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**

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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:

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

(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:

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

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:

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

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**

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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.