INORGANIC CHEMISTRY

Oxidation and Reduction

Prof. Ranjit K. Verma
University Department of Chemistry
Magadh University
Bodh Gaya-824234

(31.07.2006)

CONTENTS

Introduction
Spontaneity of a chemical reaction
Use of redox potential data
Redox stability in water
Diagrammatical & graphical summarization of redox potential data
Principles involved in extraction of the elements

Keywords
Gibbs energy, redox potential, spontaneity, redox half reaction, electrochemical series, Nernst equation, over potential, stability field of water, Disproportionation, comproportionation, Latimer diagram, Frost diagram, Pourbaix diagram, Ellingham diagram, metallurgy, pyrometallurgy, hydrometallurgy

Introduction

Oxidation and reduction are among some of the most important terms in chemistry. REDUCTION simply means electron gain ("electronation") and OXIDATION means electron loss ("de-electronation"). Both take place simultaneously and when a chemical species (atom/ion/molecule) gains one or more electrons in a chemical reaction, some other is losing electron. Together these two processes are called REDOX reaction and they constitute a major class of chemical reactions that take place around us. There may be complete transfer of electron or there may be increase or decrease in electron density (and subsequent change in bond polarization or a change in "oxidation number" of atoms) at such sites. "Redox chemistry", the chemistry of such reactions, is concerned with "electron flow" to and from a "defined" centre during a chemical reaction.

Redox reactions are encountered in almost all branches of science and many phenomena could be explained using the concept of this term. It may be a simple electrolysis or rusting and corrosion of metals (or the losing luster of the "metallic" portion of the "golden" frame of your spectacles in contact with the salty sweats on face). It may be the problem of extracting pure metal which is present as oxide in the ore. It may be environmental problems like the release of gases such as hydrogen sulfide and methane or high concentrations of metals such as Mn and Fe or non metals like arsenic and fluoride in water that is being pumped from a deep well. Myriads of phenomena move around "redox reactions". Understanding such reactions and the dependence of such phenomena on values of certain data like "electrode potential" and "Gibbs Free Energy" and the dependence of these parameters on the chemical environment such as pH, oxidation states etc is what we aim at, in the present chapter. After going through such discussions, one could explain, why sodium is a strong reducing agent and acidified potassium permanganate is a strong oxidizing agent, why fluorine is a stronger oxidizing agent than chlorine and why calcium is a stronger reducing agent than magnesium. Why sodium splits water to liberate hydrogen gas but copper does not. Why Cr^{2+} ions are not stable in aqueous solutions and undergo change to Cr^{3+} and Cr^{0} (disproportionation) while Fe^{2+} is stable. Questions on stability of simple ions (Fe^{2+}, Cr^{2+} etc.), oxoanions (FeO_4^{2-}, AsO_4^{3-} etc) and other species, are based on the redox potential data and could be answered after getting acquainted with the technique of using those data.

A redox reaction may take place in aqueous or non-aqueous media. Many of these occur in aqueous solutions or suspensions. In this medium most of the reactants and products exist as charged species (ions) and their reaction is often affected by the pH of the medium. Understanding and predicting whether such a reaction is feasible or not in solution, is of great significance. This helps us in understanding the stability and interpreting the behaviour of chemical species in those media. Such predictions and interpretations are mainly based on the values of a term known as "redox potential" for the corresponding redox processes. On the basis of redox potential values, one could easily explain the variations in chemical reactivity of substances in various media. Thus in this chapter, we shall discuss what exactly redox potential is and how to present (graphically), illustrate and use the redox potential data. But before proceeding, we shall describe some basic thermodynamic concepts which are required for our understanding of the data.

Spontaneity of a Chemical Reaction

On its own, water always flows downhill. It does so because it has a natural tendency to do so. This "natural tendency to occur" is termed "spontaneous". A chemical reaction may or may not have a natural tendency to occur. If it has this tendency *i.e*., if it takes place spontaneously, it means, the net Gibbs Free Energy (ΔG) of the reaction (at that temperature and pressure) is negative. The spontaneity of any chemical reaction is well explained by thermodynamics. At any given temperature and pressure, a negative Gibbs Energy change implies that the reaction will be spontaneous. Gibbs Free Energy, G is a state function (depends only on the thermodynamic state of the system, defined by quantities like P, T and composition). Under standard conditions, when the reactants /products are in their respective standard states, the corresponding values of G (G^0) will have particular values. Thus for a chemical reaction taking place in standard conditions (thence, at constant pressure and temperature), the value of change in $G^0(\Delta G^0)$ will have a characteristic value. This ΔG will naturally, have different values at different temperatures. It is related to temperature (T), entropy(S) and enthalpy (H) through equation (1):

$$G = H - TS \qquad \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

Hence at constant temperature,

$$\Delta G = \Delta H - T\,\Delta S \qquad \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

For any reaction,

$$\Delta G = G_{products} - G_{reactants} \qquad \ldots \ldots \ldots \ldots \ldots \ldots (3)$$

For any "spontaneous reaction", at any temperature and pressure, ΔG is negative. This means, the driving force is the tendency to move towards lower Gibbs energy. This is favoured naturally by lower enthalpy (lowering of H *i.e*., negative ΔH favours negative value of ΔG in eq.2). Similarly, higher entropy (+ve ΔS) is helpful in achieving lower G at a particular temperature and pressure. Since pressure and temperature are variables that are usually under our control, eq. (2) becomes very important in applying the concept of Gibbs energy (and spontaneity) to chemical reactions in laboratory, in nature or elsewhere. If one has to test feasibility of a decomposition reaction at any P and T, one just needs to calculate the value of ΔG and if it is negative, it is expected that the reaction will occur. If ΔG is +ve, the reaction will not proceed in the forward direction. Rather it has a tendency to move in the reverse direction. $\Delta G=0$ means the reaction equilibrium has been achieved. This concept is very much useful as it saves us from taking the trouble of actually trying the reaction. However, these thermodynamic concepts do not help us in predicting the rate of reaction i.e. whether it is fast or slow or even infinitesimally slow. For these purposes, the concepts of chemical kinetics are applied successfully. Sometimes, even –ve value of ΔG does not mean that the reaction will necessarily occur. The magnitude by which it is decreasing, matters but there may be a requirement of an initial input of excess energy etc. If ΔG is small, it means the reaction is energetically feasible and could take place if one or more of the conditions like pH, concentration, temperature are changed. The values of ΔH and ΔS do not change appreciably with eq.2 above (ΔS however, changes significantly with the state of the compound. It is large on +ve side if the state is changed from solid to liquid or

from liquid to gaseous on account of enormous increase in randomness. This could easily be understood on applying the concept : "more disorder means higher entropy".

ΔG is also related to the equilibrium constant of the reaction, K:

$$\Delta G = -RT \ln K \quad \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

Since T is never –ve, a +ve value of K implies – ve value of ΔG. Eq. (4) gives us a simple way of determining of the value of ΔG as the K-value is easily measurable for majority of the reactions. Further, electrode potential, E is related to ΔG by eq. (5):

$$\Delta G = -nFE \quad \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

where n is the number of electrons being transferred in the electrode reaction (reduction or oxidation) and F is faraday. Considering an entire electrochemical cell (two half cells *i.e.*, two electrodes –reduction taking place in one and oxidation in the other), the ΔG for the whole cell is found out. Thus a +ve value of E implies spontaneous (–ve ΔG) cell reaction.

Use of Redox Potential Data

The redox potential data are extensively used for prediction of the direction of a redox reaction under a given set of conditions. For the same, one needs to understands the following basic terms.

(a) **Redox half reaction:** Redox half reaction or the half cell reaction is the chemical reaction taking place around one electrode of a cell. Consider the two parts of a complete redox system. In one part, oxidation is taking place and in the other, reduction is taking place. The electron is transferred from one part to the other. In order to bring out such a complete redox system,

(a) the two parts(and the two species, the one undergoing oxidation and the other undergoing reduction) may form the bulk together (and electron transfer will be random) or,

(b) the two parts may be kept separated and connected by a conducting wire such that the electron released in one process, to the wire is collected by the other species and utilized in the reduction process there.

In the first type, the electron movement can not be utilized for any work. Only pV work may yield if the process results in any expansion or contraction. The situation in the second case is interesting. The electron flow in the wire can be exploited for work. It is even more efficient if the redox process in the system is taking place in a thermodynamic reversible manner. This way, more electrons could be dumped into the wire for passage to the other part. This implies more work could be exploited. Taking the two parts (of oxidation and reduction) together in either of the above ways, the system makes a complete cell.

The cell could be of two types *viz*.:

(i) Galvanic cell: The overall reaction corresponds to a decrease in G (–ve ΔG) and spontaneous reduction and oxidation are taking place in the two respective half cells. The cell reaction is unaided and spontaneous. It could be used as a source of electrical energy.

(ii) Electrolytic cell: The ΔG for the overall redox reaction is +ve and energy from outside is essential for the reaction to occur (E is –ve).

The salient features of the two types of cells may be summarized as follows (Table-1):

Table-1

Electrochemical cell type	Reaction type	Sign of ΔG	Sign of E	Equilibria	Electrode on which reduction is taking place	Oxidation electrode	Direction of flow of electron
Electrolysis	Non-spontaneous	+ve	–ve	K<1	Cathode	Anode	e^- flows to cathode
Galvanic cell(e.g. in battery)	Spontaneous	–ve	+ve	K>1	Cathode	Anode	e^- flows to cathode

The overall redox reaction is "cell reaction" and the overall e.m.f. is the cell e.m.f.. Naturally, the segments in which a reduction or an oxidation is taking place are called electrodes (cathode/anode). The chemical reactions taking place in a half cell or around an electrode are known as the electrode reactions. Half cells can form in large electrochemical cells and may also form at infinitesimally small sites where 'reduction' or 'oxidation' is taking place. The actual occurence of such reactions is governed by the corresponding electrode potential values which in turn, depend on the magnitude and sign of the corresponding values of **ΔG** (eq 2 & 5)

In the reduction half cell, the species gains electron as in

$$2H^+(aq) + 2\,e^- \rightarrow H_2\,(g)$$

or in $$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe\,(s)$$

Similarly, in an oxidation half cell, the substance loses electron as in

$$Zn\,(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$$

In either case, the oxidized and the reduced states form a couple. This couple is denoted by writing the oxidized form on the left side followed by a slash and the reduced form. Thus the three reactions shown above are written as $H^+/\,H_2$; $Fe^{2+}/\,Fe$ and $Zn^{2+}/\,Zn$, respectively. It is customary to write all the redox couples as if reduction is taking place. The format remains the same irrespective of the direction of the reaction(reduction or oxidation). In the third case, oxidation process is taking place (in acidified aqueous solutions, Zn releases $H_2$and Zn^{2+} ions) which is reverse of reduction. This anomaly is removed by putting –ve sign in the value of E^0 of the reaction In writing the net cell reaction, care is taken to balance the net electron gain with the number of electrons lost. For checking spontaneity of the cell reaction, the individual E values of the electrodes are first converted to ΔG(putting the no. of electrons, 'n' in eq. 5), the sum of the

two ΔG values is obtained from which E is calculated using the same eq. putting 'n' for the second electrode reaction.

(b) **Standard Electrode Potential:** As enunciated earlier, the driving force of any reaction is decrease in free energy (–ve ΔG). If the reactants and products are in their respective standard states at a given P and T, the change is denoted by ΔG^0 .The corresponding difference in free energy for any half cell reaction is represented as E^0. If one writes a reduction half cell reaction in which actually reduction is taking place, the ΔG^0 value will be –ve. Thus for the Zn^{2+}/ Zn couple, the E^0 value is –0.76V at 25^0C(298K) and for Fe^{2+}/ Fe couple, E^0 value is –0.44V. Similarly, the E^0 value is +0.7991V for Ag^+/ Ag couple and+0.35V for Cu^{2+}/ Cu couple (A +ve E^0 value corresponds to a –ve ΔG^0 and hence Cu^{2+} and Ag^+ both have natural tendency to get reduced). [The standard conditions have to be mentioned. In aqueous media, usually, 1 bar pressure, unit activity, 25^0C(298K) temperature and pH=0 (1M acid if H^+ is present) are taken as constituting the standard conditions.]

In practice, it is impossible to measure electrode potential of any couple in isolation. However, the e.m.f. of a cell could easily be measured which has been constructed taking it as one half cell and another half cell of known E value. It is customary to put the E^0 value at 0.00V for standard hydrogen electrode. This helps in getting the E^0 value of the other electrode which is equal to the e.m.f. of the cell thus constructed. So any electrode that has stronger tendency to reduce than H+ will have -+ve value of E and any species which has lesser tendency to reduce than H+ will have –ve value of E. In other words, the potential of the couple H^+/ H_2 has arbitrarily been put at zero to formulate a scale of electrode potential values for the other couples. Some of the standard electrode potential values (E^0) have been given in Table-2. It should be noted that the values have been calculated taking all electrode reactions as reduction reactions. The –ve value of E^0 corresponds to a +ve ΔG^0 (non-spontaneous *i.e.,* the electrode will make oxidation half cell if coupled with H-electrode for making a complete half cell).

The E^0 for the cell , Zn/ Zn^{2+}// H^+/ H_2 is calculated by taking it as a couple of Zn^{2+}/Zn and H^+/ H_2 half cells .On LHS is the oxidation half cell and on RHS is reduction half cell. So the process on the former has to be reverse of reduction. The cell e.m.f. thus, will be:

$E^o_{H^+/H_2} - E^o_{Zn^{2+}/Zn} = 0 - (-0.76V) = 0.76V$

This can be measured experimentally and confirmed. It leads to the ΔG^0 value of
$-n E^oF = -2(-0.76)F = +147kJ$

Similarly, for a cell
Zn^{2+}/ Zn// Cu^{2+}/ Cu,
$E^o_{Zn^{2+}/Zn} = -0.76V$ and $E^o_{Cu^{2+}/Cu} = +0.35V$

So the e.m.f. will be
$E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn} = +0.35V-(-0.76V) = +\ \ 1.11\ V$

And, the corresponding half cell reactions will be:

(i) $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu_{(s)}$ …… (with $E^o_{Cu^{2+}/Cu} = +0.35V$)

(ii) $Zn^{2+}(aq) + 2\ e^- \rightarrow Zn_{(s)}$ …… (with $E^o_{Zn^{2+}/Zn} = -0.76V$)

The net cell reaction will be (i) –(ii):

$Cu^{2+}(aq) + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}(aq)$ …… (with $E^o = +1.11V$)

Since the E^o for the cell reaction is +ve, ΔG^0 will be –ve ($\Delta G^0 = -n\ E^oF$) and the process will be spontaneous. If $Zn_{(s)}$ is added to an aqueous solution of Cu^{2+}, copper will be precipitated as metal and zinc will pass on to the solution as Zn^{2+} ('zinc is more reducing!')

The –ve E^o value corresponds to a couple in which the reduced species is a reducing agent (see $E^o_{Na^+/Na}$ in the table) for H^+ ions under 'standard conditions' and the +ve value means the oxidized species is an oxidizing agent(see $E^o_{F_2/F^-}$ in the table).When a metal is dipped in its aqueous solution, the passage of metal atoms from the surface of the electrode to the solution involves three phenomena *viz*. sublimation of the metal atom from metallic state(here the metallic bonding, hardness etc matter), its ionization (its ionization energy matters) and hydration of the ionized atoms(hydration energy matters). While passing into solution, the metal leaves behind electrons on the surface of the electrode. In the opposite phenomenon in which the metal ions are deposited on the surface, these three steps will be reversed. In both the cases an electrical double layer forms on the electrode. The electrode potential is the potential developing there and depends on the energetics of the three steps which can be described by a Born Haber type of cycle. In a similar way, all reduction and oxidation phenomena taking place and forming couples as described earlier can be understood.

(c) **Electrochemical Series:** The standard electrode potential values of common systems when arranged in descending order make a series. Thus the one with the highest E^o value is on the top (high +ve value means the element has strong tendency to undergo reduction and so it is a strong oxidizing agent). Similarly, the low E^o value (more on the –ve side) signifies tendency to get converted to its oxidized form and hence it is a strong reducing agent. This series is called electrochemical series. Some of the general features of this series are:

(i) The oxidized form of the couple is stronger oxidizing agent than the one below it in the series.

(ii) The reduced form of the couple is stronger reducing agent than the one above it in the series.

(iii) The reduced form of the couple that is below the H^+/H_2 couple in the series, will have a natural tendency to liberate H_2 from acidic solutions.

(iv) The reduced form of the couple below in the list will reduce the oxidized form of a couple above it in the series.

(v) The oxidized form of the couple above in the list will oxidize the reduced form of a couple below it in the series

(vi) The half-reaction with the greater reduction potential will drive the other half-reaction in the direction of oxidation

(vii) The difference between the two reduction potentials provides a quantitative description of the electromotive force of the cell.

The series is a convenient ready reckoner for predicting the direction of redox process if two couples are coupled to make a complete redox system. However, these data speak of the general tendency and spontaneity and not the rate with which the reaction will take place.

In simple terms, the electrochemical series is an arrangement of metals in their increasing reducing power such that the one in lower position in the series will reduce ions (aq) of metal in higher position.

(d) **The oxidation/reduction dilemma:** The values of electrode potential that we have discussed are 'standard electrode potentials' which are applicable under standard conditions. Prediction of any 'tendency to occur' in case of any reduction or oxidation reaction on this basis will, therefore, be correct only for standard conditions. In most of the actual reactions, the conditions are non-standard and the activity of all the species involved in the electrode reaction may not be unity. For a general electrode reaction, the electrode potential is expressed by Nernst equation (eq. 6):

$$E_{ox/red} = E^{o}_{ox/red} - (RT/nF)\ln Q \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where Q is the reaction quotient.

For a reaction of general type:

$$a\,A_{ox} + b\,B_{red} = a'\,A_{red} + b'\,B_{ox}$$

The value of the reaction quotient will be

$$Q = \frac{[A_{red}]^{a'}[B_{ox}]^{b'}}{[A_{ox}]^{a}[B_{red}]^{b}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where the subscripts denote the oxidized/reduced forms of the reactants/products in the reaction based on the thermodynamic equations (8, 9):

$$\Delta G = \Delta G^{0} + RT \ln Q \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\Delta G = -nFE \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

As already emphasized earlier, a process will be spontaneous only if $\Delta G = -ve$. Remember another equation; $\Delta G = -RT \ln K$ (eq.4). At equilibrium, ΔG will remain zero. From these facts, one can notice that

(a) For $\Delta G = -ve$, K must be +ve

(b) At equilibrium, $\Delta G = 0$ (thus E=0 and no reaction means no current will flow) and Q=K

or, $E = E^{o} - (RT/nF)\ln Q = 0$

or, $E^{o} = (RT/nF)\ln K \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$

Putting (10) in Nernst eq.,

$E = (RT/nF)[\ln K - \ln Q]$

Therefore, $E>0(\Delta G<0)$ when $Q<K$ and the reaction will move in forward direction.

(c) Putting the values of the constants at 298K,

$E = E^o - (0.0591/n) \log Q$

(d) For a couple,
$a\ A_{ox} \rightarrow a'\ A_{red}$
the electrode potential (non-standard conditions) will be:

$E = E^o - (RT/nF) \ln Q$
Where

$$Q = \frac{[A_{red}]^{a'}}{[A_{ox}]^{a}}$$

(e) As evident from the electrochemical series, a couple down in the series (lower i.e., more –ve E^0 value) will undergo reduction but if it is joined with another couple which is further down in the series, it will undergo oxidation. So, the same electrode can undergo reduction or oxidation process and this depends on which electrode it is coupled with. This fact can be understood by using the Q value for the combined redox reaction. (Q value depends upon the concentration of the reactants and the products). If putting this 'Q' in the Nernst equation gives a +ve E, the reaction will take place from L $\rightarrow$R in the overall cell reaction written for getting 'Q'. A –ve value of E implies the reaction in the reverse direction (R $\rightarrow$L)

The direction of the cell reaction can be reversed by applying an external e.m.f. of greater magnitude in opposite direction and. It will be similar to what happens when a redox couple is 'paired' with a redox couple of lower position in the electrochemical series and then with another couple which is above it in that series. Reversal of the direction of the electrode reaction means a change from oxidation reaction to reduction reaction and vice-versa.

Applications of Nernst Equation give some interesting results:
Example 1: Consider two half cell reactions:
(i) $Cd_{(s)} \rightarrow Cd^{2+}_{(aq)} + 2\ e^-$ $\quad E^0$ for the half cell or $E^0_{1/2} = -0.412V$
(ii) $2AgCl_{(s)} + 2e^- \rightarrow 2Ag_{(s)} + 2\ Cl^-_{(aq)}$ $\quad E^0_{1/2} = +0.222V$

The concn. $[CdCl_2] = 0.167$ M
Comment on the effect of lowering concn. of $CdCl_2$

The cell reaction would be:
$Cd_{(s)} + 2AgCl_{(s)} \rightarrow Cd^{2+}_{(aq)} + 2Ag_{(s)} + 2\ Cl^-_{(aq)}$ $\quad E^0 = +0.624V$

This gives the Nernst equation as:

$$E_{cell} = 0.624 - \frac{0.0591}{2} \log [Cl^-]^2 [Cd^{2+}]$$

$$E_{cell} = 0.624 - \frac{0.0591}{2} \log [0.334]^2 [0.167]$$

This means that by lowering $[CdCl_2]$, the cell reaction can be made more exothermic (The second term will decrease leading to an increase in E_{cell} and subsequently ΔG will be larger on negative side).

Example 2: Consider two half cell reactions:

(i) $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ $\quad E^0_{1/2} = 0.000V$

(ii) $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ $\quad E^0_{1/2} = -0.402V$

At what pH the cell reaction would be spontaneous?

The cell reaction would be:

$Cd^{2+}(aq) + H_2(g) \rightarrow Cd(s) + 2H^+(aq)$ $\quad E^0 = -0.402V$

This gives the Nernst equation as:

$$E_{cell} = -0.402 - \frac{0.0591}{2} \log \frac{[H^+]^2}{[Cd^{2+}]\, p_{H_2}}$$

At pH=0, if the concn. is unity, the reaction will not be spontaneous. In order to make it spontaneous at $[Cd^{2+}] = p_{H_2} = 1$, the $[H^+]$ should be incresed to make the value of E_{cell} negative.

$$E_{cell} = -0.402 - \frac{0.0591}{2} \log \frac{[H^+]^2}{(1)(1)}$$

This gives $[H^+] = 1.6 \times 10^{-7} M$

Hence, the pH should be 6.8 or above. Further, the reaction will not occur in acidic medium. Thus we can manipulate the cell reaction and the E_{cell} value by altering the pH.

(Note that a reaction having E value like this will be spontaneous at physiological pH and in presence of bases, it will be very much spontaneous.)

Redox Stability in Water

Stability of any species in any solvent depends upon several factors. It will be stable if it does not react with the solvent or other solutes present (even dissolved oxygen may react). This is also true for redox reactions. If we take water as the solvent, it may itself participate in redox reactions causing oxidation or reduction of the reduced or the oxidized form of the ion/molecule present in it. As discussed earlier, change in conditions like pH, 'presence of dissolved oxygen', concentration of the species etc. also matters. The following events will affect the redox stability of any oxidized or reduced form of any molecule or ion present in water:

(1) Reaction with water
   (a) Reduction by water
   (b) Oxidation by water
(2) Disproportionation (reaction of the solute with itself or self oxidation-reduction.
(3) Oxidation by atmospheric oxygen

(1) **Reaction with water:** Water can be oxidized to O_2 and it can also be reduced to H_2. When it is oxidized or reduced, accordingly, it will reduce or oxidize others. Thus water may act as an oxidizing agent as well as a reducing agent. Let us consider its electrode potential values for the two reactions:

(a) *Oxidation of water (to O_2):water as a reducing agent :* Oxidation of water can be seen as reverse of the corresponding reduction half reaction:

$O_2\,(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(aq)$ ... ... $E^0_{1/2}$=+1.23V

This can be represented by the couple:

$O_2, H^+ / H_2O$

Putting n=4 (since 4 electrons are involved),the Nernst equation (eq.6) becomes:

$$E_{O_2, H^+/H_2O} = E^o_{O_2, H^+/H_2O} - (RT/4F) \ln \frac{1}{p_{O_2}[H^+]^4} \quad \ldots (11)$$

where p_{O_2} is the partial pressure of O_2 and the reaction is very much dependent on pH.

Putting standard values ($E^o_{O_2H^+/H_2O}$=+1.23V; p_{O_2}= 1 bar; T=298K; RT/F=0.0591)eq (11) becomes:

$$E = 1.23 + \frac{0.0591}{4} \log [H^+]^4$$

or, E= 1.23V – 0.0591V X pH … … … … … … (12)

This equation signifies the following:

(i) The high value of the reduction potential E^o on the +ve side (+1.23V) implies that the acidified water is a poor reducing agent. The corresponding oxidation potential of water is –1.23V. It may reduce only strong oxidizing agents which form a couple having reduction potential greater than 1.23V.

(ii) Any species which has its reduction potential value higher than that of water described by the eq (12) above at a given pH can be reduced by water producing O_2.

(iii) At different pH, the required minimum value of the reduction potential of the oxidizing agent should be different (eq. 12) for getting reduced by water.

(iv) Merely getting E>0 does not lead to a reaction. In practice, it should be more than 0.6V (Overvoltage!). Secondly, transfer of 4 electrons is required which many times is not provided by couples having higher reduction potentials. Thirdly, formation of oxygen-oxygen double bonds is slow (requires catalysts!). These are the hurdles in making water act as a reducing agent.

(b) Reduction of water (to H_2): water as an oxidizing agent: Reduction of water usually appears as reaction of a metal with water or with an aqueous acid. The metal is oxidized by water or H^+ like that in the following reactions:

Oxidation by water: $M_{(s)} + H_2O_{(l)} \rightarrow M^+_{(aq)} + \frac{1}{2} H_{2(g)} + OH^-_{(aq)}$

Oxidation by H^+ ions: $M_{(s)} + H^+_{(aq)} \rightarrow M^+_{(aq)} + \frac{1}{2} H_{2(g)}$

Taking the second one, reduction of H^+ to H_2 can be represented by the couple:

H^+/H_2

And the reaction can be seen as:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \quad \ldots \ldots \ldots \quad E^0_{1/2} = 0.000 \text{ V}$$

And the Nernst equation (eq.6) will be reduced to eq (13), putting n=2 since 2 electrons are involved :

$$E = E^o - (RT/2F) \ln \frac{p_{H2}}{[H^+]^2} \qquad \ldots \ldots \ldots \ldots (13)$$

Putting the standard values ($E^o = 0.00$V; $p_{H_2} = 1$ bar; T=298K; RT/F=0.0591)eq (13) becomes:

$$E = -0.0591\text{V} \times \text{pH} \qquad \ldots \ldots \ldots \ldots \ldots \ldots (14)$$

This equation signifies the following:

(i) The potential is pH dependent.

(ii) Any couple having reduction potential value lower than this value will reduce H^+ to H_2.

(iii) The concept of 'Overvoltage requirement' applies here too.

The conditions described above for making water act as a reducing agent or as an oxidizing agent lead to the following conclusions:

**Thermodynamically, a substance will be stable in water and it will not change to its redox conjugate if its reduction potential lies between the two limits.*

** Both the limits (set by equations (12) and (14) are very much pH dependent.*

** The requirement of 'Over potential' in both the cases is over and above the two limits set by these equations.*

The range of values of the reduction potential and the pH values in which any reducible or oxidisable species will survive and remain unchanged in water is also called the stability field of water (Fig-1).Taking into account the normal pH range of natural water (4<pH<9), a region has been shown in which substances will be stable in natural water. This also explains why many minerals/ organic substances remain stable in natural water although they can form redox couples. It is simply the values of their redox potential under those pH (at 25^0 C !).

Question 1 : The electrode potential value for the acidified permanganate ion couple, MnO_4^-/Mn^{2+} is +1.51V which is outside the stability field of water (outside the 0–1.23V range). Even then, the couple does not give bubbles of O_2 in aqueous solutions?

(2.) Disproportionation: A substance may get oxidized or reduced. It can thus form two couples: A/ A_{red} and $A_{red}/A_{red/}$ which can be seen as representing the redox reactions:

$$A \xrightarrow{+e^-} A_{red} \xrightarrow{+e^-} A_{red/}$$

This is quite common in case of metal ions (and in non-metals also when the element exists in more than two oxidation states). The oxidation number of the element is simultaneously raised and lowered in solution although the electrode potential values of both the couples are well within the stability limits set by water at any pH. Such *self oxidation and reduction is known as "disproportionation"* (simultaneous increase and decrease in the oxidation number of an element at the cost of one another). A commonly cited example is the disproportionation of Cu^+ to Cu^{2+} and Cu^0:

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu^0(s)$$

The electrode potential value of the Cu^{2+}/ Cu^+ couple is +0.159V and that of the Cu^+/ Cu couple is + 0.52V. Both are within the range of stability in water (0.00V and +1.23V). Their instability is explained by pairing the two couples themselves. The value of E_{cell} then becomes 0.52–0.159 = + 0.3611V which is +ve (=> –ve ΔG) and sufficient for spontaneous process.

$Cu^+(aq) \longrightarrow Cu^{2+}(aq) + e^- \ldots \ldots \ldots E^0 = -0.159V;\ \Delta G^0 = +0.159F$

$Cu^+(aq) + e^- \longrightarrow Cu^0(s) \ldots \ldots \ldots E^0 = +0.52V;\ \Delta G^0 = -0.52F$

Net process: $2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu^0(s)\ [E^0 = +0.361V;\ \Delta G^0 = -0.361F]$

(Note that the standard electrode potentials are reduction potentials while the first reaction is that of oxidation. The reduction potential is corresponding to a +ve ΔG corresponding to the reduction process meaning that the actual process which will be going the oxidation way,

will give just the reverse value of $\Delta G = -0.159F$. Therefore, the first process of oxidation will be spontaneous and will be the overall process.)

Many such examples can be tried and we can see that the sum of the two ΔG values shall always be +ve to make the disproportionation proceed. Disproportionation is easily understood through the redox diagrams which shall be described later. There is another phenomenon, "comproportionation" which is just the reverse of disproportionation and two states change to an intermediate state.

(3.) Oxidation by atmospheric oxygen: When a species has redox instability in water, the third possibility is that of its reaction with dissolved O_2. This possibility becomes more marked if the aqueous solution is kept in open or anyway exposed to air. The most important example of atmospheric oxidation in aqueous solution is that of $Fe^{2+}_{(aq)}$. It is slowly oxidized to $Fe^{3+}_{(aq)}$ in aqueous solutions by dissolved oxygen- a reason why iron is found in nature mostly in Fe(III) state. In underground water systems, iron (II) is transformed to bicarbonate and to $FeCO_3$ on exposure to air. This on further exposure to air, gets oxidized to iron oxide giving brown deposits often visible in water streams. Secondly, Fe^{3+} is prone to hydrolysis giving acidic solution.

Presence of dissolved O_2 in water changes the redox scenario of couples through the process:

$$\tfrac{1}{2}\, O_2(g) + 2\, H^+(aq) + 2\, e^- \longrightarrow H_2\, O(l)$$

for which E^0 is +1.229V ($\Rightarrow \Delta G^0 = -nE^0F = -2 \times 1.229F = -2.458F$).

Naturally, the process is spontaneous and makes O_2 a good oxidizing agent in water. It (O_2, H^+ / H_2O) combines with the Fe^{3+}/ Fe^{2+} couple (E^0 = +0.771V which is well within the stability field of water to survive). The resultant redox process becomes:

$$4\, Fe^{2+}(aq) + O_2(g) + 4\, H^+(aq) \longrightarrow 4\, Fe^{3+}(aq) + 2\, H_2\, O(l)$$

for which the value of E^0 comes to + 1.229V –0.771 V = + 0.458 V

This is not more than the 'Overvoltage' required. Hence the process is slow but spontaneous.

Similarly, copper metal is also oxidized by moist air due to oxygen. The E^0 for Cu^{2+}/ Cu couple is + 0.34 V. The couple O_2, H^+ / H_2O combines with it to make the resultant process spontaneous:

$$\tfrac{1}{2}\, O_2(g) + 2\, H^+(aq) + 2\, e^- \longrightarrow H_2\, O(l) \quad \ldots \quad \ldots \quad \ldots \quad E^0 = +1.229V$$
$$Cu^{2+}(aq) + 2\, e^- \longrightarrow Cu(s) \quad \ldots \quad \ldots \quad \ldots \ldots \quad E^0 = +0.34V$$
$$\text{Thus for, } Cu\,(s) + \tfrac{1}{2}\, O_2(g) + 2\, H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2\, O(l) \quad E^0 = +0.89V$$

This results in slow oxidation of metallic copper to +2 state and subsequent formation of hard coating of green hydrated copper carbonate or sulfate in association with atmospheric CO_2 and SO_2.

Diagrammatical & graphical summarization of redox potential data

To know the oxidation stability of an element in a given oxidation state we need a comparative data of electrode potential values.(Table-2).

Table - 2 : Electrode potential values of some common redox systems at 25^0C

Couple	Redox reaction		Value E^0/V
Li^+/Li	$Li^+(aq) + le^-$	$Li(s)$	– 3.04
K^+/K	$K^+(aq) + le^-$	$K(s)$	– 2.93
Ca^{2+}/Ca	$Ca^{2+}(aq) + 2e^-$	$Ca(s)$	– 2.87
Na^+/Na	$Na^+(aq) + 1e^-$	$Na(s)$	– 2.71
Mg^{2+}/Mg	$Mg^{2+}(aq) + 2e^-$	$Mg(s)$	– 2.36
Al^{3+}/Al	$Al^{3+}(aq) + 3e^-$	$Al(s)$	– 1.66
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2e^-$	$Zn(s)$	– 0.76
Sn^{2+}/Sn	$Sn^{2+}(aq) + 2e^-$	$Sn(s)$	– 0.14
Pb^{2+}/Pb	$Pb^{2+}(aq) + 2e^-$	$Pb(s)$	– 0.13
H^+/H_2	$2H^+(aq) + 2e^-$	$H_2(g)$	0.00
I_2/I^-	$I_2(s) + 2e^-$	$2I^-(aq)$	+ 0.54
MnO_4^-/MnO_2,	$MnO_4^-(aq) + 2H_2O(1) + 3e^-$	$MnO_2(s) + 4OH^-(aq)$	+ 0.59
OH^-	$O_2(g) + 2H^+(aq) + 2e^-$	$H_2O_2(aq)$	+ 0.68
$O_2, H^+/H_2O_2$	$Ag^+(aq) + 1e^-$	$Ag(s)$	+ 0.80
Ag^+/Ag	$2NO_3^-(aq) + 4H^+(aq) + 2e^-$	$N_2O_4(g) + 2H_2O(1)$	+0.80
$NO_3^-, H^+/N_2O_4$	$Br_2(l) + 2e^-$	$2Br^-(aq)$	+ 1.07
Br_2/Br^-	$O_2(g) + 4H^+(aq) + 4e^-$	$2H_2O(1)$	+ 1.23
$O_2, H^+/H_2O$	$MnO_2(S) + 4H^+(aq) + 2e^-$	$Mn^{2+}(aq) + 2H_2O(1)$	+ 1.23
$MnO_2, H^+/Mn^{2+}$	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 2e^-$	$2Cr^{3+}(aq) + 2H_2O(1)$	+ 1.33
$Cr_2O_7^{2-}, H^+ / Cr^{3+}$	$Cl_2(g) + 2e$	$2Cl^-(aq)$	+ 1.36
Cl_2/Cl^-	$Au^{3+}(aq) + 3e^-$	$Au(s)$	+ 1.50
Au^{3+}/Au	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$Mn^{2+}(aq) + 4H_2O(1)$	+ 1.51
$MnO_4^-, H^+/Mn^{2+}$	$O_3(g) + 2H^+(aq) + 2e^-$	$O_2(g) + H_2O(l)$	+ 2.07
$O_3, H^+/O_2$	$F_2(g) + 2e^-$	$2F^-(aq)$	+ 2.87
F_2/F^-	**(Strongest oxidant)**	**(Weakest reductant)**	

Such tables have been organized by the voltage of the process and not by the chemical species. These are helpful if one is trying to build a cell involving two different redox couples. Just by finding out the values of their potential, one can predict the potential of the cell! But if one has to find the relative stabilities of different oxidation states of an element like Mn or Fe, one has to think on the possible redox couples that the element will form in different oxidation states and search their data. Questions like the outcome of the reaction of iron with a non-oxidizing agent like HCl (whether it will give Fe^{2+} or Fe^{3+}), become time consuming. Problems arise further when the prediction of stability has to be made under different conditions like pH etc. or that of the possible reaction of a metal in any oxidation state with an oxidant or reductant in acid or alkaline media. For handling all such problems excellent graphical/diagrammatical representations have been devised. Three such diagrams are:

(i) Latimer Diagrams
(ii) Frost Diagrams
(iii) Pourbaix Diagrams

These diagrams are convenient sources of understanding complex redox chemistry of any element in its various oxidation states and some times under different reaction conditions like pH etc. These are usually plots for oxidation states of individual elements but sometimes, more than one plot are put in a single diagram for the sake of comparisons. The variables in the three diagrams/plots have been mentioned below:

	Diagram	*Presentation style*	*The variables/plots*
1	Latimer Diagram	Flow sheet	Arrows link oxidation states forming redox couple. Standard E^0 values are written.
2	Frost Diagram	Graphical plot	nE vs. Oxidation state (Relative "Gibbs Free Energy" vs. Oxidation state)
3	Pourbaix Diagram	Graphical plot	E vs. pH

(i) Latimer Diagram: ***In Latimer diagram, values of standard redox potential connecting various oxidation states of an element are displayed.*** It is a concise reduction potential diagram and a convenient way to display all the reduction potential values for half reactions involving all the oxidation states of an element. In it, all the redox couples that the element may form are covered. Let us see how to construct such a diagram considering its important features and applications.

How to construct?

(a) The most highly oxidized form is written on the left and the most reduced form on the extreme right.

(b) On proceeding from L→ R, the species of the element towards right are in successively lower oxidation states.

(c) The standard electrode potential value for the reduction half reaction involving any pair of the species joined by an arrow is shown above the arrow.

(d) Sometimes the respective oxidation states of the element are also written below/above the species.

(e) The electrode potential values of the known redox couple (ie, for the known half cell reaction) are written on the top of the corresponding arrow. For generation of the E^0value of a combination of such processes (redox couples involving non-adjacent oxidation numbers), firstly the conversion is made to the ΔG^0 values of the corresponding redox steps. ΔG^0 of two such steps are added algebraically and the resultant ΔG value of the combined step gives the E^0 value for the combined redox process($\Delta G^0 = -nFE^0$).Because of this 'n', the process is not a simple addition of two half reactions. The potential of the resultant reaction is given by:

$$E^0_{overall} = (n_1E_1^0 + n_2E_2^0)/ (n_1 + n_2)$$

(f) Separate Latimer diagrams are constructed for an element in different media. The two popular forms are: (a) "In acidic medium" (pH=0) and (b) "In alkaline medium" (pH=14). In practice, the more important of these two examples for aqueous element chemistry is pH changes. It has become conventional to construct Latimer diagrams for the two extremes of pH = 0 and pH = 14 (respectively 1 *M* acid and 1 *M* base). A Latimer diagram can be extended to include any number of related redox systems that the element might form.

(g) The value of the redox potential depends on the value of ΔG. So, any parameter affecting the value of any process will also alter the value of E. As we know, ΔG is a state function and depends on parameters which include: (i) concentration, (ii) temperature, (iii) pH and (iv) presence of other reagents which are not inert. The presence of such reagents will affect the potential values. Such parallel values of E values are depicted by constructing a branch line in the chart showing that particular reagent. One could construct a branch in which the element forms complexes with a ligand, in its different oxidation states. For example, iron forming complexes with CN^- ligand can well be understood by constructing a branch depicting redox couples of different cyano complexes of iron in different oxidation states. Actually, two branches in a Latimer diagram reflect identical redox processes or an element in presence of the two ligand systems.

Examples:

(1) Latimer Diagram for iron (in acidic medium):

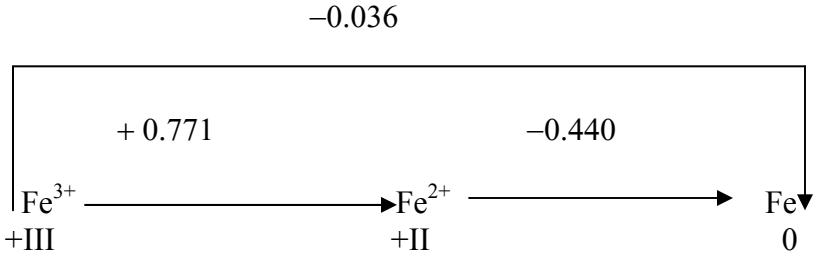
(a) From the table the standard electrode potential values of iron are taken. Then ΔG^0 values are worked out ($\Delta G^0 = -nFE^0$).

(b) Using simple algebraic additions like in case of Hess' Law of constant heat summation, ΔG^0 value for addition of two successive redox reactions is calculated. It is used for conversion to the E^0-value of the resultant of the two successive reactions. This value is written over the arrow connecting the two species of the resultant redox couple. This is also called the "skip potential" for the direct conversion.

Redox reactions	E^0values	$\Delta G^0 = -nFE^0$
$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe_{(s)}$ $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	–0.440 V + 0.771 V	–2 x F x (–0.440) –1 x F x (+0.771)
$Fe^{3+}(aq) + 3\ e^- \rightarrow Fe_{(aq)}$	+ 0.331 V (wrong!)	+ 0.109 F =–3 x F x (–0.036)

The conversion to (+II) is favoured but not from (+II) to (+III) because of the signs as described earlier. Now the E^0value for the conversion $Fe^{3+}(aq) + 3\ e^- \rightarrow Fe_{(s)}$ is worked out by using $\Delta G^0 = -nFE^0$. It is now spontaneous because of the sign.

(c) The Latimer diagram depicting the three states will thus be:



(2) Latimer Diagram for copper (in acidic medium):

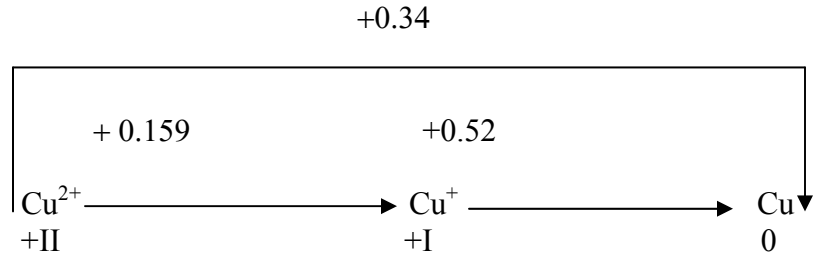
(a) In a similar way, the standard electrode potential values of copper are taken from the table. Then the ΔG^0 values are worked out.

(b) The ΔG^0 value for addition of two successive redox reactions is calculated by adding the ΔG^0 values for the two steps. Then it is converted to E^0-value of the resultant of the two successive reactions. This value is written above the arrow connecting the two species of the resultant redox couple.

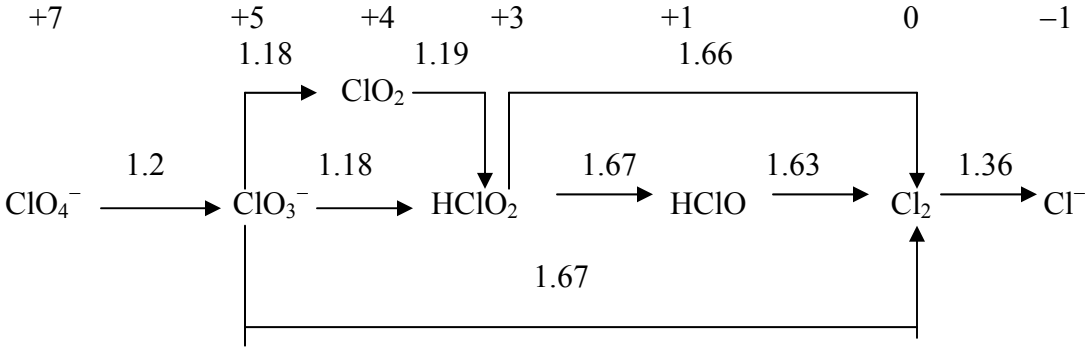
Redox reactions	E^0values	$\Delta G^0 = -nFE^0$
$Cu^+(aq) + e^- \rightarrow Cu(s)$ $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	+ 0.520 V + 0.159 V	–1 x F x (+0.520) –1 x F x (+0.159)
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+ 0.679 V (wrong!)	– 0.679 F =–2 x F x (+0.34)

It is spontaneous because of the sign.

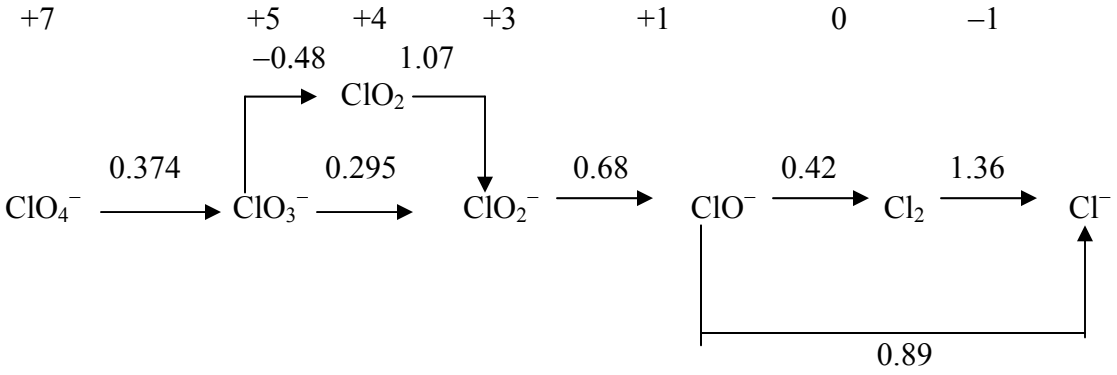
(c) The Latimer diagram depicting the three states will thus be:



(3) The Latimer diagram for chlorine in acidic solution will be:



And, the Latimer diagram for chlorine in basic solution will be:



The individual steps could easily be converted back to the redox reaction by writing first the predominant species present and then adding the other characteristic species in the acidic (H+ and H_2O) and in alkaline (OH^- and H_2O) solutions, respectively. Charge balancing is affected using the appropriate number of electrons. Thus,
The redox reaction for the ClO_4^-/ClO_3^- couple in acidic solution is:

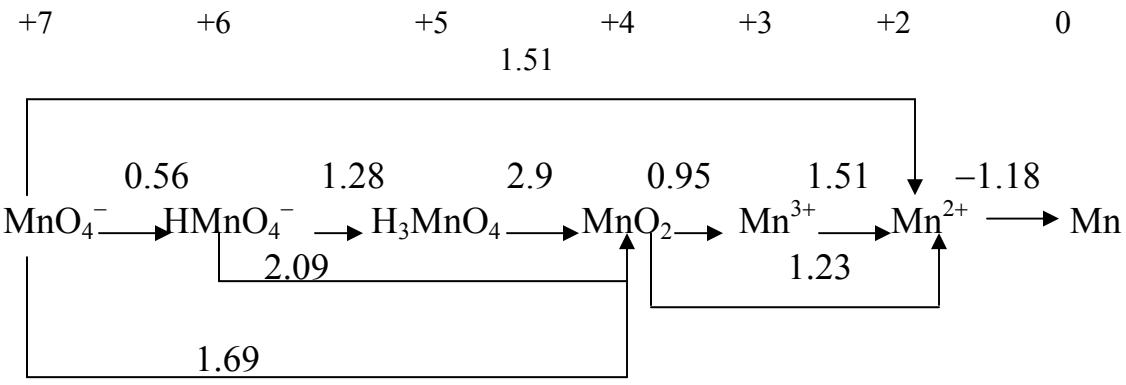
$$ClO_4^-(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow ClO_3^-(aq) + H_2O_{(l)} \quad E^0 = +1.20V$$

And in basic solution will be,

$$ClO_4^-(aq) + H_2O_{(l)} + e^- \longrightarrow ClO_3^-(aq) + OH^-(aq) \quad E^0 = +0.37V$$

Variations arise in E^0 values in the two media, due to the involvement or transfer of H^+ or OH^- in the steps. If the involvement is not there, the values remain the same ($E^o_{Cl_2/Cl^-}$ is almost the same in the two diagrams).

(4) The Latimer diagram for manganese in acidic solution is:



Features:

(a) A Latimer diagram contains sufficient information to derive the standard potentials of non-adjacent couples.

(b) It gives a quantitative picture of E^0 values at one sight.

(c) One can determine whether a species in an intermediate oxidation state will DISPROPORTIONATE (convert to the more oxidized species to its right and the more reduced species to its left) simply by comparing the redox potential for its formation *vs.* the redox potential for its reduction. *Disproportionation occurs when the E^0 value on right side is more positive than that on left.* Thus, in case of manganese, Mn^{3+} will disproportionate to Mn^{2+} and MnO_2 since the value on RHS is more +ve (1.51V) than on LHS (0.95V).

(d) More positive the electrode potential, more readily will the species on the left be reduced. Thus highly positive standard electrode potential indicates that the species on the left side of the arrow is a good oxidizing agent. A negative value of E^0 indicates that the species to the right will behave as a reducing agent.

(e) Half cell reactions can easily be written from the diagrams in the case of chlorine.

Question 2: Answer the following questions on the basis of the Latimer diagram for manganese in acidic solution given above:

(i) What will be the full half reactions for the different steps?

(ii) Calculate the E^0 value for going from MnO_4^- to Mn^{2+}.

(iii) What species will tend to disproportionate?

(iv) The E^0 values given here are for the respective reactions in standard states. i.e., $[H^+]$ =1M. Redraw Latimer diagram for pH=2.

Applications: The features of a Latimer diagram make it a very useful tool. For the sake of further illustration, let us see how oxidation of elemental copper takes place:

An overview of the Latimer diagram of copper indicates that the elemental copper will not tend to oxidation if placed in water or H^+. This could be so because of the sign of the E^0 values and hence the sign of the ΔG^0 values for the reverse reactions (oxidation). However, this could take place if some extra energy is provided to the system. This is achieved when some oxidant is put

in the system (as we have seen under the description of effects of dissolved oxygen). Let us see what happens when in the laboratory, nitric acid is used to dissolve copper wire. An additional E^0 is provided by the reaction:

$$2\ NO_3^-(aq) + 4\ H^+(aq) + 2\ e^- \longrightarrow N_2O_4(g) + 2\ H_2O(l) \qquad E^0 = +\ 0.803V$$

This makes the negative E^0 value coming for the oxidation of copper metal, to a net resultant +ve E^0 value. The ΔG value becomes negative and the hurdle is removed. The net reaction in the above case then becomes:

$$Cu(s) + 2\ NO_3^-(aq) + 4\ H^+(aq) \longrightarrow Cu^{2+}(aq) + N_2O_4(g) + 2\ H_2O(l)$$

The E^0 value is now + 0.463V. If we work out the transformation to +I state of copper, the values from the Latimer diagram and the above equation furnish $E^0 = +\ 0.283$ which justifies why the oxidation of copper metal to +I state is less likely thermodynamically.

(ii) Frost Diagram: Latimer diagram provides quantitative picture of the redox stability of an element in various oxidation states. Sometimes quick qualitative ideas are required to assess the redox properties of an element. For such purposes two graphical representations of redox properties namely, Frost diagram and Pourbaix diagram are in vogue. The graphical visualizations make the trends conceivable. Secondly, more plots (e.g., for different elements or for one element in different media) can be incorporated in a single graph for making comparisons. One is Frost diagram.

In ***Frost diagram, values of standard redox potential connecting various oxidation states of an element are displayed.*** It is a relative Gibbs free energy diagram and a convenient way to show redox properties of different oxidation states. Let us see how to construct such a diagram, what are its important features and why it is useful. It can also be constructed from Latimer diagram just by multiplying the values of E^0 with the number of electrons (n) and plotting it against the oxidation number.

How to construct?

(a) The oxidation numbers are identified as in the case of Latimer diagrams.

(b) The corresponding E^0 values and hence ΔG^0s values ($= -\ nF\ E^0$) are calculated out for ***all*** the steps. (In case of Latimer diagram, we change to ΔG^0 only if E^0 has to be calculated for non-adjacent oxidation states).

(c) Graph of nE^0/V vs. oxidation number is plotted.

(d) For the sake of comparisons, different plots of ΔG^0 (in units of nE^0) are put in the same graph. Plots of different elements can also be put in one graph for such comparisons of slopes and magnitudes.

Examples: Let us take the simple examples of iron, copper and manganese for which we have already constructed Latimer diagrams.

(1) Frost Diagram for iron (in acidic medium): The identification of the oxidation states and calculations of ΔG^0 or (nE^0) can be done and the results shown earlier, in the case of construction of Latimer diagram for iron, can be used for plotting.

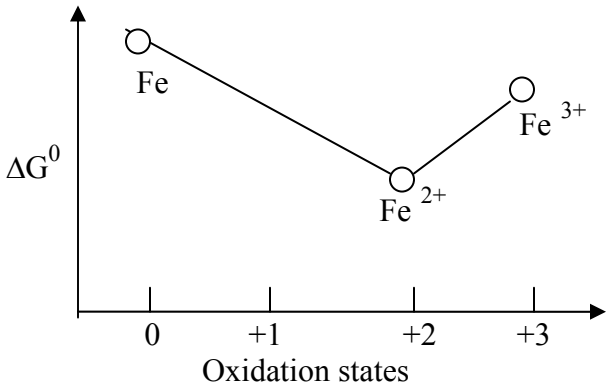


Figure 2 : Simplified Frost diagram for iron

(2) Frost Diagram for copper (in acidic medium): In a similar fashion, identification of the oxidation states and calculations of ΔG^0 or (nE^0) can be done.

Redox reactions	E^0values	$\Delta G^0 = -nFE^0$
$Cu^+(aq) + e^- \rightarrow Cu(s)$ $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	+ 0.520 V + 0.159 V	−1 x F x (+0.520) −1 x F x (+0.159)
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$		− 0.679 F =−2 x F x (+0.340)

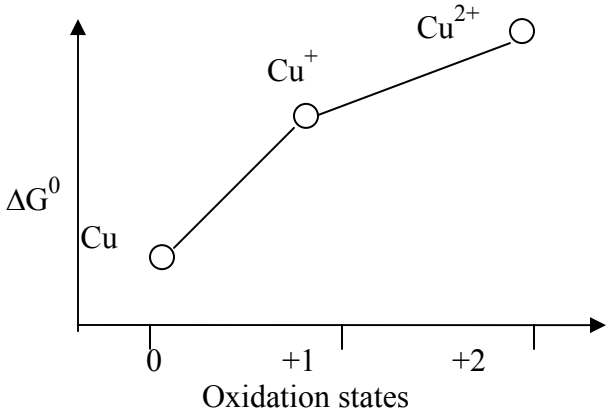


Figure 3 : Frost diagram for copper (acidic medium)

(3) Frost Diagram for manganese (in acidic medium):

Calculations of the variables:

Oxidation state	Species	The value of E^0	n E^0
0	Mn	0	0
+II	Mn^{2+}	–1.18	2 x (–1.18)=–2.36
+III	Mn^{3+}	1.5	1x 1.5+(-2.36)=–0.86
+IV	MnO_2	0.95	1x 0.95+(-0.86)=0.09
+V	H_3MnO_4	2.9	1x 2.9+0.09=2.99
+VI	$HMnO_4^-$	1.28	1x 1.28+2.99=4.27
+VII	MnO_4^-	0.56	1x 0.56+4.27=4.83

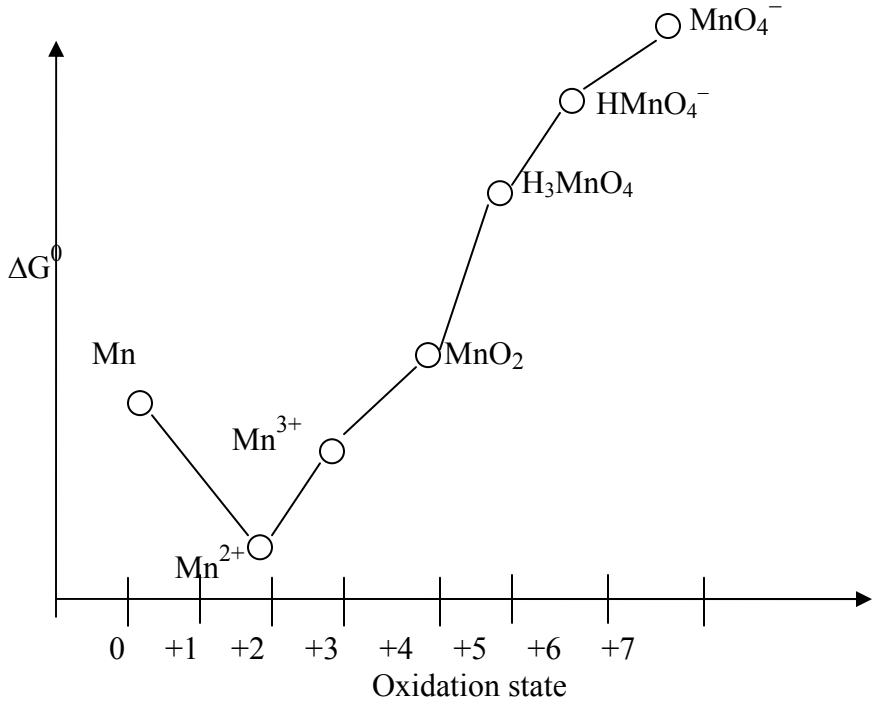


Figure 4 : Frost diagram for manganese (acidic medium)

Features of Frost Diagram:

(a) The slope of the line joining two points in a Frost diagram is equal to the standard potential value of the couple formed by the two species (represented at the two points).

(b) A Frost diagram provides quick qualitative idea of the trends in the chemical properties of element in the different oxidation states (For the exact values of E^0 i.e., for quantitative picture/values the back calculations are to be made).

(c) In common form of the diagram, the oxidation state increases from L→R but some authors put it R→L i.e., the oxidation state is put on decreasing order from L → R.

(d) Since the E^0 value is represented by the slope of the line connecting two species, steeper line corresponds to higher potential and more spontaneity. Thus

(i) The oxidizing agent in a couple (two states joined by a line) undergoes easy (more spontaneous) reduction if the slope is more positive.

(ii) Similarly, the reducing agent in the couple undergoes easier oxidation with less +ve slope.

(iii) An ion or molecule in a Frost diagram tends to disproportionate if it lies above the line connecting its two adjacent species. (Fig. 5) Here NH_2OH (N in –I state) lies above the line joining its neighbours. So it will disproportionate.

(iv) Two species will tend to comproportionate (reverse of dispropotionation) if it lies below the line connecting its two adjacent species.(As the N in NH_4NO_3 which has two oxidation states *viz.* –3 in NH_4^+ and +5 in NO_3^- (Fig 5). Thus they comproportionate to +1 in N_2O)

Applications: In view of its features, a Frost diagram finds several applications:

(1) Relative stability of a species with respect to the element in 0 state(pure element) is apparent from the slopes.
(2) The oxidizing agents and the reducing agents can easily be predicted.
(3) One can predict which of the two species is stronger oxidizing agent or which one is the stronger reducing agent in a pair(from the steepness of the curve)
(4) The unreactive redox species (which is at the minima of the curve and has little tendency to react) is easily identified. The unreactive naturally means the most stable species. (Mn^{2+} in case of the manganese curve above).
(5) The instability or the tendencies to disproportionate or to comproportionate can easily be found out.
(6) A comparative chart of different elements (for example, metals belonging to a particular periodic group) can be useful for predicting the reactivities in relative terms (Figures : 5 – 8)

Question 3:

Using the Frost Diagram for manganese (Fig. 5), identify the species that

(i) is the strongest oxidizing.

(ii) will tend to disproportionate.

Comment on the reducing behaviour of manganese metal.

(ii) Pourbaix Diagram: Problems arise when graphs are needed for comparisons under different pH conditions particularly when the redox processes are dependent on the $[H^+]$ or $[OH^-]$. Pourbaix brought out an excellent idea of constructing comparative plots involving variations in the pH.(So one need not go for different curves in acidic and alkaline media for comparison of stabilities of the same species under the two conditions)

In ***Pourbaix diagram, value of standard electrode potential E^0 is plotted against pH.***It gives the look of phase diagrams. Values at different pH are to be obtained for different redox couples of the element. It is also called predominance diagram as it gives idea of the species that will predominate under a given set of environmental conditions. (Figures : 9, 10)

Features

(a) These diagrams give a visual representation of the oxidizing and reducing abilities of the major stable compounds of an element(hence, used frequently in geochemical, environmental and corrosion studies of elements and their compounds).

(b) These are used for discussing general relation between the redox activity and the Bronsted acidity.

(c) Vertical lines separate regions in which either the reactants or the products are stable at that pH(i.e. the two regions are in acid-base equilibrium).

(d) Non-vertical lines separate species which are mutually related by redox equilibria.

(e) Horizontal lines separate species which are in redox equilibria.(no reaction is taking place involving H^+ or OH^-).The pH is constant.

(f) Regions indicate conditions under which each species is thermodynamically stable.

(g) Presence of H^+ on the left of the reduction couple is indicated by a slope from L→R of a boundary in the Pourbaix diagram.

(h) Strong oxidizing agents and oxidizing conditions are there at the top of the diagram. Strong oxidizing agent has lower boundary.

(i) Reducing agents and reducing conditions are similarly found in the bottom portion of the diagram.

(j) When the predominance area for a given oxidation state of the element disappears completely above or below a given pH and the element is in an intermediate oxidation state, the element undergoes disproportionation.

(k) If any species exists from top to bottom at a given pH, it will neither be oxidizing nor reducing at that pH.

Question 4:

On the basis of the Pourbaix diagram for iron, answer the following:

(i) At what pH, $Fe(OH)_3$ is a better oxidant, at pH=5 or at pH = 11?

(ii) At approximately what pH, Fe^{3+} will be reduced?At what pH, $Fe(OH)_2$ could easily be oxidized , 5,9 or 11?

Principles involved in the extraction of the elements

Principles of reduction and oxidation constitute the most important basis of extraction of elements from their ores. In some cases, the ore is an oxide which has to be reduced to the metal using some element which combines with oxygen of the oxide and goes out. In others, the sulfide is first converted to oxide which precedes the above process. In hydrometallurgical extractions of copper, the metal is extracted by reduction of aqueous solutions of its ions with H_2 or iron scraps. Halogens occur as halides and they are extracted by oxidation. Many modern techniques have made extraction of elements simpler, less energy and less time consuming as well as less polluting. All such techniques involve principles of oxidation-reduction and that of electrode potential. These are explained using either Ellingham diagrams or reduction potentials of the redox couple that is involved in the reduction processes.

(a) **Ellingham diagram:** *Ellingham diagram is a composite graph of ΔG^0 (Gibbs free energy) vs. T for each of the reduction and oxidation processes involved in extraction of any element, based on heating.* Normally, it includes the Gibbs energy-temperature plots for oxidation

reactions of metals and the reducing agents. In it, the number of moles of the common reactants (e.g. O_2) is the same for every reaction for the purpose of comparison. These diagrams are useful in understanding thermal reduction of an ore with a reducing element. Such processes are induced by heat and the ore is reduced to the element while the reducing agent gets oxidized. These are thus complimentary steps as in any redox process.

For testing feasibility of any reduction, there are two ways. Either one could go for the compilation of ΔG^0 data of the possible thermal redox processes. Alternatively, one could get a simple, clear and qualitative picture of the ΔG^0values of the two processes and thus that of the combined process from the Ellingham diagram in the literature. The spontaneity of the combined redox process will require a –ve ΔG^0. For trying a new method, instead of making large compilations of ΔG^0 values for heat induced redox processes of the oxide and the reducing agent, only a glance of the two plots in the diagram gives a clear, although qualitative, idea of the feasibility of the reduction. Therefore, Ellingham diagram is a very important application of the thermodynamic concept of Gibbs free energy in the extraction methodology of an element. The effort for thermal reduction varies from element to element. There is huge variation on the temperature requirement e.g., in carbon reduction of metal oxides. Rationalization of this temperature dependence is done on the basis of Ellingham diagram. Answers to many questions are obtained. e.g. "Why copper sulfide is easily reduced by carbon (or after conversion to oxide) but iron sulfide (or its oxide) is difficult to reduce?" "Why the process becomes easy when the metal obtained is in molten state?" "Why extraction of certain elements is much more difficult from oxides (e.g. Al from Al_2O_3)?"

The Ellingham diagram incorporating plots of $\Delta G^0$for oxidation (thus of reduction of the corresponding species) of some common metals and commonly used reducing agents (carbon, silicon, CO) have been given in Figure - 11. This diagram depicts Gibbs free energy of formation of oxides of elements (or that of the reduction of the oxides in the reverse way) at different temperatures. For effective interpretations, the corresponding curves for the reactions:

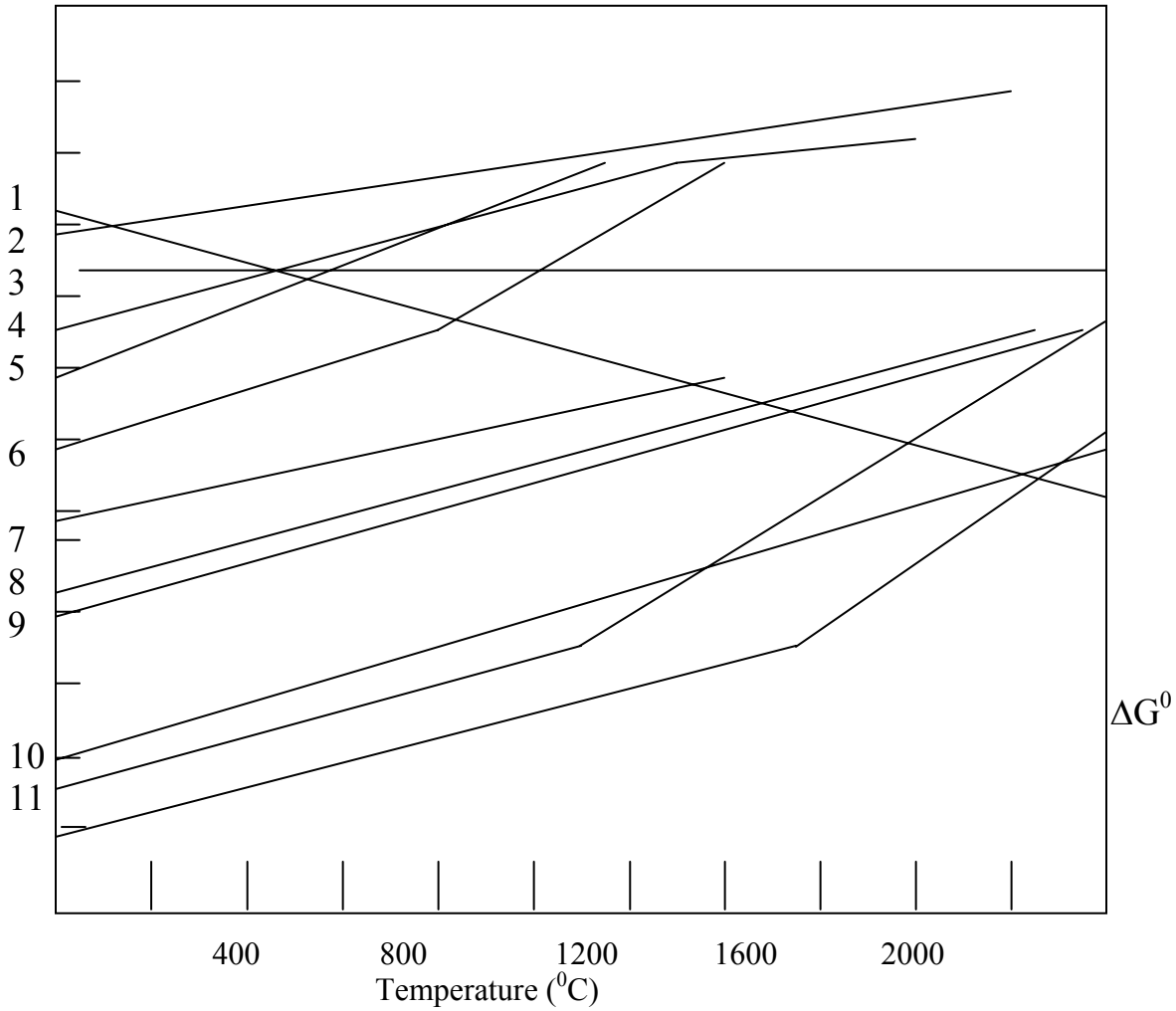
$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$
and $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$
are also incorporated in the diagram.

Interpretation: The interpretation of Ellingham diagram moves around the concept of free energy and its relation with temperature and entropy viz.
$\Delta G^0 = \Delta H^0 - T\Delta S^0$

Thermodynamics suggests that the value of ΔH^0 for any reaction is almost independent of temperature. The value of entropy (ΔS^0) also remains constant with temperature unless a change in physical state takes place (*viz*. change from solid state to liquid or from liquid to gas etc when a large increase in molecular disorders leads to a corresponding rise in entropy i.e., only then the value of ΔS is +ve).The near constancy of ΔH^0 and ΔS^0 over a temperature range implies that ΔG^0 goes on negative side on raising the temperature. Metal oxides

normally have highly ordered crystal lattice. So their formation from metal and dioxygen (O_2 is a gas and so higher entropy) leads to decrease in gaseous volume and to a –ve value of ΔS. This –ve value makes the second term +ve in the thermodynamic equation above. Rise in T further affects this term and the value of ΔG thus shifts towards +ve side with increase in temperature.

The role of the reducing agent (which forms its oxide) is to provide ΔG^0 which is negative and large enough to make the sum of the two ΔG^0 negative. For example, when C oxidizes to CO, an increase in gaseous volume means a +ve ΔS and subsequently decrease in ΔG in the equation above. Such –ve ΔG compensates and makes the process feasible. The temperature is chosen such that the sum of the two ΔG^0 in the case of the combined redox process is negative. This can easily be conceived from a simple glance of the Ellingham diagram. The point of intersection of the two plots tells us the minimum temperature needed for feasible reduction. The temperature must be higher than the one corresponding to the point of intersection in the diagram. We shall see some metallurgical techniques which are based on the Ellingham diagram.



{Figure – 11 : Ellingham diagram [(1)2C +O_2= 2CO (2) 4Cu+O_2= 2Cu_2O
(3)C +O_2= CO_2(4)2Fe + O_2= 2FeO (5) 2 CO+ O_2= 2CO_2 (6) 2Zn+O_2= 2 ZnO
(7) 2 Mn+O_2= 2MnO (8) Si+O_2= SiO_2 (9) Ti+O_2= TiO_2 (10) 4/3 Al+O_2=2/3 Al_2 O_3
(11)2Mg +O_2= 2MgO (12)2Ca +O_2= 2CaO]}

Applications : Ellingham diagram provides:

(i) a qualitative and graphical visualization of the ease of reduction of an ore with a reducing agent at different temperatures.
(ii) the possibility of using other reducing agents (for which the ΔG^0 data are available).
(iii) the optimum temperature for extraction with a given reducing agent.

(b) This gives an idea of the reactions taking place at different temperatures during heating of the ore with the reducing agent.
(c) Changes in physical states of the products of such redox processes taking place during heating are also indicated by a sudden change in the slope of the line.

(b) **Redox potential:** Redox potential (ΔE^0) data values matter in metallurgical operations involving formation of redox couples in solutions such as in electrolytic reduction. The value of redox potential of a couple of the oxidized/reduced forms of the element to be extracted should be positive to give a negative ΔG^0in the thermodynamic equation:

$\Delta G^0 = -n\, E^0 F$

If ΔE^0 value of the redox couple of the reducing agent is large enough to favour a negative ΔG^0 value for the combination of the two couples, then the combined process will be spontaneous.

In order to comprehend the applications of these two thermodynamic concepts, let us see the major types of metallurgical techniques which involve reduction or oxidation. In all of them combination of two or more reactions along with the thermodynamic states are chosen in such a way so as to yield a negative ΔG^0 value for the net process.

(i) Pyrometallurgical extractions:
(ii) Electrolytic reductions
(iii) Hydrometallurgical reductions
(iv) Oxidation

(i)Pyrometallurgical Extractions : Pyrometallurgy involves heating oxide of the metal with a reducing agent. The principle of pyrometallurgy involves thermodynamics of redox process which is easily explained through Ellingham diagram incorporating the oxidation-reduction of the metal and that of the reducing agent which is usually carbon and/or CO. In some modern metallurgical techniques another metal is also used as a reducing agent.

During the reduction of the oxide, the metal gets converted to its elemental form.

$M_xO\ (s) \rightarrow x\ M(s\ or\ l) + \frac{1}{2}O_2(g)$ ……. (i)

which can be perceived as reverse of the corresponding oxidation process for which ΔG^0 value can be expressed in the conventional way:

$$x\text{M}\ (s\ or\ l) + \tfrac{1}{2}\ \text{O}_2\ (g) \rightarrow\ \text{M}_x\text{O(s)}\ \ [\ \Delta\ \text{G}\ (M, M_xO)]\text{…….. (ii)}$$

The second reaction will be the oxidation of carbon or CO :

$$\text{CO(g)} + \tfrac{1}{2}\text{O}_2\ \text{(g)} \rightarrow\ \text{CO}_2\ \text{(g)}\ \ [\Delta\text{G}(CO, CO2)]\text{…….. (iii)}$$

$$\text{C(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow\ \text{CO(g)}\ \ [\ \Delta\text{G}(C_1CO)]\text{…….. (iv)}$$

There may be complete oxidation of carbon as in

$$\tfrac{1}{2}\text{C(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow\ \tfrac{1}{2}\text{CO}_2\ \text{(g)}\ \ [\ \Delta\text{G}(CO_1CO_2)]\text{…….. (v)}$$

On subtracting eq. (ii) [i.e. adding its negative or reverse form, eq. (i)] from one of the three equations (iii), (iv) or (v), we get the reduction equations as :

$$\text{M}_x\text{O}(s) + \text{CO}(g) \rightarrow\ x\text{M}(s\ or\ l) + \text{CO}_2\ (g)\quad \text{.....(vi)}$$

$$\text{M}_x\text{O}(s) + \text{C}(s) \rightarrow\ x\text{M}(s\ or\ l) + \text{CO}(g)\qquad \text{…….. (vii)}$$

$$\text{M}_x\text{O}(s) + \tfrac{1}{2}\text{C}(s) \rightarrow x\text{M}(s\ or\ l) + \tfrac{1}{2}\ \text{CO}_2(g)\quad \text{…….. (viii)}$$

The ΔG^0 values for these reactions can be obtained by similar subtraction of the respective ΔG^0 values. This resultant ΔG^0 value becomes negative at the point of intersection of the Ellingham plots of the two species represented by the two equations subtracted above. Thus the reduction of MxO*(s)* becomes spontaneous. The temperature at which the *C,CO* line or the *CO*, CO_2 line comes below the MxO line, the MxO can be reduced by C or CO (as the case may be) but generating CO in the first case (*C, CO* line) and CO_2 in the other case.

As pointed out earlier, the increase in amount of gases or conversion of solid to liquid (melting) or liquid to gas increases the entropy change value (ΔS^0) leading to lowering of ΔG^0 (hence –ve slope in Elingham diagram). For this reason CO is a better reducing agent at lower temperatures.

Examples :

1. Copper can easily be obtained by carbon reduction of its oxide (line 1 in Ellingham diagram above is almost at the top). ΔG^0 of CO and CO_2 formations are much lower so the net ΔG^0 (reduction of Cu_2O) and oxidation of C or CO) is on –ve side during smelting. Since a few hundred degree temperature could help C reduce Cu_2O, extraction of copper is much easier than that of even iron. This is why 'bronze age' preceded 'iron age' in history. Copper is obtained mainly as sulfide ore and sometimes as oxide ore. The sulfide ores are roasted to give oxide :

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

The oxide is reduced to metallic copper by heating with coke.

$$Cu_2O + C \rightarrow Cu + CO$$

Problems arise when the sulphide ore contains iron and the amount of copper is also low. After crushing and concentration by froth floatation method it is heated in a reverberatory furnace with silica to about 1400^0C. This way the ore melts and FeS is converted to oxide. FeO then combines with silica and forms upper layer of iron silicate. The lower layer is called copper matte. It contains Cu_2S and FeS. This liquid matte is heated in a converter. Some silica and blast of air are given to convert remaining FeS to FeO and Cu_2S to Cu_2O and finally to metallic copper. The added silica removes the residual FeO as silicate.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow FeSiO_3$$

Electrolytic method is employed for purification of copper thus obtained. Hydro-metallurgical extraction procedure is preferred for avoiding escape of SO_2 into air and other environmental problems.

2. Iron is mainly extracted in blast furnace. Oxides of iron (Fe_2O_3 or Fe_3O_4) are mixed with coke and limestone and inserted from the top. Blast of hot air is blown from the bottom. This causes combustion of coke leading to a rise in temperature up to 2000^0C. The carbon gets converted to CO in the lower part itself and the iron oxide is reduced in steps to FeO and then to Fe at different temperatures. Lime ($CaCO_3$) is also decomposed to CaO which removes silicate impurity of the ore as slag.

At 200^0C – 700^0C :

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

$$CaCO_3 \rightarrow CaO + CO_2$$

At 700^0C – 1200^0C

$$C + CO_2 \rightarrow 2CO$$

$$FeO + CO \rightarrow Fe(s) + CO_2$$

The principle of this process is easily understood by looking at the Ellingham diagram of *CO, CO_2* and *Fe, FeO*. The free energy requirements are met in the temperature range in which FeO is being converted to the metal.

3. Silicon can be prepared from SiO_2 by carbon reduction. But the Ellingham diagram suggests much higher temperature for the possible reduction:

$$SiO_2(l) + 2C(s) \rightarrow Si(l) + 2CO(g)$$

The plots for SiO_2 and *C, CO* intersect at much higher temperature and the temperature requirement of 1500^0C is met by electric arc furnace. This Si at such temperatures may form SiC with carbon which is reverted by using excess SiO_2.

$$SiO_2(l) + 2SiC(s) \rightarrow 3Si(l) + 2CO_2(g)$$

4. Titanium occurs as TiO_2 but their is no viable method for its reduction using carbon. This could be explained by Ellingham diagram of *Ti*, *TiO_2* and *C, CO*. The point of intersection corresponds to such high temperature at which the metal is very reactive and complete absence of air (O_2, N_2) has to be ensured. Carbides are also formed. Extraction of Ti is achieved by the conversion of ore to $TiCl_4$ and subsequent reduction.

$$2FeTiO_3 + 7Cl_2 + 6C \xrightarrow{900^0C} 2TiCl_4 + 2FeCl_3 + 6CO$$

For reduction of $TiCl_4$, the Ellingham diagram for halides is used. The curves for Mg and Ti cross at lower temperature and the reduction is affected in sealed tube in Ar atmosphere.

$$TiCl_4 + 2Mg \xrightarrow{950–1150^0C} Ti + 2MgCl_2$$

(ii) Electrolytic Reduction: Electrolytic reduction of any M ion is carried out using the concept of electrode potential and its relation with free energy.

$$\Delta G^0 = -nFE^0$$

The reduction of $M^{ion} \rightarrow M(s)$ requires that its E^0 value should be positive for spontaneity ($-\Delta G^0$). For any metal which is stable as its ion the potential is positive. So its reduction requires an additional energy so as to result in a net positive E^0 (and subsequently negative ΔG^0) for the resultant process. There are two ways to make ΔG^0 negative:

(1) To supply E from outside after constructing a formal cell (electrolytic reduction)

(2) Adding some couple directly to increase E.

The former is used for example, in the extraction of aluminium. Bauxite containing Al_2O_3 is extracted, purified and dehydrated. This extraction and purification involves extraction and purification involves removal by the acidic oxide SiO_2 and some amphoteric oxide Fe_2O_3. The Al_2O_3 is extracted using NaOH. The solution is neutralized using CO_2 for getting precipitates of $Al(OH)_3$ which is then dehydrated. The melt after dissolution in the final stage is electrolyzed using steel cathode and graphite anode. Graphite is useful in the reduction:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

(iii) **Hydrometallurgical Reduction:** In this technique an external redox couple is added to the solution to derive +E (hence – ve ΔG) for the combined process. Thus in the hydrometallurgical extraction of copper, copper ions are reduced by using H_2 or scrap iron. This method is effective in low grade ores which are somewhat concentrated using bacterial actions or by treatment with acids.

$$Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$$

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^{+}(aq)$$

(iv)Oxidation: Extractions based on oxidation are few. A common example is the extraction of chlorine:

$$2Cl^{-}(aq) + 2H_2O(l) \rightarrow 2\,OH^{-}(aq) + H_2(g) + Cl_2(g)$$

The ΔG^0 for this reaction is +422 kJ. Converting to E^0 (using $\Delta G^0 = -n E^0 F \Rightarrow E^0 = -\Delta G^0/nF$), we get $E^0 = 2.2V$ that needs to be applied.

The electrolysis requires an over potential and Cl_2 is obtained by electrolysis of brine. The by products are H2 and aqueous NaOH. In case of electrolysis of molten NaCl, Na is produced instead of NaOH.

Another example of oxidation based metallurgy is that of gold which occurs in such low grade ores that it has to be oxidized and dissolved as $[Au(CN)_2]^-$ ion. This is then reduced back to the metal:

$$2[Au(CN)_2]^- (aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{2-} (aq)$$

Suggested Readings:

1) M. Clyde Day and Joel Selbin, *Theoretical Inorganic Chemistry*, Affiliated EW Press,1985
2) B.Douglas, D.H.McDaniel, *Concepts and Models of Inorganic Chemistry*, John Wiley
3) N.N.Greenwood and A.Earnshaw, *Chemistry of the Elements*, Pergamon
4) R.B.Heslop and K. Jones, *Inorganic Chemistry*, Elsevier
5) J.D.Lee, *Concise Inorganic Chemistry*, Chapman and Hall
6) D.F.Shriver, P.W.Atkins and C.H.Langford, *Inorganic Chemistry*, Oxford Univ Press
7) W.M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, Prentice Hall