Electrochemical Cells at Non-Standard Conditions

Oxidation-reduction reactions in the real world rarely occur under standard conditions. Even if the cell started out with all dissolved species at $1M$ concentration, these would change as the reaction progressed; reactant concentrations decrease and those of the products increase. How can we define the potential of cells under *nonstandard conditions*?

The Nernst Equation

In 1889, Walter Nernst (1864-1941), a German scientist, developed a mathematical relationship that lets us calculate cell potentials and the direction of a spontaneous reaction at other than standard-state conditions.

The standard cell potential, E^0, is the potential measured under standard conditions, that is, with all dissolved substances having a concentration of 1.0 mol per dm^{-3}. These are almost never the conditions in a real electrochemical cell, however, so how can we predict the potential under nonstandard conditions, E?

The answer is that the standard potential, E^0, can be corrected by a factor that includes the temperature of the reaction, the number of moles of elections transferred between oxidizing and reducing agents in a balanced redox equation, n, and the concentrations of reactants and products. This relationship is called the **Nernst equation**,

$$E = E^0 - \frac{RT}{nF} \ln Q$$

where

E^0 is the standard cell potential

Q is the reaction quotient – the ratio of the activities of the products over the reactants.

At low ion concentrations, the concentrations (in mol dm^{-3}) of the ions may be used instead of the activities, because they are nearly equal. At high concentrations, the activity is actually significantly less than the concentration, and this approximation will not work.

Activities vs Concentrations

The activity of an aqueous ion is the product of its activity coefficient and its concentration:

$$a = \gamma c$$

At low ion concentrations, the coefficient, γ, is nearly equal to one, therefore $a = c$. At high concentrations, the presence of other ions causes the ions of interest to behave less like lone ions in solution and more like ions bound up in complexes or compounds. This makes them less “active”, and thus the activity coefficient decreases.

Note that the concentrations of solids and liquid solvents are considered constant and are therefore not included in the expression.

F is the Faraday constant (9.6485309 x 10^4 C mol^{-1})
R is the gas constant (8.314510 J/K mol)

When T is 298 K, we can write a modified form of the Nernst equation that we find useful in practical chemical applications.

At 25 ^0C :

$$\frac{RT}{F} = \frac{(8.314JK^{-1})(298K)}{96485\ \mathrm{C}\ mol^{-1}} = 0.0257JC^{-1} = 0.0257V$$

At 25^0C, the Nernst equation becomes

$$E = E^0 - \frac{0.0257}{n}\ln Q \qquad \text{or} \qquad E = E^0 - \frac{0.0592}{n}\log Q$$

This equation allows us to find the potential produced by a cell under nonstandard conditions or to find the concentration of a reactant or product by measuring the potential produced by a cell.

Using the Nernst Equation

Determine the cell potential at 25^0C for:

$$Fe_{(s)} + Cd^{+2}_{(aq)} \longrightarrow Fe^{(+2)}_{(aq)} + Cd_{(s)}$$

when

1. $[Fe^{+2}] = 0.010M$ and $[Cd^{+2}] = 1.0M$
2. $[Fe^{+2}] = 1.0M$ and $[Cd^{+2}] = 0.010M$

To calculate a nonstandard potential, we first need the standard potential for the cell reaction, E^0.

Oxidation:	$Fe_{(s)} \longrightarrow Fe^{+2}_{(aq)} + 2e^{-1}$	$E^0 = +0.44V$
Reduction:	$Cd^{+2}_{(aq)} + 2e^{-1} \longrightarrow Cd_{(s)}$	$E^0 = -0.40V$
Net reaction:	$Fe_{(s)} + Cd^{+2}_{(aq)} \longrightarrow Fe^{+2}_{(aq)} + Cd_{(s)}$	$E^0 = +0.04V$

Next, substitute E^0 and the conditions for solution (1) into the Nernst equation.

$$E = 0.04 - \frac{0.0257}{2} \ln \frac{[Fe^{2+}]}{[Cd^{2+}]}$$

As in chemical equilibrium calculations, the concentration of a solid does not enter into the expression. Now, using $n = 2$ (the number of moles of electrons transferred), and the ion concentrations given earlier,

$$E = +0.10V$$

The cell potential E is larger than E^0_{cell}, so the tendency to transfer electrons from $Fe_{(s)}$ to $Cd^{+2}_{(aq)}$ is greater than under standard conditions.

Examples

1. Calculate the cell potential for the reaction:

   $$2Al_{(s)} + 3MN^{+2}_{(aq)} \longrightarrow 2Al^{+3}_{(aq)} + 3Mn_{(s)}$$

   where $[Mn^{+2}] = 0.50$ mol dm^{-3}, $[Al^{+3}_{(aq)}] = 1.50$ mol dm^{-3}, $n = 6$, $(E_{cell} = 0.47V)$

2. Calculate the cell potential of the following electrochemical cell

   $Zn_{(s)} \;|\; Zn^{+2}_{(aq)}(0.001 \text{ mol } dm^{-3}) \;\|\; Ag^{+1}_{(aq)}(0.01 \text{ mol } dm^{-3}) \;|\; Ag_{(s)}$

   $(E_{cell} = 1.59V)$

3. Calculate the voltage for the following electrochemical cell

   $Zn_{(s)} \;|\; Zn^{+2}_{(aq)}(0.10 \text{ mol } dm^{-3}) \;\|\; Cu^{+2}_{(aq)}(0.010 \text{ mol } dm^{-3}) \;|\; Cu_{(s)}$

   $(E_{cell} = 1.07V)$

4. What is the cell voltage for the following electrochemical cell

   $Co_{(s)} \;|\; Co^{+2}_{(aq)}(0.1 \text{ mol } dm^{-3}) \;\|\; Ni^{+2}_{(aq)}(0.001 \text{ mol } dm^{-3}) \;|\; Ni_{(s)}$

   $(E_{cell} = -0.02V)$

E^0 and the Equilibrium Constant

The standard cell potential, E^0_{cell}, and the equilibrium constant K_c for a reaction are a measure of the tendency for a reaction to take place. It therefore seems reasonable that the two factors should be related.

Recall that the cell potential, and even the reaction direction, can change when the concentrations of products and reactants change. Thus, as reactants are converted to products in any product-favoured reaction, the value of E_cell must decline from its initial positive value to eventually reach zero. A **potential of zero** means that **no net** reaction is occuring; it is an indication that the cell has reached **equilibrium**. Thus, when $E_{net} = 0$, the Q term in the Nernst equation is equivalent to the equilibrium constant K for the reaction. So, when equilibrium has been attained the Nernst equation can be rewritten as:

$$0 = E^0 - \frac{0.0257}{n} \ln K$$

which rearranges to

$$\ln K = \frac{nE^0}{0.0257}$$

This is an extremely useful equation, because it tells us that the equilibrium constant for a reaction can be obtained from a calculation or measurement of E^0_{cell}.

$$K_c = 10^{\frac{nE^0}{0.0592}}$$

Calculate the equilibrium constant for the reaction:

$$Fe_{(s)} + Cd^{+2}_{(aq)} \longrightarrow Fe^{+2}_{(aq)} + Cd_{(s)} \qquad E^0_{cell} = +0.04V$$

What are the equilibrium concentrations of the Fe^{+2} and Cd^{+2} when the cell has reached equilibrium are given by the equilibrium expression:

$$K = 20 = [Fe^{+2}]/[Cd^{+2}]$$

Because the cell began at standard conditions, the original concentrations of both ions were $1.0M$. As the reaction proceeded to equilibrium, x mol dm^{-3} of Cd^{+2} was consumed and x mol dm^{-3} of Fe^{+2} was produced.

Therefore

$$K_c = 20 = \frac{1.0 + x}{1.0 - x}$$

Solving this we find $x = 0.9$ mol dm^{-3}. Thus, the equilibrium concentrations are: $[Fe^{+2}] = 1.0 + x = 1.9$ mol dm^{-3} and $[Cd^{+2}] = 1.0 - x = 0.10$ mol dm^{-3}.

Note:

The equation $K_c = 10^{nE^0/0.0257}$ *shows that a reaction with a positive* E^0_{cell} *has a* $K_c > 1$*, while a reaction with a negative* E^0_{cell} *has a* $K_c < 1$.

Examples

1. Calculate the equilibrium constant between silver nitrate and metallic zinc. Is the reaction complete or incomplete?

   $$Zn_{(s)} + 2Ag^{+1}_{(aq)} \longrightarrow 2Ag_{(s)} + Zn^{+2}_{(aq)} \qquad E^0 = 1.56V$$

   (Answer: $K_c = 1 \times 10^{52}$)

2. Calculate the equilibrium constant for the reaction between metallic zinc and copper(II) sulphate. Is the reaction complete? (Answer: 4.6×10^{36})

3. Consider the following equation:

   $$\frac{1}{2}Cl_{2(g)} + Br^{-1} \longrightarrow \frac{1}{2}Br_{2(l)} + Cl^{-1} \quad E^0 = 0.30V$$

   (a) Calculate the equilibrium constant for the cell reaction at equilibrium. (Answer: $K_c = 1 \times 10^5$)

   (b) What is the voltage of the cell if the concentration of Br^{-1} is increased tenfold?

4. At 25^0C $K = 9.9 \times 10^5$ for the reaction

   $$Cl_{2(aq)} + I_{2(aq)} \longrightarrow 2ICl_{(aq)}$$

   Determine E^0 for this reaction. (Answer: $0.177V$)