

Chemistry 4114 Homework solutions

- 25-1 a. Voltammetry is a general term used in electrochemistry to describe an experiment in which a potential waveform is applied to an electrode and the resulting current is measured. Polarography is a specific type of voltammetry experiment in which the electrode used is a Dropping Mercury Electrode.
- b. Linear scan polarography is a polarographic method in which the potential is varied in a linear fashion with time. Pulse polarographic methods employ a potential step potential profile that is sequenced with the drops of the Hg electrode. Pulse polarographic methods sample the current at discrete interval during the potential program, allowing one to easily discriminate against the capacitive current in the measurement. Linear scan polarography measures the current continuously during the drop growth.
- g. Laminar flow is flow in which there are well defined regions of fluid velocity over the cross section of the vessel that encloses the fluid. Generally, the flow velocity is slow near the boundaries of the container, and faster toward the middle of the container. Turbulent flow is fluid flow that is random and is not clearly defined across the dimensions of the container.
- 25-2 c. The Nernst diffusion layer is the layer of solution adjacent to the electrode in which the solution is not influence by the mechanical movement induced by stirring. Consequently, mass transport through this region of the solution up to the electrode surface can occur only by diffusion.
- e. The half-wave potential is the potential at which the current is one-half of the limiting value in a combined convection-diffusion mass transport electrochemical measurement. This is an experimental measurement that approximates the standard potential of a redox half reaction.
- 25-3 Organic redox reaction often involve proton transfer. In the absence of buffering, the release (or acceptance) of a proton can dramatically alter the pH of the solution at the electrode surface. This change in pH can cause a shift in the standard potential of the redox reaction, resulting in a change in the thermodynamics of the electrode reaction during the measurement. By buffering the solution pH, one controls the redox reaction thermodynamics by not allowing the reaction to dramatically alter the solution pH.

25-5

$$E = E_{1/2} - \frac{0.0592}{n} \log\left(\frac{i}{i_l - i}\right)$$

The number of electrons transferred is given by “n” in the above equation. If you rearrange the equation to:

$$\log\left(\frac{i}{i_l - i}\right) = -\frac{n}{0.0592}(E - E_{1/2})$$

Then make a plot of $(E - E_{1/2})$ vs. $\log\left(\frac{i}{i_l - i}\right)$, that plot should be a straight line whose slope is equal to $-\frac{n}{0.0592}$.

25-13 Anodic stripping is more sensitive than other voltammetric measurements because it involves a preconcentration step. The first stage of a stripping analysis is the deposition of the analyte atoms into the Hg drop. This results in a concentration enhancement because the Hg drop has a much smaller volume than does the surrounding solution. The analysis step is the linear potential scan from negative potential to positive potential that results in the re-oxidation of the metal atoms that were deposited into the mercury during the deposition step. The current in a voltammetric experiment is proportional to the concentration of the analyte. In an anodic stripping experiment, this is the concentration of the atoms in the Hg drop.