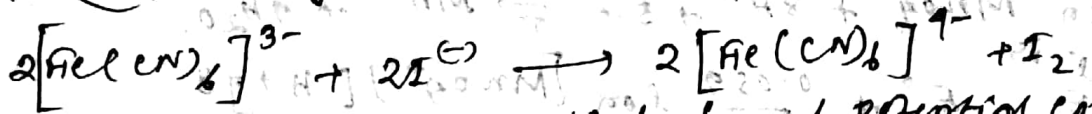


Hence the potential is raised from 0.36 volt (in neutral soln) to 0.71 volt (in 1M HCl, H₂SO₄ or HClO₄ soln).

The formal potential is now above than that of I⁻/I₂ couple. Hence the oxidation of I⁻ to I₂ by [Fe(CN)₆]³⁻ ion takes place by the following eqnⁿ;



Hence we may conclude that formal potential is over standard normal potential.

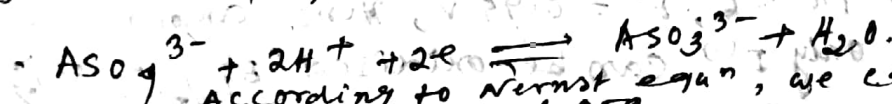
Influence of different factors on redox potential:

(1) Influence of pH of the medium:

(a) The standard reduction potential of $\text{AsO}_4^{3-}/\text{AsO}_3^{3-}$ and I_2/I^- systems are 0.56V and 0.54 volt respectively.

Hence the rxn should occur as $\text{AsO}_4^{3-} + 2\text{H}^+ + 2\text{I}^- \longrightarrow$

$\text{AsO}_3^{3-} + \text{I}_2 + \text{H}_2\text{O}$. But in reality the direction of rxn depends on the pH of the soln. The potential of the $\text{AsO}_4^{3-}/\text{AsO}_3^{3-}$ couple depends on pH.



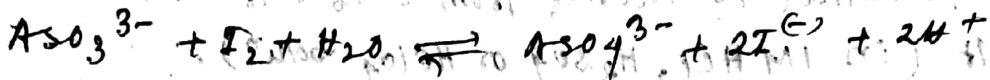
According to Nernst eqnⁿ, we can write. Therefore, $E = E^0 + \frac{0.059}{2} \log \frac{[\text{AsO}_4^{3-}][\text{H}^+]^2}{[\text{AsO}_3^{3-}]}$

$$= E^0 + 0.059 \log [\text{H}^+] + \frac{0.059}{2} \log \frac{[\text{AsO}_4^{3-}]}{[\text{AsO}_3^{3-}]}$$

$$= E^0 - 0.059 \text{pH} + \frac{0.059}{2} \log \frac{[\text{AsO}_4^{3-}]}{[\text{AsO}_3^{3-}]}$$

$$= E^0' + \frac{0.059}{2} \log \frac{[\text{AsO}_4^{3-}]}{[\text{AsO}_3^{3-}]}$$

Thus the formal potential (E^{0'}) decreases with increase of pH. In presence of excess NaHCO₃ soln (pH ≈ 8), E^{0'} becomes 0.088V which is less than 0.54 volt (standard potential of I₂/I⁻ system) under the comparable condition. Thus at pH ≈ 8, AsO_4^{3-} can not oxidise I⁻ to I₂ but I₂ can oxidise AsO_3^{3-} to AsO_4^{3-} i.e.



(b) The redox potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ couple depends on the pH of the solution.

2007
Explain $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$.

Why Cl^- is oxidised by permanganate in acidic solution only at low pH but not in neutral or medium.

$$E = E^\circ + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

$$= E^\circ + \frac{0.059 \times 8}{5} \log [\text{H}^+] + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

$$= E^\circ - \frac{0.059 \times 8}{5} \text{pH} + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

Given: $E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = 1.51 \text{ V}$

$$E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = 1.51 - 0.094 \text{pH} + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

$$E^\circ(\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$$

$$E^\circ(\text{Cl}_2/\text{Cl}^-) = E^\circ + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

Though the standard potential (E°) at pH=0 is 1.51V

with the increase of pH the formal potential (E°') decreases.

At pH=6, $E^\circ' = 0.95 \text{ V}$, hence among the halides only I^- can be oxidised ($E^\circ_{\text{I}_2/\text{I}^-} = 0.54 \text{ V}$).

($E^\circ_{\text{Br}_2/\text{Br}^-} = 1.07 \text{ V}$, $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$).

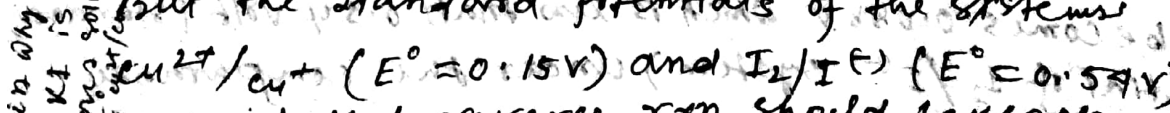
At pH=3, $E^\circ' = 1.23 \text{ V}$ and Br^- can be oxidised but Cl^- can not be oxidised.

Thus to oxidise Cl^- a much higher conc. of H^+ is required (pH < 1.5).

3. 2005. The E° values of Cu^{2+}/Cu (0.15V) and $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.54V) suggest the redox reaction of copper (II) is not possible. Explain why it is found otherwise in practice.

(2) Influence of precipitation on redox potential:

(a) The volumetric estimation of Cu by an iodometric method is based on the rxn.



But the standard potentials of the systems Cu^{2+}/Cu ($E^\circ = 0.15 \text{ V}$) and I_2/I^- ($E^\circ = 0.54 \text{ V}$) suggest that reverse rxn should take place.

Now let us consider the effect of

Main why iodine is liberated when KI is added to an aqueous soln of CuSO_4 . Although $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.15 \text{ V}$ and $E^\circ_{\text{I}_2/\text{I}^-} = 0.54 \text{ V}$.