

Nernst Equation

Skills to develop

- Explain and distinguish the cell potential and standard cell potential.
- Calculate cell potentials from known conditions (Nernst Equation).
- Calculate the equilibrium constant from cell potentials.

Nernst Equation

Electrochemistry deals with cell potential as well as energy of chemical reactions. The energy of a chemical system drives the charges to move, and the driving force give rise to the cell potential of a system called galvanic cell. The energy aspect is also related to the [chemical equilibrium](#). All these relationships are tied together in the concept of **Nernst equation**.

Walther H. Nernst (1864-1941) received the Nobel prize in 1920 "**in recognition of his work in thermochemistry**". His contribution to chemical thermodynamics led to the well known equation correlating chemical energy and the electric potential of a galvanic cell or battery.

Electric Work and Gibb's Free Energy

Energy takes many forms: mechanical work (potential and kinetic energy), heat, radiation (photons), chemical energy, nuclear energy (mass), and electric energy. A summary is given regarding the evaluation of electric energy, as this is related to electrochemistry.

Electric Work

Energy drives all changes including chemical reactions. In a redox reaction, the energy released in a reaction due to movement of charged particles give rise to a **potential difference**. The maximum potential difference is called the **electromotive force**, (**EMF**), E and the maximum electric work W is the product of charge q in Coulomb (C), and the potential ΔE in Volt (= J / C) or EMF.

$$W \text{ J} = q \Delta E \text{ C J/C (units)}$$

Note that the EMF ΔE is determined by the nature of the reactants and electrolytes, not by the size of the cell or amounts of material in it. The amount of reactants is proportional to the charge and available energy of the galvanic cell.

Gibb's Free Energy

The **Gibb's free energy** ΔG is the negative value of maximum electric work,

$$\begin{aligned}\Delta G &= - W \\ &= - q \Delta E\end{aligned}$$

A redox reaction equation represents definite amounts of reactants in the formation of also definite amounts of products. The number (n) of electrons in such a reaction equation, is related to the amount of charge transferred when the reaction is completed. Since each mole of electron has a charge of 96485 C (known as the **Faraday's constant**, F),

$$q = n F$$

and,

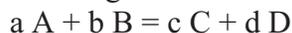
$$\Delta G = - n F \Delta E$$

At standard conditions,

$$\Delta G^\circ = - n F \Delta E^\circ$$

The General Nernst Equation

The general Nernst equation correlates the Gibbs Free Energy ΔG and the EMF of a chemical system known as the galvanic cell. For the reaction



and

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

It has been shown that

$$\Delta G = \Delta G^\circ + R T \ln Q$$

and

$$\Delta G = - n F \Delta E.$$

Therefore

$$- n F \Delta E = - n F \Delta E^\circ + R T \ln Q$$

where R , T , Q and F are the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), temperature (in K), reaction quotient, and Faraday constant (96485 C) respectively. Thus, we have

$$\Delta E = \Delta E^\circ - \frac{R T}{n F} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

This is known as the **Nernst equation**. 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.

It is interesting to note the relationship between equilibrium and the Gibbs free energy at this point. When a system is at **equilibrium**, $\Delta E = 0$, and $Q_{\text{eq}} = K$. Therefore, we have,

$$\Delta E^\circ = \frac{R T}{n F} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}, \quad (\text{for equilibrium concentrations})$$

Thus, the equilibrium constant and ΔE° are related.

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°) and log(10) conversion, the Nernst equation becomes

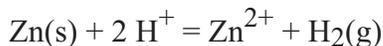
$$\Delta E = \Delta E^\circ - \frac{0.0592 \text{ V}}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

See last page for how this number is derived!

For the cell



we have a net chemical reaction of



and the standard cell potential $\Delta E^\circ = 0.763$.

If the concentrations of the ions are not 1.0 M, and the H_2 pressure is not 1.0 atm, then the cell potential ΔE may be calculated using the Nernst equation:

$$\Delta E = \Delta E^\circ - \frac{0.0592 \text{ V}}{n} \log \frac{P(\text{H}_2) [\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

with $n = 2$ in this case, because the reaction involves 2 electrons. The numerical value is 0.0592 only when $T = 298 \text{ K}$. This constant is temperature dependent. Note that the reactivity of the solid Zn is taken as 1. If the H_2 pressure is 1 atm, the term $P(\text{H}_2)$ may also be omitted. The expression for the argument of the log function follows the same rules as those for the expression of equilibrium constants and reaction quotients.

Indeed, the argument for the log function is the expression for the equilibrium constant K , or reaction quotient Q .

When a cell is at equilibrium, $\Delta E = 0.00$ and the expression becomes an equilibrium constant K , which bears the following relationship:

$$\log K = \frac{n \Delta E^\circ}{0.0592}$$

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

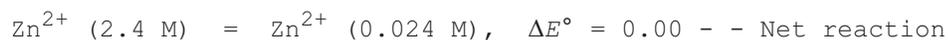
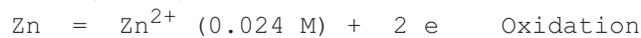
The Nernst equation also indicates that you can build a battery simply by using the same material for both cells, but by using different concentrations. Cells of this type are called **concentration cells**.

Example 1

Calculate the EMF of the cell



Solution



Using the Nernst equation:

$$\begin{aligned}\Delta E &= 0.00 - \frac{0.0592}{2} \log \frac{(0.024)}{(2.4)} \\ &= \frac{(-0.296)(-2.0)}{0.0592} \text{ V}\end{aligned}$$

Discussion

Understandably, the Zn^{2+} 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.

If you write the equation in the reverse direction,

$\text{Zn}^{2+} (0.024 \text{ M}) = \text{Zn}^{2+} (2.4 \text{ M})$,
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.

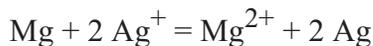
Example 2

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

Solution

Assume that you have the cell

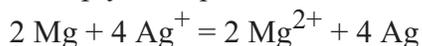
$\text{Mg} | \text{Mg}^{2+} || \text{Ag}^+ | \text{Ag}$
and the reaction is:



Using the Nernst equation

$$\Delta E = \Delta E^\circ - \frac{0.0592}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

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



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

$$\Delta E = \Delta E^\circ - \frac{0.0592}{4} \log \frac{[\text{Mg}^{2+}]^2}{[\text{Ag}^+]^4}$$

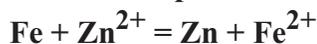
which can be simplified as

$$\Delta E = \Delta E^\circ - \frac{0.0592}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

Thus, the cell potential ΔE is not affected.

Example 3

The standard cell potential ΔE° for the reaction



is -0.353 V . If a piece of iron is placed in a 1 M Zn^{2+} solution, what is the equilibrium concentration of Fe^{2+} ?

Solution

The equilibrium constant K may be calculated using

$$\begin{aligned} K &= 10^{(n \Delta E^\circ)/0.0592} \\ &= 10^{-11.93} \\ &= 1.2 \times 10^{-12} \\ &= [\text{Fe}^{2+}]/[\text{Zn}^{2+}]. \end{aligned}$$

Since $[\text{Zn}^{2+}] = 1 \text{ M}$, it is evident that

$$[\text{Fe}^{2+}] = 1.2 \times 10^{-12} \text{ M}.$$

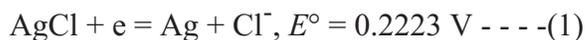
Example 4

From the standard cell potentials, calculate the solubility product for the following reaction:

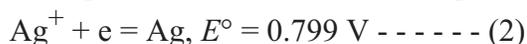


Solution

There are Ag^+ and AgCl involved in the reaction, and from the table of standard reduction potentials, you will find:



Since this equation does not contain the species Ag^+ , you need,



Subtracting (2) from (1) leads to,



Let K_{sp} be the solubility product, and employ the Nernst equation,

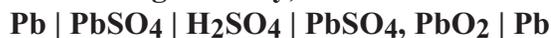
$$\log K_{sp} = (-0.577) / (0.0592) = -9.75$$

$$K_{sp} = 10^{-9.75} = 1.8 \times 10^{-10}$$

This is the value that you have been using in past tutorials. Now, you know that K_{sp} is not always measured from its solubility.

Confidence Building Questions

- In the lead storage battery,

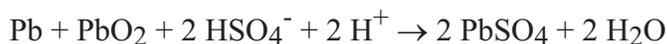


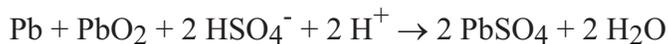
would the voltage change if you changed the concentration of H_2SO_4 ? (yes/no)

Answer ... Yes!

Hint...

The net cell reaction is





and the Nernst equation

$$\Delta E = \Delta E^\circ - (0.0592/2) \log \{1 / \{[\text{HSO}_4^-]^2 [\text{H}^+]^2\}\}.$$

- Choose the correct Nernst equation for the cell

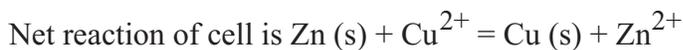


- A. $\Delta E = \Delta E^\circ - 0.0296 \log([\text{Zn}^{2+}] / [\text{Cu}^{2+}])$
- B. $\Delta E = \Delta E^\circ - 0.0296 \log([\text{Cu}^{2+}] / [\text{Zn}^{2+}])$
- C. $\Delta E = \Delta E^\circ - 0.0296 \log(\text{Zn} / \text{Cu})$
- D. $\Delta E = \Delta E^\circ - 0.0296 \log(\text{Cu} / \text{Zn})$

Answer ... A

Hint...

The cell as written has



- The standard cell potential ΔE° is 1.100 V for the cell,



If $[\text{Zn}^{2+}] = 0.01 \text{ M}$, and $[\text{Cu}^{2+}] = 1.0 \text{ M}$, what is ΔE or EMF?

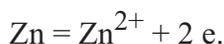
Answer ... 1.159 V

Hint...

A likely wrong result is 1.041 V.

The term that modifies ΔE is $-(0.059/n) \log\{[\text{Zn}^{2+}]/[\text{Cu}^{2+}]\}$ ($n = 2$ in this case).

Understandably, if the concentration of Zn^{2+} is low, there is more tendency for the reaction,



- The logarithm of the equilibrium constant, $\log K$, of the net cell reaction of the cell



is

- A. 1.100 / 0.0291
- B. -1.10 / 0.0291
- C. 0.0291 / 1.100
- D. -0.0291 / 1.100
- E. 1.100 / 0.0592

Answer ... A

Hint...

Use the Nernst equation in the form

$$0 = 1.100 - 0.0296 \log ([\text{Zn}^{2+}] / [\text{Cu}^{2+}])$$

The Nernst equation is useful for the determination of equilibrium constants.

Understanding is the key. Take time to understand it, there is no point in rushing.

R: Universal Gas Constant (Joules/(Mol x DegreesKelvin))

T: Temperature, (DegreesKelvin)

F: Faraday constant (Coulomb/Mol)

n: Moles of Electrons

1 Joule=1 Coulomb x Volt

$$\frac{R \times T}{n \times F}$$



$$\frac{\frac{\text{Joules}}{\text{Mol} \times \text{DegreesKelvin}} \times \frac{\text{DegreesKelvin}}{1}}{n \times \frac{\text{Coulombs}}{\text{Mol}}}$$



$$\frac{\frac{\text{Joules}}{\text{Mol} \times \text{DegreesKelvin}} \times \frac{\text{DegreesKelvin}}{1} \times \frac{\text{Mol}}{\text{Coulombs}}}{n}$$



$$\frac{\frac{\cancel{\text{Coulomb}} \times \text{Volt}}{\cancel{\text{Mol}} \times \cancel{\text{DegreesKelvin}}} \times \frac{\cancel{\text{DegreesKelvin}}}{1} \times \frac{\cancel{\text{Mol}}}{\cancel{\text{Coulombs}}}}{n}$$



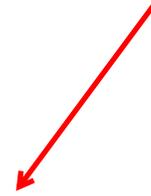
$$\frac{\text{Volts}}{\text{ElectronMoles}}$$



At 25C (298.15K):

$$\frac{8.31447 \times 298.15}{n \times 96485} = \frac{0.025693}{n} \times \ln(\text{ReactionQuotient})$$

Add in rest of equation



$$\frac{0.025693 \times \ln(10)}{n} \times \log(\text{ReactionQuotient})$$



$$\frac{0.05915}{n} \times \log(\text{ReactionQuotient})$$