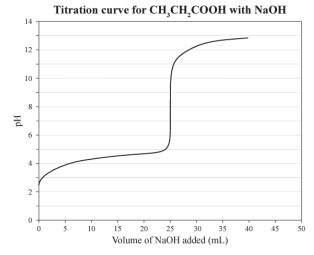
# AS 91392 Demonstrate understanding of equilibrium principles in aqueous systems Collated Titration & Titration Curve Questions

#### 2021:3

A titration was carried out by adding 0.163 mol  $L^{-1}$  sodium hydroxide, NaOH, to 20.0 mL of propanoic acid solution, CH<sub>3</sub>CH<sub>2</sub>COOH, in a conical flask. The equation for the reaction is:

$$CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$$
 
$$K_a (CH_3CH_2COOH) = 1.35 \times 10^{-5} \qquad pK_a (CH_3CH_2COOH) = 4.87$$



(a) (i) Fill in the boxes below to show all the species present in a solution of propanoic acid in order of decreasing concentration. Do not include water.

- (ii) The propanoic acid solution has a pH of 2.78 before any NaOH is added. Show, by calculation, that the initial concentration of the propanoic acid is  $0.204 \text{ mol L}^{-1}$ .
- (b) (i) Put a cross at the equivalence point on the titration curve.
  - (ii) Put ONE tick in the table below to choose the most suitable indicator for the titration.

Indicator	p <i>K</i> a	TICK ( <b>√</b> ) most suitable indicator
Thymol blue	1.70	
Methyl yellow	3.10	
Nile blue	9.70	

Explain your choice, including the consequences of choosing the other indicators.

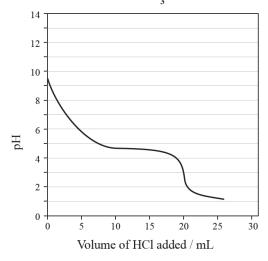
- (iii) Calculate the pH at the equivalence point.
- (c) (i) Calculate the pH of the solution in the conical flask after 29.0 mL of the NaOH solution has been added.
  - (ii) The original  $0.163 \text{ mol L}^{-1}$  NaOH solution in the burette has a pH of 13.2. Explain why this is different from the pH calculated in part (i) above. *No calculations are necessary.*

## 2020:3

A titration was carried out by adding 0.280 mol L<sup>-1</sup> hydrochloric acid, HCl, to 25.0 mL of 0.224 mol L<sup>-1</sup> sodium ethanoate solution, CH<sub>3</sub>COONa. The equation for the reaction is: CH<sub>3</sub>COONa + HCl  $\rightarrow$  CH<sub>3</sub>COOH + NaCl

$$pK_a (CH_3COOH) = 4.76 K_a (CH3COOH) = 1.74 \times 10^{-5}$$

# Titration curve for CH,COONa versus HCl



- (a) (i) List all the species present in a solution of sodium ethanoate. Do not include water.
  - (ii) Calculate the pH of the  $0.224 \text{ mol L}^{-1}$  sodium ethanoate solution before any hydrochloric acid is added.
- (b) Why are hydrochloric acid and sodium ethanoate solutions both good electrical conductors? Justify your answer, including any relevant equation(s).
- (c) (i) Calculate the pH at the equivalence point.
  - (ii) In a second titration, 25.0 mL of 0.224 mol L-1 methanamine, CH<sub>3</sub>NH<sub>2</sub>, is titrated with the same 0.280 mol L $^{-1}$  hydrochloric acid.  $K_a$  (CH<sub>3</sub>NH<sub>3</sub> $^+$ ) = 2.29 × 10 $^{-11}$   $K_a$  (CH<sub>3</sub>COOH) = 1.74 × 10 $^{-5}$  For this second titration, circle how the pH at the equivalence point will compare to the pH at the equivalence point in the titration of sodium ethanoate. Lower pH Same pH Higher pH Explain your answer. *No calculations are necessary.*

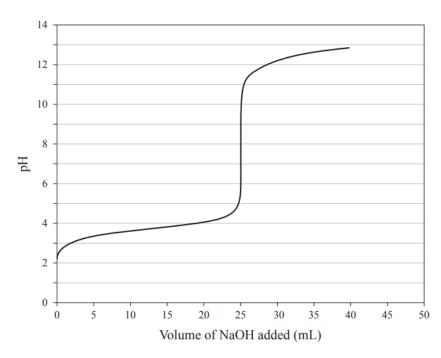
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## 2019:2

A titration was carried out by adding 0.140 mol  $L^{-1}$  sodium hydroxide, NaOH, to 20.0 mL of 0.175 mol  $L^{-1}$  methanoic acid, HCOOH.

The equation for the reaction is:  $HCOOH + NaOH \rightarrow HCOONa + H_2O$ 

$$Ka (HCOOH) = 1.82 \times 10^{-4}$$



- (a) (i) List ALL the species in solution after 12.5 mL of NaOH solution has been added. Do not include water.
  - (ii) After 12.5 mL of NaOH has been added, the solution has a pH of 3.74. Explain the significance of this pH with reference to the relative concentrations of the species present. *No calculations are necessary.*
- (b) (i) With reference to the titration curve, put a tick next to the indicator most suited to identify the equivalence point. Tick ONE below
  - ☐ Thymol blue

 $pK_a 1.70$ 

☐ Bromocresol green

 $pK_a 4.70$ 

☐ Cresol red

pK<sub>a</sub> 8.30

Explain your choice, including the consequences of choosing the other indicators.

- (ii) Calculate the pH at the equivalence point.
- (c) Calculate the pH of the solution after 28.0 mL of 0.140 mol L-1 NaOH has been added

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#### 2018:2

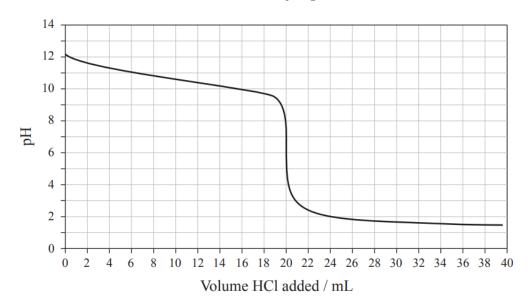
A titration was carried out by adding 0.210 mol  $L^{-1}$  hydrochloric acid, HCl, to 25.0 mL of 0.168 mol  $L^{-1}$  methanamine,  $CH_3NH_2$ .

The equation for the reaction is:

$$HCI + CH_3NH_2 \rightarrow CH_3NH_3 + + CI^-$$

pKa (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) = 10.6 Ka (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) = 
$$2.51 \times 10^{-11}$$

# Titration Curve for CH<sub>3</sub>NH<sub>2</sub> versus HCl



- (a) Between pH 9.60 11.6, the solution is a buffer.
  - (i) From the titration curve, estimate the volume of the HCl solution that must be added to the CH<sub>3</sub>NH<sub>2</sub> solution above to make a buffer solution of pH 10.0.
  - (ii) Explain how the buffer solution resists large changes in pH as the HCl solution is added between a pH of 9.60 11.6. Include an appropriate equation in your answer.
- (b) (i) List all the species present in the solution at the equivalence point in order of decreasing concentration. Do not include water.
  - (ii) Calculate the pH at the equivalence point.
- (c) Why is the solution at the equivalence point a better electrical conductor than the initial solution of methanamine?

Your answer should include relevant equation(s) and elaborate on the relative concentrations of the different species in each solution. No calculations are necessary.

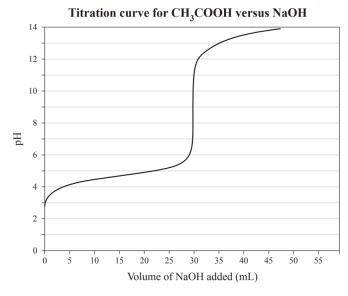
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## 2017:3

A titration was carried out by adding  $0.112 \text{ mol } L^{-1}$  sodium hydroxide solution, NaOH(aq), to 20.0 mL of ethanoic acid solution, CH<sub>3</sub>COOH(aq).

The equation for the reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(I)$$
  $K_a(CH_3COOH) = 1.74 \times 10^{-5}$ .



(a) With reference to the titration curve above, put a tick next to the indicator most suited to identify the equivalence point.

<u>Indicator</u>	рКа	Tick ONE
Methyl yellow	3.1	
Bromocresol purple	6.3	
Phenolphthalein	9.6	

- (b) (i) The ethanoic acid solution,  $CH_3COOH(aq)$ , has a pH of 2.77 before any NaOH is added. Show by calculation that the concentration of the  $CH_3COOH$  solution is 0.166 mol  $L^{-1}$ .
  - (ii) Calculate the pH of the solution in the flask after 10.0 mL of 0.112 mol  $L^{-1}$  NaOH has been added to 20.0 mL of ethanoic acid solution, CH<sub>3</sub>COOH(aq).
- (c) The equivalence point pH for the titration of ethanoic acid with sodium hydroxide is 8.79.
  - (i) Identify the chemical species present at the equivalence point, other than water.
  - (ii) In a second titration, a  $0.166 \text{ mol L}^{-1}$  methanoic acid solution, HCOOH(aq), is titrated with the NaOH solution. The equivalence point pH for this titration is 8.28.

The equivalence point pH for the CH₃COOH titration is 8.79.

Compare and contrast the pH values at the equivalence point for both titrations.

$$K_a$$
 (HCOOH) = 1.82 × 10<sup>-4</sup>  $K_a$  (CH<sub>3</sub>COOH) = 1.74 × 10<sup>-5</sup>

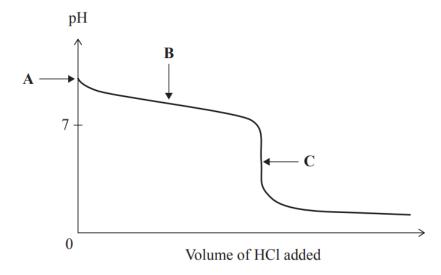
No calculations are necessary.

## 2016:3

20.00 mL of 0.320 mol  $L^{-1}$  ammonia, NH<sub>3</sub>, is titrated with 0.640 mol  $L^{-1}$  hydrochloric acid, HCl.

The equation for this reaction is:  $NH_3 + HCl \rightarrow NH_4^+ + Cl^- pK_a (NH_4^+) = 9.24$ 

The curve for this titration is given below.



- (a) Explain why the pH at the equivalence point (point C) is not 7.
- (b) Show, by calculation, that the pH at the equivalence point (point C) is 4.96.
- (c) Explain, in terms of the species present, why the pH at B (half way to the equivalence point) is 9.24.
- (d) Explain, in terms of the species present, why the pH of the solution at point C is 4.96. No calculations are necessary.

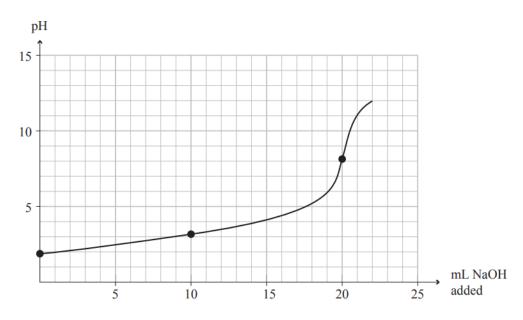
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## 2015:3

20.0 mL of 0.258 mol  $L^{-1}$  hydrofluoric acid, HF, solution is titrated with a sodium hydroxide, NaOH, solution. The equation for the reaction is:

$$HF + NaOH \rightarrow NaF + H_2O$$
  
 $pK_a (HF) = 3.17$ 

The titration curve is given below:



- (a) (i) Identify the species in solution at the equivalence point.
  - (ii) Explain why the pH at the equivalence point is greater than 7. Include an equation in your answer.
  - (iii) After a certain volume of NaOH solution has been added, the concentration of HF in the solution will be twice that of the  $F^-$ .
    - Calculate the pH of this solution, and evaluate its ability to function as a buffer.
  - (iv) Determine by calculation, the pH of the solution after 24.0 mL of 0.258 mol L<sup>-1</sup> NaOH solution has been added.
- (b) In a second titration, a 0.258 mol L<sup>-1</sup> ethanoic acid, CH₃COOH, solution was titrated with the NaOH solution. Contrast the expected pH at the equivalence point with the HF titration. pKa (CH₃COOH) = 4.76 No calculations are necessary.

#### 2014:3

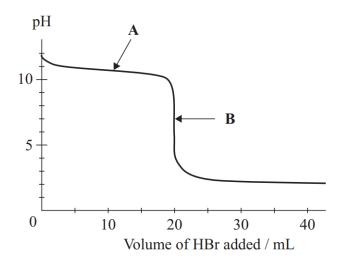
A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH<sub>3</sub>NH<sub>2</sub>, solution.

The equation for the reaction is:

$$CH_3NH_2 + HBr \rightarrow CH_3NH_3 + + Br^-$$

$$K_a (CH_3NH_3^+) = 2.29 \times 10^{-11}$$

The curve for this titration is given below:



- (a) Explain why the pH does not change significantly between the addition of 5 to 15 mL of HBr (around point A on the curve). Include any relevant equation(s) in your answer.
- (b) The aqueous methylamine,  $CH_3NH_2$ , solution has a pH of 11.8 before any HBr is added. Show by calculation that the concentration of this solution is 0.0912 mol  $L^{-1}$ .
- (c) (i) Write the formulae of the four chemical species, apart from water and OH<sup>-</sup>, that are present at the point marked B on the curve.

## 2013:3

20.0 mL of 0.0896 mol  $L^{-1}$  ethanoic acid is titrated with 0.100 mol  $L^{-1}$  sodium hydroxide. pK<sub>a</sub> (CH<sub>3</sub>COOH) = 4.76

- (a) Calculate the pH of the ethanoic acid before any NaOH is added.
- (b) Halfway to the equivalence point of the titration, the pH = pKa of the ethanoic acid.

  Discuss the reason for this.
- (c) Discuss the change in the concentration of species in solution, as the first 5.00 mL of NaOH is added to the 20.0 mL of ethanoic acid. Your answer should include chemical equations. No calculations are required.
  - (ii) Calculate the pH of the titration mixture after 5.00 mL of NaOH has been added.

#### **Answers**

#### 2021:3

- (a) (i)  $CH_3CH_2COOH > CH_3CH_2COO^- = H_3O^+ > OH^-$ 
  - (ii)  $CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO_- + H_3O^+$   $Ka = ([CH_3CH_2COO^-][H_3O^+])/[CH_3CH_2COOH]$   $1.35 \times 10^{-5} = (10^{-2.78})^2/[CH_3CH_2COOH] \quad [CH_3CH_2COOH] = 0.204 \text{ mol } L^{-1}$
- (b) (i) Cross halfway up vertical section of curve.
  - (ii) Tick for Nile blue. Nile blue changes colour over a pH range 8.70 10.70. This pH range falls within the vertical section of the curve / the pH at the equivalence point falls within this range, so Nile blue will change colour at the equivalence point. The other two indicators will both change colour before the vertical section of the curve, and will therefore be unsuitable because they will change colour before the equivalence point.
  - (iii)  $CH_3CH_2COO^- + H_2O \rightleftharpoons CH_3CH_2COOH + OH^-$  For this solution:  $[CH_3CH_2COOH] = [OH^-] = K_W / [H_3O^+]$  Using Ka to calculate pH:

$$K_{\rm a} = \frac{[{\rm H_3O^+}][{\rm CH_3CH_2COO^-}]}{[{\rm CH_3CH_2COOH}]}$$

$$1.35 \times 10^{-5} = \left(0.204 \times \frac{20}{45}\right) \times \frac{[{\rm H_3O^+}]^2}{10^{-14}}$$

$$[{\rm H_3O^+}] = 1.22 \times 10^{-9} \; {\rm mol} \; {\rm L^{-1}}$$

$${\rm pH} = 8.91$$

- (c) (i)  $n(NaOH) = cv = 0.163 \times 0.004 = 6.52 \times 10^{-4} \text{ mol}$   $c(NaOH) = 6.52 \times 10^{-4} / 0.049 = 0.0133 \text{ mol } L^{-1}$   $[H_3O^+] = 1 \times 10^{-14} / 0.0133 = 7.52 \times 10^{-13} \text{ pH} = -\log 7.52 \times 10^{-13} = 12.1$ 
  - (ii) The moles of NaOH present in the extra 4 mL of 0.163 mol  $L^{-1}$  NaOH added after the equivalence point have been diluted; i.e. total volume in conical flask is now 0.49 mL. Since  $[OH^{-}]$  has decreased, the pH also decreases.

#### 2020:3

- (a) (i) Na+, CH<sub>3</sub>COO<sup>-</sup>, CH<sub>3</sub>COOH, OH-, H<sub>3</sub>O<sup>+</sup>
  - (ii) For this solution:  $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^ [CH_3COO^-] = 0.224 \text{ mol } L^{-1}$

$$\left[\text{CH}_3\text{COOH}\right] = \left[\text{OH}^-\right] = \frac{K_{\text{w}}}{\left[\text{H}_3\text{O}^+\right]}$$

Using  $K_a$  to calculate pH:

$$K_{\rm a} = \frac{\left[{\rm H_3O^+}\right]\!\left[{\rm CH_3COO^-}\right]}{\left[{\rm CH_3COOH}\right]}$$

$$1.74 \times 10^{-5} = \frac{0.224 \times \left[ H_3 O^+ \right]^2}{10^{-14}}$$

$$[H_3O^+] = 8.81 \times 10^{-10} \text{ mol L}^{-1}$$

$$pH = 9.05$$

- (b) The electrical conductivity of a solution depends upon its concentration of mobile ions. HCl is a strong acid and therefore completely dissociates (evidence from equation) to produce a high concentration of  $Cl_{-}$  ions and  $H_3O^+$  ions in solution. HCl +  $H_2O \rightarrow Cl^{-} + H_3O^+$ 
  - Sodium ethanoate is a basic salt. It completely dissociates (evidence from equation) to produce a high concentration of Na<sup>+</sup> ions and CH<sub>3</sub>COO<sup>-</sup> ions in solution. CH<sub>3</sub>COONa  $\rightarrow$  Na<sup>+</sup> + CH<sub>3</sub>COO<sup>-</sup>

Since both solutions produce a high concentration of ions, they are both good electrical conductors.

(c) (i) 
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_{\rm a} = \frac{\left[ \text{CH}_{3}\text{COO}^{-} \right] \left[ \text{H}_{3}\text{O}^{+} \right]}{\left[ \text{CH}_{3}\text{COOH} \right]}$$

$$1.74 \times 10^{-5} = \frac{\left[H_3 O^+\right]^2}{\left(0.224 \times \frac{25}{45}\right)}$$

$$[H_3O^+] = 1.47 \times 10^{-3} \text{ mol L}^{-1}$$

$$pH = 2.83$$

(ii) Circled "Higher pH". At the equivalence point, the weak acid is present, i.e. either  $CH_3NH_3^+$  or  $CH_3COOH$ . Since  $CH_3NH_3^+$  has a smaller  $K_a$  (larger  $pK_a$ ), it is a weaker acid than  $CH_3COOH$  and will therefore dissociate to a lesser extent to produce a lower  $[H_3O^+]$ . As a result, the pH at the equivalence point will be higher for  $CH_3NH_3^+$ .

#### 2019:2

- (a) (i) Na $^+$ , HCOO $^-$ , HCOOH, OH $^-$ , H $_3$ O $^+$ 
  - (ii) After 12.5 mL NaOH has been added, it is halfway to the equivalence point. This means that [HCOOH] = [HCOO-]. Therefore pH equals pKa.
- (b) (i) Tick cresol red. Indicators change colour at a pH  $\pm 1$  of the p $K_a$ , near the p $K_a$ . Therefore, cresol red should be used as it will change near the equivalence point/steepest part of the curve, whereas thymol blue and bromocresol green will change before the equivalence point/steepest part of the curve.

(ii)

$$\begin{split} & \left[ \mathbf{H}_{3}\mathbf{O}^{+} \right] = \sqrt{\frac{K_{a} \times K_{w}}{\left[ \mathbf{CH}_{3}\mathbf{CH}_{2}\mathbf{NH}_{2} \right]}} \\ & \left[ \mathbf{H}_{3}\mathbf{O}^{+} \right] = \sqrt{\frac{1.82 \times 10^{-4} \times 1 \times 10^{-14}}{0.0778}} \\ & \left[ \mathbf{H}_{3}\mathbf{O}^{+} \right] = 4.84 \times 10^{-9} \text{ mol L}^{-1} \\ & \mathbf{pH} = -\log \left[ \mathbf{H}_{3}\mathbf{O}^{+} \right] = 8.32 \end{split}$$

OR For this solution,  $HCOO^- + H_2O \Rightarrow HCOOH + OH^-$ 

(c) After 28 mL NaOH added: n(unreacted NaOH) = cV = 0.140 x 0.003 = 4.2 x  $10^{-4}$  mol c(NaOH) = n/V =  $4.2 \times 10^{-4}$  /  $0.048 = 8.75 \times 10^{-3}$  mol L<sup>-1</sup> [H<sub>3</sub>O+] =  $1 \times 10^{-14}$  /  $8.75 \times 10^{-3}$  =  $1.14 \times 10^{-12}$  mol L<sup>-1</sup> , so pH =  $-\log 1.14 \times 10^{-12}$  = 11.9

## 2018:2

- (a) (i) Volume from curve at pH 10.0 = 15 16.0 mL [A]
  - (ii) As the HCl is added, the  $H_3O^+$  ions are neutralised by the basic component of the buffer,  $CH_3NH_2$ , according to the equation below:  $CH_3NH_2 + H_3O^+ \rightarrow CH_3NH_3^+ + H_2O$  OR  $CH_3NH_2 + HCl \rightarrow CH_3NH_3^+ + Cl^-$  Since the  $H_3O^+$  are removed from the solution, the pH of the solution does not significantly change. [A/M]
- (b) (i)  $Cl^- > CH_3NH_3^+ > CH_3NH^2 = H_3O^+ > OH^- [A/M]$ 
  - (ii)  $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$   $Ka = 2.51 \times 10^{-11} = [H_3O^+]^2 / (0.168 \times 25/45) [H_3O^+] = 1.53 \times 10^{-6} \text{ mol L}^{-1}$  $pH = -log \ 1.53 \times 10^{-6} = 5.82 [A/M/E]$
- (c) Electrical conductivity in solution requires ions. The initial solution is the weak base, methanamine. It only partially dissociates to produce a lower [ions], i.e.  $CH_3NH_3^+$  and  $OH^-$  ions. This means there is mainly  $CH_3NH_2$  present, which has no charge. The solution is therefore a poor conductor of electricity compared to the solution at the equivalence point.  $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$  The solution at the equivalence point is made up of the products from the titration /  $CH_3NH_3^+$  and  $CI^-$ . As there are more ions in solution / higher [ions] the solution at the equivalence point is a better conductor. [A/M/E]

## Other answers on NZQA site:

https://www.nzqa.govt.nz/ncea/assessment/search.do?query=Chemistry&view=reports&level=03

Email us if you really want them here but have you any idea how long it takes to type sub and superscripts?!