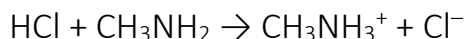


AS 91392 Demonstrate understanding of equilibrium principles in aqueous systems

Collated Buffer Questions

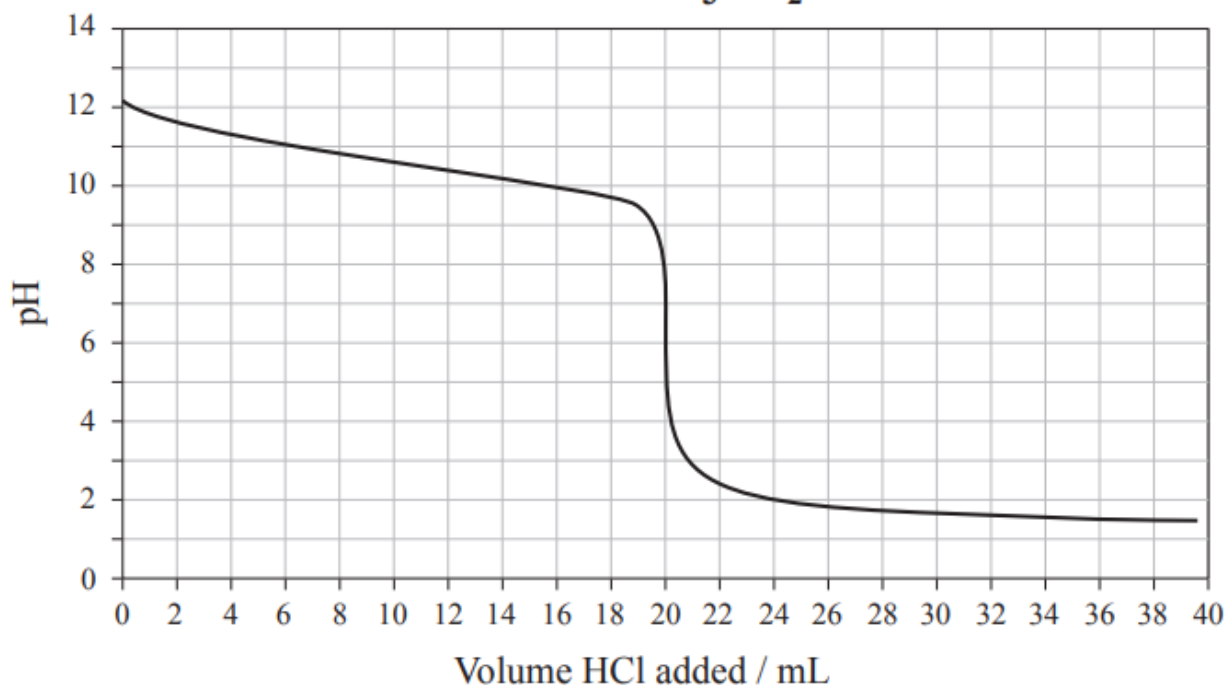
2018:2

A titration was carried out by adding  $0.210 \text{ mol L}^{-1}$  hydrochloric acid, HCl, to  $25.0 \text{ mL}$  of  $0.168 \text{ mol L}^{-1}$  methanamine,  $\text{CH}_3\text{NH}_2$ . The equation for the reaction is:



$$pK_a(\text{CH}_3\text{NH}_3^+) = 10.6 \quad K_a(\text{CH}_3\text{NH}_3^+) = 2.51 \times 10^{-11}$$

**Titration Curve for  $\text{CH}_3\text{NH}_2$  versus HCl**



- (a) Between pH 9.60 – 11.6, the solution is a buffer.
- From the titration curve, estimate the volume of the HCl solution that must be added to the  $\text{CH}_3\text{NH}_2$  solution above to make a buffer solution of pH 10.0.
  - 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.

2018:3

- (b)  $5.11 \text{ g}$  of sodium methanoate,  $\text{HCOONa}$ , was added to  $125 \text{ mL}$  of  $0.105 \text{ mol L}^{-1}$  methanoic acid,  $\text{HCOOH}$ , to make a buffer solution. Assume there is no change in the total volume.
- $$pK_a(\text{HCOOH}) = 3.74 \quad K_a(\text{HCOOH}) = 1.82 \times 10^{-4}$$
- Give the pH range over which the resulting solution will function as a buffer.

(ii) Show, by calculation, that the pH of this buffer solution is 4.50.

$$M(\text{HCOONa}) = 68.0 \text{ g mol}^{-1}$$

(iii) Evaluate whether this buffer solution will be more effective at neutralising small volumes of strong acid or strong base.

### 2017:2

(a) Ammonia,  $\text{NH}_3$ , is a weak base.  $\text{p}K_a(\text{NH}_4^+) = 9.24$   $K_a(\text{NH}_4^+) = 5.75 \times 10^{-10}$

(i) Calculate the pH of a  $0.105 \text{ mol L}^{-1}$   $\text{NH}_3$  solution.

(ii) Dilute hydrochloric acid,  $\text{HCl}$ , is added to the  $\text{NH}_3$  solution until the ratio of  $\text{NH}_3$  to  $\text{NH}_4^+$  in the solution is 5:1. Determine the pH of this solution, and evaluate its ability to resist a change in pH when small volumes of strong acid or base are added.

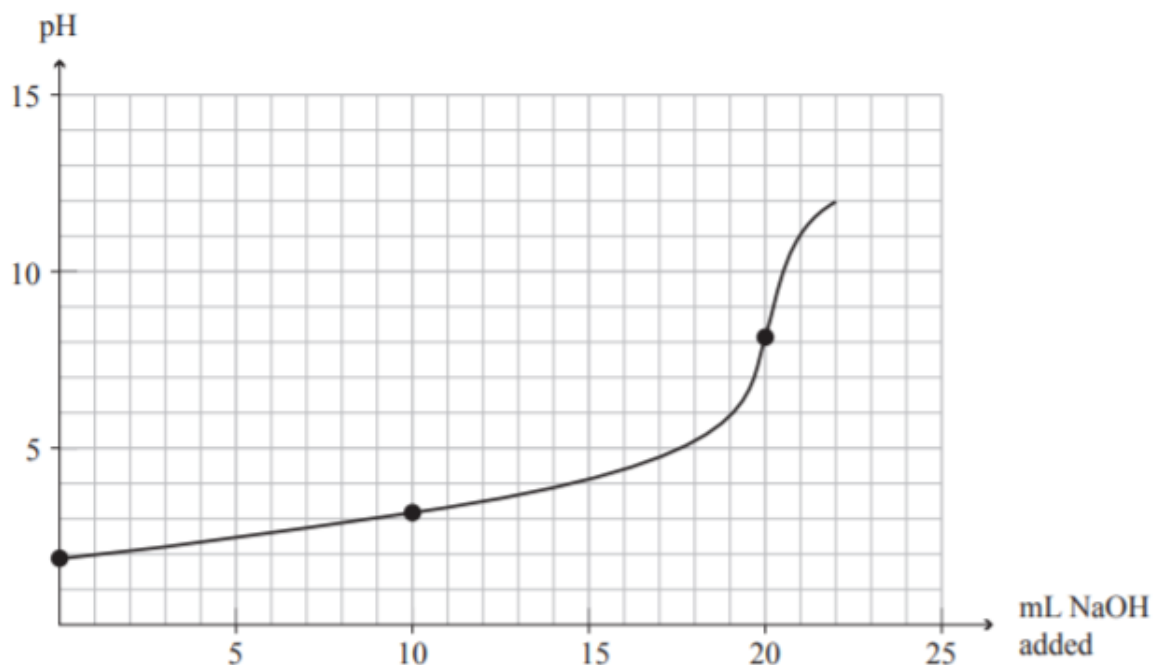
### 2016:

No separate buffer question asked.

### 2015: 3

20.0 mL of  $0.258 \text{ mol L}^{-1}$  hydrofluoric acid,  $\text{HF}$ , solution is titrated with a sodium hydroxide,  $\text{NaOH}$ , solution. The equation for the reaction is:  $\text{HF} + \text{NaOH} \rightarrow \text{NaF} + \text{H}_2\text{O}$

$\text{p}K_a(\text{HF}) = 3.17$  The titration curve is given below:



- (a) (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

**2014:1**

- (c) An aqueous solution containing a mixture of HF and sodium fluoride, NaF, can act as a buffer solution. Calculate the mass of NaF that must be added to 150 mL of 0.0500 mol L<sup>-1</sup> HF to give a buffer solution with a pH of 4.02. Assume there is no change in volume.  
 $M(\text{NaF}) = 42.0 \text{ g mol}^{-1}$   $pK_a(\text{HF}) = 3.17$

**2013:1**

- (c) (i) The following two solutions from part (a) are mixed to form a buffer solution:  
20.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub>Cl and 30.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>2</sub>  
Calculate the pH of the resultant buffer solution.  $pK_a(\text{CH}_3\text{NH}_3^+) = 10.64$
- (ii) Explain the effect on the solution formed in (i) when a small amount of acid is added

**2013:3**

20.0 mL of 0.0896 mol L<sup>-1</sup> ethanoic acid is titrated with 0.100 mol L<sup>-1</sup> sodium hydroxide.  
 $pK_a(\text{CH}_3\text{COOH}) = 4.76$

- (a) Calculate the pH of the ethanoic acid before any NaOH is added.
- (b) Halfway to the equivalence point of the titration, the pH =  $pK_a$  of the ethanoic acid. Discuss the reason for this.
- (c) (i) 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.

**2012:3**

- (a) Calculate the pH of  $0.150 \text{ mol L}^{-1}$  aqueous ammonia,  $\text{NH}_3$ .  $\text{pK}_a(\text{NH}_4^+) = 9.24$
- (b) A mixture of aqueous solutions of  $\text{NH}_3$  and ammonium chloride,  $\text{NH}_4\text{Cl}$ , can act as a buffer solution. Calculate the mass of  $\text{NH}_4\text{Cl}$  required, when added to 250 mL of a  $0.150 \text{ mol L}^{-1}$   $\text{NH}_3$  solution, to give a buffer solution with a pH of 8.60. Assume there is no change in volume.

$$M(\text{NH}_4\text{Cl}) = 53.5 \text{ g mol}^{-1} \quad \text{pK}_a(\text{NH}_4^+) = 9.24$$

- (c) Discuss the ability of the  $\text{NH}_3 / \text{NH}_4\text{Cl}$  solution to act as a buffer at a pH of 8.60. In your answer you should:
- describe the function of a buffer solution
  - evaluate its effectiveness when small amounts of acid or base are added
  - include any relevant equations.

**2011:3**

- (d) Sodium glycolate, the sodium salt of the acid, is used in skin care. Sodium glycolate can be represented as NaG.
- Calculate the amount (in moles) of sodium glycolate that must be added to 200 mL of  $1.00 \text{ mol L}^{-1}$  glycolic acid solution to produce a buffer solution that has a pH of 4.00. Assume there is no change in volume.  $\text{pK}_a(\text{HG}) = 3.83$

Answers

2018:2

- (a) (i) Volume from curve at pH 10.0 = 15 – 16.0 mL  
 (ii) As the HCl is added, the H<sub>3</sub>O<sup>+</sup> ions are neutralised by the basic component of the buffer, CH<sub>3</sub>NH<sub>2</sub>, according to the equation: CH<sub>3</sub>NH<sub>2</sub> + H<sub>3</sub>O<sup>+</sup> → CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> + H<sub>2</sub>O OR  
 CH<sub>3</sub>NH<sub>2</sub> + HCl → CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> + Cl<sup>-</sup>  
 Since the H<sub>3</sub>O<sup>+</sup> are removed from the solution, the pH of the solution does not significantly change.

2018:3

- (b) (i) The solution will function as a buffer over a pH range 2.74 – 4.74 (pK<sub>a</sub> ± 1).  
 (ii) n(HCOONa) = m/M = 5.11/68 = 0.0751 mol  
 c(HCOO<sup>-</sup>) = n/V = 0.0751/0.125 = 0.601 mol L<sup>-1</sup>  
 K<sub>a</sub> = 1.82 × 10<sup>-4</sup> = [HCOO<sup>-</sup>] [H<sub>3</sub>O<sup>+</sup>] / [HCOOH] = 0.601 × [H<sub>3</sub>O<sup>+</sup>] / 0.105  
 [H<sub>3</sub>O<sup>+</sup>] = 3.18 × 10<sup>-5</sup> mol L<sup>-1</sup>  
 pH = -log [H<sub>3</sub>O<sup>+</sup>] = 4.50  
 (iii) Since the pH of the solution falls within the buffer zone (2.74 – 4.74), it will function as a buffer. However, as the pH > pK<sub>a</sub>, / this means [HCOO<sup>-</sup>] > [HCOOH], so the buffer will be more effective against added strong acid.

2017:2

- (a) (i) [H<sub>3</sub>O<sup>+</sup>] = √ (K<sub>a</sub> × K<sub>w</sub> ÷ [NH<sub>3</sub>])  
 [H<sub>3</sub>O<sup>+</sup>] = √ (5.75 × 10<sup>-10</sup> × 1.00 × 10<sup>-14</sup> ÷ 0.105)  
 [H<sub>3</sub>O<sup>+</sup>] = 7.40 × 10<sup>-12</sup> mol L<sup>-1</sup>  
 pH = -log (7.40 × 10<sup>-12</sup>) = 11.1  
 (ii) NH<sub>4</sub><sup>+</sup> + H<sub>2</sub>O ⇌ NH<sub>3</sub> + H<sub>3</sub>O<sup>+</sup>  
 K<sub>a</sub> = [NH<sub>3</sub>][H<sub>3</sub>O<sup>+</sup>] / [NH<sub>4</sub><sup>+</sup>]  
 10<sup>-9.24</sup> = 5 × [H<sub>3</sub>O<sup>+</sup>] / 1  
 [H<sub>3</sub>O<sup>+</sup>] = 1.15 × 10<sup>-10</sup>  
 pH = 9.94

$$pK_a = 9.24$$

The solution will function as a buffer (*as it contains a weak base and conjugate acid in a 5:1 ratio / within a 1:10 ratio / within a pH range of 8.24 – 10.24*). Since the  $[NH_3] > [NH_4^+]$  /  $pH > pK_a$ , the buffer will be more effective at neutralising added strong acid.

2016: n/a

2015: 3

(a) (iii)

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

$$10^{-3.17} = \frac{1 \times [H_3O^+]}{2}$$

$$[H_3O^+] = 2 \times 10^{-3.17} = 1.35 \times 10^{-3} \text{ mol L}^{-1}$$

$$pH = -\log(1.35 \times 10^{-3}) = 2.87.$$

$$\begin{aligned} pH &= pK_a + \log [F^-] / [HF] \\ &= 3.17 + \log 0.5 \\ &= 2.87 \end{aligned}$$

Since there are significant concentrations of the weak acid and its conjugate base the solution can resist added acid or base. However, since the pH of the buffer solution is less than the  $pK_a$ ,  $[HF] > [F^-]$ , it is more effective against added base than acid.

2014: 1

(c)

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

$$10^{-3.17} = \frac{[F^-] \times 10^{-4.02}}{0.0500}$$

$$[F^-] = 0.354 \text{ mol L}^{-1}$$

$$n(\text{NaF}) = 0.354 \text{ mol L}^{-1} \times 0.150 \text{ L} = 0.0531 \text{ mol}$$

$$m(\text{NaF}) = 0.0531 \text{ mol} \times 42.0 \text{ g mol}^{-1} = 2.23 \text{ g}$$

2013:1

(c) (i)

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$[\text{H}_3\text{O}^+] = \frac{K_a [\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]}$$

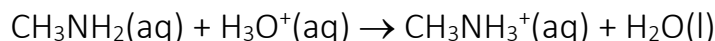
$$[\text{CH}_3\text{NH}_2] = \frac{30 \times 10^{-3} \times 1}{50 \times 10^{-3}} = 0.600 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{NH}_3^+] = \frac{20 \times 10^{-3} \times 1}{50 \times 10^{-3}} = 0.400 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 1.52705 \times 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = 10.8$$

(c) (ii) When a small amount of acid ( $\text{H}_3\text{O}^+$ ) ions are added, they will react with the  $\text{CH}_3\text{NH}_2(\text{aq})$  molecules to form  $\text{CH}_3\text{NH}_3^+(\text{aq})$  ions.



The added acid ( $\text{H}_3\text{O}^+$ ), is mostly consumed, and the pH of the solution changes very little.

2013:3

(a)  $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$  •  $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$

$$[\text{H}_3\text{O}^+] = \sqrt{1.74 \times 10^{-5} \times 0.0896} \text{ mol L}^{-1}$$

$$= 1.25 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.90$$

(b) Halfway to equivalence point, half of the ethanoic acid has been used up. There are now equimolar quantities of ethanoic acid and sodium ethanoate.

As  $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$  According to the equation when  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$

then  $K_a = [\text{H}_3\text{O}^+]$  So  $\text{p}K_a = \text{pH}$ .

(c) (i)  $\text{NaOH}(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{CH}_3\text{COONa}(\text{aq}) + \text{H}_2\text{O}(\text{l})$  (1)

$[\text{CH}_3\text{COO}^-]$  increases as it is formed in reaction (1).

$[\text{Na}^+]$  increases as NaOH is added (1).

$[\text{CH}_3\text{COOH}]$  decreases as it reacts with NaOH (1).

$[\text{H}_3\text{O}^+]$  decreases because  $[\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$  increases and  $K_a$  is a constant.

$[\text{OH}^-]$  increases because  $[\text{H}_3\text{O}^+]$  decreases and  $[\text{H}_3\text{O}^+][\text{OH}^-]$  is constant.

$$(ii) \quad n(\text{CH}_3\text{COOH at start}) = 0.0896 \times 20 \times 10^{-3} = 1.79 \times 10^{-3} \text{ mol}$$

$$n(\text{NaOH added}) = 0.1 \times 5 \times 10^{-3} = 5 \times 10^{-4} \text{ mol}$$

After 5 mL NaOH added:

$$n(\text{CH}_3\text{COOH}) = 1.29 \times 10^{-3} \text{ mol}$$

$$n(\text{CH}_3\text{COO}^-) = 5.00 \times 10^{-4} \text{ mol}$$

$$[\text{CH}_3\text{COOH}] = 0.0516 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{COO}^-] = 0.0200 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 4.48 \times 10^{-5} \text{ mol L}^{-1} \quad \text{pH} = 4.35$$

### 2012:3

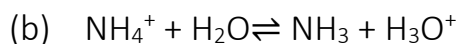


$$K_a = 10^{-9.24} = 5.75 \times 10^{-10}$$

$$K_b = [\text{OH}^-]^2 / [\text{NH}_3] = K_w / K_a = 1.74 \times 10^{-5}$$

$$[\text{OH}^-] = \sqrt{(1.74 \times 10^{-5} \times 0.150)} = 1.61 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = 6.19 \times 10^{-12} \text{ mol L}^{-1} \quad \text{pH} = 11.2$$



$$[\text{NH}_4^+] = [\text{NH}_3] [\text{H}_3\text{O}^+] / K_a$$

$$[\text{NH}_4^+] = 0.150 \times 10^{-8.60} / 10^{-9.24}$$

$$[\text{NH}_4^+] = 0.655 \text{ mol L}^{-1}$$

$$n(\text{NH}_4^+) = 0.655 \text{ mol L}^{-1} \times 0.250 \text{ L} = 0.164 \text{ mol}$$

$$m(\text{NH}_4\text{Cl}) = 0.164 \text{ mol} \times 53.5 \text{ g mol}^{-1} = \mathbf{8.76 \text{ g}}$$

Note: allow use of  $\text{pH} = \text{pK}_a + \log [\text{NH}_3] / [\text{NH}_4^+]$

(c) A buffer is a solution that undergoes a minimal change of pH when small amounts of acid or base are added. Added acid will react with  $\text{NH}_3$  so there is almost no change in



Added base will react with  $\text{NH}_4^+$  so that there is almost no change in  $[\text{OH}^-]$ :  $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$

(These equations show that the ratio of  $\text{NH}_3$ :  $\text{NH}_4^+$  changes slightly, but this does not significantly affect the pH.)

Since the pH of the buffer is lower than the  $\text{pK}_a$  of  $\text{NH}_4^+$ , the  $[\text{NH}_4^+]$  will be higher than the  $[\text{NH}_3]$ . This means the buffer will be more effective against added base.



2011:3

(d)  $[\text{H}_3\text{O}^+] = 1.00 \times 10^{-4} \text{ mol L}^{-1}$ .

$$[\text{G}^-] = \frac{K_a \times [\text{HG}]}{[\text{H}_3\text{O}^+]} = 1.48 \text{ mol L}^{-1}$$

Thus in 200 mL =  $0.2 \times 1.48 = 0.296 \text{ mol}$

*Alternative method*

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{weak base}]}{[\text{weak acid}]}$$

$$4.00 = 3.83 + \log_{10} \frac{[\text{base}]}{[\text{acid}]}$$

$$\log_{10} [\text{base}] = 0.17$$

$$[\text{base}] = 1.48 \text{ mol L}^{-1}$$

Thus, in 200 mL =  $0.2 \times 1.48 = 0.296 \text{ mol}$