

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:



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

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

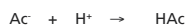
By definition the pK_a is the pH value at equimolar concentrations of salt and acid, in this case 4.74.

(This can be verified by substituting 0.05 mol/L for $[\text{Ac}^-]$ and $[\text{HAc}]$ 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.

$$4.74 = \text{pK}_a + \log_{10} \frac{0.05}{0.05}$$

Since $0.05/0.05 = 1$ and $\log_{10} 1$ is 0, then $\text{pK}_a = 4.74$

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



(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 $\text{pK}_a = 4.74$) then solve for the new pH.

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

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

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

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

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

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

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

$$\text{Final pH} = 4.74 + \log_{10} \frac{0.0375}{0.0459}$$

$$= 4.74 + \log_{10} 0.817$$

$$= 4.74 + (-0.088)$$

$$= 4.65 \text{ (to 3 sig figs)}$$

(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 1.0×10^{-14} and the dissociation constant of lactic acid (K_a) is 1.38×10^{-4} .)