

# FEASIBILITY OF REDOX REACTIONS THROUGH FORMAL REDOX POTENTIAL VALUES

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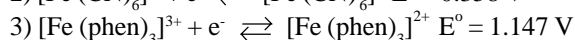
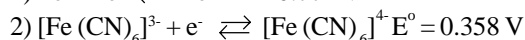
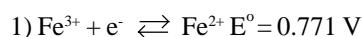
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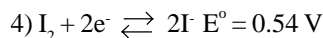
In a complexation reaction, where one or more of the components of the redox couple are involved, it is very difficult to have the exact knowledge of the activities to determine the standard redox potential values. Therefore, at specified concentration Nerst equation may be modified to calculate the formal potential by replacing the activities to concentrations (Braun 1985). The various parameters exploited for facilitating such reactions have been complexation of the reacting species, nature of acid or base and pH, formation of hydroxo complexes with metal ions, formation of hydronium salt of anionic metal complexes (Bailer *et al* 1973; Farrukh and Naqvi 2002; Kimura 1999). In addition to that, the factors described below also alter the respective standard redox potential values. (1)  $E^\circ$  decreases with increasing the oxidation number of an element due to an increase in ionization potential. (2)  $E^\circ$  also decreases within a period as ionization potential increases with increasing atomic number. (3) Ionization potential values of the transition metal series increase with increasing atomic number, accordingly  $E^\circ$  values get decreased within a period.

Redox potential values are the indicators of stability or instability of metal ions and these get altered as the nature of the medium and the species being dissolved is varied (Ayodele *et al* 2000; Cotton and Wilkinson 1980; Dindi and Sudarsan 2001). Thus the redox potential values are expected to decrease or increase as the metal ion stabilizes or destabilizes itself through chemical interactions in the medium. If we consider the following half cells involving +3 and +2 oxidation states of iron of the Ferric / Ferrous, Ferricyanide / Ferrocyanide and Ferriphenanthroline / Ferrophenantroline systems (Weast 1980-1981),



It can be seen that the redox potentials of all these half-cells are different. Equilibrium 1 involves bare iron (III) whereas equilibrium 2 pertains to same oxidation state of iron complexed with  $\text{CN}^-$  ion. These two half-cells do not have same redox potential. This is because the oxidized form (left hand side of equation 2) gets stabilized through interaction with  $\text{CN}^-$  ion, as compared to the reduced form (right hand side of equation 2) and that the redox potential of equation 2 is less than the value shown in equation 1 where no such chemical interaction has taken place. On the other hand when iron(III) complexed with phenanthroline, it gets destabilized as compared to reduced form of the same complex (equation 3) and when it is without such chemical interactions (equation 1), its redox potential gets enhanced. The quantum of variation of redox potential values largely depends upon the nature of the ligands, interacting with the either of the oxidizing or reducing species involved in the redox equilibrium (Jeffry *et al* 1994).

However, it is very important to note that formal redox potentials rather than standard redox potentials are to be considered when one tries to establish the feasibility of any electron transfer process. This can be illustrated by considering the two half cells of Ferricyanide/Ferrocyanide (equation 2) and iodine/iodide systems.



At standard conditions (considering standard redox potential values) iodine would oxidize Ferrocyanide whereas, in 1 M HCl (considering formal potential values, i.e. at 1 M specified concentration) Ferricyanide / Ferrocyanide system has potential of 0.706 V which leads to the reverse reaction of iodide ion with Ferricyanide.

Ferrophenantroline  $[\text{Fe}(\text{phen})_3]^{2+}$  was prepared by adding ligand (Phenanthroline) in slight excess to avoid mono or bi complex formation, to ferrous ammonium sulfate solution of required concentration, resulting into a wine red solution of Ferrophenantroline. All acids (A.R. grade, Merck) were standardized with standard NaOH (NaOH was standardized with oxalic acid prior to use) and were diluted to appropriate dilutions of 0.5 M, 1.0 M and 1.5 M.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  (A.R. grade, Merck) were used for the measurement of potentials of  $\text{Fe}^{3+} / \text{Fe}^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$  systems. Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , was standardized iodometrically (Jeffry *et al* 1994).

The stock solutions of each were prepared having a concentration of 0.1M in 0.5M, 1.0M and 1.5M of each acid. The stock solutions were subsequently diluted to  $1 \times 10^{-3}\text{M}$  concentrations with standard solutions of each acid.

25 ml of  $\text{FeCl}_3$  ( $1 \times 10^{-3}\text{M}$ ) was taken in a beaker and the burette

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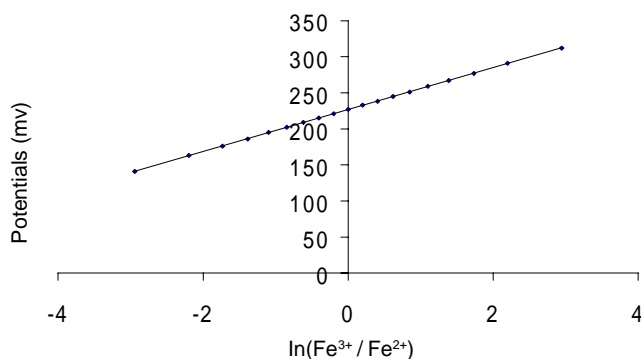
**Table 1**  
Variation of formal potentials of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{phen})_3]^{3+}/[\text{Fe}(\text{phen})_3]^{2+}$  systems in different acids at 30°C

Medium / Strength	$\text{Fe}^{3+}/\text{Fe}^{2+}$			$[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$			$[\text{Fe}(\text{phen})_3]^{3+}/[\text{Fe}(\text{phen})_3]^{2+}$		
	0.5M	1.0M	1.5M	0.5M	1.0M	1.5M	0.5M	1.0M	1.5M
HClO <sub>4</sub>	0.737V	0.746V	0.759V	0.704V	0.707V	0.709V	1.038V	1.073V	1.082V
HCl	0.712V	0.739V	0.746V	0.700V	0.706V	0.700V	1.025V	1.064V	1.071V
HNO <sub>3</sub>	0.703V	0.738V	0.744V	0.640V	0.682V	0.692V	1.013V	1.059V	1.067V
H <sub>2</sub> SO <sub>4</sub>	0.698V	0.716V	0.731V	0.630V	0.673V	0.688V	1.006V	1.038V	1.055V
H <sub>3</sub> PO <sub>4</sub>	0.631V	0.639V	0.644V	0.623V	0.667V	0.683V	0.997V	1.011V	1.017V

was charged with  $1 \times 10^{-3} \text{ M Na}_2\text{S}_2\text{O}_3$ . Bright platinum electrode was used as an indicator. Electrode immersed in  $\text{FeCl}_3$  solution and an SCE reference electrode immersed in the saturated solution of potassium chloride formed the other half cell. The salt bridge of KCl connected these two half-cells.

Magnetic stirrer in the beaker continuously stirred solution and the potential difference between the electrodes were read with the aid of potentiometer (Kent EIL 7020). The potential difference and volume of  $\text{Na}_2\text{S}_2\text{O}_3$  in the burette were recorded after each addition. Potentials were plotted as ordinates (y-axis) and  $\ln([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$  as abscissas (x-axis) using Nerst equation of  $E = E^\circ + RT/nF \ln([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$ . A straight line was obtained with a positive slope and intercept on y-axis as displaced in Fig 1. Formal potentials ( $E^\circ$ ), potentials at unit concentrations of both  $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ , were calculated from the intercept at  $\ln([\text{Fe}^{3+}]/[\text{Fe}^{2+}]) = 0$ , using the formula,  $E^\circ = E^\circ_{\text{intercept}} + E^\circ_{\text{SCE}}$ , ( $E^\circ_{\text{SCE}} = 0.244 \text{ V}$ ). Same process was repeated for  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{phen})_3]^{3+}/[\text{Fe}(\text{phen})_3]^{2+}$  systems by taking 25 ml of each  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$  separately in the beaker and titrating against  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ .

Formal potentials of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{phen})_3]^{3+}/[\text{Fe}(\text{phen})_3]^{2+}$  systems have been investigated



**Fig 1.** Relationship between potentials and  $\ln(\text{Fe}^{3+}/\text{Fe}^{2+})$  to calculate the formal potential values using Nerst equation.

in different acidic medium and the results are shown in Table 1. These results lead us to conclude the following:

Formal potential values of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $[\text{Fe}(\text{phen})_3]^{3+}/[\text{Fe}(\text{phen})_3]^{2+}$  systems have been recorded to be lower than their standard redox potentials ( $E^\circ = 0.771 \text{ V}$  and  $1.14 \text{ V}$ , respectively), pertaining to bare oxidation states of iron. This pattern suggests that  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  ions stabilize  $\text{Fe}^{3+}$  as well as  $[\text{Fe}(\text{phen})_3]^{3+}$  against reduction more than these stabilize  $\text{Fe}^{2+}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$  against oxidation, vindicates the literature which suggests that stability constants of  $\text{Fe}^{3+}$  as well as  $[\text{Fe}(\text{phen})_3]^{3+}$  complexes with these ions are more than those of corresponding  $\text{Fe}^{2+}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$  complexes. The close values of redox potentials in different acid mediums indicate that there is not much difference in complexation capability of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ ,  $[\text{Fe}(\text{phen})_3]^{3+}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$  with these different acid ligands. Formal potential values were found to be more in  $\text{HClO}_4$  and less in  $\text{H}_3\text{PO}_4$  indicating that complexation is least in  $\text{HClO}_4$  and greatest in  $\text{H}_3\text{PO}_4$  with both of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ ,  $[\text{Fe}(\text{phen})_3]^{3+}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$ . This is due to perchlorate ion has very slight tendency to serve as a ligand in complexes (weak ligand due to high electronegativity of both chlorine and oxygen) if compared by sulfur in  $\text{SO}_4^{2-}$  (Cotton and Wilkinson 1970).

Formal potential values for  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  system in different acid solutions were found to be greater than standard redox potential ( $E^\circ = 0.358 \text{ V}$ ) showing that protonation occurs in acidic medium which stabilizes  $[\text{Fe}(\text{CN})_6]^{4-}$  against oxidation more than it stabilizes  $[\text{Fe}(\text{CN})_6]^{3-}$  against reduction. Stability constant of  $\text{H}[\text{Fe}(\text{CN})_6]^{3-}$  ( $2 \times 10^4 \text{ M}^{-1}$ ) is much greater than that of  $\text{H}[\text{Fe}(\text{CN})_6]^{2-}$  ( $< 10 \text{ M}^{-1}$ ), so the activity of the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is decreased to a greater extent than that of the  $[\text{Fe}(\text{CN})_6]^{3-}$  ion upon decreasing pH (Kimura *et al* 1999). Due to much more difference in the stability constants of both protonated forms, significant variation in the standard and formal potential is observed. Formal potential values got slightly increased when medium changed from weak

acid to stronger acid due to higher protonation in stronger acid.

**Key words:** Formal potential, Redox reactions, Complexing ions, pH, Nerst equation.

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