• Codeine, a cough suppressant extracted from crude opium, is a weak base with a  $pK_b = 5.79$ . What is the pH of a 0.020 M solution of codeine?

As codeine, is a weak base and so [OH<sup>-</sup>] must be calculated. for example using a reaction table:

	codeine	H <sub>2</sub> O	+	<b>codeineH</b> <sup>+</sup>	OH.
initial	0.020	large		0	0
change	- <i>x</i>	negligible		+x	+x
final	0.020 - x	large		x	x

The equilibrium constant  $K_b$  is given by:

$$K_{\rm b} = \frac{[\rm codeineH^+][OH^=]}{[\rm codeine]} = \frac{x^2}{(0.020 - x)}$$

As  $pK_b = -\log_{10}K_b = 5.79$ ,  $K_b = 10^{-5.79}$ . Hence,

$$\frac{x^2}{(0.020-x)} = 10^{-5.79}$$

As  $K_b$  is very small,  $0.020 - x \sim 0.020$  and hence:

$$x^2 = 0.020 \times 10^{-5.79}$$
 or  $x = 1.8 \times 10^{-4} \text{ M} = [\text{OH}^-(\text{aq})]$ 

Hence, the pOH is given by:

$$pOH = -log_{10}[OH^{-}] = -log_{10}[1.8 \times 10^{-4}] = 3.74$$

Finally, pH + pOH = 14.00 so

pH = 14.0 - 3.74 = 10.26

Answer: 10.26

• A buffer solution is formed with 0.250 M CH<sub>3</sub>COOH and 0.350 M CH<sub>3</sub>COONa. What is the pH of this buffer solution? ( $K_a$  of acetic acid =  $1.8 \times 10^{-5}$  M.)

The pH of a buffer solution is given by the Henderson-Hasselbalch equation:

$$\mathbf{pH} = \mathbf{pK}_{\mathbf{a}} + \log\left(\frac{\mathbf{base}}{\mathbf{acid}}\right)$$

As  $pK_a = -log_{10}K_a = -log_{10}(1.8 \times 10^{-5}) = 4.74$ . With [base] = [CH<sub>3</sub>COONa] = 0.350 M and [acid] = [CH<sub>3</sub>COOH] = 0.250 M,

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$$pH = 4.74 + log\left(\frac{0.350}{0.250}\right) = 4.89$$

As the buffer contains a higher concentration of base than acid, the  $pH > pK_a$ .

Answer: 4.89

Calculate the pH of the solution formed when  $6.3 \times 10^{-2}$  mol of NaOH is added to 1.0 L of the buffer solution.

In a 1.0 L solution of the buffer, there is 0.250 mol of CH<sub>3</sub>COOH and 0.350 mol of CH<sub>3</sub>COO<sup>-</sup>.

The OH<sup>-</sup> will react with the CH<sub>3</sub>COOH to produce CH<sub>3</sub>COO<sup>-</sup>. The concentration of the former will therefore decrease whilst the concentration of the latter will increase. After the OH<sup>-</sup> is added:

number of moles of CH<sub>3</sub>COOH =  $(0.250 - 6.3 \times 10^{-2})$  M = 0.187 mol number of moles of CH<sub>3</sub>COO<sup>-</sup> =  $(0.350 + 6.3 \times 10^{-2})$  M = 0.413 mol

As the volume of solution does not change, these are also the new acid and base concentrations. Hence, the buffer now has:

$$pH = 4.74 + \log\left(\frac{0.413}{0.187}\right) = 5.09$$

As base has been added, there is an increase in the pH. As it is being added to a buffer system, this change is small. Addition of this quantity of base to water would increase the pH by 1.20 units.

Answer: 5.09