Marks 7

Calculate the pH of a 0.010 M solution of aspirin at 25 °C. The pK_a of aspirin is 3.5 at this temperature.

As aspirin is a weak acid, [H_3O^+] must be calculated using a reaction table:

	$C_9H_8O_4$(aq)	H_2O	$\rightleftharpoons$	H_3O^+	$C_9H_7O_4^-$
initial	**0.010**	**large**		**0**	**0**
change	**$-x$**	**negligible**		**$+x$**	**$+x$**
final	**$0.010 - x$**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][C_9H_7O_4^-(aq)]}{[C_9H_8O_4(aq)]} = \frac{x^2}{0.010 - x}$$

As pK_a = $-\log_{10}K_a$, $K_a = 10^{-3.5}$ and is very small, $0.010 - x \sim 0.010$ and hence:

$x^2 = 0.010 \times 10^{-3.5}$ **or** $x = 1.8 \times 10^{-3}$ M = [H_3O^+]

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(1.8 \times 10^{-3}) = 2.8$$

pH = **2.8**

Ammonia, NH_3, is a weak base in water. Write the equation for the acid/base reaction between aspirin and ammonia.

$$C_9H_8O_4(aq) + NH_3(aq) \rightarrow C_9H_7O_4^-(aq) + NH_4^+(aq)$$

What is the expression for the equilibrium constant, K, for this reaction?

$$K = \frac{[NH_4^+(aq)][C_9H_7O_4^-(aq)]}{[NH_3(aq)][C_9H_8O_4(aq)]}$$

Rewrite this expression in terms of the K_a of aspirin and the K_a of NH_4^+. (Hint: multiply by [H^+]/[H^+] = 1) Hence calculate the value of K. The pK_a of NH_4^+ is 9.2.

For $C_9H_8O_4$, K_a ($C_9H_8O_4$) $= \dfrac{[H_3O^+][C_9H_7O_4^-(aq)]}{[C_9H_8O_4(aq)]} = 10^{-3.5}$

For NH_3, K_a (NH_4^+) $= \dfrac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]} = 10^{-9.2}$

$$K = \frac{[\mathrm{NH_4}^+(\mathrm{aq})][\mathrm{C_9H_7O_4}^-(\mathrm{aq})]}{[\mathrm{NH_3}(\mathrm{aq})][\mathrm{C_9H_8O_4}(\mathrm{aq})]} = \frac{[\mathrm{NH_4}^+(\mathrm{aq})]}{[\mathrm{NH_3}(\mathrm{aq})][\mathrm{H}^+(\mathrm{aq})]} \times \frac{[\mathrm{H}^+(\mathrm{aq})][\mathrm{C_9H_7O_4}^-(\mathrm{aq})]}{[\mathrm{C_9H_8O_4}(\mathrm{aq})]}$$

$$= \quad (1 / K_a\ (\mathrm{NH_3})) \quad \times \quad K_a\ (\mathrm{C_9H_8O_4})$$

$$K = (1 / 10^{-9.2}) \times (10^{-3.5}) = 10^{5.7} = 5.0 \times 10^5$$

Answer: $\mathbf{5.0 \times 10^5}$

Would aspirin dissolve in a solution of ammonia? Explain your answer.

The equilibrium constant for the reaction of ammonia and aspirin is very large: aspirin will dissolve.

Marks 6

- Solution A consists of a 0.050 M aqueous solution of benzoic acid, C_6H_5COOH, at 25 °C. Calculate the pH of Solution A. The pK_a of benzoic acid is 4.20.

As benzoic acid is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	C_6H_5COOH	$\rightleftharpoons$	H^+	$C_6H_5COO^-$
initial	**0.050**		**0**	**0**
change	$-x$		$+x$	$+x$
final	$0.050 - x$		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{x^2}{0.050 - x}$$

As pK_a = $-\log_{10}K_a$, $K_a = 10^{-4.20}$ and is very small, $0.050 - x \sim 0.050$ and hence:

$x^2 = 0.050 \times 10^{-4.2}$ **or** $x = 1.78 \times 10^{-3}$ M $= [H^+]$

Hence, the pH is given by:

$\text{pH} = -\log_{10}[H^+] = -\log_{10}(1.78 \times 10^{-3}) = 2.75$

pH = **2.75**

Other than water, what are the major species present in solution A?

K_a is very small and the equilibrium lies almost completely to the left. The major species present are water and the undissociated acid: C_6H_5COOH

Solution B consists of a 0.050 M aqueous solution of ammonia, NH_3, at 25 °C. Calculate the pH of Solution B. The pK_a of NH_4^+ is 9.24.

NH_3 is a weak base so $[OH^-]$ must be calculated by considering the equilibrium:

	NH_3	H_2O	$\rightleftharpoons$	NH_4^+	OH^-
initial	**0.050**	**large**		**0**	**0**
change	$-y$	**negligible**		$+y$	$+y$
final	$0.050 - y$	**large**		y	y

The equilibrium constant K_b is given by:

ANSWER CONTINUES ON THE NEXT PAGE

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{y^2}{(0.050 - y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 – 9.24 = 4.76$

As $pK_b = 4.76$, $K_b = 10^{-4.76}$. K_b is very small so $0.050 – y \sim 0.050$ and hence:

$y^2 = 0.050 \times 10^{-4.76}$ or $y = 9.32 \times 10^{-4}$ M = $[OH^-]$

Hence, the pOH is given by:

$pOH = -\log_{10}[OH^-] = \log_{10}[9.32 \times 10^{-4}] = 3.03$

Finally, pH + pOH = 14.00 so

pH = 14.00 – 3.03 = 10.97

pH = **10.97**

Other than water, what are the major species present in solution B?

K_b is very small and the equilibrium lies almost completely to the left. The major species present are water and the unprotonated weak base: NH_3

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
5

Write the equation for the reaction that occurs when benzoic acid reacts with ammonia?

$C_6H_5COOH(aq) + NH_3(aq) \rightarrow C_6H_5COO^-(aq) + NH_4^+(aq)$

Write the expression for the equilibrium constant for the reaction of benzoic acid with ammonia?

$$K = \frac{[C_6H_5COO^-(aq)][NH_4^+(aq)]}{[C_6H_5COOH(aq)][NH_3(aq)]}$$

What is the value of the equilibrium constant for the reaction of benzoic acid with ammonia?

Multiplying the expression above by $[H^+]$ / $[H^+]$ gives:

$$K = \frac{[C_6H_5COO^-(aq)][NH_4^+(aq)]}{[C_6H_5COOH(aq)][NH_3(aq)]} \cdot \frac{[H^+(aq)]}{[H^+(aq)]}$$

$$= \frac{[H^+(aq)][C_6H_5COO^-(aq)]}{[C_6H_5COOH(aq)]} \cdot \frac{[NH_4^+(aq)]}{[NH_3(aq)][H^+(aq)]}$$

$$= K_a \times \frac{K_b}{[H^+(aq)][OH^-(aq)]} = \frac{K_a \times K_b}{K_w}$$

$$= \frac{(10^{-4.20}) \times 10^{-4.76}}{(10^{-14})} = 1.1 \times 10^5$$

Answer: **1.1×10^5**

What are the major species in the solution that results from dissolving equimolar amounts of benzoic acid and ammonia in water?

The equilibrium strong favours products so the major species are:

$C_6H_5CO_2^-(aq)$, $NH_4^+(aq)$, $H_2O(l)$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 4

- What is the pH of a 0.1 M solution of ammonium chloride, given the K_b for ammonia is 1.8×10^{-5}.

The ammonium ion, NH_4^+, is the conjugate acid of NH_3. The K_a of a conjugate acid and base are related by:

$$K_a \times K_b = 10^{-14.00}$$

Hence,

$$K_a = 10^{-14.00} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

NH_4^+ is a weak acid so $[H_3O^+]$ must be calculated using the equilibrium:

	NH_4^+	H_2O	$\rightleftharpoons$	NH_3	H_3O^+
initial	**0.1**	**large**		**0**	**0**
change	$-x$	**negligible**		$+x$	$+x$
final	$0.1 - x$	**large**		x	x

The equilibrium constant K_a is given by:

$$K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{(0.1-x)} = 5.6 \times 10^{-10}$$

As K_b is *very* small, $0.1 - x \sim 0.1$ and hence:

$$x^2 = 0.1 \times 5.6 \times 10^{-10} \text{ or } x = 7.5 \times 10^{-6} \text{ M} = [H_3O^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+] = \log_{10}[7.5 \times 10^{-6}] = 5.1$$

pH = **5.1**

What is the ratio of ammonia to ammonium ion in this solution?

From above, $[NH_3] = x$ M $= 7.5 \times 10^{-6}$ M and $[NH_4^+] = (0.1 - x)$ M = 0.1 M. Hence:

$$[NH_3] / [NH_4^+] = 7 \times 10^{-5}$$

Answer: **7×10^{-5}**

Marks 4

- What is the pH of a solution which is 0.10 M in both acetic acid and sodium acetate? The K_a for acetic acid is 1.8×10^{-5}.

By definition, $pK_a = -\log_{10}K_a$. Hence:

$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$

Using the Henderson-Hasselbalch equation, $pH = pK_a + \log \frac{[base]}{[acid]}$

With [base] = [acetate] = 0.10 M and [acid] = [acetic acid] = 0.10 M, therefore:

$pH = 4.74 + \log \frac{0.10}{0.10} = 4.74$

Answer: **4.74**

What is the final pH if 0.010 mol of HCl is added to 1.0 L of the above solution?

Using number of moles = concentration × volume, the number of moles of acetate and acetic acid originally present in 1.0 L of a 0.10 M solutions are:

$n_{acetate} = 0.10 \text{ mol L}^{-1} \times 1.0 \text{ L} = 0.10 \text{ mol}$
$n_{acetic\ acid} = 0.10 \text{ mol L}^{-1} \times 1.0 \text{ L} = 0.10 \text{ mol}$

The added H_3O^+ from HCl will react with the acetate to produce more acetic acid:

acetate + H_3O^+ → acetic acid + H_2O

Hence, after addition of HCl, the amount of acetate will decrease and the amount of acetic acid will increase:

$n_{acetate} = (0.10 - 0.010) \text{ mol} = 0.09 \text{ mol}$
$n_{acetic\ acid} = (0.10 + 0.010) \text{ mol} = 0.11 \text{ mol}$

Using concentration = number of moles / volume, their concentrations will become:

[acetate] = 0.09 mol / 1.0 L = 0.09 M
[acetic acid] = 0.11 mol / 1.0 L = 0.11 M

Using the Henderson-Hasselbalch equation,

$pH = 4.74 + \log \frac{0.09}{0.11} = 4.65$

Answer: **4.65**

Marks 7

- The pK_a of formic acid, HCO_2H, is 3.77. What is the pH of a 0.20 M solution of formic acid?

As formic acid is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	HCO_2H	H_2O	$\rightleftharpoons$	H_3O^+	HCO_2^-
initial	**0.20**	**large**		**0**	**0**
change	$-x$	**negligible**		$+x$	$+x$
final	$0.20 - x$	**large**		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = \frac{x^2}{0.20 - x}$$

As pK_a = $-\log_{10}K_a$, $K_a = 10^{-3.77}$ and is very small, $0.20 - x \sim 0.20$ and hence:

$$x^2 = 0.20 \times 10^{-3.77} \quad \text{or} \quad x = 5.8 \times 10^{-3}\ \text{M} = [H_3O^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(5.8 \times 10^{-3}) = 2.23$$

pH = **2.23**

Give the equation for the reaction of formic acid with solid sodium hydroxide.

$HCOOH(aq) + NaOH(s) \rightarrow HCO_2^-(aq) + Na^+(aq) + H_2O(l)$

Calculate the ratio of formate ion / formic acid required to give a buffer of pH 4.00.

Using the Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$4.00 = 3.77 + \log\frac{[HCO_2^-]}{[HCO_2H]}$$

$$\text{So, } \frac{[HCO_2^-]}{[HCO_2H]} = 10^{0.23} = 1.70$$

Answer: **1.70**

ANSWER CONTINUES ON THE NEXT PAGE

What amount (in mol) of sodium hydroxide must be added to 100.0 mL of 0.20 M HCO_2H to prepare a solution buffered at pH 4.00?

If the concentration of OH^- which is added is x M then this will react with HCO_2H to produce HCO_2^- so that:

$[HCO_2H] = (0.20 - x)$ M and
$[HCO_2^-] = x$ M

From above, if pH = 4.00, then $\frac{[HCO_2^-]}{[HCO_2H]} = 1.70$. Hence:

$$\frac{x}{0.20 - x} = 1.70 \quad \text{so } x = 0.13$$

To achieve $[OH^-(aq)] = 0.13$ mol L^{-1} in 100.0 mL, the number of moles of NaOH that must be added is:

number of moles = concentration × volume
= 0.13 mol L^{-1} × 0.1000 L = 0.013 mol

Answer: **0.013 mol**

Marks 8

- Solution A consists of a 1.00 M aqueous solution of HOCl at 25 °C. The pK_a of HOCl is 7.54. Calculate the pH of Solution A.

As HOCl is a weak acid, [H^+(aq)] must be calculated by considering the equilibrium:

	HOCl(aq)	$\rightleftharpoons$	OCl^-(aq)	H^+(aq)
initial	**1.00**		**0**	**0**
change	**-*x***		**+*x***	**+*x***
final	**1.00 – *x***		***x***	***x***

The equilibrium constant K_a is given by:

$$K_a = \frac{[OCl^-(aq)][H^+(aq)]}{[HOCl]} = \frac{x^2}{(1.00 - x)}$$

As pK_a = 7.54, $K_a = 10^{-7.54}$. K_a is very small so 1.00 – x ~ 1.00 and hence:

$x^2 = 1.00 \times 10^{-7.54}$ **or** x **= 0.000170 M = [H^+(aq)]**

Hence, the pH is given by:

pH = –log$_{10}$[H^+(aq)] = –log$_{10}$[0.000170] = 3.77

pH = **3.77**

At 25 °C, 1.00 L of Solution B consists of 74.4 g of NaOCl dissolved in water. Calculate the pH of Solution B.

The molar mass of NaOCl is:

molar mass = (22.99 (Na) + 16.00 (O) + 35.45 (Cl)) g mol^{-1} = 74.44 g mol^{-1}

The number of moles present in 74.4 g is therefore:

number of moles = mass / molar mass = (74.4 g) / (74.44 g mol^{-1}) = 0.999 mol

If this is present in 1.00 L, then [OCl^-] = 0.999 M.

As it is a weak base, [OH^-] must be calculated by considering the equilibrium:

	OCl^-	H_2O	$\rightleftharpoons$	HOCl	OH^-
initial	**0.999**	**large**		**0**	**0**
change	**-*y***	**negligible**		**+*y***	**+*y***
final	**0.999 – *y***	**large**		***y***	***y***

ANSWER CONTINUES ON THE NEXT PAGE

The equilibrium constant K_b is given by:

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]} = \frac{y^2}{(0.999 - y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 - 7.54 = 6.46$

As $pK_b = 6.46$, $K_b = 10^{--6.46}$. K_b is very small so $0.999 - y \sim 0.999$ and hence:

$y^2 = 0.999 \times 10^{-6.46}$ **or** $y = 0.000589$ **M** $= [OH^-]$

Hence, the pOH is given by:

$pOH = -\log_{10}[OH^-] = \log_{10}[0.000589] = 3.23$

Finally, pH + pOH = 14.00 so

$pH = 14.00 - 3.23 = 10.77$

pH = **10.77**

Solution B (0.40 L) is poured into Solution A (0.60 L). What amount of NaOH (in mol) must be added to give a solution, after equilibration, with a pH of 8.20?

The number of moles of HOCl in 0.60 L is:

number of moles = concentration × volume
= (1.00 mol L^{-1}) × (0.60 L) = 0.60 mol

The number of moles of OCl^- in 0.60 L is:

number of moles = concentration × volume
= (0.999 mol L^{-1}) × (0.40 L) = 0.40 mol

The added NaOH will react with the HOCl to form more OCl^-:

$HOCl(aq) + OH^-(aq) \rightarrow OCl^-(aq) + H_2O(l)$

If x mol of NaOH is added then this reaction will lead to:

number of moles of HOCl = $(0.60 - x)$ mol
number of moles of OCl^- = $(0.40 + x)$ mol

ANSWER CONTINUES ON THE NEXT PAGE

The solution has a volume of 1.00 L so:

[HOCl] = (0.60 – x) M and [OCl$^-$] = (0.40 + x) M

Using the Henderson-Hasselbalch equation with pH = 8.20:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{OCl^-(aq)}]}{[\mathrm{HOCl(aq)}]} = 7.54 + \log\frac{(0.40+x)}{(0.60-x)} = 8.20$$

$$\log\frac{(0.40+x)}{(0.60-x)} = 0.66 \quad \text{or} \quad \frac{(0.40+x)}{(0.60-x)} = 10^{0.66} = 4.57$$

Solving this gives x = 0.42 mol.

Answer: **0.42 mol**

Marks 4

- Citric acid, $C_6H_8O_7$, has three pK_a values: pK_{a1} = 3.13, pK_{a2} = 4.76 and pK_{a3} = 6.40. Explain, giving exact volumes and concentrations, how to make 1.0 L of a citrate-based buffer with pH 5.58.

The desired pH is equally close to pK_{a2} and pK_{a3} so the best buffer could use either of these equilibria. Using pK_{a3} corresponds to using the equlibrium:

$$HCit^{2-}(aq) \rightleftharpoons H^+(aq) + Cit^{3-}(aq)$$

Using the Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = 6.40 + \log\frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]}$$

At pH = 5.58,

$$\log\frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]} = (5.58 - 6.40) = -0.82$$

$$\frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]} = 0.15$$

As 1.0 L of the buffer is required,

$[Cit^{3-}] = n_{Cit3-} / 1.0$ M
$[HCit^{2-}] = n_{HCit2-} / 1.0$ M

So,

$$\frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]} = \frac{n_{\text{Cit}^{3-}}}{n_{\text{HCit}^{2-}}} = 0.15$$

There are *many* ways to construct the buffer to achieve this ratio when the acid and base are mixed.

If the two solutions have the same initial concentrations, then the ratio of the *volumes* used is 0.15. The volumes add up to 1000 mL:

volume of $HCit^{2-}$ = x L volume of Cit^{3-} = 1.0 – x L

So,

$$\frac{V_{\text{Cit}^{3-}}}{V_{\text{HCit}^{2-}}} = \frac{1.0 - x}{x} = 0.15$$

$x = 0.87$

Hence, 870 mL of $HCit^{2-}$ and 130 mL of Cit^{3-} are used.

Marks 7

- A 20.0 mL solution of nitrous acid (HNO_2, pK_a = 3.15) was titrated to its equivalence point with 24.8 mL of 0.020 M NaOH. What is the concentration of the HNO_2 solution?

The number of moles of OH^- added at the equivalence point is:

number of moles = concentration × volume
= (0.020 mol L^{-1})(0.0248 L) = 0.00050 mol

This must also be equal to the number of moles of HNO_2 present in 20.0 mL. Its concentration is therefore:

concentration = number of moles / volume
= (0.00050 mol) / (0.020 L) = 0.025 M

Answer: **0.025 M**

What was the pH at the start of the titration?

As HNO_2 is a weak acid, $[H^+(aq)]$ must be calculated by considering the equilibrium:

	$HNO_2(aq)$	$\rightleftharpoons$	$NO_2^-(aq)$	$H^+(aq)$
initial	0.025		0	0
change	$-x$		$+x$	$+x$
final	$0.025 - x$		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[HNO_2^-(aq)][H^+(aq)]}{[HNO_2]} = \frac{x^2}{(0.025 - x)}$$

As pK_a = 3.15, $K_a = 10^{-3.15}$. K_a is very small so $0.025 - x \sim 0.025$ and hence:

$x^2 = 0.025 \times 10^{-3.15}$ **or** $x = 0.0042$ **M = $[H^+(aq)]$**

Hence, the pH is given by:

pH = $-\log_{10}[H^+(aq)] = -\log_{10}[0.0042] = 2.38$

pH = **2.38**

ANSWER CONTINUES ON THE NEXT PAGE

What was the pH after (a) 12.4 mL and (b) 24.8 mL of the NaOH had been added?

When OH^- reacts with HNO_2, the amount of HNO_2 decreases *and* the amount of its conjugate base, NO_2^-, increases.

(a) 12.4 mL represents the half equivalence point. When this much OH^- is added, the amount of HNO_2 is reduced to half its initial value and an *equal* amount of NO_2^- is produced. With $[HNO_2(aq)] = [NO_2^-(aq)]$, the Henderson-Hasselbalch equation gives the pH as:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = 3.15 + \log(1) = 3.15$$

(b) 24.8 mL represents the equivalence point. When this much OH^- is added, the amount of HNO_2 is reduced zero and all of the initial HNO_2 is now present as NO_2^-. From above, the amount of NO_2^- is therefore 0.00050 mol. The total volume is now (20.0 + 24.8) mL = 44.8 mL so:

$$[NO_2^-(aq)] = (0.00050 \text{ mol}) / 0.0448 \text{ L}) = 0.0112 \text{ M}$$

As $NO_2^-(aq)$ is a weak base, the pH must be calculated using a reaction table:

	$NO_2^-(aq)$	$H_2O(l)$	$\rightleftharpoons$	$HNO_2(aq)$	$OH^-(aq)$
initial	**0.0112**	**large**		**0**	**0**
change	$-y$	**negligible**		$+y$	$+y$
final	$0.0112 - y$	**large**		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[HNO_2(aq)][OH^-(aq)]}{[NO_2^-(aq)]} = \frac{y^2}{(0.0112-y)}$$

For an acid and its conjugate base:

$$\mathrm{p}K_a + \mathrm{p}K_b = 14.00$$

$$\mathrm{p}K_b = 14.00 - 3.15 = 10.85$$

As $\mathrm{p}K_b = 10.85$, $K_b = 10^{-10.85}$. K_b is very small so $0.0112 - y \sim 0.0112$ and hence:

$y^2 = 0.0112 \times 10^{-10.85}$ **or** $y = 0.000000397 \text{ M} = [OH^-]$

Hence, the pOH is given by:

$$\mathrm{pOH} = -\log_{10}[OH^-] = \log_{10}[0.000000397] = 6.40$$

Finally, pH + pOH = 14.00 so pH = 14.00 – 6.40 = 7.60

(a) 12.4 mL: pH = **3.15**	(b) 24.8 mL: pH = **7.60**

ANSWER CONTINUES ON THE NEXT PAGE

Qualitatively, how would each of these three pH values be affected if 5 mL of water were added to the 20.00 mL of nitrous acid before beginning the titration?

The initial pH would increase slightly as the nitrous acid solution would be more dilute.

The pH at half-equivalence point would *not* change (as pH = pK_a).

The final pH would decrease slightly as the NO_2^- solution produced would also be more dilute.

Marks 8

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using $[Co(NH_3)_5(OH_2)]^{3+}$ as an example.

Co^{3+} has a high charge and is relatively small: it has a high charge density. When attached to water, it polarises the O–H bond in the aqua ligand.

This weakens the O–H bond causing the complex to be acidic in aqueous solution.

Solution A consists of a 0.10 M aqueous solution of $[Co(NH_3)_5(OH_2)](NO_3)_3$ at 25 °C. Calculate the pH of Solution A. The pK_a of $[Co(NH_3)_5(OH_2)]^{3+}$ = 5.69.

As $[Co(NH_3)_5(OH_2)]^{3+}$ is a weak acid, $[H_3O^+]$ must be calculated using a reaction table (acid = $[Co(NH_3)_5(OH_2)]^{3+}$ and base = $[Co(NH_3)_5(OH)]^{2+}$

	acid	H_2O	$\rightleftharpoons$	H_3O^+	base
initial	**0.10**	**large**		**0**	**0**
change	**-x**	**negligible**		**+x**	**+x**
final	**0.10 – x**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.10-x}$$

As pK_a = -log$_{10}K_a$, $K_a = 10^{-5.69}$ and is very small, 0.10 – x ~ 0.10 and hence:

$x^2 = 0.10 \times 10^{-5.69}$ or $x = 4.5 \times 10^{-4}$ M = $[H_3O^+]$

Hence, the pH is given by:

pH = $-\log_{10}[H_3O^+] = -\log_{10}(4.5 \times 10^{-4}) = 3.35$

pH = **3.35**

At 25 °C, 1.00 L of Solution B consists of 28.5 g of $[Co(NH_3)_5(OH)](NO_3)_2$ dissolved in water. Calculate the pH of Solution B.

The molar mass of $[Co(NH_3)_5(OH)](NO_3)_2$ is:

**molar mass = (58.93 (Co) + 7 × 14.01 (N) + 7 × 16.00 (O) + 16 × 1.008 (H)) g mol^{-1}
= 285.128 g mol^{-1}**

The number of moles present in 28.5 g is therefore:

number of moles = mass / molar mass = (28.5 g) / (285.128 g mol^{-1}) = 0.100 mol

ANSWER CONTINUES ON THE NEXT PAGE

If this is present in 1.00 L, then [base] = 0.100 M.

As it is a weak base, [OH$^-$] must be calculated by considering the equilibrium:

	base	H_2O	$\rightleftharpoons$	acid	OH^-
initial	0.100	large		0	0
change	$-y$	negligible		$+y$	$+y$
final	$0.100 - y$	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100 - y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 5.69 = 8.31$$

As $pK_b = 8.31$, $K_b = 10^{-8.31}$. K_b is very small so $0.100 - y \sim 0.100$ and hence:

$$y^2 = 0.100 \times 10^{-8.31} \text{ or } y = 2.21 \times 10^{-5} \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[2.21 \times 10^{-5}] = 4.65$$

Finally, pH + pOH = 14.00 so

$$\text{pH} = 14.00 - 4.65 = 9.35$$

pH = **9.35**

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a pH = 7.00.

The ratio of acid to conjugate base needed can be calculated using the Henderson-Hasselbalch equation, $\text{pH} = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$:

$$7.00 = 5.69 + \log\frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{1.31} = 20.4$$

As the base and acid have the same concentration, this is also the ratio of the volumes needed. As $V_{acid} + V_{base} = 1.0$ L and $V_{base} / V_{acid} = 20.4$:

$$V_{acid} = 0.047 \text{ L and } V_{base} = 0.953 \text{ L}$$

Marks 8

- Solution A consists of a 0.020 M aqueous solution of propionic acid, $C_3H_6O_2$, at 25 °C. Calculate the pH of Solution A. The pK_a of propionic acid is 4.87.

As $C_3H_6O_2$ is a weak acid, $[H^+]$ must be calculated by considering the equilibrium:

	$C_3H_6O_2$	$\rightleftharpoons$	$C_3H_5O_2^-$	H^+
initial	**0.020**		**0**	**0**
change	$-x$		$+x$	$+x$
final	$0.020 - x$		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[C_3H_5O_2^-][H^+]}{[C_3H_6O_2]} = \frac{x^2}{(0.020-x)}$$

As pK_a = 4.87, $K_a = 10^{-4.87}$. K_a is very small so $0.020 - x \sim 0.020$ and hence:

$$x^2 = 0.020 \times 10^{-4.87} \quad \text{or} \quad x = 0.000519 \text{ M} = [H^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H^+] = -\log_{10}[0.000519] = 3.28$$

Answer: **pH = 3.28**

At 25 °C, 1.00 L of Solution B consists of 2.24 g of potassium propionate ($KC_3H_5O_2$) dissolved in water. Calculate the pH of Solution B.

The molar mass of $KC_3H_5O_2$ is:

molar mass = (39.10 (K) + 3×12.01 (C) + 5×1.008 (H) + 2×16.00 (O)) g mol^{-1}
= 112.17 g mol-1

Thus, 2.24 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{2.24 \text{ g}}{112.17 \text{ g mol}^{-1}} = 0.0200 \text{ mol}$$

If this is dissolved in 1.0 L, $[C_3H_5O_2^-]_{initial}$ = 0.0200 M.

As $C_3H_5O_2^-$ is a weak base, $[C_3H_5O_2^-]$ must be calculated by considering the equilibrium:

ANSWER CONTINUES ON THE NEXT PAGE

	$C_3H_5O_2^-$	H_2O	$\rightleftharpoons$	$C_3H_6O_2$	OH^-
initial	**0.0200**	**large**		**0**	**0**
change	$-y$	**negligible**		$+y$	$+y$
final	$0.0200 - y$	**large**		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[C_3H_6O_2][OH^-]}{[C_3H_5O_2^-]} = \frac{y^2}{(0.0200 - y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 - 4.87 = 9.13$

As $pK_b = 9.13$, $K_b = 10^{--9.13}$. K_b is very small so $0.0200 - y \sim 0.0200$ and hence:

$y^2 = 0.0200 \times 10^{-9.13}$ **or** $y = 0.000000385$ **M** $= [OH^-]$

Hence, the pOH is given by:

$pOH = -\log_{10}[OH^-] = \log_{10}[0.000000385] = 5.41$

Finally, pH + pOH = 14.00 so

$pH = 14.00 - 5.41 = 8.59$

Answer: **pH = 8.59**

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

Combining the two solutions will double the overall volume, to 2.00 L. As a result, the concentration of both the acid and base will halve: [acid] = 0.010 M and [base] = 0.0100 M.

The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 4.87 + \log\frac{0.0100}{0.010} = 4.87$$

Answer: **pH = 4.87**

If you wanted to adjust the pH of Solution C to be exactly equal to 5.00, which component in the mixture would you need to increase in concentration?	**More base is needed: add $KC_3H_5O_2$**

Marks
7

- Solution A consists of a 0.020 M aqueous solution of aspirin (acetylsalicylic acid, $C_9H_8O_4$) at 25 °C. Calculate the pH of Solution A. The pK_a of aspirin is 3.52.

As $C_9H_8O_4$ is a weak acid, $[H^+]$ must be calculated by considering the equilibrium:

	$C_9H_8O_4$	$\rightleftharpoons$	$C_9H_7O_4^-$	H^+
initial	**0.020**		**0**	**0**
change	$-x$		$+x$	$+x$
final	$0.020 - x$		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[C_9H_7O_4^-][H^+]}{[C_9H_7O_{24}]} = \frac{x^2}{(0.020 - x)}$$

As pK_a = 3.52, $K_a = 10^{-3.52}$. K_a is very small so $0.020 - x \sim 0.020$ and hence:

$x^2 = 0.020 \times 10^{-3.52}$ **or** $x = 0.00246$ **M** $= [H^+]$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H^+] = -\log_{10}[0.00246] = 2.61$$

Answer: **2.61**

At 25 °C, 1.00 L of Solution B consists of 4.04 g of sodium acetylsalicylate ($NaC_9H_7O_4$) dissolved in water. Calculate the pH of Solution B.

The molar mass of $NaC_9H_7O_4$ is:

molar mass = (22.99 (Na) + 9×12.01 (C) + 7×1.008 (H) + 4×16.00 (O)) g mol^{-1}
= 202.136 g mol-1

Thus, 4.04 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{4.04 \text{ g}}{202.136 \text{ g mol}^{-1}} = 0.0200 \text{ mol}$$

If this is dissolved in 1.0 L, $[C_9H_7O_4^-]_{initial} = 0.0200$ M.

As $C_9H_7O_4^-$ is a weak base, $[C_9H_7O_4^-]$ must be calculated by considering the equilibrium:

ANSWER CONTINUES ON THE NEXT PAGE

	$C_9H_7O_4^-$	H_2O	$\rightleftharpoons$	$C_9H_8O_4$	OH^-
initial	**0.0200**	**large**		**0**	**0**
change	**-*y***	**negligible**		**+*y***	**+*y***
final	**0.0200 – *y***	**large**		***y***	***y***

The equilibrium constant K_b is given by:

$$K_b = \frac{[C_9H_8O_4][OH^-]}{[C_9H_7O_4^-]} = \frac{y^2}{(0.0200-y)}$$

For an acid and its conjugate base:

$\mathrm{p}K_a + \mathrm{p}K_b = 14.00$

$\mathrm{p}K_b = 14.00 - 3.52 = 10.48$

As $\mathrm{p}K_b = 10.48$, $K_b = 10^{-10.48}$. K_b is very small so $0.0200 - y \sim 0.0200$ and hence:

$y^2 = 0.0200 \times 10^{-10.48}$ **or** $y = 0.000000814$ **M** $= [OH^-]$

Hence, the pOH is given by:

$\mathrm{pOH} = -\log_{10}[OH^-] = \log_{10}[0.000000814] = 6.09$

Finally, pH + pOH = 14.00 so
pH = 14.00 – 6.09 = 7.91

Answer: **7.91**

Solution B (200.0 mL) is mixed with Solution A (400.0 mL) and water (200.0 mL) to give Solution C. Calculate the pH of Solution C after equilibration at 25 °C.

400.0 mL of solution A (the acid) contains:

number of moles = concentration × volume = $(0.0200 \text{ mol L}^{-1}) \times (0.4000 \text{ L})$
= 0.00800 mol

200.0 mL of solution B (the base) contains:

number of moles = concentration × volume = $(0.0200 \text{ mol L}^{-1}) \times (0.2000 \text{ L})$
= 0.00400 mol

The final solution has a total volume of (200.0 + 400.0 + 200.0) mL = 800.0 mL.

The concentrations of acid and base in the final solution are:

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$$\textbf{concentration of acid} = \frac{\textbf{number of moles}}{\textbf{volume}} = \frac{\textbf{0.00800 mol}}{\textbf{0.8000 L}} = \textbf{0.0100 M}$$

$$\textbf{concentration of base} = \frac{\textbf{number of moles}}{\textbf{volume}} = \frac{\textbf{0.00400 mol}}{\textbf{0.8000 L}} = \textbf{0.00500 M}$$

The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation:

$$\mathbf{pH = p}\boldsymbol{K}_{\mathbf{a}} + \mathbf{log}\frac{[\mathbf{base}]}{[\mathbf{acid}]} = \mathbf{3.52 + log}\frac{\mathbf{0.00500}}{\mathbf{0.0100}} = \mathbf{3.22}$$

Answer: **3.22**

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?	**To lower the pH, more acid is required: solution A**

Marks

- Calculate the pH of a 0.20 M solution of potassium fluoride. The pK_a of HF is 3.17. **3**

As F^- is a weak base, $[OH^-]$ must be calculated by considering the equilibrium:

	F^-	H_2O	$\rightleftharpoons$	OH^-	HF
initial	**0.20**	**large**		**0**	**0**
change	**-*x***	**negligible**		**+*x***	**+*x***
final	**0.20 – *x***	**large**		***x***	***x***

The equilibrium constant K_b is given by:

$$K_b = \frac{[OH^-][HF]}{[F^-]} = \frac{x^2}{0.20 - x}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 3.17 = 10.83$$

As $pK_b = 10.83$, $K_b = 10^{-10.83}$. K_b is very small so $0.20 - x \sim 0.20$ and hence:

$$x^2 = 0.20 \times 10^{-10.83} \quad \text{or} \quad x = 0.0000017 \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = -\log_{10}[0.0000017] = 5.76$$

Finally, pH + pOH = 14.00 so

$$pH = 14.00 - 5.76 = 8.24$$

Answer: **pH = 8.24**

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the pK_a of iodic acid, HIO_3, is 0.79, how many moles of sodium iodate, $NaIO_3$, would need to be added to this solution to raise its pH to 2.00? **3**

Using pH = $-\log_{10}[H^+(aq)]$,

$$[H^+(aq)]_{initial} = 10^{-1.22} = 0.060 \text{ M}$$

$$[H^+(aq)]_{final} = 10^{-2.00} = 0.010 \text{ M}$$

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The change of (0.060 – 0.010 M) = 0.050 M occurs due to the reaction with IO_3^-(aq) to produce HIO_3(aq). If [IO_3^-(aq)] = *x*, the reaction table is:

	H^+(aq) +	IO_3^-(aq)	$\rightleftharpoons$	HIO_3(aq)
initial	**0.060**	***x***		**0**
change	**-0.050**	**-0.050**		**+0.050**
final	**0.010**	***x* – 0.050**		**0.050**

As pK_a = 0.79 = -log$_{10}K_a$:

$$K_a = \frac{[H^+(aq)][IO_3^-(aq)]}{[HIO_3(aq)]} = \frac{(0.010)\times(x-0.050)}{0.050} = 10^{-0.79}$$

Thus, *x* = 0.86 M = [IO_3^-(aq)]$_{initial}$. This concentration corresponds to a 300.0 mL solution so the number of moles that have been added is:

number of moles = concentration × volume
= (0.86 M) × (0.3000 L) = 0.26 mol

Answer: **0.26 mol**

Marks 5

- Buffers made of mixtures of $H_2PO_4^-$ and HPO_4^{2-} are used to control the pH of soft drinks. What is the pH of a 350 mL drink containing 6.0 g of NaH_2PO_4 and 4.0 g of Na_2HPO_4?

  For phosphoric acid, H_3PO_4, pK_{a1} = 2.15, pK_{a2} = 7.20 and pK_{a3} = 12.38.

The formula masses of NaH_2PO_4 and Na_2HPO_4 are:

$$\boldsymbol{M(NaH_2PO_4) = (22.99\ (Na) + 2\times1.008\ (H) + 30.97\ (P) + 4\times16.00\ (O))\ g\ mol^{-1} = 119.976\ g\ mol^{-1}}$$

$$\boldsymbol{M(Na_2HPO_4) = (2\times22.99\ (Na) + 1.008\ (H) + 30.97\ (P) + 4\times16.00\ (O))\ g\ mol^{-1} = 141.958\ g\ mol^{-1}}$$

Hence, the number of moles of each present are:

$$\boldsymbol{n(NaH_2PO_4) = \text{mass / formula mass} = 6.0\ g / 119.976\ g\ mol^{-1} = 0.050\ mol}$$

$$\boldsymbol{n(Na_2HPO_4) = 4.0 / 141.958\ g\ mol^{-1} = 0.028\ mol}$$

As both are present in the same solution, the ratio of their concentrations is the same as the ratio of these amounts. There is no need to calculate the concentrations, although it does not change the answer.

The relevant equilibrium for this buffer is

$$\boldsymbol{H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)}$$

This corresponds to the second ionization of H_3PO_4 so pK_{a2} is used with the base acid being $H_2PO_4^-$ (from NaH_2PO_4) and the base being HPO_4^{2-} (from Na_2HPO_4). The pH can be calculated using the Henderson-Hasselbalch equation:

$$\boldsymbol{pH = pK_a + \log([base]/[acid]) = pK_{a2} + \log([HPO_4^{2-}]/[H_2PO_4^-]) = 7.20 + \log(0.028/0.050) = 6.95}$$

Briefly describe how this buffer system functions. Use equations where appropriate.

The buffer contains an acid ($H_2PO_4^-$) and its conjugate base (HPO_4^{2-}) and is able to resist changes in pH when H^+ or OH^- is added.

If H^+ is added, the base reacts with it to remove it according to the equilibrium:

$$\boldsymbol{HPO_4^{2-}(aq) + H^+(aq) \rightleftharpoons H_2PO_4^-(aq)}$$

ANSWER CONTINUES ON THE NEXT PAGE

If OH^- is added, the acid reacts with it to remove it according to the equilibrium:

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^-(aq) + H_2O(l)$$

As long the amounts of the acid and base present are not exceeded, the changes in pH will be small.

Is this buffer better able to resist changes in pH following the addition of acid or of base? Explain your answer.

Maximum buffering occurs when equal amounts of base and acid are present. This buffer has less base than acid present. As a result, it is less able to resist cope with the addition of H^+.

Larger changes in pH result from the addition of acid.

Marks 8

- Solution A consists of a 0.20 M aqueous solution of formic acid, HCOOH, at 25 °C. Calculate the pH of Solution A. The pK_a of HCOOH is 3.75.

The reaction table is:

	HCOOH(aq)	$H_2O(l)$	$\rightleftharpoons$	$HCOO^-(aq)$	$H_3O^+(aq)$
start	**0.20**	**large**		**0**	**0**
change	**-x**	**-x**		**+x**	**+x**
equilibrium	**0.20-x**	**large**		**x**	**x**

As $pK_a = -\log_{10}(K_a) = 3.75$, $K_a = 10^{-3.75}$ and:

$$K_a = \frac{[HCOO^-(aq)][H_3O^+(aq)]}{[HCOOH(aq)]} = \frac{(x)(x)}{(0.20 - x)} = \frac{x^2}{(0.20 - x)} = 10^{-3.75}$$

As K_a is very small, x is tiny and 0.20 – x ~ x. Hence,

$$K_a \sim \frac{x^2}{(0.20)} = 10^{-3.75} \quad \text{or } x^2 = (0.20) \times (10^{-3.75}) \text{ so } x = [H_3O^+(aq)] = 6.0 \times 10^{-4}\text{ M}$$

As $pH = -\log_{10}([H_3O^+(aq)]$:

$pH = -\log_{10}(6.0 \times 10^{-4}) = 2.22$

Answer: **2.22**

ANSWER CONTINUES ON NEXT PAGE

At 25 °C, 1.00 L of Solution B consists of 13.6 g of sodium formate, $NaHCO_2$, dissolved in water. Calculate the pH of Solution B.

The molar mass of $NaHCO_2$ is

(22.99 (Na)) + (1.008 (H)) + (12.01 (C)) + (2 × 16.00 (O)) = 68.008

The solution thus contains $\frac{\text{mass}}{\text{molar mass}} = \frac{13.6}{68.008} = 0.200\,\text{mol}$

As this is dissolved in 1.00 L, the concentration is 0.200 M. The reaction table is now:

	$HCOO^-(aq)$	$H_2O(l)$	$\rightleftharpoons$	$HCOOH(aq)$	$OH^-(aq)$
start	0.200	large		0	0
change	-y	-y		+y	+y
equilibrium	0.200-y	large		y	y

As $pK_a + pK_b = 14.00$, $pK_b = 14.00 - 3.75 = 10.25$, $K_b = 10^{-10.25}$ and:

$$K_b = \frac{[HCOOH(aq)][OH^-(aq)]}{[HCOO^-(aq)]} = \frac{(y)(y)}{(0.200-y)} = \frac{y^2}{(0.200-y)} = 10^{-10.25}$$

Again K_b is very small, y is tiny and 0.200 – y ~ y. Hence, $y^2 = (0.200) \times (10^{-10.25})$

so $y = [OH^-(aq)] = 3.35 \times 10^{-6}$ M and $pOH = -\log_{10}([OH^-(aq)] = 5.47$

As pH + pOH = 14.00, pH = 14.00 – 5.47 = 8.52

Answer: **8.52**

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

After mixing solution A (1.00 L) and solution B (1.00 L), the total volume is 2.00 L. This halves the concentration of the both the acid and the base.

$$[\text{acid}] = \frac{0.20}{2} = 0.10\text{ M and [base]} = \frac{0.200}{2} = 0.100\text{ M}$$

Solution C contains a weak acid (HCOOH) and its conjugate base ($HCOO^-$). It is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation can be used:

$$pH = pK_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.75 + \log_{10}\left(\frac{0.100}{0.10}\right) = 3.75$$

Answer: **3.75**

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

[HCOOH] would be increased (the acid)

Marks
4

- Buffer systems are frequently used in chemistry. What is a buffer system and how does it function? Use equations where appropriate.

Buffer systems resist changes in pH: a buffer will maintain a relatively constant pH when acid or base is added.

They consist of mixtures of a weak acid (HA) and its conjugate base (A^-) in high concentration.

If acid is added, the system can respond by removing it using A^-:

$$\mathbf{H^+(aq) + A^-(aq) \rightarrow HA(aq)}$$

If base is added, the system can respond by removing it using HA:

$$\mathbf{OH^-(aq) + HA(aq) \rightarrow H_2O(l) + A^-(aq)}$$

What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 4.00? The K_a of acetic acid is 1.8×10^{-5} M.

The pH of a buffer system made from a mixture of the weak acid (HA) and its conjugate base (A^-) is described by the equation:

$$\mathbf{pH = pK_a + \log\frac{[A^-(aq)]}{[HA(aq)]}}$$

For acetic acid, $K_a = 1.8 \times 10^{-5}$ or $pK_a = -\log(K_a) = 4.74$. To obtain pH = 4.00:

$$\mathbf{4.00 = 4.74 + \log\frac{[A^-(aq)]}{[HA(aq)]} \text{ and so } \frac{[A^-(aq)]}{[HA(aq)]} = 10^{-0.74} = 0.18}$$

Alternatively, $\mathbf{\frac{[HA(aq)]}{[A^-(aq)]} = \frac{1}{0.18} = 5.56}$

Answer: **5.56: 1**

Marks 8

- Solution A consists of a 0.25 M aqueous solution of hydrazoic acid, HN_3, at 25 °C. Calculate the pH of Solution A. The pK_a of HN_3 is 4.63.

As $pK_a = -\log(K_a) = 4.63$, $K_a = 10^{-4.63} = 2.34 \times 10^{-5}$. The reaction table is:

	$HN_3(aq)$	$\rightleftharpoons$	$H^+(aq)$	$N_3^-(aq)$
t = 0	**0.25**		**0**	**0**
change	**-x**		**+x**	**+x**
equilibrium	**0.25 – x**		**x**	**x**

Hence, $K_a = \dfrac{[H^+(aq)][N_3^-(aq)]}{[HN_3]} = \dfrac{(x)(x)}{(0.25\text{-}x)} = \dfrac{x^2}{(0.25\text{-}x)} = 2.34 \times 10^{-5}$

As K_a is very small, very little HN_3 dissociates and x is tiny so (0.25 – x) ~ 0.25

Hence, $\dfrac{x^2}{(0.25)} = 2.34 \times 10^{-5}$ **or** $x = [H^+(aq)] = 2.42 \times 10^{-3}$ **M**

As $pH = -\log[H^+(aq)]$:

$pH = -\log(2.42 \times 10^{-3}) = 2.62$

Answer: **2.62**

(ANSWER CONTINUES ON THE NEXT PAGE)

At 25 °C, 1.00 L of Solution B consists of 13.0 g of sodium azide (NaN_3) dissolved in water. Calculate the pH of Solution B.

The relevant reaction is now: $N_3^-(aq) + H_2O(l) \rightleftharpoons HN_3(aq) + OH^-(aq)$

As N_3^- is the conjugate base of HN_3, the equilibrium constant for this reaction is K_b where $pK_a + pK_b = 14.00$.

Hence, using pK_a from above:

$$pK_b = 14.00 - 4.63 = 9.37 \text{ or } K_b = 10^{-9.37} = 4.27 \times 10^{-10}.$$

The molar mass of NaN_3 is (22.99 (Na)) + (3 × 14.01 (N)) = 65.02. The number of moles in 13.0 g is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{13.0}{65.02} = 0.200 \text{ mol}$$

As this is dissolved in 1.00 L, $[N_3^-(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.200}{1.00} = 0.200\,M$

The relevant reaction table is now:

	$N_3^-(aq)$	$H_2O(l)$	$\rightleftharpoons$	$HN_3(aq)$	$OH^-(aq)$
t = 0	0.200			0	0
change	-x			+x	+x
equilibrium	0.200 – x			x	x

The equilibrium constant $K_b = \frac{[NH_3(aq)][OH^-(aq)]}{[N_3^-(aq)]} = \frac{(x)(x)}{(0.200\text{-}x)} = \frac{x^2}{(0.200\text{-}x)}$

K_b is small so the amount of $N_3^-(aq)$ which is protonated is tiny and hence 0.200 – x ~ 0.200.

Hence, $\frac{x^2}{(0.200)} = 4.27\times10^{-10}$ **or** $x = [OH^-(aq)] = 9.24 \times 10^{-6}$ **M**

As pOH = -log[OH(aq)] = -log(9.24 × 10^{-6}) = 5.03

As pH + pOH = 14:

pH = 14 – 5.03 = 8.97

Answer: **8.97**

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

Solution C is a buffer system as it contains both a weak acid (HN_3) and its conjugate base (N_3^-(aq). The pH can be obtained from the Henderson-Hasselbalch equation:

$$\mathbf{pH = pK_a + \log\frac{[A^-(aq)]}{[HA(aq)]}}$$

Using pK_a = 4.63, [HA(aq)] = [HN_3(aq)] = 0.25 M and [A^-(aq)] = [N_3^-(aq)] = 0.200 M:

$$\mathbf{pH = (4.63) + \log\frac{(0.200)}{(0.25)} = 4.53}$$

Answer: **4.53**

If you wanted to adjust the pH of Solution C to be exactly equal to 4.00, which component in the mixture would you need to increase in concentration?

To lower the pH, the acid concentration (HN_3) is increased

Marks 6

- Calculate the pH of a 0.200 M solution of acetic acid, CH_3COOH, at 25 ºC. (The pK_a of acetic acid is 4.76).

As acetic acid is a weak acid, $[H_3O^+]$ must be calculated:

	CH_3COOH	H_2O	$\rightleftharpoons$	H_3O^+	CH_3COO^-
initial	**0.200**	**large**		**0**	**0**
change	**$-x$**	**negligible**		**$+x$**	**$+x$**
final	**$0.200 - x$**	**large**		**x**	**x**

The equilibrium constant K_a is given by: $K_a = \dfrac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \dfrac{x^2}{0.2 - x}$

As pK_a = 4.76 = $-\log_{10}K_a$ so $K_a = 10^{-4.76}$. As K_a is very small, $0.200 - x \sim 0.200$ and hence:

$x^2 = 0.200 \times 10^{-4.76}$ **or** $x = 0.0019$ **M** $= [H_3O^+]$

Hence, the pH is given by:

$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}[0.0019] = 2.73$

pH = **2.73**

Solid sodium acetate, $NaCH_3CO_2$, (0.15 mol) was dissolved in 0.500 L of 0.200 M acetic acid and the volume made up to 750 mL with water. What is the pH of the resulting solution?

The solution contains a weak acid (acetic acid) and its conjugate base (acetate). 0.15 mol of acetate is present in 750 mL so its concentration is:

[base] = (0.15 mol) / (0.750 L) = 0.20 M

500 mL of 0.200 M acid contains (0.5 L) × (0.200 M) = 0.100 mol. The concentration of the acid in 750 mL is therefore:

[acid] = (0.100 mol) / (0.750 L) = 0.133 M

The Henderson-Hasselbalch equation can be used for this buffer:

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 4.76 + \log_{10}\left(\frac{0.20}{0.133}\right) = 4.94$$

pH = **4.94**

ANSWER CONTINUES ON THE NEXT PAGE

How much more $NaCH_3CO_2$ needs to be dissolved in the above solution to give a final pH of 5.00?

A pH of 5.00 will be obtained when:

$$\mathbf{pH = 4.76 + \log_{10}\left(\frac{[base]}{[acid]}\right) = 5.00 \text{ or } \log_{10}\left(\frac{[base]}{[acid]}\right) = 0.24}$$

Hence,

$$\mathbf{\left(\frac{[base]}{[acid]}\right) = 10^{0.24} = 1.74 \text{ or } [base] = 1.74 \times [acid] = 1.74 \times 0.133 = 0.232\ M}$$

The number of moles of base in 750 mL is therefore (0.232 M) × (0.750 L) = 0.174 mol.

As 0.15 mol was added originally, an additional (0.17 – 0.15) = 0.02 mol is required.

Answer: **0.02 mol**