- Phenylketonuria is an inherited disorder in which phenylacetic acid, $C_6H_5CH_2COOH$, (simplified here to HPAc) accumulates in the blood. A study of the acid shows that the pH of a 0.12 M HPAc solution is 2.60. What is the pK_a of phenylacetic acid?

3

As HPAc is a weak acid, the equilibrium for its dissociation can be studied using an 'ICE' table:

	HPAc	$\rightleftharpoons$	PAc$^-$	H$^+$
initial	0.12		0	0
change	-x		+x	+x
final	0.12 – x		x	x

By definition, pH = -log$_{10}$[H$^+$(aq)] so [H$^+$(aq)] = 10$^{-2.60}$ M. From the reaction table, x = [H$^+$(aq)]$_{eq}$ so:

   [HPAc]$_{eq}$ = 0.12 – x = (0.12 – 10$^{-2.60}$) M = 0.12 M (to 2 s.f.)
   [H$^+$(aq)]$_{eq}$ = x = 10$^{-2.60}$ M
   [PAc$^-$(aq)]$_{eq}$ = x = 10$^{-2.60}$ M

The equilibrium constant K_a is given by:

$$K_a = \frac{[HPac^-][H^+]}{[HPAc]} = \frac{(10^{-2.60})(10^{-2.60})}{(0.12)} = 5.26 \times 10^{-5}$$

By definition, pK_a = -log$_{10}K_a$ so:

   pK_a = -log$_{10}$(5.26 × 10^{-5}) = 4.28

Answer: **4.28**

- A sample of hydrofluoric acid (0.10 M, 25.0 mL) is titrated with 0.10 M NaOH. The pK_a of hydrofluoric acid, HF, is 3.17. Calculate the pH at the following four points.

before any NaOH is added

At this point, the solution contains only a weak acid. As HF is a weak acid, $[H^+]$ must be calculated by considering the equilibrium:

	HF	⇌	F$^-$	H$^+$
initial	0.10		0	0
change	-x		+x	+x
final	0.10 – x		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[F^-][H^+]}{[HF]} = \frac{x^2}{(0.10-x)}$$

As pK_a = 3.17, $K_a = 10^{-3.17}$. K_a is very small so 0.10 – x ~ 0.10 and hence:

$$x^2 = 0.10 \times 10^{-3.17} \quad \text{or} \quad x = 0.00822 \text{ M} = [H\cdot]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H\cdot] = -\log_{10}[0.00822] = 2.09$$

pH = **2.09**

when half of the HF has been neutralised

At this point, half of the original HF has been converted to its conjugate base F$^-$. The pH can be calculated using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\textbf{base}]}{[\textbf{acid}]} = 3.17 + \log\frac{[F^-]}{[HF]} = 3.17 + + \log(1) = 3.17$$

pH = **3.17**

at the equivalence point

At this point, all of the original HF has been converted to F$^-$. The number of moles of HF originally present is:

number of moles of HF = concentration × volume
= (0.10 mol L^{-1}) × (0.025 L) = 0.0025 mol

This is equal to the amount of F$^-$ present at equivalence. As 25.0 mL of NaOH has been added at this point, the total volume is now (25.0 + 25.0) mL = 50.0 mL. The concentration of F$^-$ is therefore:

ANSWER CONTINUES ON THE NEXT PAGE

As F⁻ is a weak base. [OH⁻] must be calculated using a reaction table.

	F⁻	**H₂O**	⇌	**HF**	**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:

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{y^2}{(0.050-y)}$$

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 0.050 – y ~ 0.050 and hence:

$$y^2 = 0.050 \times 10^{-10.83} \text{ or } y = 8.59 \times 10^{-7} \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = \log_{10}[8.59 \times 10^{-7}] = 6.07$$

Finally, pH + pOH = 14.00 so

$$pH = 14.00 - 6.07 = 7.93$$

pH = **7.93**

after the addition of 37.5 mL of NaOH

This volume of 0.10 M NaOH contains

> **number of moles of NaOH = concentration × volume**
> **= (0.10 mol L⁻¹) × (0.0375 L) = 0.00375 mol**

From above, there was original 0.0025 mol of HF present so the excess of OH⁻ is:

excess moles of OH⁻ = (0.00375 – 0.0025) mol = 0.00125 mol

This is present in a total volume of (25.0 + 37.5) mL = 62.5 mL, so its concentration is:

ANSWER CONTINUES ON THE NEXT PAGE

$[OH^-]$ = number of moles / volume
= (0.00125 mol) / (0.0625 L) = 0.020 mol L^{-1}

Hence,

pOH -= $-\log_{10}[OH^-]$ = $-\log_{10}(0.020)$ = 1.70

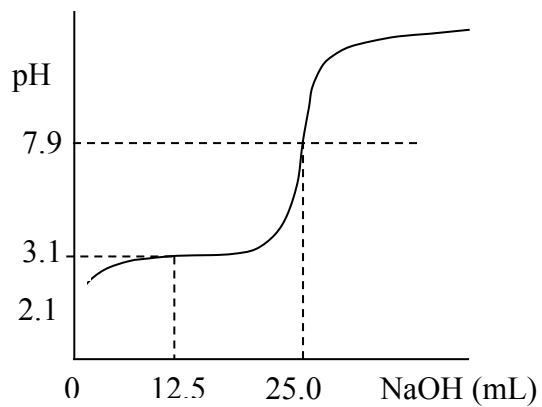Lastly, pH = 14.00 – pOH:

pH = 14.00 – 1.70 = 12.30

pH = **12.30**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Sketch the titration curve.

**Marks
2**

Putting the 4 points from 2014-N-7 together gives the titration curve:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

	Marks
• Explain the following terms or concept.	**1**

Lewis base

A species that can form a bond by donating a lone pair of electrons, *e.g.* **H_2O.**

• What amount of NaOH (in mol) needs to be added to 250 mL of 0.10 M acetic acid to give a solution with a pH of 5.00? The pK_a of acetic acid is 4.76.

If the concentration of OH⁻ which is added is x M then this will react with acetic acid to produce its conjugate base, acetate, so that:

> **[acid] = (0.10 – x) M and**
> **[base] = x M**

The Henderson-Hasselbalch equation can be used to work out the ratio of these needed for a pH of 5.00:

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

$$5.00 = 4.76 + \log\frac{x}{0.10 - x}$$

Hence:

$$\frac{x}{0.10 - x} = 10^{0.24} \quad \text{so } x = 0.0634$$

To achieve [OH⁻(aq)] = 0.0634 mol L⁻¹ in 250 mL, the number of moles of NaOH that must be added is:

> **number of moles = concentration × volume**
> **= 0.0634 mol L⁻¹ × 0.250 L = 0.016 mol**

Answer: **0.016 mol**

	Marks
• Explain the following terms or concepts.	**1**

Isoelectric point

The pH at which a protein or amino acid has no net charge, *i.e.* it contains equal amounts of positive and negative charges.

Marks
3

- Phenylketonuria is an inherited disorder in which phenylacetic acid, $C_6H_5CH_2COOH$, (simplified here to HPAc) accumulates in the blood. If untreated, it can cause mental retardation and death. A study of the acid shows that the pH of a 0.12 M HPAc solution is 2.60. What is the pK_a of phenylacetic acid?

As HPAc is a weak acid, the equilibrium for its dissociation can be studied using an 'ICE' table:

	HPAc	$\rightleftharpoons$	PAc$^-$	H$^+$
initial	**0.12**		**0**	**0**
change	**-x**		**+x**	**+x**
final	**0.12 – x**		**x**	**x**

By definition, pH = -log$_{10}$[H$^+$(aq)] so [H$^+$(aq)] = $10^{-2.60}$ M. From the reaction table, x = [H$^+$(aq)]$_{eq}$ so:

[HPAc]$_{eq}$ = 0.12 – x = (0.12 – $10^{-2.60}$) M = 0.12 M (to 2 s.f.)
[H$^+$(aq)]$_{eq}$ = x = $10^{-2.60}$ M
[PAc$^-$(aq)]$_{eq}$ = x = $10^{-2.60}$ M

The equilibrium constant K_a is given by:

$$K_a = \frac{[\text{HPac}^-][\text{H}^+]}{[\text{HPAc}]} = \frac{(10^{-2.60})(10^{-2.60})}{(0.12)} = 5.26 \times 10^{-5}$$

By definition, pK_a = -log$_{10}K_a$ so:

pK_a = -log$_{10}$(5.26 × 10^{-5}) = 4.28

Answer: **4.28**

Marks
4

- Buffer 1 is a solution containing 0.08 M NH_4Cl and 0.12 M NH_3. Buffer 2 is a solution containing 0.15 M NH_4Cl and 0.05 M NH_3. The acid dissociation constant of the ammonium ion is 5.50×10^{-10}. What are the pH values of each of the buffer solutions?

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

$pK_a = -\log_{10}(5.50 \times 10^{-10}) = 9.26$

Using the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\frac{[base]}{[acid]} = 9.290 + \log\frac{[NH_3]}{[NH_3Cl]}$$

For buffer 1:

$$pH = 9.26 + \log\frac{0.12}{0.08} = 9.44$$

For buffer 2:

$$pH = 9.26 + \log\frac{0.05}{0.15} = 8.78$$

| Buffer 1 pH = **9.44**	Buffer 2 pH = **8.78**

Which buffer is better able to maintain a steady pH on the addition of small amounts of both a strong acid and strong base? Explain.

Buffer 1 is better able to maintain a steady pH because its pH is closer to the pK_a of NH_4^+. This is because it has relatively high concentrations of both NH_4^+ and NH_3 which can react with any added OH^- or H^+ respectively.

**Marks
4**

- Explain the role played by the lungs and the kidneys in maintaining blood pH at a constant value of 7.4.

The most important buffer system in the blood is the hydrogencarbonate / carbonic acid system:

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$$
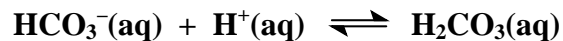
If the amount of H^+ exceeds the capacity of the buffering system (*e.g.* during vigorous exercise), the lungs can help by removing $CO_2(g)$. CO_2 is linked to the buffer system via

$$H_2CO_3(aq) \rightleftharpoons H_2O + CO_2(g)$$
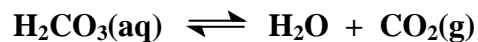
Thus removal of $CO_2(g)$ will shift the HCO_3^-/H_2CO_3 equilibrium to the right, reducing H^+.

If the blood becomes too basic, the kidneys can help by excreting HCO_3^-. This will shift the buffer equilibrium to the left, producing more H^+.

- Sketch the titration curve (pH against mL of added base) when 25.0 mL of 0.10 M hydrofluoric acid (HF) with a pK_a of 3.17 is titrated with 0.10 M NaOH. Calculate the pH at the following four points:
    (i) before any NaOH is added;
    (ii) when half of the HF has been neutralised;
    (iii) at the equivalence point; and
    (iv) 50% beyond the equivalence point, *i.e.* when 1.5 times the equivalence volume has been added.

(i) At this point, the solution contains only a weak acid.

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

	HF	⇌	F$^-$	H$^+$
initial	0.10		0	0
change	-x		+x	+x
final	0.10 – x		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[F^-][H^+]}{[HF]} = \frac{x^2}{(0.10-x)}$$

As pK_a = 3.17, $K_a = 10^{-3.17}$. K_a is very small so 0.10 – x ~ 0.10 and hence:

$$x^2 = 0.10 \times 10^{-3.17} \quad \text{or} \quad x = 0.00822 \text{ M} = [H^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H^+] = -\log_{10}[0.00822] = 2.09$$

(ii) At this point, half of the original HF has been converted to its conjugate base F$^-$. The pH can be calculated using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 3.17 + \log\frac{[F^-]}{[HF]} = 3.17 + + \log(1) = 3.17$$

(iii) At this point, all of the original HF has been converted to F$^-$. The number of moles of HF originally present is:

number of moles of HF = concentration × volume
= (0.10 mol L^{-1}) × (0.025 L) = 0.0025 mol

This is equal to the amount of F$^-$ present at equivalence. As 25.0 mL of NaOH has been added at this point, the total volume is now (25.0 + 25.0) mL = 50.0 mL. The concentration of F$^-$ is therefore:

$[F^-]$ = number of moles / volume = (0.0025 mol) / (0.050 L) = 0.050 mol L^{-1}

As F⁻ is a weak base. [OH⁻] must be calculated using a reaction table.

	F⁻	H₂O	⇌	HF	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:

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{y^2}{(0.050-y)}$$

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 $0.050 - y \sim 0.050$ and hence:

$$y^2 = 0.050 \times 10^{-10.83} \text{ or } y = 8.59 \times 10^{-7} \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = \log_{10}[8.59 \times 10^{-7}] = 6.07$$

Finally, pH + pOH = 14.00 so

$$pH = 14.00 - 6.07 = 7.93$$

(iv) At this point, there is excess strong base present. Addition of 1.5 times the equivalence volume corresponds to addition of (1.5×25.0) mL = 37.5 mL. This volume of 0.10 M NaOH contains

number of moles of NaOH = concentration × volume
$$= (0.10 \text{ mol L}^{-1}) \times (0.0375 \text{ L}) = 0.00375 \text{ mol}$$

From (iii), there was original 0.0025 mol of HF present so the excess of OH⁻ is:

excess moles of OH⁻ = (0.00375 – 0.0025) mol = 0.00125 mol

This is present in a total volume of (25.0 + 37.5) mL = 62.5 mL, so its concentration is:

[OH⁻] = number of moles / volume
$$= (0.00125 \text{ mol}) / (0.0625 \text{ L}) = 0.020 \text{ mol L}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

Hence,

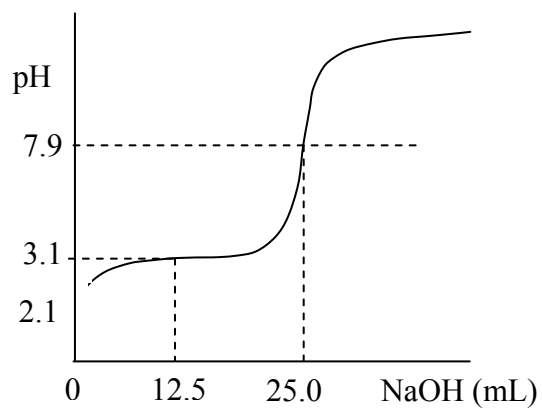$$pOH -= -\log_{10}[OH^-] = -\log_{10}(0.020) = 1.70$$

Lastly, pH = 14.00 – pOH:

$$pH = 14.00 - 1.70 = 12.30$$

Putting these 4 points together gives the titration curve:

Marks
3

- Tris(hydroxymethyl)aminomethane is commonly used to make buffer solutions. It has a base ionisation constant of 1.26×10^{-6}. What is the pH of a 0.05 M aqueous solution of this compound?

The base ionization constant refers to the reaction below for which the reaction table is:

	tris	+ H$_2$O	⇌	trisH$^+$	OH$^-$
Initial	**0.05**			**0**	**0**
Change	**-x**			**+x**	**+x**
Equilibrium	**0.05 - x**			**x**	**x**

As pK_b = -log$_{10}K_b$, at equilibrium,

$$K_b = \frac{[\text{trisH}^+][\text{OH}^-]}{[\text{tris}]} = \frac{(x)(x)}{(0.05-x)} = \frac{x^2}{(0.05-x)} = 1.26 \times 10^{-6}$$

As K_b is so small, x will be tiny and $0.05 - x \sim 0.05$ and so

$$x^2 = 1.26 \times 10^{-6} \times 0.05 \text{ or } x = [\text{OH}^-] = 2.5 \times 10^{-4} \text{ M}$$

Hence, pOH = -log$_{10}$[OH$^-$] = -log$_{10}$(2.5 × 10^{-4}) = 3.60 and so:

$$\text{pH} = 14.00 - \text{pOH} = 10.4$$

Answer: **10.4**

- The ionisation constant of water, K_w, at 37 °C is 2.42×10^{-14}. What is the pH for a neutral solution at 37 °C?

1

By definition, K_w = [H$^+$(aq)][OH$^-$(aq)]. Water ionizes to produce equal amounts of H$^+$(aq) and OH$^-$(aq). Let [H$^+$(aq)] = [OH$^-$(aq)] = y:

$$K_w = (y)(y) = y^2 = 2.42 \times 10^{-14}$$

$$y = 1.56 \times 10^{-7} \text{ M} = [\text{H}^+(\text{aq})]$$

$$\text{pH} = -\log_{10}[\text{H}^+(\text{aq})] = -\log_{10}(1.56 \times 10^{-7}) = 6.81$$

Answer: **6.81**

- Calculate the pH of a 0.10 mol L^{-1} solution of HF. (The pK_a of HF is 3.17.)

**Marks
6**

HF is a weak acid so the equilibrium concentrations need to be calculated using a reaction table:

	HF	$\rightleftharpoons$	H$^+$(aq)	F$^-$(aq)
Initial	0.10		0	0
Change	-x		+x	+x
Equilibrium	0.10 − x		x	x

As pK_a = -log$_{10}$$K_a$, at equilibrium,

$$K_a = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]} = \frac{(x)(x)}{(0.10-x)} = \frac{x^2}{(0.10-x)} = 10^{-3.17}$$

As K_a is so small, x will be tiny and 0.10 − x ~ 0.10 and so

$$x^2 = 10^{-3.17} \times 0.10 \text{ or } x = [H^+(aq)] = 0.00822 \text{ M}$$

As pH = -log$_{10}$[H$^+$(aq)],

$$pH = -log_{10}(0.00822) = 2.09$$

Answer: **2.09**

What mass of NaF needs to be added to 100.0 mL of the above solution to make a buffer with a pH of 3.00?

Using the Henderson-Hasselbalch equation for the pH of the buffer:

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

To make a buffer with pH = 3.00 and [acid] = [HF] = 0.10 M:

$$3.00 = 3.17 + \log\left(\frac{[F^-]}{0.10}\right) \text{ or } \log\left(\frac{[F^-]}{0.10}\right) = =0.17$$

Hence,

$$[F^-] = 0.10 \times 10^{-0.17} = 0.068 \text{ M}$$

The number of moles in 100.0 mL is thus 0.0068 mol. As NaF will dissolve to give one F$^-$ per formula unit, this is also the number of moles of NaF required.

ANSWER CONTINUES ON THE NEXT PAGE

The formula mass of NaF is (22.99 (Na) + 19.00 (F)) g mol^{-1} = 41.99 g mol^{-1}. The mass of NaF required is thus:

mass = number of moles × formula mass
= (0.0068 mol) × (41.99 g mol^{-1}) = 0.28 g

Answer: **0.28 g**

Explain why HCl is a much stronger acid than HF.

Cl is a much larger atom than F and is less electronegative. The H–Cl bond is therefore much longer and weaker than the H–F bond. The H–Cl bond is therefore easier to break and it is the stronger acid.

HF is actually a weak acid. F is smaller and more electronegative than O, so the H–F bond is stronger than the O–H bond. There is consequently little dissociation of HF when it is dissolved in water.

- 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

As pH = -log$_{10}$([H$_3$O$^+$(aq)],

[H$_3$O$^+$(aq)]$_{initial}$ = 10$^{-1.22}$ = 0.0600 and [H$_3$O$^+$(aq)]$_{final}$ = 10$^{-2.00}$ = 0.0100

The reaction table is:

	IO$_3$$^-$(aq)	H$_3$O$^+$(aq)	⇌	HIO$_3$	H$_2$O
initial	x	0.0600		0	large
final	x – 0.0500	0.0100		0.0500	large

The solution contains a weak acid (HIO$_3$ and its conjugate base (IO$_3$$^-$). It is a buffer and can be treated using the Henderson-Hasselbalch equation,

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

$$2.00 = 0.79 + \log_{10}\left(\frac{(x - 0.0500)}{0.0500}\right)$$

x = 0.865 M

This concentration is present in 300.0 mL of solution so the number of moles of IO$_3$$^-$ which has been added is,

number of moles = concentration × volume = 0.865 × 0.3000 = 0.260 mol

Answer: **0.260 mol**

3

- Explain why the acidity of hydrogen halides *increases* with increasing halogen size (*i.e.*, K_a (HCl) < K_a (HBr) < K_a (HI)), while the acidity of hypohalous acids *decreases* with increasing halogen size (*i.e.*, K_a (HOCl) > K_a (HOBr) > K_a (HOI)).

For the hydrogen halides, the length of the H-X bond increases and hence gets weaker as the halogen gets bigger,. The weaker the bond, the more easily the H$^+$ dissociates.

For the hypohalous acids, as the electronegativity of the halide increases, the more electron density it pulls from the O-H bond towards itself. This results in the O-H bond becoming more polar and increasing the ease with which the H$^+$ will be lost.

**Marks
5**

- The K_a of benzoic acid is 6.3×10^{-5} M at 25 °C.

  Calculate the pH of a 0.0100 M aqueous solution of sodium benzoate (C_6H_5COONa).

As benzoic acid is a weak acid, its conjugate base, $C_6H_5COO^-$, is a weak base and so $[OH^-]$ must be calculated using the reaction table:

	$C_6H_5COO^-$	H_2O	$\rightleftharpoons$	OH^-	C_6H_5COOH
initial	0.0100	large		0	0
change	-x	negligible		+x	+x
final	0.0100 – x	large		x	x

The equilibrium constant K_b is given by:

$$K_b = \frac{[OH^-][C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{x^2}{0.0100 - x}$$

For an acid and its conjugate base in aqueous solution, $K_a \times K_b = K_w = 10^{-14}$. Hence,

$$K_b = \frac{10^{-14}}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$$

As K_b is very small, $0.0100 - x \sim 0.0100$ and hence:

$$x^2 = 0.0100 \times (1.6 \times 10^{-10}) \quad \text{or} \quad x = 1.3 \times 10^{-6} \text{ M} = [OH^-(aq)]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = -\log_{10}[1.3 \times 10^{-6}] = 5.9$$

Finally, pH + pOH = 14.0 so

$$pH = 14.0 - 5.9 = 8.1$$

Answer: **pH = 8.1**

Answer: **pH = 4.1**

ANSWER CONTINUES ON THE NEXT PAGE

A buffer solution is prepared by adding 375 mL of this 0.0100 M aqueous solution of sodium benzoate to 225 mL of 0.0200 M aqueous benzoic acid. Calculate the pH of the buffer solution.

375 mL of a 0.0100 of benzoate contains,

moles of benzoate = volume×concentration = 0.375×0.0100 = $3.75×10^{-3}$ mol

225 mL of a 0.0200 of benzoic acid contains,

moles of benzoic acid = 0.225×0.0200 = $4.50×10^{-3}$ mol

The mixture has a volume of (375 + 225) = 600 mL so the concentrations of benzoate (base) and benzoic acid (acid) are:

$$[\text{base}] = \frac{\text{number of moles}}{\text{volume}} = \frac{3.75 \times 10^{-3}}{0.600} = 6.25 \times 10^{-3} \text{ M}$$

$$[\text{acid}] = \frac{4.50 \times 10^{-3}}{0.600} = 7.50 \times 10^{-3} \text{ M}$$

As pK_a = -$\log_{10}K_a$,

$$pK_a = -\log_{10}(6.3 \times 10^{-5}) = 4.2$$

The pH of the buffer can be calculated using the Henderson-Hasselbalch equation,

$$pH = pK_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 4.2 + \log_{10}\left(\frac{6.25 \times 10^{-3}}{7.50 \times 10^{-3}}\right) = 4.1$$

Answer: **pH = 4.1**

**Marks
3**

- The active ingredient in aspirin is the monoprotic acid, acetylsalicylic acid ($HC_9H_7O_4$) that has a K_a of 3.3×10^{-4} M at 25 °C. What is the pH of a solution obtained when a tablet containing 200 mg of acetylsalicylic acid is dissolved in 125 mL of water?

The molar mass is $(8 \times 1.008$ (H)) + (9×12.01) + $(4 \times 16.00$ (O)) g mol^{-1} = 180.154 g mol^1 so 200 mg contains:

$$n(HC_9H_7O_4) = \frac{\text{mass}}{\text{molar mass}} = \frac{(200 \times 10^{-3}\,\text{g})}{(180.154\,\text{g mol}^{-1})} = 1.11 \times 10^{-3}\,\text{mol}$$

When this amount is dissolved in 125 mL, the concentration is:

$$n[HC_9H_7O_4] = \frac{\text{number of moles}}{\text{volume}} = \frac{(1.11 \times 10^{-3}\,\text{mol})}{(125/1000\,\text{L})} = 8.88 \times 10^{-3}\,\text{M}$$

The reaction table is:

	$HC_9H_7O_4$	H_2O	$\rightleftharpoons$	H_3O^+	$C_9H_7O_4^-$
initial	8.88×10^{-3}	large		0	0
change	$-x$	negligible		$+x$	$+x$
final	$8.88 \times 10^{-3} - x$	large		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+(aq)][C_9H_7O_4^-(aq)]}{[HC_9H_7O_4(aq)]} = \frac{x^2}{(8.88 \times 10^{-3} - x)} = 3.3 \times 10^{-4}$$

K_a is not sufficiently small in comparison to the initial concentration of acid that any approximation to this equation can be made. Hence, the quadratic expression must be solved:

$$x^2 = (3.3 \times 10^{-4} \times 8.88 \times 10^{-3}) - (3.3 \times 10^{-4})x$$

$$x^2 + (3.3 \times 10^{-4})x - (2.9 \times 10^{-6})$$

With $a = 1$, $b = +3.3 \times 10^{-4}$ and $c = -2.9 \times 10^{-6}$, the roots are:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(3.3 \times 10^{-4}) \pm \sqrt{(3.3 \times 10^{-4})^2 - (4 \times 1 \times -2.9 \times 10^{-5})}}{(2 \times 1)}$$

Only the positive root has physical significance so $x = 1.55 \times 10^{-3}$

$[H_3O^+(aq)] = x = 1.55 \times 10^{-3}$ M, pH = $-\log_{10}([H_3O^+(aq)])$ = $-\log_{10}(1.55 \times 10^{-3})$ = **2.81**

Answer: **pH = 2.81**

ANSWER CONTIUNES ON THE NEXT PAGE

- A standard test for the presence of chloride ion in water involves the appearance of a precipitate of AgCl upon addition of 1 mL of $AgNO_3$ (0.03 M) to 100 mL of the water sample. What is the minimum concentration of Cl^- detectable by this method? $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ M^2.

The number of moles of $Ag^+(aq)$ in 1 mL of 0.03 M $AgNO_3$ is:

$$n(Ag^+(aq)) = \text{concentration} \times \text{volume} = (0.03 \text{ M}) \times (1 \times 10^{-3} \text{ L}) = 3 \times 10^{-5} \text{ mol}$$

In the test, this amount is present in (100 + 1) = 101 mL so its concentration is:

$$[Ag^+(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{(3 \times 10^5 \text{ mol})}{(101 \times 10^{-3} \text{ L})} = 3 \times 10^{-4} \text{ M}$$

The solubility equilibrium and product for AgCl are given by:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+(aq)][Cl^-(aq)] = 1.8 \times 10^{-10}$$

Hence,

$$[Cl^-(aq)] = \frac{K_{sp}}{[Ag^+(aq)]} = \frac{(1.8 \times 10^{-10})}{(3 \times 10^{-4})} = 6 \times 10^{-7} \text{ M}$$

If $[Cl^-(aq)]$ is less than this value, AgCl will not precipitate.

Answer: $[Cl^-(aq)] = = 6 \times 10^{-7}$ **M**

Marks
7

- Uric acid, $C_5H_5N_4O_3$, is a weak diprotic acid with a low solubility of 70 mg L^{-1}. The extremely painful inflammation known as gout occurs when crystals of uric acid are deposited in the joints. Given that the pH of a saturated solution of uric acid is 4.58, calculate the pK_{a1} of uric acid at 25 °C?

As pH = $-\log_{10}([H_3O^+(aq)])$ 4.58, $[H_3O^+(aq)] = 10^{4.58} = 2.63 \times 10^{-5}$ M.

The molar mass of uric acid is:

$((5\times12.01\ (C)) + (5\times1.008\ (H)) + (4\times14.01\ (N)) + (3\times16.00\ (O))$ g mol^{-1}
$= 169.13$ g mol^{-1}

A one litre solution contains 70 mg corresponding to

number of moles = $\dfrac{(70\times10^{-3}\ \text{g})}{(169.13\ \text{g mol}^{-1})} = 4.1\times10^{-4}$ mol .

For this weak acid, the reaction table is:

	$C_5H_5N_4O_3$	H_2O	$\rightleftharpoons$	H_3O^+	$C_5H_4N_4O_3^-$
initial	4.1×10^{-4}	large		0	0
final	$(4.1\times10^{-4}) - (2.63 \times 10^{-5})$	large		2.63×10^{-5}	2.63×10^{-5}

The equilibrium constant K_{a1} is given by:

$$K_{a1} = \frac{[H_3O^+(aq)][C_5H_4N_4O_3^-(aq)]}{[C_5H_5N_4O_3(aq)]} = \frac{(2.63\times10^{-5})\times(2.63\times10^{-5})}{(3.9\times10^{-4})} = 1.8 \times 10^{-6}$$

Hence, p$K_{a1} = -\log_{10}K_{a1} = -\log_{10}(1.8 \times 10^{-6}) = 5.7$

Answer: **pK_{a1} = 5.7**

The monosodium salt of uric acid is slightly more soluble, 8×10^{-4} g mL^{-1}. Calculate the solubility product constant, K_{sp}, of sodium urate at 25 °C. Assume no hydrolysis of the urate ion occurs.

The formula mass of the monosodium salt, $NaC_5H_4N_4O_3$ is 22.99 (Na) + (5×12.01 (C)) + (4×1.008 (H)) + (4×14.01 (N)) + (3×16.00 (O)) = 191.112. The molar solubility is:

molar solubility = $\dfrac{\text{solubility}}{\text{formula mass}} = \dfrac{(8\times10^{-4}\ \text{g mL}^{-1})}{(191.112\ \text{g mol}^{-1})}$

$= = 4\times10^{-6}$ mol mL$^{-1} = 4\times10^{-3}$ M

Hence, $K_{sp} = [Na^+(aq)][C_5H_4N_4O_3^-(aq)] = (4 \times 10^{-3}) \times (4 \times 10^{-3}) = 2 \times 10^{-5}$

Answer: **$K_{sp} = 2 \times 10^{-5}$**

ANSWER CONTIUNES ON THE NEXT PAGE

Suggest a possible reason why the pH of blood plasma remains near 7.4 even when saturated with uric acid.

Blood is buffered by a CO_3^{2-} / HCO_3^- buffering system which resists changes in pH.

**Marks
2**

- The formulation of a pharmaceutical to be delivered by injection includes sodium chloride to make it isotonic with blood plasma. Why is this necessary?

An isotonic solution has the same concentration of particles as in cell fluid so water particles leave the cell at the same rate that they enter it and there is no change in the osmotic pressure. A non-isotonic solution would lead to a change in the osmotic pressure and hence a change in the cell volume.

- A solution of volume 2.00 L was prepared by mixing equal volumes of nitric acid (0.10 M) and sulfuric acid (0.10 M). To this, sodium hydroxide (10.0 g) was added. Assuming no volume change, what is the pH of the final solution?

3

Nitric acid, HNO_3, dissociates completely to give 1 mol of $H^+(aq)$ for every mole of acid. The number of moles in 1.00 L of a 0.10 M solution of $HNO_3(aq)$ is:

$n(H^+(aq))$ = **volume × concentration = 1.00 L × 0.10 M = 0.100 mol**

Sulfuric acid, H_2SO_4, dissociates completely to give 2 mol of $H^+(aq)$ for every mole of acid. The number of moles in 1.00 L of a 0.10 M solution of $H_2SO_4(aq)$ is:

$n(H^+(aq))$ = **2 × 1.00 × 0.10 = 0.200 mol**

The total number of moles of $H^+(aq)$ is thus (0.100 + 0.200) mol = 0.300 mol.

The formula mass of NaOH is 22.99 (Na) + 16.00 (O) + 1.008 (H) g mol^{-1} = 39.998 g mol^{-1} so 10.0 g contains:

$$n(OH^-(aq)) = \frac{mass}{formula\,mass} = \frac{10.0\,g}{39.998\,g\,mol^{-1}} = 0.250\,mol$$

The number of moles of $H^+(aq)$ after the addition of NaOH is thus:

$n(H^+(aq))$ = **(0.300 – 0.250) mol = 0.050 mol**

This amount is dissolved in a volume of 2.00 L so the final concentration is:

$$[H^+(aq)] = \frac{number\,of\,moles}{volume} = \frac{0.050\,mol}{2.00\,L} = 0.0250\,M$$

As pH = -log$_{10}$([H$^+$(aq)],

pH = -log$_{10}$(0.0250) = 1.6

pH = 1.6

ANSWER CONTIUNES ON THE NEXT PAGE

- Acetic acid (100 mL, 0.20 M) is mixed with solid sodium hydroxide (0.010 mol). Calculate the final pH of the solution. pK_a of acetic acid = 4.76

3

Assuming that the addition of solid sodium hydroxide causes no volume change, the initial [OH⁻(aq)] is:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}} = \frac{0.010\,\text{mol}}{(100/1000)\,\text{L}} = 0.10\,\text{M}$$

Acetic acid and sodium hydroxide react together in a 1:1 ratio:

	CH$_3$COOH	OH⁻	⇌	CH$_3$COO⁻	H$_2$O
initial	0.20	0.10		0	large
final	(0.20 – 0.10) = 0.10	0		0.10	large

The solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used:

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 4.76 + \log_{10}\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\right)$$

As [acid] = [base], $\log_{10}\left(\dfrac{[\text{base}]}{[\text{acid}]}\right) = \log_{10}(1) = 0$ **and so**

$$\text{pH} = \text{p}K_a = 4.76$$

pH = **4.76**