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Reactivity series, activity series and electrochemical series
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This *Science note* aims to inform readers of the differences between the related electrochemical terms – reactivity series, activity series and electrochemical series – and to give pre-university teachers a deeper understanding of the origin and concept of electrode potential (including single-ion thermodynamics) and the factors affecting their values.

Introduction/justification

Students often spot the small differences in the order of metals in a reactivity series and the electrochemical series and want to know the reasons for the difference in ordering. A reactivity series is usually based on kinetics although this order is often correlated with energetics. An activity series and an electrochemical series are based on thermodynamics.

It should be noted that the term 'activity' has two meanings: one in the context of an activity series and the other as an effective thermodynamic concentration that takes into account deviations from ideal behaviour.

Students may also attempt to correlate the orders of metallic elements with electronegativity measurements and values of ionisation energies and find some discrepancies. This topic may be a suitable topic for an Individual Investigation component of the IB chemistry programme combining practical and theoretical work. It could also be a 'stretch and challenge' theoretical exercise where students can be asked to comment on plotted data from their data booklet or textbook.

Reactivity series

Students are often introduced to the concept of a reactivity series via 'displacement' reactions in aqueous solutions, reacting metals with dilute acid, and then with metal cations, and perhaps heating powdered metals with metal compounds and carbon.

The reactivity series is based on empirical data where the 'reactivity' of metals with acids and cations is probably based on relative rates, but the displacements between metals with carbon and hydrogen are probably based on energetics.
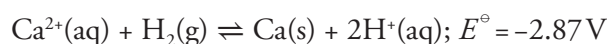
Standard electrode potential

The standard electrode potential, $E^\ominus$, is a quantitative measure of the tendency of reactants in their standard states to form products in their standard states for a particular redox reaction (under standard conditions: any temperature – usually 298 K, a molar concentration of ions (ignoring activity) and a pressure of 1 bar (only important in the case of a gas)). (The bar is a unit of pressure defined as 100 kPa; it is about equal to the atmospheric pressure on Earth at sea level.)

A standard electrode potential is a convenient way of presenting equilibrium and Gibbs free energy data, to which it is related by the expressions $\Delta G^\ominus = -zFE^\ominus$ and $\Delta G^\ominus = -RT\ln K$, where z represents the charge and F is the charge in coulombs carried by 1 mole of electrons (*c.* 96 500 C mol^{-1}). Hence, the electrochemical series is based on the principles of thermodynamics. $\Delta G^\ominus$ is usually used for chemical reactions and $E^\ominus$ is used for half-cell reactions.

Standard electrode potentials are presented in a table (often as an electrochemical series) not for complete reactions but as half-reactions relative to the standard hydrogen electrode (SHE), so the information is presented as compactly as possible. The half-cell reactions are always written as a reduction process, for example:

$$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s); E^\ominus = -2.87\,V$$
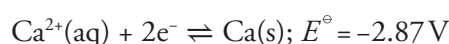
is shorthand for the reaction described by the following ionic equation:

$$Ca^{2+}(aq) + H_2(g) \rightleftharpoons Ca(s) + 2H^+(aq); E^\ominus = -2.87\,V$$

or

$$\Delta G^\ominus = -2 \times (-2.87)F\,kJ = 553\,910\,J\,mol^{-1} = +554\,kJ\,mol^{-1}$$

The negative sign for the electrode potential (equivalent to a positive value for the Gibbs free energy change) indicates that there is a strong tendency for the reaction to proceed spontaneously (under standard conditions) from right to left (backwards). An alternative statement is that the equilibrium constant, K, is very small for the forward reaction. $\Delta G^\ominus = -5.7\ln K \approx 10^{-100}\,kJ\,mol^{-1}$, showing that based on the principles of thermodynamics the reduction of hydrated calcium ions by hydrogen molecules (under standard conditions) hardly proceeds at all.

The factors that influence the standard reduction electrode potentials of metal ions can be investigated by considering the formation of the hydrated metal ion as the result of three processes in an energy cycle (Figure 1): atomisation of the metal atoms, ionisation of the gaseous metal atoms and hydration of the gaseous metal ions.
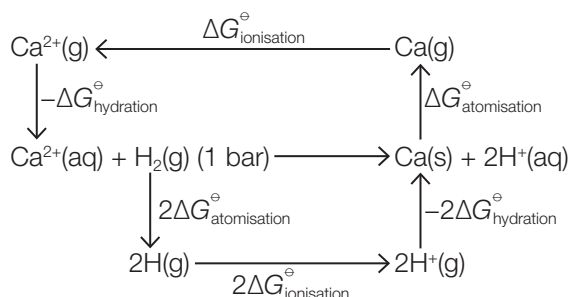
Figure 1 An energy cycle representing the standard reduction potential of aqueous calcium ions

This, of course, may not be the mechanism of the electrode process, but it is its thermodynamic equivalent since the initial and final states are the same. The complete breakdown of the reaction is shown in Figure 1. The free energy change for the reaction, $\Delta G^{\ominus}$, is given by:

$$\Delta G^{\ominus} = 2(\Delta G^{\ominus}_{atomisation} + \Delta G^{\ominus}_{ionisation} - \Delta G^{\ominus}_{hydration})_{hydrogen} - (\Delta G^{\ominus}_{atomisation} + \Delta G^{\ominus}_{ionisation} - \Delta G^{\ominus}_{hydration})_{calcium}$$

and the standard reduction potential is given by:

$$E^{\ominus} = -\Delta G^{\ominus}/zF = (1/zF) \times (\Delta G^{\ominus}_{atomisation} + \Delta G^{\ominus}_{ionisation} - \Delta G^{\ominus}_{hydration})_{calcium} - (1/F) \times (\Delta G^{\ominus}_{atomisation} + \Delta G^{\ominus}_{ionisation} + \Delta G^{\ominus}_{hydration})_{hydrogen}$$

where $\Delta G^{\ominus}_{atomisation} = 203\,kJ\,mol^{-1}$; $\Delta G^{\ominus}_{ionisation} = 1314\,kJ\,mol^{-1}$; $\Delta G^{\ominus}_{hydration} = -1088\,kJ\,mol^{-1}$ (data from Trasatti and IUPAC Commission on Electrochemistry, 1986).

For hydrogen,

$$(1/F) \times (\Delta G^{\ominus}_{atomisation} + \Delta G^{\ominus}_{ionisation} - \Delta G^{\ominus}_{hydration})$$

is equal to 4.44 V, and therefore

$$E^{\ominus} = -4.44 + (1/zF) \times (\Delta G^{\ominus}_{atomisation} + \Delta G^{\ominus}_{ionisation} - \Delta G^{\ominus}_{hydration})_{calcium}$$

It should be noted that the value of 4.44 V will be unfamiliar to many teachers and it is not a thermodynamic value but an absolute value (from summing the individual $\Delta G^{\ominus}$ values in the energy cycle); 0 V on this scale refers to electrons at rest in a vacuum. Teachers will be more familiar with the value of 0.00 V from the more usual thermodynamic scale of oxidation–reduction potentials, i.e. relative to the SHE.

There is no simple experiment that allows you to accurately measure thermodynamic properties of a single ion as it is transferred between two phases. The problem relates to the orientation of the solvent molecules at a phase boundary. When you transfer an ion from vacuum to water, there are two energy components that must be considered: the close-range interactions of the ion with the solvent and the fact that there is always a preferential orientation of solvent molecules at the surface leading to a potential difference between the two phases called the surface potential. Single electrode potentials traditionally are considered to be not meaningful thermodynamic quantities, but some authors (e.g. Rockwood, 1986, 2015) disagree.

The entropy changes during these redox processes are relatively small compared with the enthalpy changes for these reactions. We can conclude (as an approximation) that the value of the electrode potential depends mainly on the relative sizes of the enthalpies of atomisation, ionisation and hydration, between metals.

For large negative electrode potentials, the enthalpies of atomisation and ionisation (which are always positive (endothermic)) and the enthalpy of hydration (which are always negative (exothermic)) may be large. This is a simple but useful 'model' for pre-university students.

Electrochemical series

When the standard reduction electrode potentials are arranged in order of magnitude, conventionally with the largest negative value at the top, the electrochemical series is obtained.

Students will note that this closely resembles the reactivity series that can be generated empirically from observations of reactions in which elements and compounds are involved.

The electrochemical series provides a means of finding the cell potentials (electromotive force) of a large number of possible electrochemical cells from a much smaller number of measurements (standard reduction potentials).

It should be emphasised to students that all the data in the table refer to aqueous solutions where all ion concentrations are $1\,mol\,dm^{-3}$ (strictly speaking, unit activity), the pressure is 1 bar and the temperature is 25 °C (298 K). They may not be valid under non-standard conditions of temperature and ion concentrations. However, because of the logarithmic relation in the Nernst equation,

$$E = E^{\ominus} + (RT/zF) \times \ln([oxidised\ form]/[reduced\ form])$$

only very large changes in concentration have much effect on the values of electrode potentials. They may also give the correct predictions for redox reactions in the gaseous or solid state. (It should be noted that using concentrations in the Nernst equation is an approximation and they should be replaced by activities, but the approximation is valid if the concentrations are dilute.)

The standard reduction electrode potentials are shown in Figure 2.

Oxidised species $\rightleftharpoons$ Reduced species	$E^{\ominus}$ (V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.04
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$H_2O(l) + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-(aq)$	−0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.45
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.26
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq)$	+0.40
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52
$\frac{1}{2}I_2(s) + e^- \rightleftharpoons I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$\frac{1}{2}Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.09
$\frac{1}{2}O_2(g) + 2H_2(aq) + 2e^- \rightleftharpoons H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O(l)$	+1.51
$\frac{1}{2}F_2(g) + e^- \rightleftharpoons F^-(aq)$	+2.87

Figure 2 The electrochemical series (standard electrode potentials); data from International Baccalaureate Organization (2014)

Trends in electrode potential data

The alkali metals (Group 1) have high electrode potentials owing to their relatively small enthalpy changes of atomisation and low ionisation energies, which cause the electrode potentials to be large and negative despite their low hydration energies.

It should be noted that ionisation energy, electronegativity, electron affinity and standard electrode potential all measure attraction for electrons, but in different situations. The ionisation energy is the minimum energy required to remove a mole of electrons from a mole of gaseous atom to form a mole of unipositive ions. The electronegativity measures the affinity of an atom for electrons in a covalent bond. The electron affinity is the energy change (in molar quantities) of a gaseous atom for accepting an electron into its

valence shell to form an anion in the gaseous state. The electrode potential indicates the reducing and oxidising power at an electrode in aqueous solution (under standard conditions). Some correlation between the terms is expected but not detailed agreement.

Students should be reminded that the electrode potential depends on three energy changes whose sum need not vary smoothly from element to element, even if the three enthalpy changes themselves vary fairly smoothly, since the magnitude of change differs. This can be demonstrated by students plotting enthalpies of atomisation, enthalpies of hydration and the first ionisation energies of the Group 1 elements (alkali metals) and their sum against atomic number.

In any comparison of electrode potentials, all three enthalpy changes must be taken into account since no individual enthalpy change (factor) can explain the trends in electrode potential. Students often spot lithium at the top of the electrochemical series and apparently out of place. Lithium has the most negative reduction potential because its hydration energy is much larger than any other alkali metal as a result of its relatively small radius and hence high charge density.

The Group 2 metals appear high in the reactivity series, with calcium above sodium. Although their ionisation energies (sum of first and second) are higher than those of the alkali metals, their enthalpies of atomisation are relatively small and their hydration enthalpies are relatively large, owing to their much higher charge density.

The transition elements have relatively large ionisation energies and very large atomisation enthalpies, which, despite these elements' higher hydration enthalpies, reduce their electrode potentials below those of Group 2 metals.

Electrode potentials and ionisation energies

It common for students to consider the 'ease with which metal atoms lose electrons'. However, large amounts of energy are required to remove electrons from all atoms. Ionisation energies are always endothermic – energy has to be absorbed and work done to remove electrons. Similarly, it is not wise for students to connect the order of the metals in the electrochemical series (based on electrode potentials) with ionisation energies.

A comparison of ionisation energies and standard electrode potentials (standard reduction potentials) shows that the 'order of ease of formation' is not the same (Figure 3). For divalent ions, the ionisation energy is the sum of the first and second ionisation energies. For aluminium, the ionisation energy is the sum of the first, second and third ionisation energies.

The two sets of data cannot be expected to be the same because the ionisation energies refer to

Orders of activity

based on ionisation energies	based on standard reduction electrode potentials
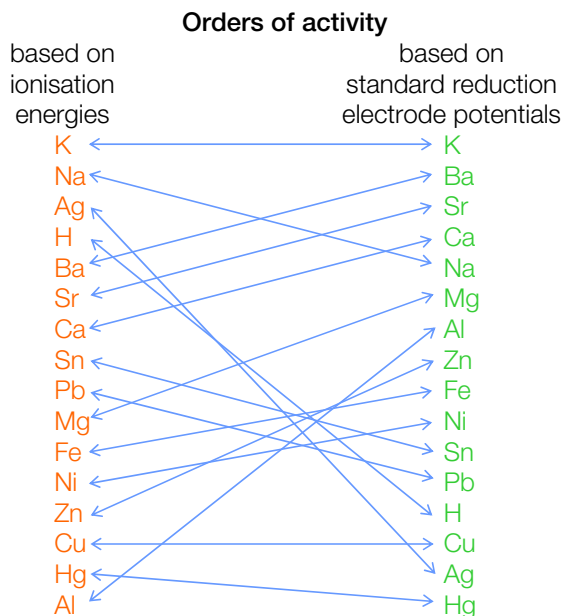
Figure 3 A comparison of ionisation energies and standard electrode potentials

$$M(g) \rightarrow M^{z+}(g) + ze^-$$

and, as discussed previously, electrode potentials refer to
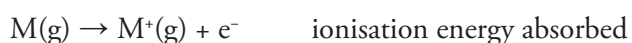
$$M(s) \rightarrow M^{z+}(aq) + ze^-$$

Enthalpies of vaporisation and hydration obviously play a part in electrode potentials but not in ionisation energies.

The overall change represented by

$$M(s) \rightarrow M^+(aq) + e^-$$

can be separated, as described previously (in the form of an energy cycle), into

$M(s) \rightarrow M(g)$	sublimation energy absorbed
$M(g) \rightarrow M^+(g) + e^-$	ionisation energy absorbed
$M^+(g) \rightarrow M^+(aq)$	hydration energy released

The ionisation energy is only *one component* of the total energy transfer that takes place at an electrode in aqueous solution.

Activity series

The term activity series is an unfortunate term, since 'activity' is usually associated with rates of reactions, which is controlled by activation energy. However, all true activity series, such as the electrochemical series, are based on thermodynamic criteria: electrode potentials (which are measures of spontaneity or feasibility) or Gibbs free energy of formation, for example, metal oxides. Figure 4 shows the activity series based on standard electrode potential data.

Acknowledgements

Increasing activity

Li
Cs
Rb
K
Ba
Sr
Ca
Na
Mg
Be
Al

C

Zn
Cr
Fe
Cd
Co
Ni
Sn
Pb

H

Sb
As
Bi
Cu
Ag
Pd
Hg
Pt
Au

Figure 4 Activity series based on standard electrode potential data; data from IBO (2014)

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Further reading

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