Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

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Paper Title: Inorganic Chemistry (Section B)

Unit: 6 (Oxidation and Reduction)

Module Name: Diagrammatic presentation of potential data: Latimer diagram

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Notes

Diagrammatic Presentation of Potential Data

- There are several diagrammatic presentations which give summaries of useful redox potential data depicting relative stabilities of compounds in which one element exists in a series of different oxidation states.
- Two such diagrammatic representations are

  1) the Latimer diagrams and

  2) the Frost diagrams.
- These diagrams furnish a good deal of information in a compact form.

Latimer diagram

- Latimer diagram of an element presents the standard reduction potential values (E° values) for a series of compounds of that element in which the element is in different oxidation states.
- Different species given in the Latimer diagram have arrows in between them and E° values involving the two immediate (adjacent) species are written over the arrows.
- The oxidation state (O.S.) of the element concerned is written under the species.

- The species having the element in the highest O.S. is written on the extreme left and the species having the element in the lowest O.S. is written on the extreme right.
- Thus, on proceeding from left to right in a Latimer diagram, the O.S. of the element concerned goes on decreasing.
- Latimer diagram contains the notations for the reduction half-cell reactions.
- In a given adjacent pair of species, the left hand species is reduced to right hand species.
- For example,

1. **Latimer diagram for chlorine in acidic solution is written as:**

$$ClO_4^- \xrightarrow{+1.20V} ClO_3^- \xrightarrow{+1.18V} HClO_2 \xrightarrow{+1.65V} HClO \xrightarrow{+1.67V} Cl_2 \xrightarrow{+1.36V} Cl^-$$

Cl = +7 +5 +3 +1 0 -1

In this diagram, the notation (change) $ClO_4^- \rightarrow ClO_3^-$, represents the reduction half-reaction given as:

$$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O, \quad E° = +1.20\ V$$

Similarly, Reduction half-cell reactions for other notations can be written as:

$$ClO_3^- + 3H^+ + 2e^- \rightarrow HClO_2 + H_2O, \quad E° = +1.18\ V$$

$$HClO_2 + 2H^+ + 2e^- \rightarrow HClO + H_2O, \quad E° = +1.65\ V$$

$$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O, \quad E° = +1.67\ V$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-, \quad E° = +1.36\ V$$

- A Latimer diagram here, is thus, converted into a reduction half-cell reaction by including the predominant species present in acidic solution (viz. H^+ ion and H_2O) and balancing the equation by adding appropriate number of electrons.
- The solution in the above cases is acidic with pH = 0.

2. **Latimer diagram for chlorine in basic medium is written as:**

$$ClO_4^- \xrightarrow{+0.37V} ClO_3^- \xrightarrow{+0.30V} ClO_2^- \xrightarrow{+0.68V} ClO^- \xrightarrow{+0.42V} Cl_2 \xrightarrow{+1.36V} Cl^-$$

$$\text{Cl} = +7 \qquad +5 \qquad +3 \qquad +1 \qquad 0 \qquad -1$$

Reduction half reactions for different changes shown are:

$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$, $E° = +0.37$ V

$ClO_3^- + H_2O + 2e^- \rightarrow ClO_2^- + 2OH^-$, $E° = +0.30$ V

$ClO_2^- + H_2O + 2e^- \rightarrow ClO^- + 2OH^-$, $E° = +0.68$ V

$2ClO^- + 2H_2O + 2e^- \rightarrow Cl_2 + 4OH^-$, $E° = +0.42$ V

$Cl_2 + 2e^- \rightarrow 2Cl^-$, $E° = +1.36$ V

In basic solution (pH = 14), the predominant species are OH^- and H_2O which are hence included to balance the equation for the above half-cell reactions.

3. Fe exists in different oxidation states like +6, +3, +2 and 0.

Latimer diagram showing these oxidation states can be written as:

$$FeO_4^{2-} \xrightarrow{+2.20V} Fe^{3+} \xrightarrow{+0.77V} Fe^{2+} \xrightarrow{-0.47V} Fe^0$$

$$\text{Fe} = +6 \qquad +3 \qquad +2 \qquad 0$$

Reduction half-cell reactions for different changes shown are:

$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$, $E° = +2.20$ V

$Fe^{3+} + e^- \rightarrow Fe^{2+}$, $E° = +0.77$ V

$Fe^{2+} + 2e^- \rightarrow Fe^0$, $E° = -0.47$V

4. Latimer diagram for Oxygen

$$O_2 \xrightarrow{+0.70V} H_2O_2 \xrightarrow{+1.76V} H_2O$$

$$\text{O} = 0 \qquad -1 \qquad -2$$

Reduction half reactions for different changes shown are:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2, \quad E° = +0.70\ V$$

$$H_2O_2 + 2H^+ + e^- \rightarrow 2H_2O, \quad E° = +1.76\ V$$

5. Latimer diagram from the reduction half reactions for Manganese in acidic medium:

Given,

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}, \qquad E° = +0.56\ V$$

$$MnO_4^{2-} + 4H^+ + 2e^- \rightarrow MnO_2 + 2H_2O, \quad E° = +2.26\ V$$

$$MnO_2 + 4H^+ + e^- \rightarrow Mn^{3+} + 2H_2O, \quad E° = +0.95\ V$$

$$Mn^{3+} + e^- \rightarrow Mn^{2+}, \qquad E° = 1.51\ V$$

$$Mn^{2+} + 2e^- \rightarrow Mn^0, \qquad E° = -1.14\ V$$

Latimer diagram will be,

$$MnO_4^- \xrightarrow{+0.56V} MnO_4^{2-} \xrightarrow{+2.26V} MnO_2 \xrightarrow{+0.95V} Mn^{3+} \xrightarrow{+1.15V} Mn^{2+} \xrightarrow{-1.19V} Mn^0$$

Mn = +7	+6	+4	+3	+2	0