Quadrant II – Transcript and Related Materials

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Module Name: Stability of various oxidation states (Latimer Diagram) for Mn, Fe and Cu.

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Notes

A **Latimer diagram** of a chemical element is a summary of the standard electrode potential data of that element. This type of diagram is named after Wendell Mitchell Latimer, an American chemist.

This Reduction Potential Diagram list the various forms of an element in different oxidation states. When an element exists in multiple oxidation states, it is convenient to display all of the reduction potentials for the reduction half cells in a single reduction potential diagram.

The most oxidized species is to the extreme left and the most reduced species on the right. Oxidation number decrease from left to right and the E^0 values are written above the line joining the species involved in the couple. High positive standard reduction potential implies the specie can be easily reduced and is hence a good oxidizing agent. A negative E° implies that the species on the right is oxidized to the species on the left and is hence a good reducing agent.

The Latimer diagram can tell us whether an oxidation state of an element is stable with respect to disproportionation. Element is simultaneously oxidized and reduced are said to disproportionate.

$$2\,M^{+}(aq) \longrightarrow M(s) + M^{2+}(aq)$$

'The potential on the left of a species is less than the potential on the right- the species can oxidize and reduce itself, a process known as ***disproportionation'***.

$$A_1^{5+} \xrightarrow{w} A_2^{3+} \xrightarrow{x} A_3^{1+} \xrightarrow{y} A_4^{0} \xrightarrow{z} A_5^{1-}$$

A general representation of a Latimer diagram of a specie A is given above. The specie exists in five different oxidation state: +5 in A_1, +3 in A_2, +1 in A_3, 0 in A_4, -1 in A_5.

The highest oxidation state is +5 in A_1 which is written on the left. The lowest oxidation state is -1 in A_5, which is on the right. The potential for the reduction of the different species are given above the arrow. The potential 'w' is for the reduction of A_1^{5+} to A_2^{3+}.

$$\underset{+7}{MnO_4^-} \xrightarrow{+0.56} \underset{+6}{MnO_4^{2-}} \xrightarrow{+1.51} \underset{+4}{MnO_2} \xrightarrow{+2.26} \underset{+3}{Mn^{3+}} \xrightarrow{+0.95} \underset{+2}{Mn^{2+}} \xrightarrow{-1.18} \underset{0}{Mn}$$

Given above is the Latimer diagram of manganese in acidic solution. From this diagram the following can be inferred:

- Manganese exist in six different oxidation state
- MnO_4^-, MnO_4^{2-}, MnO_2, Mn^{3+}, Mn^{2+} and Mn
- The highest oxidation state is +7 in MnO_4^-
- The lowest oxidation state is 0 in Mn metal
- Except for the reduction of Mn^{2+} to Mn, all the reduction potentials are positive.
- All the species can be reduced spontaneously except Mn^{2+}
- Mn metal will undergo oxidation spontaneously.

A Latimer diagram can be converted to a half cell reaction by introducing the predominant specie in acidic solution, H^+ and H_2O and then balancing the equation. (for basic solutions OH^- and H_2O). Consider a part of the Latimer diagram for Manganese.

$$MnO_4^- \longrightarrow HMnO_4^-$$

Since the Latimer diagram is in acidic solution it can be balances as follows,

$$MnO_4^-(aq) + e^- \longrightarrow MnO_4^{2-}(aq) \qquad E^o = 0.56\ V$$

Similarly,

$$MnO_2 \xrightarrow{+0.90} Mn^{3+}$$

$$MnO_2(aq) + 4H^+(aq) + e^- \longrightarrow Mn^{3+}(aq) + 2H_2O(l) \qquad E^o = 0.95\ V$$

The reduction potential for non-adjacent species in the Latimer diagram can also be obtained. Let us take a part of the Latimer diagram as shown below

$$MnO_2 \xrightarrow{+1.51} Mn^{3+} \xrightarrow{+0.95} Mn^{2+}$$

The first step is to Identify the two redox couples; in this case it is $MnO_2 \rightarrow Mn^{3+}$ and $Mn^{3+} \rightarrow Mn^{2+}$. The oxidation states of Manganese in these three species are +4, +3 and +2, respectively.

Now we will write the balanced equation for the two couples

$$MnO_2(aq) + 4H^+(aq) + e^- \longrightarrow Mn^{3+}(aq) + 2H_2O(l) \qquad E^o = +0.95\ V$$

$$Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+}(aq) \qquad E^o = +1.5\ V$$

Adding the two reactions will give us the overall reaction for the reduction of MnO_2 to Mn^{2+}.

$$MnO_2(aq) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$$

This tells us the reaction that is taking place. Now we need to obtain the reduction potential for the reaction. Since potentials are not additive, we male use of the relation between reduction potential and Gibbbs free energy.

$$\Delta G = -nFE^o$$

$$\Delta G = \Delta G_1 + \Delta G_1$$

$$-nFE^o = -n'FE'^o - n''FE''^o$$

$$E^o = \frac{n'E^{o\prime} + n''E^{o\prime\prime}}{n}$$

Appling this equation, n’ = number of electrons in the first reaction (1), n’’ = number of electrons in the second reaction (1) and n = number of electrons in the overall reaction (2).

E_o' is the reduction potential for the first reaction (+0.95V), E_o'' is the reduction potential for the second reaction (+1.5V), E_o' is the reduction potential for the overall reaction which has to be calculated. Substituting these values in the equation gives a reduction potential of **E^o = +1.225 V.**

Let us now identify the species in the Latimer diagram of Manganese that are susceptible to disproportionation. For this we will make use of the rule that **‘If the potential on the left of a species is less than the potential on the right-** the species can oxidize and reduce itself, and the specie will ***disproportionate’***.

$$\underset{+7}{MnO_4^-} \xrightarrow{+0.56} \underset{+6}{MnO_4^{2-}} \xrightarrow{+1.51} \underset{+4}{MnO_2} \xrightarrow{+2.26} \underset{+3}{Mn^{3+}} \xrightarrow{+0.95} \underset{+2}{Mn^{2+}} \xrightarrow{-1.18} \underset{0}{Mn}$$

Consider the specie MnO_4^{2-} , the potential to its left is 0.56V and the potential to its right is 2.26 V. The potential on the left of a species is less than the potential on the right and so MnO_4^{2-} will disproportionate. Similarly, for other species, MnO_2 will disproportionate while Mn^{3+} and Mn^{2+} are stable to disportionation.

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