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Standard electrode potential

In electrochemistry, **standard electrode potential** (E^\ominus) is defined as *The value of the standard emf of a cell in which molecular hydrogen under standard pressure is oxidized to solvated protons at the left-hand electrode.*^[1]

The basis for an electrochemical cell, such as the galvanic cell, is always a redox reaction which can be broken down into two half-reactions: oxidation at anode (loss of electron) and reduction at cathode (gain of electron). Electricity is generated due to electric potential difference between two electrodes. This potential difference is created as a result of the difference between individual potentials of the two metal electrodes with respect to the electrolyte. (Reversible electrode is an electrode that owes its potential to changes of a reversible nature, in contrast to electrodes used in electroplating which are destroyed during their use.) It is the measure of reducing power of any element or compound.

Although the overall potential of a cell can be measured, there is no simple way to accurately measure the electrode/electrolyte potentials in isolation. The electric potential also varies with temperature, concentration and pressure. Since the oxidation potential of a half-reaction is the negative of the reduction potential in a redox reaction, it is sufficient to calculate either one of the potentials. Therefore, standard electrode potential is commonly written as standard reduction potential. At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called the electrode potential. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as standard electrode potential. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a galvanic cell, the half-cell in which oxidation takes place is called anode and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called cathode and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the on position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

Contents

Calculation

Standard reduction potential table

See also

References

Further reading

External links

Calculation

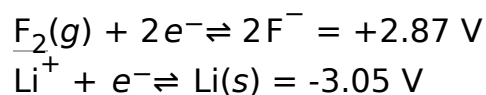
The electrode potential cannot be obtained empirically. The galvanic cell potential results from a *pair* of electrodes. Thus, only one empirical value is available in a pair of electrodes and it is not possible to determine the value for each electrode in the pair using the empirically obtained galvanic cell potential. A reference electrode, standard hydrogen electrode (SHE), for which the potential is *defined* or agreed upon by convention, needed to be established. In this case the standard hydrogen electrode is set to 0.00 V and any electrode, for which the electrode potential is not yet known, can be paired with standard hydrogen electrode—to form a galvanic cell—and the galvanic cell potential gives the unknown electrode's potential. Using this process, any electrode with an unknown potential can be paired with either the standard hydrogen electrode or another electrode for which the potential has already been derived and that unknown value can be established.

Since the electrode potentials are conventionally defined as reduction potentials, the sign of the potential for the metal electrode being oxidized must be reversed when calculating the overall cell potential. The electrode potentials are independent of the number of electrons transferred—they are expressed in volts, which measure energy per electron transferred—and so the two electrode potentials can be simply combined to give the overall *cell* potential even if different numbers of electrons are involved in the two electrode reactions.

For practical measurements, the electrode in question is connected to the positive terminal of the electrometer, while the standard hydrogen electrode is connected to the negative terminal.^[2]

Standard reduction potential table

The larger the value of the standard reduction potential, the easier it is for the element to be reduced (gain electrons); in other words, they are better oxidizing agents. For example, F₂ has a standard reduction potential of +2.87 V and Li⁺ has −3.05 V:



The highly positive standard reduction potential of F₂ means it is reduced easily and is therefore a good oxidizing agent. In contrast, the greatly negative standard reduction potential of Li⁺ indicates that is not easily reduced. Instead, Li_(s) would rather undergo oxidation (hence it is a good reducing agent). Zn²⁺ has a standard reduction potential of −0.76 V and thus can be oxidized by any other electrode whose standard reduction potential is greater than −0.76 V (e.g. H⁺(0 V), Cu²⁺(0.34 V), F₂(2.87 V)) and can be reduced by any electrode with standard reduction potential less than −0.76 V (e.g. H₂(−2.23 V), Na⁺(−2.71 V), Li⁺(−3.05 V)).

In a galvanic cell, where a spontaneous redox reaction drives the cell to produce an electric potential, Gibbs free energy Δ*G*[°] must be negative, in accordance with the following equation:

$$\Delta G^\circ_{\text{cell}} = -nFE^\circ_{\text{cell}}$$

where *n* is number of moles of electrons per mole of products and *F* is the Faraday constant, ~96485 C/mol. As such, the following rules apply:

If *E*[°]_{cell} > 0, then the process is spontaneous (galvanic cell)

If *E*[°]_{cell} < 0, then the process is nonspontaneous (electrolytic cell)

Thus in order to have a spontaneous reaction (Δ*G*[°] < 0), *E*[°]_{cell} must be positive, where:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

where E°_{anode} is the standard potential at the anode and $E^{\circ}_{\text{cathode}}$ is the standard potential at the cathode as given in the table of standard electrode potential.

See also

- [Nernst equation](#)
- [Solvated electron](#)
- [Pourbaix diagram](#)

References

1. IUPAC, *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book") (1997). Online corrected version: (2006–) "standard electrode potential, E° (<https://goldbook.iupac.org/S05912.html>)". doi:10.1351/goldbook.S05912 (<https://doi.org/10.1351%2Fgoldbook.S05912>)
2. IUPAC definition of the electrode potential (<http://goldbook.iupac.org/E01956.html>)

Further reading

- Zumdahl, Steven S., Zumdahl, Susan A (2000) *Chemistry* (5th ed.), Houghton Mifflin Company. ISBN 0-395-98583-8
- Atkins, Peter, Jones, Loretta (2005) *Chemical Principles* (3rd ed.), W.H. Freeman and Company. ISBN 0-7167-5701-X
- Zu, Y, Couture, MM, Kolling, DR, Crofts, AR, Eltis, LD, Fee, JA, Hirst, J (2003) *Biochemistry*, 42, 12400-12408
- Shuttleworth, SJ (1820) *Electrochemistry* (50th ed.), Harper Collins.

External links

- Standard Electrode Potentials table (<http://hyperphysics.phy-astr.gsu.edu/hbase/Tables/electpot.html>)
- Redox Equilibria (<http://www.chemguide.co.uk/physical/redoxeqia/introduction.html>)
- Chemistry of Batteries (<http://www.science.uwaterloo.ca/~cchieh/cact/c123/battery.html>)
- Electrochemical Cells (<http://hyperphysics.phy-astr.gsu.edu/HBASE/Chemical/electrochem.html#c1>)
- STEP in Non-aqueous solvent (<http://www.tandfonline.com/doi/abs/10.1080/14786440908564891>)

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