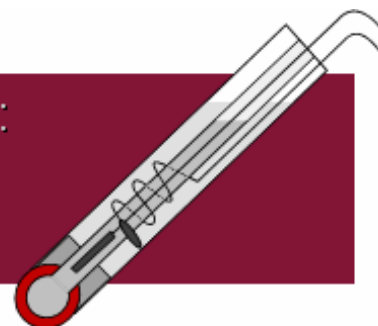


Analytical Electrochemistry : Potentiometry

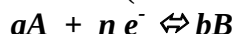
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The Nernst Equation

The technique of *potentiometry* involves the measurement of cell potentials under conditions of no current flow. In the electrochemical cell, if a high impedance device like a voltmeter, is placed between the indicator and reference electrodes, no current will flow between the two compartments. As we have seen, it is possible under these conditions to measure the potential difference that exists between the two electrodes. For cells with all reactants present at unit activity, the measured cell potential (neglecting junction potential effects) will be the *standard cell potential*, E^0_{cell} . As a reminder, *activity* defines an “effective concentration” for a particular species, and takes into account all the *interionic interactions* that the ions experience in the solution, not just a count of the number of molecules of a species per liter (molarity). In real applications of potentiometry, reactant activities are seldom (read *never*) equal to unity, and measured cell potentials move away from those that result from the tabulated values of E^0 .

A fundamental expression for characterizing redox systems under equilibrium conditions is the Nernst equation. One usually has encountered this expression early in their study of electrochemistry, perhaps in a general chemistry course long ago. The Nernst equation allows the calculation of relative activities of the species in a redox reaction as a function of the measured electrode potential (E) and the standard reduction potential (E^0) for the half reaction. For the general redox reaction (written as a reduction)



the Nernst equation takes the form

$$E = E^0 - (RT/nF) \log [(\mathcal{A}_B)^b / (\mathcal{A}_A)^a]$$

where R is the gas constant ($8.314 \text{ (V} \cdot \text{C)/(K} \cdot \text{mol)}$), T is temperature in K, n is the stoichiometric number of electrons involved in the process, F is the Faraday constant ($96,485 \text{ C/equivalent}$) and $\mathcal{A}_B$ and $\mathcal{A}_A$ are the activities of the reduced and oxidized members of the redox pair, respectively. At 25°C , the value of (RT/F) is equal to 0.0592 , and the Nernst equation becomes

$$E = E^0 - (0.0592/n) \log [(\mathcal{A}_B)^b / (\mathcal{A}_A)^a]$$

In practical usage, it is convenient to replace activities in the Nernst equation with concentrations. Because E^0 values are *standard reduction potentials* they are not

appropriate when concentration values are used. (For a review of standard potentials and electrochemical cells, you can access the companion “Concepts” module at www.asdlib.org). Instead, it is proper to use *formal potentials*, $E^{0'}$, which are half-cell potentials measured when the concentration (not activity) ratio of $[B]/[A]$ is unity and concentrations of other solution species are specified and fixed. These values provide corrections for activity effects under the cell conditions for which they have been measured, and should be used whenever they are available. Tables containing formal potentials for many redox reactions are readily available. If an $E^{0'}$ value is unavailable, the use of E^0 generally results in a reasonably small error.

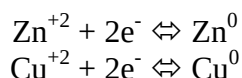
Substituting $E^{0'}$ and concentration terms for activities, the Nernst equation for the general reaction above (at 25 °C) becomes

$$E = E^{0'} - (0.0592 / n) \log ([B]^b / [A]^a)$$

where square brackets represent concentrations in moles/L.

The Nernst equation can be applied to each of the half reactions in an electrochemical cell in turn, allowing the calculation of cathode and anode potentials at varying values of concentrations. The two half reaction potentials are then combined as before to determine the value of the overall cell potential.

Consider the following half reactions for an electrochemical cell:



If instead of unit activities, assume the cell concentrations of Zn^{+2} and Cu^{+2} were set at 0.00100 M and 0.00500 M respectively by dissolving the appropriate amount of each nitrate salt in the respective half-cells. The Nernst equation can now be used to calculate each of the half cell potentials at this concentration. (E^0 values will be used in this example instead of $E^{0'}$.) As the solid electrodes are both the elemental form of the element, the activity for each (and hence the concentration term) is reduced to 1.0.

Anode: $E_a = E^0 - (0.0592 / n) \log ([\text{Products}] / [\text{Reactants}])$

$$= -0.763 \text{ V} - (0.0592/2) \log ([0.00100] / [1])$$

$$= -0.674 \text{ V}$$

Cathode: $E_c = 0.339 \text{ V} - (0.0592/2) \log ([0.00500] / [1])$

$$= 0.339 \text{ V} - (0.0592/2) \log ([0.00500] / [1])$$

$$= 0.407 \text{ V}$$

The overall cell potential (now E_{cell} instead of E^0_{cell}) is calculated as follows:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.407 \text{ V} - (-0.674 \text{ V}) = +1.08 \text{ V}$$

In practice, potentiometric measurements involve at least one reference electrode whose composition and potential are fixed, and the concepts of anode and cathode are of only peripheral importance. Most measurements will include the use of a calibration plot for which only the magnitude of measured potential is related directly to analyte activity.