Solutions to Exercises – chapter 10

10.1) Why must all electroanalytical cells contain a reference electrode?

In order to obtain a stable reference potential from an electrode, no current must be allowed to flow across the solution / electrode interface. Current will obviously flow through the counter and working electrodes; for this reason a third dedicated reference electrode may be introduced into the cell. No current flows through this electrode and so a stable reference potential may be obtained.

10.2) Why is the normal hydrogen electrode now very rarely used?

The normal hydrogen electrode historically was the first reference electrode to be developed and described. This necessitated the use of flowing hydrogen gas which is both cumbersome and presents an explosion risk. Today a number of reference electrodes such as the standard calomel electrode and / or the silver/silver chloride electrode may be used – these are far easier to use in practice and give extremely good performance in terms of reproducibility.

10.3) Describe three forms of mass transport to electrode surfaces.

Diffusion – mass transport down a concentration gradient.

Migration – movement of material due to the influence of an electrical field.

Convection – forced physical movement of material (e.g. via stirring, or due to density changes – for example when a solution is heated).

10.4) From the two half cell equations below determine the cell potential:

$Fe^{3+} + e^{-} = Fe^{2+}$ $E^0 = 0.771$ V

$I^{-}_{3} + 2e^{-} = 3I^{-}$ $E^0 = 0.5355$V

Cell potential = 0.771-0.5355V = 0.2355V

10.5) From the two half cell equations below determine the cell potential:

$Fe^{3+} + e^{-} = Fe^{2+}$ $E^0 = 0.771$ V

$Zn^{2+} + 2e^{-} = Zn$ $E^0 = -0.763$V

Cell potential = 0.771-(-0.763)V = 1.534V

10.6) From the two half cells equations below determine the cell potential:

$I_{2(aq)} + 2e^{-} = 2I^{-}$ $E^0 = 0.6197$ V

$Sn^{4+} + 2e^{-} = Sn^{2+}$ $E^0 = 0.154$ V

Cell potential = 0.6197-0.154V = 0.4657V

10.7) A pH 3 aqueous solution contains 1x10^{-3} M CrO_7^{2-} and 1.5x10^{-2} M Cr^{3+}. Calculate the potential of the half cell reaction.

(E^0 = 1.33 V: $Cr_2O_7^{2-}$ + 14H^+ 6e^- ⇆ 2Cr^{3+} 7H_2O)

$E = E^0 – (2.302RT / nF) \log_{10} [Red/Ox]$

$E = 1.33 – 0.0118 \log_{10} \{(1x10^{-3})/1.52x10^{-2} \text{ x } (10^{-3})^8\}$ V

E = 1.333 – 0.269

∴E = 1.064V

10.8) The potential of a cell with respect to a SCE reference electrode is: - 0.845 V. Calculate the potential with respect to a SHE. (The cell potential using the SHE is 0.242V less negative than SCE).

Cell potential = -0.845 + 0.242V = <u>-0.603V</u>

10.9) The potential of a half cell with respect to a SCE reference electrode is: - 0.793 V. Calculate the potential with respect to a Ag/AgCl electrode. (The cell potential using the Ag/AgCl is 0.014V less negative than SCE).

Cell potential = -0.793 + 0.014V = <u>-0.779V</u>

10.10) A pH electrode is recording a pH of 6.1: Acid added to the solution and the potential of the pH electrode increases by 177mV. What is the pH of the new solution?

An increase of 59mV corresponds to a 10-fold increase in the [H+].

An increase in 177mV corresponds to 177/59 pH units = 3 pH units.

The new pH will therefore be 6.1+ 3 = pH 9.1

10.11) Explain why ion selective electrodes exhibit logarithmic responses with respect to analyte concentration.

Ion selective electrodes exhibit logarithmic responses due to the log term of the Nernst equation: ie:

$$E = E^0 – (2.302RT / nF) \log_{10} [Red/Ox]$$

Ion selective electrodes are potentiostatic and respond to the concentration of a particular ion, the concentration of which, determines the potential of the electrode.

10.12) Why are electrolytes often added to samples for electroanalysis?

Electrolytes are often added to samples to lower the resistance or impedance of the solution by offering ions for charge conduction through the electrolyte solution.

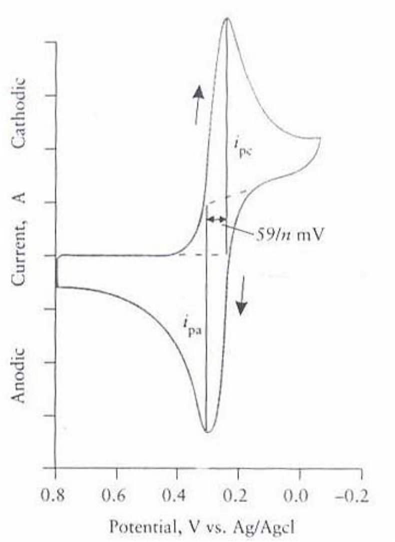
10.13) Explain is meant by a chemically modified electrode.

A chemically modified electrode is an electrode, the surface of which has been chemically modified in some way – for example, by coating with a polymer or immobilised reagent layer.

10.14) What advantages can be gained by using micro-electrodes? What possible drawbacks can be encountered using micro-electrodes?

Micro-electrodes offer stir independent responses, for example, when used within sensors, since the rate of diffusional mass transport will exceed mass transport via concentration. Micro-electrodes also offer lower limits of detection than can be obtained using macroscopic electrodes.

10.15) Sketch a cyclic voltammogram for a diffusion controlled reversible one electron process; how will the shape of this voltammogram differ for a two electron process?



The peak separation will be halved i.e. the peak separation will change from being 59mV to being 59/2: ie 29.5mV.

10.16) What are the advantages and disadvantages associated with using a dropping mercury electrode in comparison to solid electrodes?

Principal Advantages:

A DME uses mercury which always offers a clean electrode surface. Mercury offers moreover favourable electrode kinetics to many redox couples.

Principal Disadvantages:

A new mercury drop is constantly being formed. This grows until it reaches a critical drop weight when the drop falls from the capillary electrode; a new drop then begins to grow and the process repeats itself. The current grows and falls in a zig-zag like manner as shown within Fig 10.10 of book.