Marks 4

- Citric acid, $C_6H_8O_7$, has three pK_a values: pK_{a1} = 3.13, pK_{a2} = 4.76 and pK_{a3} = 6.40. Explain, giving exact volumes and concentrations, how to make 1.0 L of a citrate-based buffer with pH 5.58.

The desired pH is equally close to pK_{a2} and pK_{a3} so the best buffer could use either of these equilibria. Using pK_{a3} corresponds to using the equlibrium:

$$HCit^{2-}(aq) \rightleftharpoons H^+(aq) + Cit^{3-}(aq)$$

Using the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\frac{[base]}{[acid]} = 6.40 + \log\frac{[Cit^{3-}]}{[HCit^{2-}]}$$

At pH = 5.58,

$$\log\frac{[Cit^{3-}]}{[HCit^{2-}]} = (5.58 - 6.40) = -0.82$$

$$\frac{[Cit^{3-}]}{[HCit^{2-}]} = 0.15$$

As 1.0 L of the buffer is required,

$$[Cit^{3-}] = n_{Cit3-} / 1.0 \text{ M}$$
$$[HCit^{2-}] = n_{HCit2-} / 1.0 \text{ M}$$

So,

$$\frac{[Cit^{3-}]}{[HCit^{2-}]} = \frac{n_{Cit^{3-}}}{n_{HCit^{2-}}} = 0.15$$

There are *many* ways to construct the buffer to achieve this ratio when the acid and base are mixed.

If the two solutions have the same initial concentrations, then the ratio of the *volumes* used is 0.15. The volumes add up to 1000 mL:

volume of $HCit^{2-}$ = x L **volume of Cit^{3-} = 1.0 – x L**

So,

$$\frac{V_{Cit^{3-}}}{V_{HCit^{2-}}} = \frac{1.0-x}{x} = 0.15$$

$$x = 0.87$$

Hence, 870 mL of $HCit^{2-}$ and 130 mL of Cit^{3-} are used.