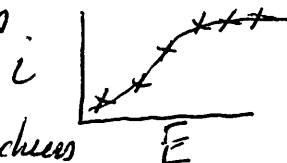


Problems Chapter 25

25.2 a) voltammogram - recording of the current that flows through a working electrode as a function of the applied potential.

$$i \sqrt{E}$$

b) hydrodynamic voltammetry - used for the detection and determination of oxidizable or reducible species exiting a column from LC or in flow injection analysis. The voltammogram is recorded as a series of points based on the current at different potentials.

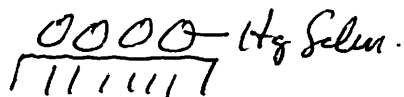


c) Nernst diffusion layer - the thickness of a depletion layer growing outward from an electrode during a reaction where concentrations of reactants and products are different.

$$l = \sqrt{Dt}$$

l = diffusion layer thickness, cm
 D = diffusion coefficient, cm²/s
 t = time, s

d) mercury thin film electrode - droplets of liquid Hg formed on a solid electrode. Often used for anodic stripping voltammetry.



e) half wave potential - potential at half the limiting current

$$i \sqrt{E - E_{1/2}}$$

$$E_{1/2} \approx E^0$$

f) Voltammetric sensor - when an electrode has been modified to impart some molecular recognition chemistry on the surface, it can provide selectivity in the voltammetric method.

25-3. High supporting electrolyte concentration is used in most electroanalytical measurements to impart high conductivity to the solution connecting the electrodes. It is also added to minimize the effects of migration on mass transport, when a charged analyte is being studied. When the concentration of electrolyte exceeds analyte by $\sim 100\times$, then the fraction of current caused by analyte is near zero.

25-4. The reference potential is placed close to the working electrode in voltammetric measurements to minimize the potential drop between the working and counter electrodes

$$E_{\text{TRUE}} = E_{\text{APPL}} - iR$$

By placing the reference close to the working electrode, iR becomes a small value and the true potential applied to the working electrode is E_{APPL} .

25-7. The purpose for the electrodeposition step in ASV is to preconcentrate the metal. The amount of metal deposited, $M^{+n} + ne^- \rightleftharpoons M$, controls the magnitude of the stripping current. Important variables include E_{dep} , time and stirring.

The redox reaction is

a)



$$E_{O/H_2O} = E^{\circ}_{O/H_2O} + \frac{0.0592}{2} \log \frac{[O][H^+]^2}{[H_2O]} - E_{red}$$

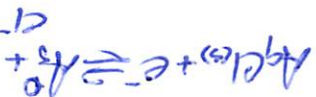
$$E_{O/H_2O} = E_{O/H_2O}^{\circ} + \frac{0.0592}{2} \log \frac{1}{[H^+]^2} - E_{red}$$

$$E_{H_2} = E^{\circ}_{O/H_2O} + \frac{0.0592}{2} \log [H^+]^2 - E_{red}$$

same $P_{O_2} = P_{H_2}$

$$E_{H_2} = 0.599V + \frac{0.0592}{2} \log (1.0 \times 10^{-7})^2 - E_{red}$$

$$E_{red} = 0.244V$$



$$E_{H_2} = 0.185V - 0.244V = -0.059V$$

b)

at $pH = 4.0$ $[H^+] = 1.0 \times 10^{-4} M$

same as above $P_{O_2} = P_{H_2}$

$$E_{H_2} = 0.599V + \frac{0.0592}{2} \log (1.0 \times 10^{-4})^2 - E_{red}$$

$$E_{red} = 0.244V$$



$$E_{H_2} = 0.362V - 0.244V = 0.118V$$

Making adjustment were possible shifts E_{H_2} to more positive values

Remember:

