Deacon's Challenge
No 98 - Answer

A buffer solution (pH 4.74) contains acetic acid (0.05 mol/L) and sodium acetate (0.05 mol/L) i.e. it is a 0.1M acetate buffer. Calculate the pH after addition of 2 mL of 0.025M hydrochloric acid to 10 mL of the buffer.

The dissociation to be considered is:

$$HAc \rightarrow H^+ + Ac^-$$

and the concentrations of all species are related by the Henderson Hasselbalch equation:

$$pH = pK_a + \log_{10} \frac{[Ac^-]}{[HAc]}$$

By definition the pK_a is the pH value at equimolar concentrations of salt and acid, in this case 4.74.

(This can be verified by substituting 0.05 mol/L for [Ac^-] and [HAc] into the above equation and calculating pK_a. The small amount of Ac^- liberated from the slight dissociation of the weak acid HAc is negligible and can be ignored.

$$4.74 = pK_a + \log_{10} \frac{0.05}{0.05}$$

Since 0.05/0.05 = 1 and $\log_{10}1$ is 0, then pK_a = 4.74)

Addition of HCl to this buffer converts some of the acetate ions into acetic acid:

$$Ac^- + H^+ \rightarrow HAc$$

(The minute amount of Ac^- liberated by dissociation of the HAc produced is negligible and can be ignored)

The next step is to calculate the adjusted concentrations of Ac^- and HAc, substitute these into the Henderson-Hasselbalch equation (using pK_a = 4.74) then solve for the new pH.

$$\text{Final } [Ac^-] = \text{Initial } [Ac^-] - \text{Added } [HCl]$$

$$\text{Final } [HAc] = \text{Initial } [HAc] + \text{Added } [HCl]$$

Allowance must be made for the dilution resulting from mixing 10 mL buffer with 2 mL HCl (total volume = 12 mL):

$$\text{Initial } [Ac^-] = \frac{\text{Initial } [HAc] \times 10}{12} = \frac{0.05 \times 10}{12} = 0.0417 \text{ mol/L}$$

$$\text{Added } [HCl] = \frac{\text{Initial } [HCl] \times 2}{12} = \frac{0.025 \times 2}{12} = 0.0042 \text{ mol/L}$$

$$\text{Final } [Ac^-] = 0.0417 - 0.0042 = 0.0375 \text{ mol/L}$$

$$\text{Final } [HAc] = 0.0417 + 0.0042 = 0.0459 \text{ mol/L}$$

$$\begin{aligned} \text{Final pH} &= 4.74 + \log_{10} \frac{0.0375}{0.0459} \\ &= 4.74 + \log_{10} 0.817 \\ &= 4.74 + (-0.088) \\ &= \mathbf{4.65} \text{ (to 3 sig figs)} \end{aligned}$$

(If the HCl was diluted with water instead of buffer then the pH would be $-\log_{10} 0.0042$ = 2.4 which illustrates the efficiency of buffering.)

Question 99

Stating any assumptions you make calculate the pH of the following solutions:

0.01 M NaOH
0.02 M lactic acid
A solution obtained by mixing 10 mL of solution a) with 10 mL of solution b)

(The ionic product of water (K_W) is 1.0 x 10^{-14} and the dissociation constant of lactic acid (K_a) is 1.38 x 10^{-4}.)