# Electrochemistry

**Unit15B:** Nernst Equation

### Knowledge/Understanding Goals:

* how to work with galvanic & electrolytic cells under non-standard conditions using the Nerst Equation.

**The Nernst Equation**

The voltaic cells we have discussed so far have all been at standard conditions of 1 atm, 25⁰C, and 1M solutions. But what happens when 1M solutions are not utilized in the cells? To calculate the theoretical potential of such cells, the following equation is applied:

***R T* [C]c [D]d [Ox]**

***E* = *E*° - ----- ln** QQ **= --------- = ---**

***n F* [A]a [B]b [Red]**

This is known as the **Nernst equation**. where *R, T, Q* and *F* are the gas constant (8.314 J mol-1 K-1), temperature (in K), reaction quotient, and Faraday constant (96485 C) respectively.

The equation allows us to calculate the cell potential of any galvanic cell for any concentrations. Some examples are given in the next section to illustrate its application. (Ex: Cu + Ag+ → Ag + Cu2+, 1.2M AgNO3 & 0.77M Cu(NO3)2, 313K)

### The Nernst Equation at 298 K

At any specific temperature, the Nernst equation derived above can be reduced into a simple form. For example, at the standard condition of 298 K (25°), the Nernst equation becomes

**0.0592 V [C]c [D]d**

***E* = *E*° - --------- log** QQ **= ---------**

***n* [A]a [B]b**

Please note that log (based 10) is applicable here instead of the natural logoritm, ln. n equals the moles of electrons in motion according to the half-reaction.

**The Nernst Equation at Equilibrium & 298K**

When a cell is at equilibrium, Δ*E* = 0.00 and the Q expression becomes an equilibrium constant *K*, which bears the following relationship:

***n* Δ*E*°**

**log *K* = --------**

**0.0592**

where **Δ***E*° is the difference of standard potentials of the half cells involved. A battery containing any voltage is not at equilibrium.

The Nernst equation also indicates that you can build a battery simply by using the same material for both cells, but by using different concentrations. Cells of this type are called **concentration cells**.

### Example 1

**Calculate the EMF of the cell**

**Zn(s) | Zn2+** **(0.024 M) || Zn2+** **(2.4 M) | Zn(s)**

***Discussion***

Understandably, the Zn2+ ions try to move from the concentrated half-cell to a dilute solution. In reality, to even out the concentration of ions in each half-cell, ions will be converted into neutral metal (reduced) in the concentrated cell while ions will be created from neutral metal (oxidized) in the dilute cell. The ions themselves are not in motion, the electrons are.

***Solution***

Zn2+ (2.4 M) + 2 e- → Zn Reduction

Zn → Zn2+ (0.024 M) + 2 e- Oxidation

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Zn2+ (2.4 M) → Zn2+ (0.024 M), Δ*E*° = 0.00

Note, Δ*E*° = 0.00 for this type of cell. The potential of Zn oxidation is equal and opposite to the potential of Zn reduction.

Using the Nernst equation:

0.0592 (0.024)

Δ*E* = 0.00 - ------- log --------

2 (2.4)

= (-0.296)(-2.0)

= 0.0592 V

Understandably, the Zn2+ ions try to move from the concentrated half-cell to a dilute solution. That driving force gives rise to 0.0592 V.

From here, you can also calculate the energy of dilution.

Zn2+ (0.024 M) = Zn2+ (2.4 M),

its voltage will be -0.0592 V. At equilibrium concentrations in the two half cells will have to be equal, in which case the voltage will be zero.

Previously, we discussed that cell potential (ΔE) is unaffected by molar coefficients and should not be multiplied by the same factor. We can show why using the Nernst equation.

### Example 2

**Show that the voltage of an electric cell is unaffected by multiplying the reaction equation by a positive number.**

Assume that you have the cell at STP

Mg | Mg2+ || Ag+ | Ag

and the reaction is:

Mg + 2 Ag+ = Mg2+ + 2 Ag

Using the Nernst equation

0.0592 [Mg2+]

Δ*E* = Δ*E*° - ------ log --------

2 [Ag+]2

If you multiply the equation of reaction by 2, you will have

2 Mg + 4 Ag+ = 2 Mg2+ + 4 Ag

Note that there are 4 electrons involved in this equation, and now *n* = 4 in the Nernst equation:

0.0592 [Mg2+]2

Δ*E* = Δ*E*° - ------ log --------

4 [Ag+]4

which can be simplified as

0.0592 [Mg2+]

Δ*E* = Δ*E*° - ------ log --------

2 [Ag+]2

Thus, the cell potential Δ*E* is not affected as the Nernst equations which describe each molar scenario are identical.