uc3m | Universidad Carlos III de Madrid

OpenCourseWare (2023)

CHEMISTRY II

Verónica San Miguel Arnanz

Teresa Pérez Prior

Berna Serrano Prieto

Department of Materials Science and Engineering and Chemical Engineering

ELECTROCHEMISTRY I

1. INTRODUCTION

Electrochemistry constitutes the realm of chemistry dedicated to the transformation between electrical energy and chemical energy. Within this domain, electrochemical processes predominantly involve redox (oxidation-reduction) reactions. These reactions manifest in two distinctive scenarios: converting energy released by a spontaneous reaction into electricity and using electrical energy to instigate nonspontaneous reactions. Electrochemistry offers a versatile set of techniques for observing chemical reactions and assessing solution properties, including determining the pKa of acids and the thermodynamic characteristics of reactions. Beyond its traditional applications, electrochemistry extends its reach to monitoring essential biological functions such as brain and heart activity, evaluating blood pH, and detecting pollutants in water supplies.

Redox reactions, inherent in processes like metal corrosion and energy storage and production systems, involve the transfer of electrons. By harnessing the principles of electrochemistry, we can delve into a broad spectrum of applications, ranging from traditional chemical analyses to the intricate dynamics of biological systems and environmental monitoring.

2. REDOX EQUATIONS

In redox reactions, electrons undergo transfer from one substance to another. An illustrative instance of a redox reaction is the interaction between silver and zinc. The fundamental approach to composing and balancing redox reaction equations is separating the reduction and oxidation processes. A half-reaction entails the oxidation or reduction part of a reaction considered independently.

Electrochemical reactions, constituting redox processes, involve converting released energy from a spontaneous reaction into electricity or vice versa. These redox reactions share similarities with acid-base reactions, as both are fundamentally concerned with the transfer of electrons between species.

Understanding the oxidation number of an element, which signifies the charges an atom in a molecule would have if electrons were completely transferred, is crucial. This oxidation number indicates the electrons' count lost, gained, or shared due to chemical bonds. Monitoring changes in the oxidation state informs us about the occurrence of oxidation or reduction. Oxidation entails electron loss, leading to an increase in the oxidation number, whereas reduction involves electron gain, causing a decrease in the oxidation number. Knowledge of the oxidation numbers of involved elements is imperative for writing half-reactions and determining overall redox reactions.

The process of balancing redox reactions involves the same steps as for an acidic medium to balance reactions in a basic medium, encompassing steps 1 to 4 and incorporating additional steps from 5 to 7. Balancing chemical reactions using the *ion-electron method* in an acidic medium involves a systematic approach:

Step 1: Write the unbalanced equation for the reaction in ionic form.

Step 2: Separate the equation into two half-reactions.

Step 3: Independently balance the atoms (excluding O and H) in each half-reaction.

Step 4: Introduce H_2O to balance the oxygen atoms and H^+ to balance the hydrogen atoms.

Step 5: Add electrons to one side of each half-reaction to equalize the charges. Adjust the number of electrons by multiplying one or both half-reactions as needed.

Step 6: Combine the two half-reactions and balance the final equation by inspection, ensuring that electrons on both sides cancel each other.

Step 7: Confirm that the equation maintains consistency in the types and quantities of atoms and charges on both sides.

For the ion-electron method in the basic medium (which starts from Step 4), follow these additional steps:

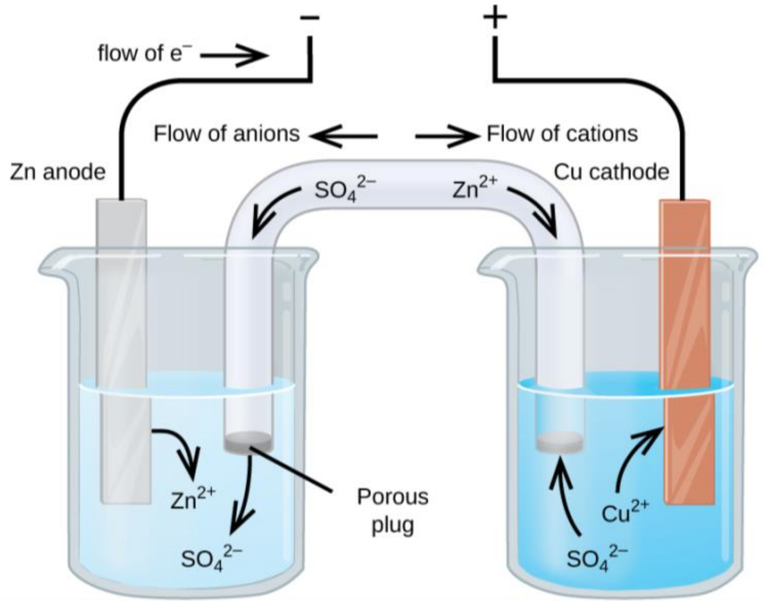
Step 4-5: Add an equal number of OH^- ions to both sides of the equation for each H^+ ion present. Combine H^+ and OH^- ions where they appear on the same side to form H_2O.

These steps systematically guide the balancing process, ensuring the conservation of mass and charge in the balanced chemical equation.

3. ELECTROCHEMICAL CELLS

An electrochemical cell is the experimental apparatus for harnessing electricity through a spontaneous redox reaction, known as either a Galvanic or Voltaic cell, that generates an electric current The key components of such a cell include: i) Electrolyte: A solution containing ions; ii) Electrodes: the site of the oxidation process is the Anode and the site of the reduction process is the Cathode; iii) Salt bridge, often an inverted U tube with an inert electrolyte solution like KCl or NH_4NO_3, ensures the necessary flow of cations and anions between electrode compartments.

An exemplary Galvanic cell is the Daniell cell, featuring a zinc bar immersed in a zinc sulfate solution and a copper bar immersed in a copper sulfate solution (Figure 1). The cell exploits the simultaneous oxidation of zinc to Zn^{2+} and the reduction of Cu^{2+} to copper, facilitated by the transfer of electrons through an external wire. A salt bridge is utilized to prevent a direct reaction between Cu^{2+} ions and the zinc bar. It prevents the buildup of charge imbalances hindering the cell's operation. The overall redox reaction leads to the external flow of electrons from the anode to the cathode, with cations moving toward the anode in the solution.



Redox Reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

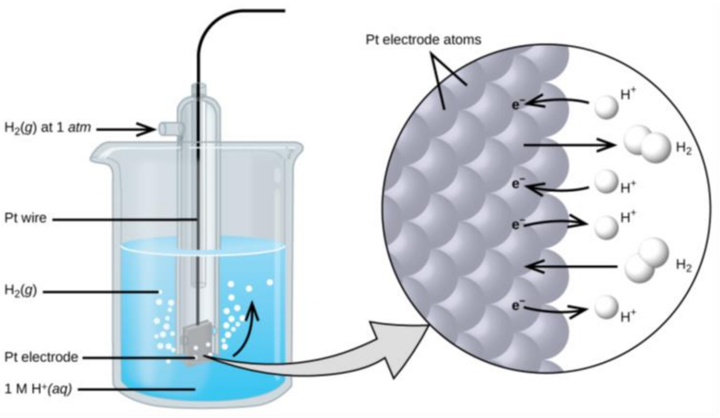
Source: Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, https://openstax.org/details/books/chemistry-2e.

Figure 1. Daniell cell representation.

Chemists use a cell diagram notation to represent the structure of electrode compartments in a galvanic cell. For the Daniell cell, assuming concentrations of Zn^{2+} and Cu^{2+} ions are 1 M, the cell diagram is expressed as Zn (s) | Zn^{2+}(ac) (1 M) || Cu^{2+}(ac) (1 M) | Cu (s). Vertical lines denote phase boundaries and double vertical lines indicate the salt bridge. The anode is positioned to the left in the schematic, with other components listed in the order encountered from the anode to the cathode.

It is not feasible to measure the potential of a single electrode independently. However, by arbitrarily assigning the potential of a specific electrode as zero, it becomes a reference point for determining the relative potentials of other electrodes. The Standard Hydrogen Electrode (SHE)serves as this reference, particularly for measuring and tabulating the potentials of various redox half-reactions.

In practical terms, hydrogen gas is introduced into a hydrochloric acid solution at 25 °C, employing a platinum electrode that serves dual purposes (Figure 2). The platinum surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. Firstly, it provides a surface facilitating the dissociation of hydrogen molecules. Secondly, it acts as an electrical conductor connecting to the external circuit. Under standard-state conditions, where the pressure of H_2 is 1 atm and the HCl solution concentration is 1 M, the potential for reducing H^+ at 25 °C is conventionally set at zero.



$$2H^+(1M)+2e^- \rightarrow H_2(1\ \ atm)$$

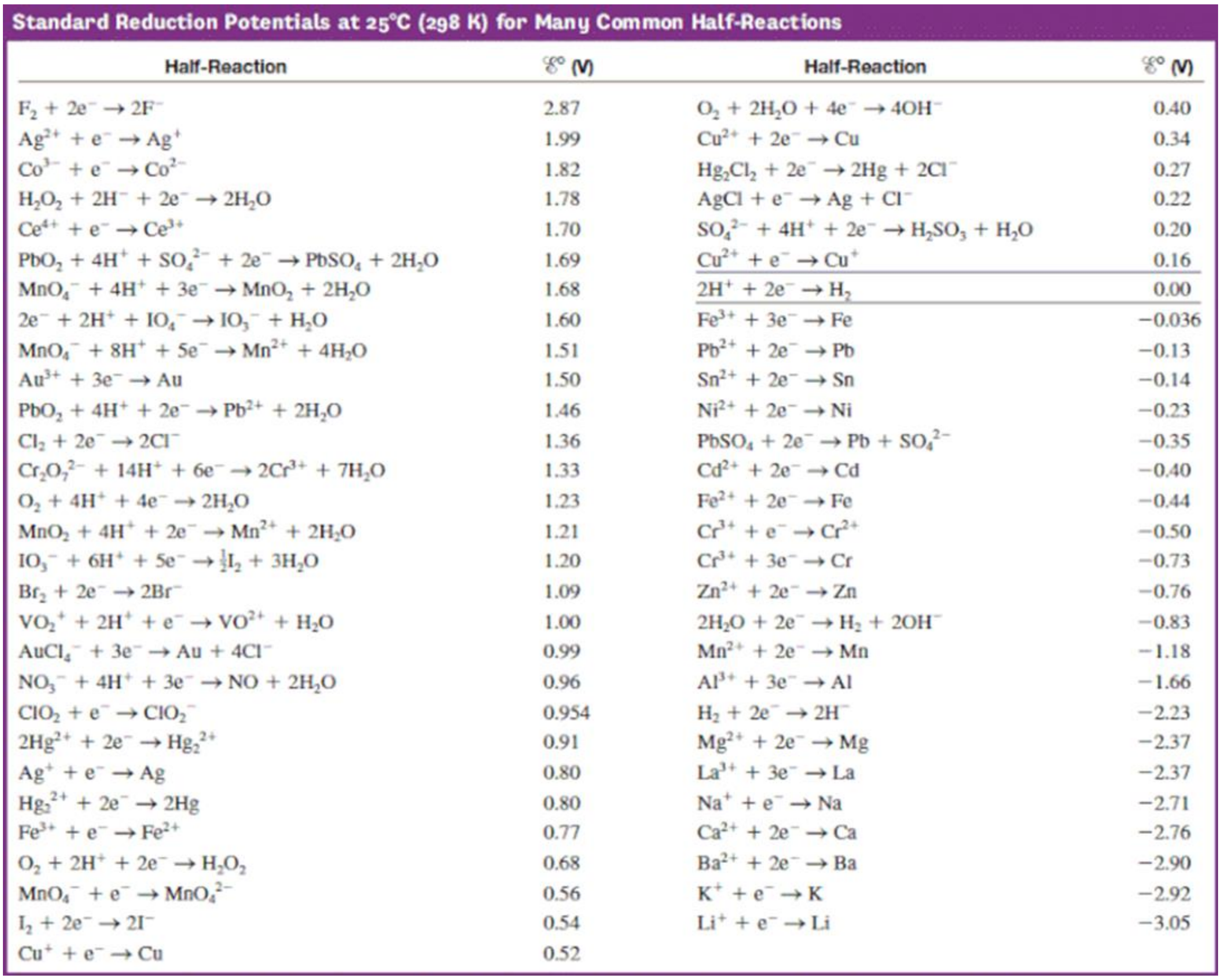
$$E^0_{2H^+/H_2}=0\ \ V$$

Source: Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, https://openstax.org/details/books/chemistry-2e.

Figure 2. Standard Hydrogen Electrode representation.

Experimentally, the potential difference between the anode and the cathode is measured using a voltmeter, and this reading is referred to as cell voltage or electromotive force (emf), denoted as E. Standard reduction potentials for various half-cell reactions are listed in the Table 1, with the SHE having a standard reduction potential of zero volts. Below the SHE, negative standard reduction potentials increase, while above it, positive standard reduction potentials increase.

Table 1. Standard Reduction Potentials.



Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathcal{E}^{\circ}$ (V)	Half-Reaction	$\mathcal{E}^{\circ}$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Source: Hjswg1994, CC BY-SA 4.0, https://commons.wikimedia.org/wiki/File:%ED%91%9C%EC%A4%80%ED%99%98%EC%9B%90%EC%A0%84%EC%9C%84.gif.

In standard state conditions, reducing agents (oxidized at the anode) strengthen from top to bottom, whereas oxidizing agents (reduced at the cathode) strengthen from bottom to top. Considering standard reduction potentials, the lithium cation is identified as the weakest oxidizing agent, indicating its reluctance to undergo reduction. Consequently, metallic lithium emerges as the strongest reducing agent, preferring oxidation as the anode.

Key considerations for standard reduction potentials include reversibility of reactions, the sign of E^0 for oxidation reactions (reversed reactions), stoichiometric coefficient variations not impacting E^0, and the relationship between E^0 and the tendency for reduction (cathodic character) or oxidation (anodic character).

4. SPONTANEITY OF REDOX REACTIONS AND EQUILIBRIUM CONSTANTS

Our next focus is on understanding the connection between the standard potential of the cell and thermodynamic parameters such as Free Energy and equilibrium constants. In an electrochemical cell, the conversion of chemical energy to electrical energy is a pivotal process. The electrical energy, in this case, is the result of the electromotive force (emf) of the cell multiplied by the total electrical charge (in coulombs) passing through the cell (volts × coulombs = joules). The measured emf signifies the maximum voltage achievable by the cell. This value aids in calculating the maximum amount of electrical energy that can be derived from the chemical reaction. This energy, expressed as electrical work (w_{max}), corresponds to the maximum useful work attainable from the reaction. In essence, the change in free energy (ΔG) represents the maximum amount of work extractable from a reaction. This relationship can be expressed as:

$$\Delta G = -nFE_{cell}$$

Here, both n and F are positive quantities, and ΔG is negative for a spontaneous process, implying that E_{cell} must be positive. (F, the Faraday constant, signifies the electrical charge in 1 mole of electrons; n is the number of moles of electrons traversing the circuit.) This holds true for reactions where reactants and products are in their standard states.

Now, we can establish a link between E^0_{cell} and the equilibrium constant (K) of a redox reaction. The free energy change for a reaction and its equilibrium constant are related as follows:

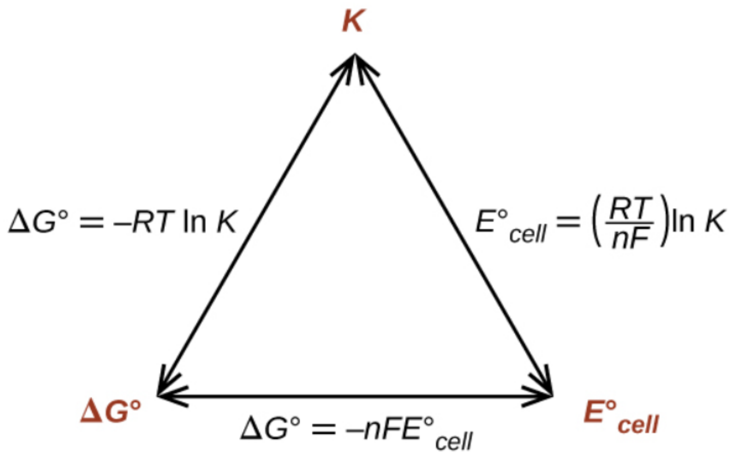
$$\Delta G^0 = -RT \ln K$$

Therefore, combining these equations yields:

$$E^0_{cel} = \frac{RT}{nF} \ln K$$

In the context of electrochemical data, one of the most valuable applications of standard potentials lies in calculating equilibrium constants. This approach allows us to determine the equilibrium constants for various reactions expressed as two half-reactions. The value of E^0_{cell} remains constant, irrespective of how the equation is formulated. However, the value of ΔG depends on the stoichiometric coefficients in the chemical equation.

In summary, the relationships among E^0_{cell}, ΔG^0, and K are characterized in the Figure 3, providing insights into the spontaneity of a redox reaction. These relationships allow us to calculate any two of the three quantities if one is known, offering a comprehensive understanding of the reaction's thermodynamics and equilibrium composition.



Source: Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, https://openstax.org/details/books/chemistry-2e.

Figure 3. Schematic representation of the relation between three important thermodynamic properties.

5. THE NERNST EQUATION

Standard-state conditions can be challenging to maintain and, in some cases, impossible. Nevertheless, a mathematical relationship exists between a cell's electromotive force (emf) and the concentrations of reactants and products in a redox reaction under non-standard-state conditions. This relationship is derived below.

Consider a redox reaction of the type $aA+bB \rightleftharpoons cC+dD$. Under conditions that deviate from standard state, the Gibbs free energy change (ΔG) is used instead of ΔG° to predict the reaction direction. The relationship between them, derived from thermodynamics, is given by:

$$\Delta G = \Delta G^0 + RT \ln Q$$

Here, Q is the reaction quotient, and considering: $\Delta G = -nFE$, the equation becomes:

$$-nFE = -nFE^0 + RT \ln Q$$

Dividing through by −nF, we get:

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

As a reaction progresses towards equilibrium, the concentrations of reactants and products change, and ΔG approaches zero. Consequently, in a working electrochemical cell, as reactants are consumed, the cell potential (E) decreases until it reaches zero at equilibrium. At this point, the cell generates no potential difference, and the reaction ceases to do work.

To understand the quantitative relationship between cell potential and concentration, the Nernst equation is used. This equation expresses how the cell potential varies with the composition of species in the cell. For a concentration cell, where the two electrodes have the same material but differ in ion concentrations, the Nernst equation is crucial. It is employed to estimate cell potentials under nonstandard conditions and find concentrations.