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# Positive-negative sign rule for ion-terms in E.M.F of electrochemical cells and its application to potentiometric titration

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Let us have an electrochemical cell represented as follows

(—) Left-hand half-cell || Right-hand half-cell (+)

We propose the following formulas (eqs. (1) and (2) which are easily deducible from the classical Nernst equation) for the E.MF.(E) of a complete cell—

$$E = (E^\circ_R - E^\circ_L) \overset{+}{\underset{-}{\text{or}}} \sum^{\text{All rev. ions}} \frac{mRT}{nF} \ln(\text{Ion}). \qquad \ldots \quad (1)$$

where $E_R^\circ$ and $E_L^\circ$ are the standard electrode potential (reduction) of the right-hand and the left-hand half-cell respectively, $m$ is the co-efficient of the ion in the half-cell equation written as reduction and the other symbols have their usual significance. The summation is over all reversible ions.

Now we formulate the following sign rule : The sign before an ion term (in eq. (1)) is given by the product of the oxidation rank of the ion and the polarity of the electrode, the oxidation rank of an ion being considered positive (+) for a simple positive ion (or an oxidant of a redox couple) and negative for a simple negative ion (or a reductant of a redox couple), i.e.

Sign of an ion-term = Sign of oxidation rank × polarity of the electrode ... (2)

This is shown in tabular form below.

| | Sign preceding the ion-term | |
|---|---|---|
| | For simple positive(+) ion or ox.- ion in redox pair symbol (+) | For simple negative ion(−) or red.- ion in redox pair symbol (−) |
| **Positive electrode (+)** | (+) | (−) |
| **Negative electrode (−)** | (−) | (+) |

Stated simply (i) reversible cations will have (+) sign in right-hand half-cells and (−) sign in left-hand half cells; reversible anions will have sign just opposite to above; (ii) in ionic redox pairs oxidant ions will have same sign as simple cations and reductant ions as simple anions, irrespective of the nature of their charges.

Now, our eq. (1) backed by our sign rule (eq. (2)) is capable of taking care of all electrochemical cells as illustrated by a couple of representative cases below.

*Example* 1 : **Bismuth-Bismuth oxide electrode against Stannate-Stannite electrode in alkaline solution.**

*Step* (*i*). **Cell Representation*** :

$$(-)\ \mathrm{Pt}\,|\,\mathrm{HSnO_2^-},\ \mathrm{Sn(OH)_6^{-2}},\ \mathrm{OH^-Bi_2O_3(s)}\,|\,\mathrm{Bi}\ (+)$$

*Step* (*ii*). **Reduction Reactions**** :

$$(R)\quad \mathrm{Bi_2O_3}(s)+3\mathrm{H_2O}+6e = 2\mathrm{Bi}(s)+6\mathrm{OH^-}$$

$$(L)\quad \mathrm{Sn(OH)_6^{-2}}+2e - \mathrm{HSnO_2^-}+\mathrm{H_2O}+3\mathrm{OH^-}.$$

*Step* (*iii*). **Table for sign of ion-terms**

| (1) Ion | (2) Oxidation rank symbol | (3) $m$ | (4) $n$ | (5) Electrode sign | (6) Sign of ion-term col.2 × col.5 |
|---|---|---|---|---|---|
| $\mathrm{OH^-}$ | (−) | 6 | 6 | (+) | (−) |
| $\mathrm{Sn(OH)_6^{-2}}$ | (+) | 1 | 2 | (−) | (−) |
| $\mathrm{HSnO_2^-}$ | (−) | 1 | 2 | (−) | (+) |
| $\mathrm{OH^-}$ | (−) | 3 | 2 | (−) | (+) |

*Step* (*iv*). **Applying eq. (1) we get for the E.M.F. of the complete cell,**

$$E = (E^0{}_{Bi_2O_3\to 2B^i} - E^0{}_{Sn(OH)_6^{-2}\to HSnO_2^-}) - \frac{6RT}{6F}\ln(\mathrm{OH^-})$$

$$-\frac{RT}{2F}\ln(\mathrm{Sn(OH)_6})^{-2}+\frac{RT}{2F}\ln(\mathrm{HSnO_2^-})+\frac{3RT}{2F}\ln(\mathrm{OH^-})$$

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* ***Note*** **1—In cell representation it is preferable to have the half-cell with higher $E^0$ on the right-hand side, because it is more likely for such electrode to be the positive electrode of the set-up. However, this is a matter of convenience only, because if a wrong choice has been made $E$ will turn out to be negative but still all the conclusions will be algebraically correct.**

** ***Note*** **2—Both the cell reactions are to be represented as reduction reactions (i.e., electrons on the left-hand side) irrespective of the actual reactions in the half-cells.**

$$E = (E^0_{Bi_2O_3\rightarrow 2Bi} - E^0_{Sn(OH)_6^{-2}\rightarrow HSnO_2^-}) - \frac{RT}{2F}\ln(\mathrm{Sn(OH)_6})^{-2}$$

$$+\frac{RT}{2F}\ln(\mathrm{HSnO_2^-}) + \frac{RT}{2F}\ln(\mathrm{OH^-}),$$

where $E^0$'s are the S.E.P. (reduction) of the half-cells.

Furthermore, (i) the number of electrons in ($R$) need not be the same as in ($L$) and (ii) it does not matter whether one writes $Hg_2Cl_2+2\epsilon = 2Hg+2Cl^-$ or $\frac{1}{2}Hg_2Cl_2+\epsilon = Hg+Cl^-$ as long as the equation is a balanced one.

*Example* 2. Silver-Silver chloride electrode against a Cadmium-amalgum electrode.

Following the sign rule, the E.M.F. expression for this simple cell can be directly written as

$$E = (E^0_{AgCl\rightarrow Cl^-} - E^0_{Cd^{++}\rightarrow Cd}) - \frac{RT}{F}\ln(\mathrm{Cl^-}) - \frac{RT}{2F}\ln(\mathrm{Cd^{++}})$$

where $E^0$'s are the S.E.P. (reduction) of the electrodes as clearly pointed out in the subscripts.

It may be pointed out that our sign-rule has no application in single electrode potential which is always given by a Nernst-type equation, e.g,

$$E_{(R\ or\ L)} = E^0 - \frac{RT}{nF}\ln K',$$

where $K'$ is the activity quotient of the reduction equation. So, an alternative formula for $E$ is

$$E = (E_R{}^0 - E_L{}^0) - \frac{RT}{F}\ln\frac{(K'_R)^{1/n_R}}{(K'_L)^{1/n_L}} \quad \ldots \quad (3)$$

which is as good as eq. (1) but somewhat less convenient.

## E.M.F. CHANGE DURING POTENTIOMETRIC TITRATION

Our sign rule is also applicable to predict how the observed E.M.F. changes during potentiometric titration (or on addition of a reversible ion). Since oxidants

| Titration Cell | Change of observed E.M.F. during | |
|---|---|---|
| | **Titration with an oxidant (+) (or simple cation)** | **Titration with a reducant (−) (or a simple anion)** |
| **Positive Half-cell (Right-hand)** (+) | (+) | (−) |
| **Negative Half-cell (Left-hand)** (−) | (−) | (+) |

have (+) rank symbol it follows that on adding an oxidant as titrant at the positive (+) half-cell, the observed E.M.F. increases and at the negative (−) electrode, it decreases. The opposite holds good for titration with a reductant. This is summarised below.

*Example* 1 : *Acid-Base titration*—

Cell representation : (−) Glass ‖ $H^+$ Calomel (+); Titrant : **Alkali**.

We are titrating here with $OH^-$ [Symbol (−)], in the negative half-cell (−); since (−)×(−) = (+), we predict that the observed E.M.F. will monotonically increase during titration.

*Example* 2 : *Redox titration*—(i) Titration with Permanganate ion (ii) Titration with Titanous ion.

(i) Since $MnO_4^-$ has a positive oxidation rank (+), our rule predicts that the observed E.M.F. will increase with progress of titration if the titration vessel is the positive half-cell and would decrease in a negative half-cell. (ii) The opposite is true in titration with titanous (or ferrous) ion because being a reductant its oxidation rank is negative (−).

*Example* 3 : *Precipitation titration*—

Suppose we titrate $Cl^-$ ion by adding silver nitrate, the indicator electrode being Ag/AgCl. According to our rule the titrant is a simple (+) ion. Therefore, if the titration is carried out at a positive electrode, the E.M.F. would increase during titration and just the opposite would happen at a negative electrode.

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