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^- required in the titration is:

number of moles = concentration × volume

= (0.020 mol L^{-1}) × (0.0248 L) = 4.96 × 10^{-4} mol

This is equal to the number of moles of HNO_2 in 20.0 mL. Hence, the concentration of HNO_2 is equal to:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}} = \frac{4.96 \times 10^{-4}\ \text{mol}}{0.0200\ \text{L}} = 0.025\ \text{M}$$

Answer: **0.025 M**

What was the pH at the start of the titration?

HNO_2 is a weak acid so the equilibrium concentrations need to be calculated using a reaction table:

	HNO_2	H_2O	$\rightleftharpoons$	$H_3O^+(aq)$	$NO_2^-(aq)$
Initial	**0.025**	**large**		**0**	**0**
Change	**-*x***			**+*x***	**+*x***
Equilibrium	**0.025 – *x***			***x***	***x***

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

$$K_a = \frac{[H_3O^+(aq)][NO_2^-(aq)]}{[HNO_2(aq)]} = \frac{(x)(x)}{(0.025-x)} = \frac{x^2}{(0.025-x)} = 10^{-3.15}$$

As K_a is so small, *x* will be tiny and 0.025 – *x* ~ 0.025 and so

$x^2 = 10^{-3.15} \times 0.025$ or $x = [H_3O^+(aq)] = 0.00421$ M

As pH = -log$_{10}$[H_3O^+(aq)],

pH = -log$_{10}$(0.00421) = 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?

(a) **12.4 mL represents the half equivalence point. At this point, $[HNO_2(aq)] = [NO_2^-(aq)]$ and pH = pK_a. Hence pH = 3.15**

(b) **24.8 mL represents the equivalence point. At this point, all of the HNO_2 has been converted into NO_2^- so:**

number of moles of NO_2^- = 4.96×10^{-4} mol

The total volume of the solution is (20.0 + 24.8) mL = 44.8 mL. Hence:

$$[NO_2^-(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{4.96 \times 10^{-4}}{0.0448 \text{ L}} = 0.0111 \text{ M}$$

The solution contains a weak base. The pH needs to be calculated using a reaction table.

	NO_2^-	H_2O	$\rightleftharpoons$	$HNO_2(aq)$	$OH^-(aq)$
Initial	**0.0111**	**large**		**0**	**0**
Change	$-y$			$+y$	$+y$
Equilibrium	$0.0111 - y$			y	y

As pK_a + pK_b = 14.00, pK_b = 14.00 – 3.15 = 10.85. At equilibrium,

$$K_b = \frac{[HNO_2(aq)][OH^-(aq)]}{[NO_2^-(aq)]} = \frac{(y)(y)}{(0.025-y)} = \frac{y^2}{(0.025-y)} = 10^{-10.85}$$

As K_b is so small, y will be tiny and $0.025 - y \sim 0.025$ and so

$$y^2 = 10^{-10.85} \times 0.025 \text{ or } y = [OH^-(aq)] = 3.96 \times 10^{-7} \text{ M}$$

As pOH = $-\log_{10}[OH^-(aq)]$,

$$\text{pOH} = -\log_{10}(3.96 \times 10^{-7}) = 6.40$$

Finally, as pH + pOH = 14.00,

$$\text{pH} = 14.00 - 6.40 = 7.60$$

(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 0.020 M NH_3 had been used in place of the NaOH solution? The pK_b of NH_3 is 4.76.

The initial pH is unchanged as no base is present.

As pK_b for NH_3 is 4.76, pK_a for its conjugate acid NH_4^+ is (14.00 – 4.76) = 9.24. The half equivalence point is in the acidic region of the titration (it is at pH = 3.15 for the weak acid / strong base titration above). This pH is considerably lower the pK_a value of NH_4^+ and so essentially all of the NH_3 will be present as NH_4^+ and it will not contribute to [H_3O^+(aq). The pH at the half-equivalence point will be the same as it depends only on the pK_a of HNO_2.

The pH at the equivalence point will be lower. At equivalence, the solution will contain NO_2^- as in the HNO_2 / OH^- titration. It will also contain NH_4^+, the conjugate acid of NH_3. As this is weakly acid, the pH will be lowered.