

Disproportionation Reaction

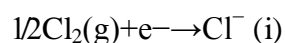
Disproportionation is a chemical reaction, typically a redox reaction, where a molecule is transformed into two or more dissimilar products. In a redox reaction, the species is simultaneously oxidized and reduced to form at least two different products.

Explanation:

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This is best illustrated by an actual example. Chlorine gas is known to undergo disproportionation in alkaline conditions to give chloride and chlorate ions.

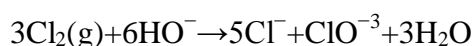
Reduction



Oxidation



And $5 \times (\text{i}) + (\text{ii})$ gives:

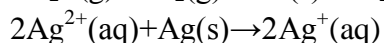
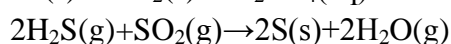
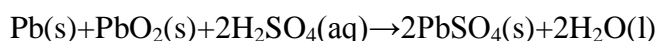


Which is balanced with respect to mass and charge, as is always required. Clearly zerovalent chlorine gas has undergone reduction to chloride ion, and oxidation to chlorate ion; i.e. a disproportionation reaction.

Comproportionation Reaction

A reaction in which an element in a higher oxidation state reacts with the same element in a lower oxidation state to give the element in an intermediate oxidation state is known as comproportionation or symproportionation.

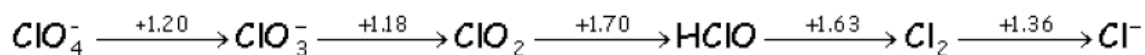
Example:



Latimer diagrams

A Latimer diagram provides us a concise way of presenting a great deal of information about the various oxidation states of the elements. Below is a Latimer diagram for chlorine in acid solution. The

potentials that are given are the reduction potential for going from the species at the left of a line to the one at the right of the line.



The arrow connecting ClO_4^- and ClO_3^- represents the half-reaction



You can easily use a Latimer diagram to determine the reduction potential for half-reactions between non-adjacent species. This procedure is different from what you are accustomed to doing when you add two half-reactions in order to generate an overall reaction with no excess electrons. In that case, you simply add the E° 's for the two half reactions. In the case of making a new half-reaction, a reaction that has electrons on one side or the other, you need to remember that the relation between free energy and E° is $\Delta G^\circ = -nF E^\circ$. Therefore when you add two half-reactions where the electrons do not cancel, the potential of the resultant reaction is given by

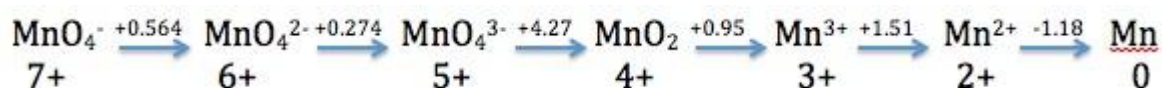
$$E^\circ_{\text{overall}} = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_1 + n_2}$$

As an example, to go from HClO to Cl^- the potential would be given by $E^\circ = (1.63+1.36)/2 = 1.50\text{V}$

You can also use Latimer diagrams to predict whether or not a particular form of an element will be stable in solution, or will undergo a disproportionation reaction. Look at a species in a Latimer diagram. If the potential going to the right is more positive than that going to the left, the species is unstable and will undergo, slowly or quickly, a disproportionation reaction. For example, looking at the diagram above you can see that ClO_2 will disproportionate to HClO and ClO_3^- . The Latimer diagram will not tell us if the disproportionation will be fast or slow, that is kinetics.

Example:

Mn in Acid

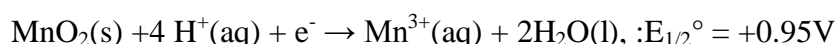


The Latimer diagram for Mn illustrates its standard reduction potentials (in 1 M acid) in oxidation states from +7 to 0.

The Latimer diagram compresses into shorthand notation all the standard potentials for redox reactions of the element Mn. For example, the entry that connects Mn^{2+} and Mn gives the potential for the half-cell reaction:



and the entry connecting Mn^{4+} and Mn^{3+} represents the reaction:



We can also calculate values for **multi-electron reactions** by first adding $\Delta G^\circ (= -nFE^\circ)$ values and then dividing by the total number of electrons

For example, for the 5-electron reduction of MnO_4^- to Mn^{2+} , we write

$$E^\circ = \frac{1(0.564) + 1(0.274) + 1(4.27) + 1(0.95) + 1(1.51)}{5} = +1.51\text{V}$$

and for the three-electron reduction of $\text{MnO}_4^-(\text{aq})$ to $\text{MnO}_2(\text{s})$,

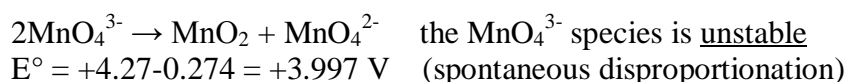
$$E^\circ = \frac{1(0.564) + 1(0.274) + 1(4.27)}{3} = +1.70\text{V}$$

Remember to divide by the number of electrons involved in the oxidation number change (5 and 3 for the above equations).

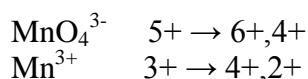
Thermodynamically stable and unstable oxidation states

An unstable species on a Latimer diagram will have a lower standard potential to the left than to the right.

Example:



Which Mn species are unstable with respect to disproportionation?



So stable species are: MnO_4^- , MnO_4^{2-} , MnO_2 , Mn^{2+} , and Mn^0 .

But MnO_4^{2-} is also unstable - why?

$\text{MnO}_4^{2-} \rightarrow \text{MnO}_2$ It undergoes a multi-electron transfer!

So overall, $2\text{MnO}_4^{2-} \rightarrow \text{MnO}_4^- + \text{MnO}_2 \quad E^\circ = 2.272 - 0.564 = \underline{+1.708 \text{ V}}$

Frost diagrams:

In a Frost diagram, we plot $\Delta G^\circ F (= nE^\circ)$ vs. oxidation number. The zero oxidation state is assigned a nE° value of zero.

Stable and **unstable oxidation states** can be easily identified in the plot. Unstable compounds are higher on the plot than the line connecting their neighbors. Note that this is simply a graphical representation of what we did with the Latimer diagram to determine which oxidation states were stable and unstable.

The **standard potential** for any electrochemical reaction is given by the **slope** of the line connecting the two species on a Frost diagram. For example, the line connecting Mn^{3+} and MnO_2 on the Frost diagram has a slope of +0.95, the standard potential of MnO_2 reduction to Mn^{3+} . This is the number that is written above the arrow in the Latimer diagram for Mn. Multielectron potentials can be calculated easily by connecting the dots in a Frost diagram.

