

- 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:

- before any NaOH is added;
- when half of the HF has been neutralised;
- at the equivalence point; and
- 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	$\rightleftharpoons$	F <sup>-</sup>	H <sup>+</sup>
<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>final</b>	<b>0.10 - x</b>		<b>x</b>	<b>x</b>

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  $0.10 - x \sim 0.10$  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:

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

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

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

**(iii) At this point, all of the original HF has been converted to F<sup>-</sup>. The number of moles of HF originally present is:**

$$\begin{aligned} \text{number of moles of HF} &= \text{concentration} \times \text{volume} \\ &= (0.10 \text{ mol L}^{-1}) \times (0.025 \text{ L}) = 0.0025 \text{ mol} \end{aligned}$$

This is equal to the amount of F<sup>-</sup> 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<sup>-</sup> is therefore:

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

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

	$F^-$	$H_2O$	$\rightleftharpoons$	$HF$	$OH^-$
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  $(1.5 \times 25.0) \text{ mL} = 37.5 \text{ mL}$ . This volume of 0.10 M NaOH contains

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

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

$$\text{excess moles of } OH^- = (0.00375 - 0.0025) \text{ mol} = 0.00125 \text{ mol}$$

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

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

ANSWER CONTINUES ON THE NEXT PAGE

Hence,

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

Lastly,  $\text{pH} = 14.00 - \text{pOH}$ :

$$\text{pH} = 14.00 - 1.70 = 12.30$$

Putting these 4 points together gives the titration curve:

