- A sample of hydrofluoric acid (0.10 M, 25.0 mL) is titrated with 0.10 M NaOH. The pK_a of hydrofluoric acid, HF, is 3.17. Calculate the pH at the following four points.

before any NaOH is added

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	$\rightleftharpoons$	$\mathbf{F^-}$	$\mathbf{H^+}$
initial	**0.10**		**0**	**0**
change	**-x**		**+x**	**+x**
final	**0.10 – x**		**x**	**x**

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:

$$x^2 = 0.10 \times 10^{-3.17} \quad \text{or} \quad x = 0.00822 \text{ M} = [H\cdot]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H\cdot] = -\log_{10}[0.00822] = 2.09$$

pH = **2.09**

when half of the HF has been neutralised

At this point, half of the original HF has been converted to its conjugate base F^-. The pH can be calculated using the Henderson-Hasselbalch equation:

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

pH = **3.17**

at the equivalence point

At this point, all of the original HF has been converted to F^-. The number of moles of HF originally present is:

number of moles of HF = concentration × volume
= (0.10 mol L^{-1}) × (0.025 L) = 0.0025 mol

This is equal to the amount of F^- 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^- is therefore:

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

	F⁻	H₂O	⇌	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:

$y^2 = 0.050 \times 10^{-10.83}$ or $y = 8.59 \times 10^{-7}$ 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

$pH = 14.00 - 6.07 = 7.93$

pH = **7.93**

after the addition of 37.5 mL of NaOH

This volume of 0.10 M NaOH contains

number of moles of NaOH = concentration × volume
= (0.10 mol L⁻¹) × (0.0375 L) = 0.00375 mol

From above, there was original 0.0025 mol of HF present so the excess of OH⁻ is:

excess moles of OH⁻ = (0.00375 – 0.0025) mol = 0.00125 mol

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

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[OH⁻] = number of moles / volume
        = (0.00125 mol) / (0.0625 L) = 0.020 mol L⁻¹

Hence,

pOH -= -log₁₀[OH⁻] = -log₁₀(0.020) = 1.70

Lastly, pH = 14.00 – pOH:

pH = 14.00 – 1.70 = 12.30

pH = **12.30**

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