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
$1/2Cl_2(g)+e^- \rightarrow Cl^-$ (i)

Oxidation
$1/2Cl_2(g)+6HO^- \rightarrow ClO^{-3}+5e^-+3H_2O$ (ii)

And 5×(i)+(ii) gives:

$3Cl_2(g)+6HO^- \rightarrow 5Cl^-+ClO^{-3}+3H_2O$

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:

$Pb(s)+PbO_2(s)+2H_2SO_4(aq) \rightarrow 2PbSO_4(s)+2H_2O(l)$
$2H_2S(g)+SO_2(g) \rightarrow 2S(s)+2H_2O(g)$
$2Ag^{2+}(aq)+Ag(s) \rightarrow 2Ag^+(aq)$

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.

$$ClO_4^- \xrightarrow{+1.20} ClO_3^- \xrightarrow{+1.18} ClO_2 \xrightarrow{+1.70} HClO \xrightarrow{+1.63} Cl_2 \xrightarrow{+1.36} Cl^-$$

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

$$ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_3^-(aq) + H_2O(l) \qquad E^\circ = 1.20V$$

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^0'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 Eo is D Go = -nF Eo. Therefore when you add two half-reactions where the electrons do not cancel, the potential of the resultant reaction is given by

$$E^\circ_{overall} = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_1 + n_2}$$

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

<u>Mn in Acid</u>

$$\begin{array}{ccccccccccccc} MnO_4^- & \xrightarrow{+0.564} & MnO_4^{2-} & \xrightarrow{+0.274} & MnO_4^{3-} & \xrightarrow{+4.27} & MnO_2 & \xrightarrow{+0.95} & Mn^{3+} & \xrightarrow{+1.51} & Mn^{2+} & \xrightarrow{-1.18} & Mn \\ 7+ & & 6+ & & 5+ & & 4+ & & 3+ & & 2+ & & 0 \end{array}$$

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:

$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$, $E_{1/2}^{\circ} = -1.18V$

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

$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+}(aq) + 2H_2O(l)$, :$E_{1/2}° = +0.95V$

We can also calculate values for **multi-electron reactions** by first adding ΔG°(=-nFE°) 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

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

and for the three-electron reduction of $MnO_4^-(aq)$ to $MnO_2(s)$,

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

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:

$2MnO_4^{3-} \rightarrow MnO_2 + MnO_4^{2-}$ the MnO_4^{3-} species is unstable
E° = +4.27-0.274 = +3.997 V (spontaneous disproportionation)

Which Mn species are unstable with respect to disproportionation?

MnO_4^{3-} $5+ \rightarrow 6+,4+$
Mn^{3+} $3+ \rightarrow 4+,2+$

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

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

$MnO_4^{2-} \rightarrow MnO_2$ It undergoes a multi-electron transfer!

So overall, $2MnO_4^{2-} \rightarrow MnO_4^- + MnO_2$ $E° = 2.272 - 0.564 = \underline{+1.708\ V}$

Frost diagrams:

In a Frost diagram, we plot $\Delta G°/F$ (= $nE°$) 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.