Chem Factsheet

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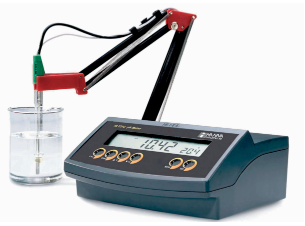
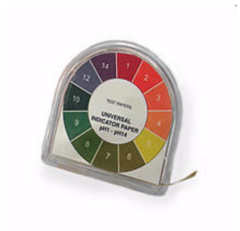
Calculating pH

pH is a measure of the acidity or alkalinity of an aqueous solution with a scale commonly ranging from 0 to 14 and being estimated by indicators (e.g. Universal indicator paper) or measured more accurately by a pH meter. Solutions with pH values less than 7 are said to be acidic whilst solutions with pH values greater than 7 are said to be alkaline. Hence, solutions with pH values equal to 7 are said to be neutral.





> *These familiar values (<7, 7 and >7) apply only if the temperature of the solution is 298K (25°C). Some of the consequences of this temperature dependence will be considered later!*

This FactSheet concentrates on calculating pH values rather than measuring them. In order to be able to complete such calculations, there follows a summary of the essential definitions related to the nature and behaviour of acids and bases.

	Idea	Definition
1	Acid	A **proton (H^+) donor**
2	Base	A **proton acceptor**
3	Alkali	A solution containing a **water soluble base** and consequently an excess of **OH^- ions**.
4	Strong	An acid (e.g.HCl, HNO_3, H_2SO_4, H_3PO_4) or a base (e.g. NaOH, $Ba(OH)_2$) which is **fully ionised** in aqueous solution
5	Weak	An acid (e.g.any carboxylic acid [RCOOH], phenol [C_6H_5OH]) or a base (e.g. NH_3, any amine [RNH_2]) which is **partially ionised** in aqueous solution
6	K_w	K_w is the "Ionic Product of Water" where $\mathbf{K_w = [H^+] \times [OH^-] = 1.00 \times 10^{-14}}$ mol^2dm^{-6} at 298K
7	pH	$\mathbf{-log_{10}[H^+]}$
8	pOH	$\mathbf{-log_{10}[OH^-]}$
9	K_a	The equilibrium constant referring to the partial (equilibrium) ionisation of a weak acid (HA), $HA \rightleftharpoons H^+ + A^-$ $\mathbf{K_a = \frac{[H^+] \times [A^-]}{[HA]}}$ mol dm^{-3} (usually at 298K).
10	K_b	The equilibrium constant referring to the partial (equilibrium) ionisation of a weak base (B) $B + H_2O \rightleftharpoons BH^+ + OH^-$ $\mathbf{K_b = \frac{[BH^+] \times [OH^-]}{[B]}}$ mol dm^{-3} (usually at 298K).
11	pK_a	$\mathbf{-log_{10} K_a}$
12	pK_b	$\mathbf{-log_{10} K_b}$
13	Buffer	A solution which **resists changes in pH** when small amounts of acid or base are added or the solution is diluted.
14	Acidic buffer	A buffer solution which has a working **pH below 7** at 298K. Typically it consists of a mixture of a weak acid (e.g. HCOOH) and a salt of the same acid (e.g. HCOONa). Produced by simply mixing the weak acid with the salt or by partially neutralising a sample of the weak acid (HCOOH) using a strong base (NaOH).
15	Alkaline buffer	A buffer solution which has a working **pH above 7** at 298K. Typically it consists of a mixture of a weak base (e.g. NH_3) and a salt of the same base (e.g. NH_4Cl). Produced by simply mixing the weak base with the salt or by partially neutralising a sample of the weak base (NH_3) using a strong acid (HCl).

> *At 298K, for any given solution,* ***pH + pOH = 14****.*
> *This is derived by taking log_{10} of both sides of $[H^+] \times [OH^-] = 1.00 \times 10^{-14}$*

Worked examples of the various types of pH calculation follow. Further examples are included for you to practise the techniques.

> ***Exam Hint:-*** *quote pH values to* ***2 decimal places****.*

Calculation 1: The pH of Water

Calculate the pH of pure water at 298K. State and explain how this value will change as the temperature rises.

In pure water, a few molecules are ionised : $H_2O \rightleftharpoons H^+ + OH^-$

$\rightarrow [H^+] = [OH^-]$ since the ions are produced in ratio 1:1

$\rightarrow K_w = [H^+] \times [OH^-] = [H^+]^2 = 1.00 \times 10^{-14}$

$\rightarrow [H^+] = \sqrt{1.0 \times 10^{-14}} = 1.00 \times 10^{-7}$ mol dm^{-3}

$\rightarrow pH = -log_{10}(1.00 \times 10^{-7}) =$ **7.00**.

The ionisation of water involves bond breaking. It is therefore an endothermic process and, according to Le Chatelier's Principle, will be favoured a higher temperature. Hence, as temperature rises the concentration of H^+ ions will increase and the pH value will therefore decrease. e.g. If $[H^+]$ increases from 1.0×10^{-7} mol dm^{-3} to 1.05×10^{-7} mol dm^{-3}, the new pH will be $-\log_{10}(1.05 \times 10^{-7}) = 6.98$.

*In this and subsequent pH calculations, the **H^+ and OH^- ions derived from the ionisation of water are considered negligible**. In pure water, $[H^+]$ and $[OH^-]$ are only 1.00×10^{-7} mol dm^{-3} (see above) and in an acidic or alkaline solution the H^+ and OH^- ions derived from water will be even less because the ionisation equilibrium $[H_2O \rightleftharpoons H^+ + OH^-]$ will be pushed to the left.*

Calculation 2: The pH of a Solution of a Strong Acid

This type of calculation would apply to acids such as HCl, HNO_3, H_2SO_4 and H_3PO_4.

Calculate the pH of a 0.12 mol dm^{-3} of the strong acid H_nA for:
(a) n = 1 (b) n = 2 (c) n = 3.

H_nA will be fully ionised : $H_nA \rightarrow nH^+ + A^{n-}$
$\rightarrow [H^+] = n \times [H_nA]$
$\rightarrow$ For (a), $[H^+] = 1 \times 0.12 = 0.12$ mol dm^{-3} $\rightarrow$ pH $= -\log_{10}(0.12) =$ **0.92**
and for (b), $[H^+] = 2 \times 0.12 = 0.24$ mol dm^{-3} $\rightarrow$ pH $= -\log_{10}(0.24) =$ **0.62**
and for (c), $[H^+] = 3 \times 0.12 = 0.36$ mol dm^{-3} $\rightarrow$ pH $= -\log_{10}(0.36) =$ **0.44**

Calculation 3: The pH of a Solution of a Strong Base

This type of calculation would apply to bases such as NaOH, KOH and $Ba(OH)_2$

Calculate the pH of a 0.07 mol dm^{-3} of the strong base $M(OH)_n$ for (a) n = 1 (b) n = 2.

Method 1	Method 2
$M(OH)_n$ will be fully ionised. $M(OH)_n \rightarrow nOH^- + M^{n+}$ $\rightarrow [OH^-] = n \times [M(OH)_n]$	$M(OH)_n$ will be fully ionised. $M(OH)_n \rightarrow nOH^- + M^{n+}$ $\rightarrow [OH^-] = n \times [M(OH)_n]$
For (a), $[OH^-] = 1 \times 0.07 = 0.07$ mol dm^{-3} $[H^+] = K_w/[OH-] = 1.00 \times 10^{-14} / 0.07$ $\rightarrow$pH $= -\log_{10}(1.00 \times 10^{-14} / 0.07) =$ **12.85**	For (a), $[OH^-] = 1 \times 0.07 = 0.07$ mol dm^{-3} $\rightarrow$ pOH $= -\log_{10}(0.07) = 1.15$ $\rightarrow$ pH = 14 – 1.15 = **12.85**
For (b), $[OH^-] = 2 \times 0.07 = 0.14$ mol dm^{-3} $[H^+] = K_w/[OH^-] = 1.00 \times 10^{-14} / 0.14$ $\rightarrow$ pH $= -\log_{10}(1.00 \times 10^{-14} / 0.14) =$ **13.15**	For (b), $[OH^-] = 2 \times 0.07 = 0.14$ mol dm^{-3} $\rightarrow$ pOH $= -\log_{10}(0.14) = 0.85$ $\rightarrow$ pH = 14 – 1.15 = **13.15**

Calculation 4: The pH of a Solution of a Weak Acid (HA)

This type of calculation applies to acids such as methanoic acid (HCOOH), ethanoic acid (CH_3COOH) and phenol (C_6H_5OH). Here a value for Ka must be available since the ionisation of a weak acid is an equilibrium process.

Equilibrium	HA	$\rightleftharpoons$	H^+	+	A^-
Initial concentration /mol dm^{-3}	C		0		0
			(Ignoring H^+ ion from H_2O – see earlier)		
Equilibrium concentration /mol dm^{-3}	C - x		x		x

$$\rightarrow \text{Ka} = \frac{[H^+] \times [A^-]}{[HA]} = \frac{x^2}{C-x}$$

$$\rightarrow x = [H^+] = \sqrt{}\text{Ka} \times (C-[H^+])$$

Using this equation to find $[H^+]$, and hence the pH, would involve solving a quadratic equation. However, by making a reasonable approximation, this equation can be made much easier to solve. This approximation involves assuming that the value of x is insignificant compared to the value of C. This is reasonable for most weak acids since very few molecules are actually ionised. Hence, $(C-[H^+])$ can be replaced with just C!

$$\rightarrow \text{Ka} = \frac{[H^+] \times [A^-]}{[HA]} \approx \frac{x^2}{C}$$

$\rightarrow x = [H^+] \approx \sqrt{}(K_a \times C)$.
This is the relationship most often used to calculate the pH of a weak acid.

Calculation 5 : Calculate the pH of:

(a) 0.14 mol dm^{-3} methanoic acid (HCOOH) which has K_a 1.82×10^{-4} mol dm^{-3} at 298K
(b) 0.074 mol dm^{-3} phenol (C_6H_5OH) which has K_a 1.57×10^{-10} mol dm^{-3} at 298K

For (a)
$[H^+] \approx \sqrt{}(K_a \times C) = \sqrt{}(1.82 \times 10^{-4} \times 0.14) = 5.0477 \times 10^{-3}$
$\rightarrow$ pH $= -\log_{10}(5.0477 \times 10^{-3}) =$ **2.30**

(Note : Had the approximation not been made, solving the quadratic equation would give pH 2.29 (to 2dp) for this solution)

For (b)
$[H^+] \approx \sqrt{}(K_a \times C) = \sqrt{}(1.57 \times 10^{-10} \times 0.074) = 3.4085 \times 10^{-6}$
$\rightarrow$ pH $= -\log_{10}(3.4085 \times 10^{-6}) =$ **5.47**

(Note : Had the approximation not been made, solving the quadratic equation would give pH 5.47 (to 2dp) for this solution)

Calculation 6: The pH of a Solution of a Weak Base (B)

This type of calculation applies to bases such as ammonia (NH_3) and aminomethane (CH_3NH_2).
Here a value for Kb must be available since the ionisation of a weak base (B) is an equilibrium process.

Equilibrium		B	+	H_2O	⇌	BH^+	+	OH^-
Initial concentration	/mol dm^{-3}	C				0		0
				(Ignoring OH^- ion from H_2O – see earlier)				
Equilibrium concentration	/mol dm^{-3}	C - x				x		x

$$\rightarrow \ Kb = \frac{[BH^+] \times [OH^-]}{[B]} = \frac{x^2}{C-x}$$

$$\rightarrow \ x = [OH^-] = \sqrt{} \ K_b \times (C-[OH^-])$$

As in the previous case, using this equation to find $[OH^-]$, and hence the pH, would involve solving a quadratic equation. However, by making a similar approximation, this equation can be simplified to **$[OH^-] \approx \sqrt{}(K_b \times C)$**
This is the relationship most often used to calculate the pH of a weak base.

Calculate the pH of:
(a) 0.097 mol dm^{-3} ammonia (NH_3) which has K_b 1.80 × 10^{-5} mol dm^{-3} at 298K
(b) 0.11 mol dm^{-3} aminoethane ($C_2H_5NH_2$) which has K_b 5.63 × 10^{-4} mol dm^{-3} at 298K

Method 1	Method 2
$[OH^-] \ = \approx \sqrt{}(K_b \times C)$	$[OH^-] \ = \approx \sqrt{}(K_b \times C)$
For (a), $[OH^-] = \sqrt{}(1.80 \times 10^{-5} \times 0.097)$ $= \ 1.321 \text{ x } 10^{-3}$ mol dm^{-3} $[H^+] = K_w/[OH\text{-}] = 1.00 \times 10^{-14} / 1.321 \times 10^{-3}$ $\rightarrow pH = -\log_{10}(1.00 \times 10^{-14} / 1.321\text{--} \times 10^{-3})$ = **11.12**	For (a), $[OH^-] = \sqrt{}(1.80 \times 10^{-5} \times 0.097)$ $= \ 1.321 \times 10^{-3}$ mol dm^{-3} $\rightarrow pOH = -\log_{10}(1.321 \times 10^{-3})$ = 2.88 → pH = 14 – 2.88 = **11.12**
For (b), $[OH^-] = \sqrt{}(5.63 \times 10^{-4} \times 0.11)$ $= \ 7.869 \times 10^{-3}$ mol dm^{-3} $[H^+] = K_w/[OH\text{-}] = 1.00 \times 10^{-14} / 7.869 \times 10^{-3}$ $\rightarrow pH = -\log_{10}(1.00 \times 10^{-14} / 7.869 \times 10^{-3})$ = **11.89**	For (b), $[OH^-] = \sqrt{}(5.63 \times 10^{-4} \times 0.11)$ $= \ 7.869 \times 10^{-3}$ mol dm^{-3} $\rightarrow pOH = -\log_{10}(7.869 \times 10^{-3})$ = 2.11 → pH = 14 – 2.10 = **11.89**

Calculation 7: The pH of a Diluted Solution of a Acid or Base

If V_1 cm^3 of a solution of an acid or base is diluted to V_2 cm^3 by addition of water then the effective concentration of the acid or base becomes (the original concentration × V_1 / V_2).

This new concentration can then be used as in calculations 2-6 [good further practice for those calculations!], depending on whether the solution is an acid or a base and whether it is weak or strong.

(a) Calculate the pH of a 0.52 mol dm^{-3} solution of the strong acid H_2SO_4 after 25.0cm^3 of it is diluted to 100.0cm^3.

$[H_2SO_4]$ after dilution = 0.52 × 25/100 = 0.13 mol dm^{-3}
H_2SO_4 will be fully ionised : $H_2SO_4 \ \rightarrow \ 2H^+ \ + \ SO_4^{2-}$
$\rightarrow \ [H^+] \ = 2 \times [H_2SO_4] \ = \ 2 \times 0.13 = 0.26$ mol $dm^{-3} \rightarrow pH = -\log_{10}(0.26) =$ **0.59**

(b) Calculate the pH of a 0.064 mol dm^{-3} solution of the strong base NaOH after 40.0cm^3 of it is added to 80.0cm^3 of water.

Method 1	Method 2
[NaOH] after dilution = 0.064 × 40/120 = 0213 mol dm^{-3} NaOH will be fully ionised : $NaOH \rightarrow \ Na^+ \ + \ OH^-$ $\rightarrow [OH^-] \ = 0213\text{---}$ mol dm^{-3} $[H^+] = K_w/[OH^-] = 1.00 \times 10^{-14} / 0213\text{---}$ $\rightarrow pH \ = -\log_{10}(1.00 \times 10^{-14} / 0213\text{---})$ = **12.33**	[NaOH] after dilution = 0.064 × 40/120 = 0213 mol dm^{-3} NaOH will be fully ionised : $NaOH \rightarrow Na^+ \ + \ OH^-$ $\rightarrow \ [OH^-] \ = 0213\text{---}$ mol dm^{-3} $\rightarrow \ pOH = -\log_{10}(0213) = 1.67$ → pH = 14 – 1.67 = **12.33**

(c) Calculate the pH of a 0.35 mol dm^{-3} solution of the weak acid CH_3COOH [K_a = 1.85 × 10^{-5} mol dm^{-3}] after 10.0cm^3 of it is diluted to 250.0cm^3.

$[CH_3COOH]$ after dilution = 0.35 × 10/250 = 0.014 mol dm^{-3}
$[H^+] \approx \sqrt{} \ (K_a \times C) = \ \sqrt{}(1.85 \times 10^{-5} \times 0.014) = 5.089 \times 10^{-4}$
$\rightarrow pH = -\log_{10}(5.089 \times 10^{-4}) =$ **3.29**

(d) Calculate the pH of a 0.12 mol dm^{-3} solution of the weak base NH_3 [K_b = 1.80 × 10^{-5} mol dm^{-3}] after mixing it with an equal volume of water.

Method 1	Method 2
$[NH_3]$ after dilution = 0.12 × 1/2 = 0.06 mol dm^{-3} $[OH^-] \approx \sqrt{}(K_b \times C)$ $\rightarrow [OH^-] = \sqrt{}(1.80 \times 10^{-5} \times 0.06)$ $= 1.0392 \times 10^{-3}$ mol dm^{-3} $\rightarrow [H^+] = K_w/[OH\text{-}] = 1.00 \times 10^{-14}/1.0392 \times 10^{-3}$ $\rightarrow$ pH = $-\log_{10}(1.00 \times 10^{-14} / 1.0392 \times 10^{-3})$ = **11.02**	$[NH_3]$ after dilution = 0.12 × 1/2 = 0.06 mol dm^{-3} $[OH^-] \approx \sqrt{}(K_b \times C)$ $\rightarrow [OH^-] = \sqrt{}(1.80 \times 10^{-5} \times 0.06)$ $= 1.0392 \times 10^{-3}$ mol dm^{-3} $\rightarrow$ pOH = $-\log_{10}(1.08 \times 10^{-3})$ = 2.98 $\rightarrow$ pH = 14 – 2.98 = **11.02**

Calculation 8: The pH of an Acidic Buffer Solution

Rem. An acidic buffer is mixture of a weak acid (e.g. HCOOH) and a salt of same acid (e.g. HCOONa)

DO NOT *use $[H^+] \approx \sqrt{}(K_a \times C)$ to calculate a buffer pH! The concentrations of H^+ and A^- are only equal in a solution of the PURE acid. In a buffer, the concentration of A^- is much higher because of the presence of the salt of the acid, HA.*

The weak acid is partially ionised but the salt is fully ionised.

$HCOOH \rightleftharpoons HCOO^- + H^+$ and $HCOONa \rightarrow HCOO^- + Na^+$

$$Ka = \frac{[H^+] \times [HCOO^-]}{[HCOOH]}$$

But [HCOOH] = Moles of HCOOH in excess / Volume of mixture in dm^3

and $[HCOO^-]$ = Moles of HCOONa formed / Volume of mixture in dm^3

[Note : $HCOO^-$ from HCOOH is negligible since the salt pushes the HCOOH equilibrium further to the left.]

$$\rightarrow K_a = \frac{[H^+] \times [HCOONa]}{[HCOOH]}$$

$$\rightarrow [H+] = \frac{K_a \times [HCOOH]}{[HCOONa]}$$

$$= \frac{K_a \times \text{ Moles of HCOOH in excess / Volume of mixture in dm}^3}{\text{Moles of HCOONa formed / Volume of mixture in dm}^3}$$

$$= \frac{K_a \times \text{ Moles of HCOOH in excess}}{\text{Moles of HCOONa formed}} \text{ since the volume will cancel.}$$

This can then be used to calculate the pH as usual.

Calculate the pH of the acidic buffer solution produced by mixing 40.0cm^3 of 0.20 mol dm^{-3} HCOOH (K_a = 1.82 × 10^{-4} mol dm^{-3} at 298K) with 10.0cm^3 of 0.30 mol dm^{-3} NaOH.

Moles of HCOOH used = 0.20 × 40.0 / 1000 = 0.008

Moles of NaOH used = 0.30 × 10.0 / 1000 = 0.003

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

→ Moles of HCOOH in excess = 0.008 – 0.003 = 0.005

and moles HCOONa formed = Moles NaOH reacted = 0.003

$$\mathbf{[H^+]} = \frac{\mathbf{K_a \times \text{ Moles of HCOOH in excess}}}{\mathbf{\text{Moles of HCOONa formed}}}$$

$$= \frac{1.82 \times 10^{-4} \times 0.005}{0.003} = 3.033 \times 10^{-4} \text{ mol dm}^{-3}$$

→ pH = $-\log_{10}(3.033 \times 10^{-4})$ = **3.52**

Calculation 9: The pH of an Alkaline Buffer Solution

Rem. An alkaline buffer is a mixture of a weak base (e.g. NH_3) and a salt of same acid (e.g. NH_4Cl).

The weak base is partially ionised but the salt is fully ionised.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \text{ and } NH_4Cl \rightarrow NH_4^+ + Cl^- ; \; K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_3]}$$

But $[NH_3]$ = Moles of NH_3 in excess / Volume of mixture in dm^3

and $[NH_4^+]$ = Moles of NH_4Cl formed / Volume of mixture in dm^3

[Note : NH_4^+ from NH_3 is negligible since the salt pushes the NH_3 equilibrium further to the left.]

$$\rightarrow K_b = \frac{[OH\text{-}] \times [NH_4Cl]}{[NH_3]} \qquad \rightarrow [OH\text{-}] = \frac{K_b \times [NH_3]}{[NH_4Cl]}$$

$$= \frac{K_b \times \text{ Moles of } NH_3 \text{ in excess / Volume of mixture in dm}^3}{\text{Moles of } NH_4Cl \text{ formed / Volume of mixture in dm}^3}$$

$$= \frac{Kb \times \text{ Moles of } NH_3 \text{ in excess}}{\text{Moles of } NH_4Cl \text{ formed}} \text{ since the volume will cancel.}$$

This can then be used to calculate the pH as usual, via K_w or using pOH.

Calculate the pH of the alkaline buffer solution produced by mixing 25.0cm^3 of 0.15 mol dm^{-3} NH_3 ($K_b = 1.80 \times 10^{-5}$ mol dm^{-3} at 298K) with 15.0cm^3 of 0.10 mol dm^{-3} HCl.

Moles of NH_3 used = 0.15 × 25.0 / 1000 = 0.00375 Moles of HCl used = 0.10 × 15.0 / 1000 = 0.00150

The equation for the neutralisation is: $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$ → Moles of NH_3 in excess = 0.00375 – 0.00150 = 0.00225
and moles NH_4Cl formed = Moles HCl reacted = 0.00150

$$[OH^-] = \frac{\mathbf{K_b \times \text{Moles of } NH_3 \text{ in excess}}}{\mathbf{\text{Moles of } NH_4Cl \text{ formed}}} = \frac{1.80 \times 10^{-5} \times 0.00225}{0.00150} = 2.70 \times 10^{-5} \text{ mol dm}^{-3}$$

Method 1	Method 2
$\rightarrow [H^+] = K_w/[OH^-] = 1.00 \times 10^{-14} / 2.70 \times 10^{-5}$ $\rightarrow$ pH $= -\log_{10}(1.00 \times 10^{-14} / 2.70 \times 10^{-5}) = \mathbf{9.43}$	$\rightarrow$ pOH $= -\log_{10}(2.70 \times 10^{-5}) = 4.57$ $\rightarrow$ pH $= 14 - 4.57 = \mathbf{9.43}$

Calculation 10: The pH of a Mixture of an Acid with a Base

These calculations can follow various routes depending on whether the acid or the base is in excess in the mixture, whether the acid and/or base are strong or weak and what volumes of each are mixed. The permutations that you might be expected

A	**Excess strong acid** with a strong base e.g. **HCl** + KOH	Calculate the number of moles of excess acid. Hence, using the total volume of the mixture, determine its concentration in the mixture. Hence calculate the pH as in **calculation 2**
B	**Excess strong acid** with a weak base e.g. **HCl** + NH_3	
C	**Excess weak acid** with a strong base e.g. **HCOOH** + NaOH	This mixture corresponds to an **acid buffer** since it will contain the excess weak acid along with the salt produced by neutralisation. Calculate the pH as in **calculation 8**.
D	**Excess weak acid** with a weak base e.g. **HCOOH** + NH_3	Not applicable at A level
E	**Excess strong base** with a strong acid e.g. **KOH** + HCl	Calculate the number of moles of excess base. Hence, using the total volume of the mixture, determine its concentration in the mixture. Hence calculate the pH as in **calculation 3**.
F	**Excess strong base** with a weak acid e.g. **NaOH** + CH_3COOH	
G	**Excess weak base** with a strong acid e.g. $\mathbf{NH_3}$ + HCl	This mixture corresponds to an **alkaline buffer** since it will contain the excess weak base along with the salt produced by neutralisation. Calculate the pH as in **calculation 9**.
H	**Excess weak base** with a weak acid e.g. $\mathbf{NH_3}$ + HCOOH	Not applicable at A level

Calculation 11: The pH of a Diluted Buffer Solution

For acidic buffer

$$[H^+] = \frac{K_a \text{ x Moles of weak acid}}{\text{Moles of salt of weak acid}}$$

For alkaline buffer

$$[OH^-] = \frac{K_b \text{ x Moles of weak base}}{\text{Moles of salt of weak base}}$$

There is no calculation here! The equations above show that $[H^+]$ / $[OH^-]$ depends on the ratio of weak acid / base to salt of weak acid / base. This ratio, and hence the pH, does not change when water is added.

Calculation 12: The pH of an Acidic Buffer Solution after adding some Strong Acid or Base

If a small amount of strong acid is added to an acidic or alkaline buffer, its pH will decrease but only slightly.

Calculate the pH of the acidic buffer solution containing 40.0cm^3 of 0.20 mol dm^{-3} HCOOH ($K_a = 1.82 \times 10^{-4}$ mol dm^{-3} at 298K) and 10.0cm^3 of 0.30 mol dm^{-3} NaOH <u>after</u> (a) 10.0cm^3 of 0.1 mol dm^{-3} HCl (b) 10.0cm^3 of 0.1 mol dm^{-3} NaOH has been added.

Look back to calculation 8. This buffer starts at pH 3.52 and contains 0.005 moles of HCOOH with 0.003 moles of HCOONa.

(a) Moles HCl added = moles H^+ added = 0.10 × 10.0 / 1000 = 0.001
These H^+ ions combine with $HCOO^-$ (from salt) to form more HCOOH. $HCOO^- + H^+ \rightarrow HCOOH$
→ Moles of HCOOH now in solution = 0.005 + 0.001 = 0.006
and moles of HCOONa now in solution = 0.003 - 0.001 = 0.002

$$[H^+] = \frac{\mathbf{K_a \text{ x Moles of HCOOH}}}{\mathbf{\text{Moles of HCOONa}}} = \frac{1.82 \times 10^{-4} \times 0.006}{0.002} = 5.46 \times 10^{-4} \text{ mol dm}^{-3}$$

→ New pH = $-\log_{10}(5.46 \times 10^{-5})$ = **3.26**
(Note: addition of the same acid to 50cm^3 of water would change the pH from 7.00 to 1.79)

(b) Moles NaOH added = moles OH^- added
= 0.10 × 10.0 / 1000 = 0.001
These OH^- ions convert some HCOOH to $HCOO^-$ (the salt).
$HCOOH + OH^- \rightarrow HCOO^- + H_2O$
→ Moles of HCOOH now in solution = 0.005 - 0.001 = 0.004
and moles of HCOONa now in solution = 0.003 + 0.001 = 0.004

$$[H^+] = \frac{\mathbf{K_a \times \text{Moles of HCOOH}}}{\mathbf{\text{Moles of HCOONa}}} = \frac{1.82 \times 10^{-4} \times 0.004}{0.004} = 1.82 \times 10^{-4} \text{ mol dm}^{-3}$$

→ New pH = $-\log_{10}(1.82 \text{ x } 10^{-4})$ = **3.74**

Calculation 13: The pH of an Alkaline Buffer Solution after adding some Strong Base or Base

If a small amount of strong base is added to an acidic or alkaline buffer, its pH will increase but only slightly.

Calculate the pH of the alkaline buffer solution containing 25.0cm^3 of 0.15 mol dm^{-3} NH_3 ($K_b = 1.80 \times 10^{-5}$ mol dm^{-3} at 298K) and 15.0cm^3 of 0.10 mol dm^{-3} HCl <u>after</u> (a) 5.00cm^3 of 0.1 mol dm^{-3} HCl (b) 5.00cm^3 of 0.1 mol dm^{-3} NaOH has been added.

Look back at calculation 9. This buffer starts at pH 9.43 and contains 0.00375 moles of NH_3 with 0.00150 moles of NH_4Cl.

(a) Moles HCl added = moles H^+ added = 0.10 × 5.0 / 1000 = 0.0005

These H^+ ions combine with NH_3 to form more NH_4Cl (the salt).

$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

$\rightarrow$ Moles of NH_3 now in solution = 0.00375 - 0.0005 = 0.00325

and moles of NH_4Cl now in solution = 0.00150 + 0.0005 = 0.0020

$$\mathbf{[OH^-]} = \frac{\mathbf{K_b \times Moles\ of\ NH_3}}{\mathbf{Moles\ of\ NH_4Cl}} = \frac{1.80 \times 10^{-5} \times 0.00325}{0.0020} = 2.925 \times 10^{-5}\ \text{mol dm}^{-3}$$

Method 1	Method 2
$\rightarrow [H^+] = K_w/[OH^-] = 1.00 \times 10^{-14} / 2.925 \times 10^{-5}$	$\rightarrow pOH = -\log_{10}(2.925 \times 10^{-5}) = 4.53$
$\rightarrow pH = -\log_{10}(1.00 \times 10^{-14} / 2.925 \times 10^{-5}) =$ **9.46**	$\rightarrow$ New pH = 14 – 4.53 = **9.46**

(b) Moles NaOH added = moles OH^- added = 0.10 × 5.0 / 1000 = 0.0005

These OH^- ions convert some NH_4^+ (from the salt) to NH_3.

$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

$\rightarrow$ Moles of NH_3 now in solution = 0.00375 + 0.0005 = 0.00425

and moles of NH_4Cl now in solution = 0.0015 - 0.0005 = 0.0010

$$\mathbf{[OH^-]} = \frac{\mathbf{K_b \times Moles\ of\ NH_3}}{\mathbf{Moles\ of\ NH_4Cl}} = \frac{1.80 \times 10^{-5} \times 0.00425}{0.0010} = 7.65 \times 10^{-5}\ \text{mol dm}^{-3}$$

Method 1	Method 2
$\rightarrow [H^+] = K_w/[OH^-] = 1.00 \times 10^{-14} / 7.65 \times 10^{-5}$	$\rightarrow pOH = -\log_{10}(7.65 \times 10^{-5}) = 4.12$
$\rightarrow pH = -\log_{10}(1.00 \times 10^{-14} / 7.65 \times 10^{-5}) =$ **9.88**	$\rightarrow$ New pH = 14 – 4.12 = **9.88**

Practice Questions

1. A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and $100cm^3$ of distilled water were added. Calculate the pH of the new solution formed at 298K.
2. A 25.0 cm^3 sample of 0.620 mol dm^3 nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added. Calculate the pH of the solution formed at 298K.
3. At 42°C, the value of K_w is 3.46×10^{14} mol^2dm^{-6}. Calculate the pH of pure water at this temperature.
4. The value of K_a for weak acid (HA) is 1.93×10^{-4} mol dm^{-3} at 25°C. Calculate the pH of a 0.0560 mol dm–3 solution of HA at 25°C.
5. The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25°C. A buffer solution is prepared containing 2.35×10^{-2} mol of methanoic acid and 1.84×10^{-2} mol of sodium methanoate in $1.00dm^3$ of solution. Calculate the pH of this buffer solution at 25°C. A 5.00 cm^3 sample of 0.100 mol dm^{-3} hydrochloric acid is added to this buffer solution. Calculate the new pH of the buffer solution after this addition.
6. Calculate the pH of the buffer solution formed when $10.00cm^3$ of 0.100 mol dm^{-3} potassium hydroxide are added to $25.00cm^3$ of 0.430 mol dm^{-3} ethanoic acid at 298K. (K_a for $CH_3COOH = 1.85 \times 10^{-5}$ mol dm^{-3} at 298K)
7. Calculate the pH of 0.140 $moldm^{-3}$ aqueous sodium hydroxide at 50°C. The value of K_w is 5.48×10^{-14} mol^2dm^{-6} at 50°C.
8. Calculate the pH of the solution formed when $25.0cm^3$ of 0.150 mol dm^{-3} aqueous sulfuric acid are added to 30.0 cm^3 of 0.200 mol dm^{-3} aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.

Answers

1. See calculation 7(a) → 1.79
2. See calculation 10E. Find moles of acid. Find moles of alkali. Calculate moles in excess (here NaOH). Calculate [NaOH] using total volume. Calculate pH as per calculation 3 → 12.85
3. See calculation 1 → 6.73
4. See calculation 4 → 2.49
5. See calculation 8 → 3.64 ; See calculation 12 → 3.62
6. See calculation 8 → 3.74
7. See calculation 3 →12.41
8. See calculation 10A. Find moles of acid. Find moles of alkali. Calculate moles in excess (here H_2SO_4) remembering reaction ratio. Calculate $[H_2SO_4]$ using total volume. Calculate $[H^+]$ and pH as per calculation 2 → 1.59

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