CH1011 Tutorial 9 Answers

1. How would you make up a buffer solution?
   Illustrate your answer using acetic acid (CH_3COOH; pKa = 4.74).

A buffer solution is made by mixing equal, strong concentrations of a weak acid and the salt of the conjugate base of this acid where the desired pH is the pKa value of the acid. Varying the amounts of acid and base allows for the alteration of the pH to slightly different values according to the Henderson-Hasselbach equation.
For instance 0.5M CH_3COOH (weak acid) and 0.5M $CH_3COO^-Na^+$ when mixed would form a buffer solution with a pH around 4.74.

2. Explain why the pH of rainwater is not neutral (pH 7.0).

Rainwater is composed of water vapour that has condensed around small cloud condensation nuclei (small particles that float about in the air) to form cloud drops which have then coalesced to form raindrops. The raindrops contain water that is in equilibrium with the gases in the atmosphere. CO_2, SO_2 (SO_3) and NOx (NO, NO_2) are the main gases that are water soluble and equilibrate with rainwater. In the raindrop further reaction occurs to form H_2CO_3, H_2SO_4, or HNO_3. In an unpolluted atmosphere the carbonic acid sets the pH at around 5.6, in polluted regions the formation of the mineral acids may lower the pH to 2.0.
In the raindrop these acids are neutralised by any basic mineral dust that has ended up in the raindrop and ammonia that is also present in the atmosphere.

3. Calculate the hydrogen ion concentration, pH and pOH for a 0.200 M solution of propanoic acid (HPr, pK_a = 4.89).

Equation: $HPr + H_2O \rightleftharpoons Pr^- + HO^+$

Ka $= 10^{(-pKa)}$ - as $pKa = -\log_{10}Ka$
$= 1.29e-5$

$[H+] = \sqrt{Ka \times [HA]} = \sqrt{1.29e-5 \times 0.200} = 0.00161$ mol dm^{-3}

- check 100 x Ka << [HA]
  100 x 1.29 e-5 << 0.2 therefore it was valid to use the above approximation

$pH = -\log_{10}[H+] = -\log_{10}(0.00161) = 2.79$

$pOH = 14 - pH = 11.21$

4. Explain the chemical basis for the COD test and why the COD test is important in environmental monitoring.

In a water body that contains significant organic pollutants the microbial population can consume more oxygen than is available in the water resulting in a large DO drop. Once the DO approaches zero then most organisms that require O_2 to respire will die (eg. fishkills).

$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$

Normal values in unpolluted water for the COD are around 2mg /L, high values are found in organically polluted water 1000s mg /L.

The COD test is similar in that it involves oxidation of the residual DOC but it differs in that a strong chemical oxidant (e.g. H^+/Cr_2O_7) is added in excess and the amount in excess is determined by back titration with standard Fe^{2+} solution.

Organic reaction: $Cr_2O_7^{2-}$ consumes organic matter in a quantitative relationship:

$$C_6H_{12}O_6(s) + 4Cr_2O_7^{2-} + 32H^+ \rightarrow 6CO_2\uparrow + 8Cr^{3+} + 22H_2O$$

Titration reaction: used work out the remaining $Cr_2O_7^{2-}$

$Cr_2O_7^{2}- + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$ (titrant)

The titration works out the amount of $Cr_2O_7^{2-}$ consumed, this is subtracted from the original amount of $Cr_2O_7^{2-}$. The empirical relationship 4 moles of $Cr_2O_7^{2}$ is equivalent to 6 moles of O_2 is used to along with the molar mass of O2 to calculated the COD in mg /L.

The advantage of the COD method is that it takes only two hours at reflux to carry out the $Cr_2O_7^{2-}$ oxidation, which means it is the most appropriate method for testing industrial waste effluent. Other tests such as the BOD take 5 days.

5. Reverse osmosis is a useful process in obtaining freshwater from marine water. How does this process work and what are the disadvantages?

In **Reverse Osmosis** the solvent passes through a semi-permeable membrane from a region of low solvent (here water) concentration to one of higher concentration (e.g. from salt solution to pure water). This is achieved by applying a pressure on the low solvent concentration side of the membrane which is greater than the natural osmotic pressure of the system. $p_{ext} > \pi$

The problem with reverse osmosis is that it is energy intensive, while portable hand pump versions are useful for emergency use the provision of municipal scale drinking water supply based on R.O. water is only possible where a relatively cheap energy source can be used to supply the high pressures required to push the saline water against the membrane at a reasonable rate.