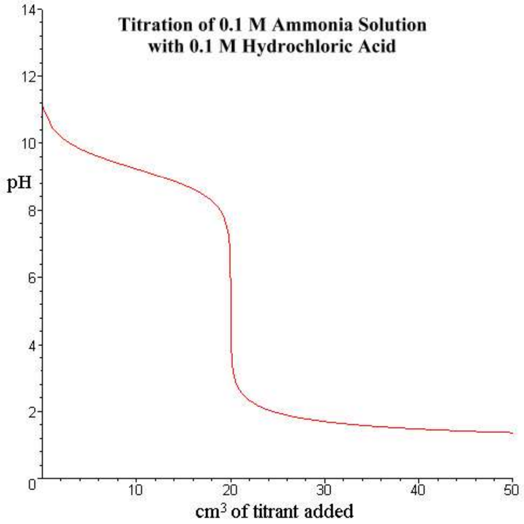
Figure 8.2



In the third part of the experiment there is a solution of a weak base in the conical flask. The titrant is a solution of a strong acid. As a result the pH starts high, drops to a weakly acidic value at the equivalence point and then drops further once the strong acid is in excess.

The variation in pH is shown in figure 8.3.

Figure 8.3



METHOD

Your experiment will consist of three parts. First you will titrate hydrochloric acid (in a conical flask) with sodium hydroxide solution (from a burette). Secondly you will titrate ethanoic acid solution with the same sodium hydroxide solution. Finally you will titrate ammonia solution with the hydrochloric acid solution, the hydrochloric acid solution now replacing the sodium hydroxide in the burette.

In two cases (the titration of hydrochloric acid with sodium hydroxide and the titration of ethanoic acid with sodium hydroxide) you will calculate the pH that would be expected at every stage of the titration and plot theoretical graphs of the calculated values along side the measured values using the same axes. You may do all your calculations and plot your points using a spread sheet such as Excel. Join the points with a smooth curve by hand. Do not connect the points with straight lines.

1) Place 20 cm^3 of 0.1 M hydrochloric acid in a conical flask using a pipette.
2) Measure the approximate pH of the solution using a pH meter if it is available. Alternatively use broad range pH paper to get a rough idea of the pH, and then use narrow range indicator paper covering this pH to refine your measurement. Record the pH in the results table.
3) Add 1 cm^3 of 0.1 M sodium hydroxide solution from a burette, mix thoroughly, and measure and record the pH of the solution as in step (2).
4) Add a further 4 cm^3 of sodium hydroxide solution from the burette so as to make the total volume added up to 5 cm^3 as in the table, mix thoroughly, and again measure the pH.
5) Continue in this way until a total of 45 cm^3 of alkali have been added. Record all your pH values in the results table.
6) Measure 20 cm^3 of 0.1 M ethanoic acid into a clean conical flask. Repeat the above procedure.
7) Rinse out the burette first with distilled water and then with hydrochloric acid solution. Measure 20 cm^3 of 0.1 M ammonia solution into a clean conical flask and titrate with hydrochloric acid from the burette, measuring the pH according to Table 8.6.
8) Calculate the values necessary to complete the results tables.
9) Plot graphs of your measured pH values alongside your calculated ones (where appropriate) to see how they agree. Be careful to distinguish the various points clearly. Include a key on your graph. Use a separate piece of graph paper for each pair of substances.

RESULTS

Titration of hydrochloric acid with sodium hydroxide solution

Conc. of stock solution of acid = _______________ mol dm^{-3}

Conc. of base = _______________ mol dm^{-3}

Aliquot volume (i.e. volume of acid titrated) = ____________________ cm^3

Expected equivalence point (volume of base required to neutralise the acid)

= ____________________ cm^3

Note that equation (7.2) will be required to calculate the pH up to the equivalence point, and equation (8.2) thereafter. The pH at the equivalence point should be that of the water used.

Table 8.2: Before equivalence point

Total volume of NaOH(aq) added /cm^3	*Volume of HCl(aq) remaining*[9]	*Total volume of soln. /cm^3*	*Conc. of excess acid*[10] */mol dm^{-3}*	*Calculated pH (eqn. 7.2)*	*Measured pH*
0					
1					
5					
10					
15					
18					

Table 8.3: After equivalence point

Total volume of NaOH(aq) added /cm^3	*Volume of NaOH(aq) used up*[11]	*Volume of NaOH(aq) remaining*	*Total vol of soln. /cm^3*	*Conc. of excess base*[10] */mol dm^{-3}*	*Calculated pH (equation 8.2)*	*Measured pH*
22						
25						
35						
45						

Titration of ethanoic acid with sodium hydroxide solution

pK_a value for ethanoic acid (acetic acid, CH_3COOH) = 4.76

Conc. of NaOH(aq) = _______________ mol dm^{-3}

Conc. of CH_3COOH(aq) = _______________ mol dm^{-3}

Aliquot volume = ___________________ cm^3

Expected equivalence point = ___________________ cm^3

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[9] If NaOH and HCl concs. are the same, this is given by volume of HCl(aq) – volume of NaOH(aq).

[10] Calculated using equation (1.9)

[11] If NaOH and HCl concs. are the same, this is equal to the volume of HCl(aq) originally present.

pH at 0 cm^3 of base added is measured as = ________________________

and calculated (equation 7.3) as:

= ________________________

Table 8.4: Before equivalence point

Total volume of NaOH(aq) added /cm^3	*Volume of $CH_3COOH(aq)$ remaining*[12]	*Volume of $CH_3COO^-(aq)$ produced*[13]	*Total vol of soln. /cm^3*	*Conc. of excess CH_3COOH /mol dm^{-3}*	*Conc. of CH_3COO^-*	*Calculated pH (equation 8.1)*	*Measured pH*
1							
5							
10							
15							
18							

At equivalence point

pH at equivalence point is calculated (equation 8.3) to be:

= ________________________

(You are not required to measure this since any error in the stated concentrations of the stock solutions would affect the value greatly.)

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[12] If the conc. of CH_3COOH and NaOH are the same, this is given by volume of $CH_3COOH(aq)$ – volume of NaOH(aq).

[13] If the conc. of CH_3COOH and NaOH are the same, this is equal to the volume of NaOH(aq) added.

Table 8.5: After the equivalence point

Total volume of NaOH(aq) added /cm^3	*Volume of NaOH(aq) in excess.*	*Total volume of solution /cm^3*	*Concentration of OH$^-$ /mol dm^{-3}*	*Calculated pH (equation 8.2)*	*Measured pH*
22					
30					
45					

Table 8.6: Titration of ammonia with dilute hydrochloric acid

Total volume of HCl added /cm^3	*0*	*1*	*5*	*10*	*15*	*18*	*22*	*25*	*35*	*45*
Measured pH										

PROBLEMS

1) Practice drawing sketch graphs of the various types of titration curve that you have produced. These are: strong acid/strong base, weak acid/strong base, and weak base/strong acid. A sketch graph has no scales, though the origin should be correctly indicated. What is important is the form of the curve, i.e. where it is flat, or where it is steep, as well as the type of curvature: concave or convex, points of inflexion, maxima and minima etc.
2) Derive each of the equations (7.1, 7.2, 8.2, 8.3, and 8.4) for calculating pH. You will have to start with the appropriate dissociation equation and table of concentrations.
3) For the titration of ethanoic acid with sodium hydroxide explain why the various equations are used for calculating the pH at various stages in the titration, making clear why each equation only applies to a certain situation, and not to the other situations. For example, why does equation (8.4) apply only to the pH at the equivalence point and not to the pH before or after this point?
4) On your graphs indicate the volume of titrant added when the pH of the solution is equal to the pK$_a$ value of the weak acid. (Hint: consider equation 8.1.) Describe how this may be used in a method for measuring the pK$_a$ of a weak acid without having to know its concentration explicitly.