• The structure of common aspirin, acetylsalicylic acid, is shown below. It has a pK_a value of 3.5.



Calculate the pH of a solution in which one normal adult dose (0.65 g) is dissolved in 250 mL of water.

The chemical formula of acetylsalicylic acid is C₉H₈O₄. It has a molar mass of $(9 \times 12.01 \text{ (C)} + 8 \times 1.008 \text{ (H)} + 4 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 180.154 \text{ g mol}^{-1}$.

The number of moles present corresponds to:

number of moles = mass / molar mass = $(0.65 \text{ g}) / (180.154 \text{ g mol}^{-1}) = 0.00361 \text{ mol}$

The concentration when this amount is dissolved in 250 mL of water is therefore:

[aspirin] = number of moles / volume = (0.00361 mol) / (0.25 L) = 0.0144 M

As aspirin is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	C ₉ H ₈ O ₄	H ₂ O	 H_3O^+	C ₉ H ₇ O ₄
initial	0.0144	large	0	0
change	- <i>x</i>	negligible	+ <i>x</i>	+ <i>x</i>
final	0.144 – <i>x</i>	large	x	x

The equilibrium constant K_a is given by:

$$K_{\rm a} = \frac{[{\rm H}_3{\rm O}^+][{\rm C}_9{\rm H}_7{\rm O}_4^-]}{[{\rm C}_9{\rm H}_7{\rm O}_4]} = \frac{x^2}{0.0144 - x}$$

As $pK_a = -\log_{10}K_a$, $K_a = 10^{-3.5}$ and is very small, $0.0144 - x \sim 0.0144$ and hence:

$$x^2 = 0.0144 \times 10^{-3.5}$$
 or $x = 2.1 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$

Hence, the pH is given by:

$$pH = -log_{10}[H_3O^+] = -log_{10}(2.1 \times 10^{-3}) = 2.7$$

Answer: 2.7

If blood has a pH of 7.4, what percentage of aspirin is present in the deprotonated form in a solution consisting of one normal adult dose in 250 mL of blood?

Using the Henderson – Hasselbalch equation,

$$\mathbf{pH} = \mathbf{pK}_{\mathbf{a}} + \log \frac{[\mathbf{base}]}{[\mathbf{acid}]}$$

At a pH of 7.4

$$7.4 = 3.5 + \log \frac{[base]}{[acid]}$$
 so $\frac{[base]}{[acid]} = 10^{3.9} = 7900$

The deprotonated, conjugate base form completely dominates at this pH.

Answer: 100% base

Solutions of aspirin are unstable due to hydrolysis. If 0.26 g of a normal adult dose remains after 4 hours, what is the half-life of aspirin?

The number of moles present after 4 hours corresponds to:

number of moles = mass / molar mass = $(0.26 \text{ g}) / (180.154 \text{ g mol}^{-1}) = 0.00144 \text{ mol}$

The concentration when this amount is dissolved in 250 mL of water is therefore:

[aspirin] = number of moles / volume = (0.00144 mol) / (0.25 L) = 0.00577 M

The amount present after time t is related to the amount initially present through the equation:

 $\ln[\mathbf{A}] = \ln[\mathbf{A}]_0 - kt$

From above, [A]₀ = 0.0144 M. As [A] = 0.00577 M with *t* = 4 hours:

 $\ln(0.00577) = \ln(0.0144) - k \times 4$

k = 0.23

Finally, the half life, $t_{1/2}$, is given by

 $t_{1/2} = \ln 2 / k = 3$ hours

Answer: **3 hours**