

- Trichloroacetic acid,  $\text{CCl}_3\text{COOH}$ , a corrosive acid used to precipitate proteins, has a  $K_a$  of 0.16 M. What is the pH of a 0.050 M solution of trichloroacetic acid?

Hint: If  $ax^2 + bx + c = 0$ , then  $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

The reaction table is:

	$\text{CCl}_3\text{COOH}$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{CCl}_3\text{COO}^-$
initial	0.050	large		0	0
change	-x	negligible		+x	+x
final	$0.050 - x$	large		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CCl}_3\text{COO}^-(\text{aq})]}{[\text{CCl}_3\text{COOH}(\text{aq})]} = \frac{x^2}{0.050 - x} = 0.16$$

$K_a$  is not sufficiently small that any approximation to this equation can be made. Hence, the quadratic expression must be solved:

$$x^2 = (0.16 \times 0.050) - 0.16x \text{ or } x^2 + 0.16x - 0.0080$$

With  $a = 1$ ,  $b = +0.16$  and  $c = -0.0080$ , the roots are:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.16 \pm \sqrt{(0.16)^2 - (4 \times 1 \times -0.0080)}}{(2 \times 1)} = \frac{-0.16 \pm 0.24}{2}$$

Only the positive root has physical significance so  $x = \frac{-0.16 + 0.24}{2} = 0.04$

As  $[\text{H}_3\text{O}^+(\text{aq})] = x = 0.04 \text{ M}$  and  $\text{pH} = -\log_{10}([\text{H}_3\text{O}^+(\text{aq})])$ :

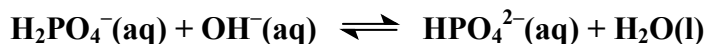
$$\text{pH} = -\log_{10}(0.04) = 1.4$$

Answer: **pH = 1.4**

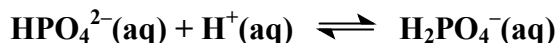
**Marks**  
**6**

- The  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  ions play a major role in maintaining the intracellular pH balance. Write balanced equations to show how a solution containing these ions can act as a buffer.

**The presence of  $\text{H}_2\text{PO}_4^-(\text{aq})$  means that the solution can remove  $\text{OH}^-(\text{aq})$ :**



**The presence of  $\text{HPO}_4^{2-}(\text{aq})$  means that the solution can remove  $\text{H}^+(\text{aq})$ :**



For phosphoric acid,  $K_{a1} = 7.1 \times 10^{-3}$  M,  $K_{a2} = 6.3 \times 10^{-8}$  M,  $K_{a3} = 4.2 \times 10^{-13}$  M. At what pH would the  $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$  buffer system be most effective? Why?

**Buffers are most effective when  $[\text{acid}] = [\text{base}]$  at which point  $\text{pH} = \text{p}K_a$ . For this system, this requires  $[\text{H}_2\text{PO}_4^-(\text{aq})] = [\text{HPO}_4^{2-}(\text{aq})]$ . This acid / base equilibrium corresponds to  $K_{a2}$ :**



**Thus,  $\text{pH} = \text{p}K_{a2} = -\log_{10}(6.3 \times 10^{-8}) = 7.20$**

Calculate the ratio of  $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$  needed to give a solution buffered to a pH of 7.35.

**Using the Henderson-Hasselbalch equation:**

$$\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \text{ or } \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - \text{p}K_a$$

**Thus:**

$$\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - \text{p}K_{a2} = 7.35 - 7.20 = 0.15$$

$$\left( \frac{[\text{base}]}{[\text{acid}]} \right) = 10^{0.15} = 1.4 \text{ or } \left( \frac{[\text{acid}]}{[\text{base}]} \right) = \frac{1}{1.4} = 0.71$$

- Find the concentration of  $\text{H}_3\text{O}^+$  in a 0.60 M aqueous solution of nitrous acid. The acid dissociation constant of  $\text{HNO}_2$  is  $K_a = 7.1 \times 10^{-4}$  M.

Marks  
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The reaction table is:

	$\text{HNO}_2$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{NO}_2^-$
initial	0.60	large		0	0
change	-x	negligible		+x	+x
final	$0.60 - x$	large		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{NO}_2^-(\text{aq})]}{[\text{HNO}_2(\text{aq})]} = \frac{x^2}{0.60 - x} = 7.1 \times 10^{-4}$$

$K_a$  is very small compared to the initial concentration of  $\text{HNO}_2$  so that  $0.60 - x \sim 0.60$  and so:

$$x^2 \sim (7.1 \times 10^{-4}) \times (0.60) \text{ so } x = [\text{H}_3\text{O}^+(\text{aq})] = x = 0.021 \text{ M}$$

Answer: 0.021 M

- An aqueous solution of a weak acid has  $[\text{H}_3\text{O}^+] = 2.54 \times 10^{-4}$  M. Find the pH and pOH of the solution.

1

Using  $\text{pH} = -\log_{10}([\text{H}_3\text{O}^+(\text{aq})])$  and  $\text{pH} + \text{pOH} = 14.00$ :

$$\text{pH} = -\log_{10}(2.54 \times 10^{-4}) = 3.60$$

$$\text{pOH} = 14.00 - 3.60 = 10.40$$

pH = 3.60

pOH = 10.40

- Ammonia,  $\text{NH}_3$ , is a Brønsted-Lowry base and a Lewis base, but not an Arrhenius base. Why?

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A Brønsted-Lowry base is a proton ( $\text{H}^+$ ) acceptor:  $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$

A Lewis base is a species that can donate a lone pair:  $:\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$

An Arrhenius base is one that *contains*  $\text{OH}^-$  ions that are released on dissolution in water. Ammonia *generates*  $\text{OH}^-$  ions in its reaction with water but does not contain them in its formula and hence it is not an Arrhenius base.

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

**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<sup>+</sup> 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<sup>+</sup> will be lost.**

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

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

**Marks**  
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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:

	$C_6H_5COO^-$	$H_2O$	$\rightleftharpoons$	$OH^-$	$C_6H_5COOH$
<b>initial</b>	<b>0.0100</b>	<b>large</b>		<b>0</b>	<b>0</b>
<b>change</b>	<b>-x</b>	<b>negligible</b>		<b>+x</b>	<b>+x</b>
<b>final</b>	<b>0.0100 - x</b>	<b>large</b>		<b>x</b>	<b>x</b>

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,**

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

**225 mL of a 0.0200 of benzoic acid contains,**

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

**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,**

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

**Answer: pH = 4.1**

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the  $pK_a$  of iodic acid,  $\text{HIO}_3$ , is 0.79, how many moles of sodium iodate,  $\text{NaIO}_3$ , would need to be added to this solution to raise its pH to 2.00?

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

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

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

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

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

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

The change of  $(0.060 - 0.010 \text{ M}) = 0.050 \text{ M}$  occurs due to the reaction with  $\text{IO}_3^-$  (aq) to produce  $\text{HIO}_3$ (aq). If  $[\text{IO}_3^-(\text{aq})] = x$ , the reaction table is:

	$\text{H}^+(\text{aq}) +$	$\text{IO}_3^-(\text{aq})$	$\rightleftharpoons$	$\text{HIO}_3(\text{aq})$
initial	0.060	$x$		0
change	-0.050	-0.050		+0.050
final	0.010	$x - 0.050$		0.050

As  $\text{p}K_a = 0.79 = -\log_{10}K_a$ :

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{IO}_3^-(\text{aq})]}{[\text{HIO}_3(\text{aq})]} = \frac{(0.010) \times (x - 0.050)}{0.050} = 10^{-0.79}$$

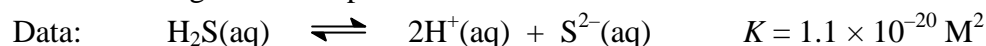
Thus,  $x = 0.86 \text{ M} = [\text{IO}_3^-(\text{aq})]_{\text{initial}}$ . This concentration corresponds to a 300.0 mL solution so the number of moles that have been added is:

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (0.86 \text{ M}) \times (0.3000 \text{ L}) = 0.26 \text{ mol} \end{aligned}$$

Answer: **0.26 mol**

**Marks**  
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- The pH of a solution can be controlled by adding small amounts of gaseous HCl. Assuming no change in volume, calculate what the pH of the solution must be to just dissolve 1.00 g of NiS suspended in 1.0 L of water.



$$K_{\text{sp}}(\text{NiS}) = 1.0 \times 10^{-22} \text{ M}^2$$

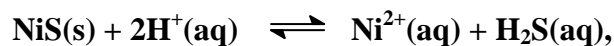
For the dissolution  $\text{NiS}(\text{s}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$ ,

$$K_{\text{sp}} = [\text{Ni}^{2+}(\text{aq})][\text{S}^{2-}(\text{aq})].$$

For the acid dissociation,  $\text{H}_2\text{S}(\text{aq}) \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{S}^{2-}(\text{aq})$ ,

$$K = \frac{[\text{H}^+(\text{aq})]^2[\text{S}^{2-}(\text{aq})]}{[\text{H}_2\text{S}(\text{aq})]}$$

Combining these two equilibria gives, for the overall reaction,



$$K_{\text{eq}} = \frac{[\text{Ni}^{2+}(\text{aq})][\text{H}_2\text{S}(\text{aq})]}{[\text{H}^+(\text{aq})]^2} = \frac{K_{\text{sp}}}{K} = \frac{1.0 \times 10^{-22}}{1.1 \times 10^{-20}} = 9.1 \times 10^{-3}$$

The formula mass of NiS is (58.69 (Ni) + 32.07 (S))  $\text{g mol}^{-1} = 90.76 \text{ g mol}^{-1}$ . The amount in 1.00 g is therefore,

$$\text{number of moles} = \frac{\text{mass}(\text{g})}{\text{molar mass}(\text{g mol}^{-1})} = \frac{1.00 \text{ g}}{90.76 \text{ g mol}^{-1}} = 0.0110 \text{ mol}$$

In the dissolution  $\text{NiS}(\text{s}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$ , so if 0.0110 mol of NiS(s) completely dissolves in 1.0 L,  $[\text{Ni}^{2+}(\text{aq})] = 0.011 \text{ M}$ . From the overall reaction, each mole of NiS which dissolves produces one mole of  $\text{H}_2\text{S}(\text{aq})$  so  $[\text{H}_2\text{S}(\text{aq})] = 0.011 \text{ M}$ . Hence,

$$[\text{H}^+(\text{aq})]^2 = \frac{(0.011 \text{ M})(0.011 \text{ M})}{9.1 \times 10^{-3}} \quad \text{or} \quad [\text{H}^+(\text{aq})] = 0.12 \text{ M}$$

$$\text{pH} = -\log_{10}[\text{H}^+(\text{aq})] = -\log_{10}(0.12) = 0.94$$

$$\text{pH} = 0.94$$



- Calculate the pH of a  $0.10 \text{ mol L}^{-1}$  solution of HF. (The  $\text{p}K_{\text{a}}$  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	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	$\text{F}^-(\text{aq})$
<b>Initial</b>	<b>0.10</b>		<b>0</b>	<b>0</b>
<b>Change</b>	<b>-x</b>		<b>+x</b>	<b>+x</b>
<b>Equilibrium</b>	<b><math>0.10 - x</math></b>		<b>x</b>	<b>x</b>

As  $\text{p}K_{\text{a}} = -\log_{10}K_{\text{a}}$ , at equilibrium,

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

As  $K_{\text{a}}$  is so small,  $x$  will be tiny and  $0.10 - x \sim 0.10$  and so

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

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

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

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:

$$\text{pH} = \text{p}K_{\text{a}} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

To make a buffer with  $\text{pH} = 3.00$  and  $[\text{acid}] = [\text{HF}] = 0.10 \text{ M}$ :

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

Hence,

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

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

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

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{formula mass} \\ &= (0.0068 \text{ mol}) \times (41.99 \text{ g mol}^{-1}) = 0.28 \text{ g} \end{aligned}$$

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 solution is prepared by dissolving 0.050 mol of acetic acid, 0.020 mol of sodium acetate and 0.0010 mol of HCl in water to give a final volume of 250 mL. The  $pK_a$  of acetic acid is 4.76. What is the pH of this solution?

**Marks**  
**3**

**HCl will react with the acetate to produce acetic acid:**



As 0.020 mol of  $\text{CH}_3\text{CO}_2^-$  is initially present, the number of moles after this reaction is  $(0.020 - 0.0010)$  mol = 0.019 mol.

As 0.050 mol of  $\text{CH}_3\text{COOH}$  is initially present, the number of moles after this reaction is  $(0.050 + 0.0010)$  mol = 0.051 mol.

The final volume is 250 mL so the concentrations are:

$$[\text{CH}_3\text{CO}_2^-(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.019 \text{ mol}}{0.250 \text{ L}} = 0.076 \text{ M}$$

$$[\text{CH}_3\text{COOH}(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.051 \text{ mol}}{0.250 \text{ L}} = 0.204 \text{ M}$$

The pH of the solution containing both an acid ( $\text{CH}_3\text{COOH}$ ) and its conjugate base ( $\text{CH}_3\text{CO}_2^-$ ) is given by the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.76 + \log \frac{0.076}{0.204} = 4.33$$

$$\text{pH} = 4.33$$

**Marks**  
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- A 20.0 mL solution of nitrous acid ( $\text{HNO}_2$ ,  $\text{p}K_a = 3.15$ ) was titrated to its equivalence point with 24.8 mL of 0.020 M NaOH. What is the concentration of the  $\text{HNO}_2$  solution?

The number of moles of  $\text{OH}^-$  required in the titration is:

number of moles = concentration  $\times$  volume

$$= (0.020 \text{ mol L}^{-1}) \times (0.0248 \text{ L}) = 4.96 \times 10^{-4} \text{ mol}$$

This is equal to the number of moles of  $\text{HNO}_2$  in 20.0 mL. Hence, the concentration of  $\text{HNO}_2$  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?

$\text{HNO}_2$  is a weak acid so the equilibrium concentrations need to be calculated using a reaction table:

	$\text{HNO}_2$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq})$	$\text{NO}_2^-(\text{aq})$
<b>Initial</b>	<b>0.025</b>	<b>large</b>		<b>0</b>	<b>0</b>
<b>Change</b>	<b>-x</b>			<b>+x</b>	<b>+x</b>
<b>Equilibrium</b>	<b>0.025 - x</b>			<b>x</b>	<b>x</b>

As  $\text{p}K_a = -\log_{10}K_a$ , at equilibrium,

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{NO}_2^-(\text{aq})]}{[\text{HNO}_2(\text{aq})]} = \frac{(x)(x)}{(0.025-x)} = \frac{x^2}{(0.025-x)} = 10^{-3.15}$$

As  $K_a$  is so small,  $x$  will be tiny and  $0.025 - x \sim 0.025$  and so

$$x^2 = 10^{-3.15} \times 0.025 \text{ or } x = [\text{H}_3\text{O}^+(\text{aq})] = 0.00421 \text{ M}$$

As  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(\text{aq})]$ ,

$$\text{pH} = -\log_{10}(0.00421) = 2.38$$

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?

(a) 12.4 mL represents the half equivalence point. At this point,  $[\text{HNO}_2(\text{aq})] = [\text{NO}_2^-(\text{aq})]$  and  $\text{pH} = \text{p}K_a$ . Hence  $\text{pH} = 3.15$

(b) 24.8 mL represents the equivalence point. At this point, all of the  $\text{HNO}_2$  has been converted into  $\text{NO}_2^-$  so:

$$\text{number of moles of } \text{NO}_2^- = 4.96 \times 10^{-4} \text{ mol}$$

The total volume of the solution is  $(20.0 + 24.8) \text{ mL} = 44.8 \text{ mL}$ . Hence:

$$[\text{NO}_2^-(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{4.96 \times 10^{-4}}{0.0448 \text{ L}} = 0.0111 \text{ M}$$

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

	$\text{NO}_2^-$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HNO}_2(\text{aq})$	$\text{OH}^-(\text{aq})$
Initial	0.0111	large		0	0
Change	-y			+y	+y
Equilibrium	$0.0111 - y$			y	y

As  $\text{p}K_a + \text{p}K_b = 14.00$ ,  $\text{p}K_b = 14.00 - 3.15 = 10.85$ . At equilibrium,

$$K_b = \frac{[\text{HNO}_2(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NO}_2^-(\text{aq})]} = \frac{(y)(y)}{(0.025 - y)} = \frac{y^2}{(0.025 - y)} = 10^{-10.85}$$

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

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

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

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

Finally, as  $\text{pH} + \text{pOH} = 14.00$ ,

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

(a) 12.4 mL:  $\text{pH} = 3.15$

(b) 24.8 mL:  $\text{pH} = 7.60$

ANSWER CONTINUES ON THE NEXT PAGE

Qualitatively, how would each of these three pH values be affected if 0.020 M  $\text{NH}_3$  had been used in place of the NaOH solution? The  $\text{p}K_b$  of  $\text{NH}_3$  is 4.76.

**The initial pH is unchanged as no base is present.**

**As  $\text{p}K_b$  for  $\text{NH}_3$  is 4.76,  $\text{p}K_a$  for its conjugate acid  $\text{NH}_4^+$  is  $(14.00 - 4.76) = 9.24$ . The half equivalence point is in the acidic region of the titration (it is at  $\text{pH} = 3.15$  for the weak acid / strong base titration above). This pH is considerably lower the  $\text{p}K_a$  value of  $\text{NH}_4^+$  and so essentially all of the  $\text{NH}_3$  will be present as  $\text{NH}_4^+$  and it will not contribute to  $[\text{H}_3\text{O}^+(\text{aq})]$ . The pH at the half-equivalence point will be the same as it depends only on the  $\text{p}K_a$  of  $\text{HNO}_2$ .**

**The pH at the equivalence point will be lower. At equivalence, the solution will contain  $\text{NO}_2^-$  as in the  $\text{HNO}_2 / \text{OH}^-$  titration. It will also contain  $\text{NH}_4^+$ , the conjugate acid of  $\text{NH}_3$ . As this is weakly acid, the pH will be lowered.**