

## 4.5: Redox Reactions with Coupled Equilibria

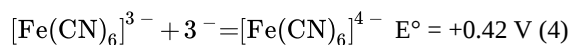
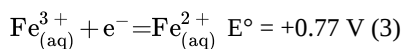
### Redox Reactions with Coupled Equilibria

Coupled equilibria (solubility, complexation, acid-base, and other reactions) change the value of  $E^\circ$ , effectively by changing the concentrations of free metal ions. We can use the Nernst equation to calculate the value of  $E^\circ$  from the equilibrium constant for the coupled reaction. Alternatively, we can measure the half-cell potential with and without the coupled reaction to get the value of the equilibrium constant. This is one of the best ways to measure  $K_{sp}$ ,  $K_a$ , and  $K_d$  values.

As an example, we consider the complexation of  $Fe^{2+}$  and  $Fe^{3+}$  by  $CN^-$  ions:



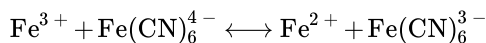
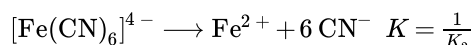
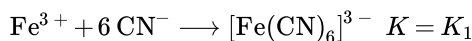
Which oxidation state of Fe is more strongly complexed by  $CN^-$ ? We can answer this question by measuring the standard half-cell potential of the  $[Fe(CN)_6]^{3-/4-}$  couple and comparing it to that of the  $Fe^{3+/2+}$  couple:



Iron(III) is **harder to reduce** (i.e.,  $E^\circ$  is **less positive**) when it is complexed to  $CN^-$

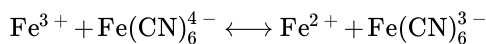
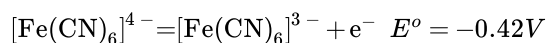
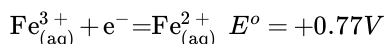
This implies that the equilibrium constant for complexation reaction (Equation 4.5.1) should be **smaller** than that for reaction (Equation 4.5.2). How much smaller?

We can calculate the ratio of equilibrium constants by adding and subtracting reactions:



The equilibrium constant for this reaction is the product of the two reactions we added, i.e.,  $K = K_1/K_2$ .

But we can make the same overall reaction by combining reactions (3) and (4)



In this case, we can calculate  $E^\circ = 0.77 - 0.42 = +0.35 \text{ V}$

It follows from  $nFE^\circ = -\Delta G^\circ = RT \ln K$  that

$$E^\circ = \frac{RT}{nF} \ln \frac{K_1}{K_2}$$

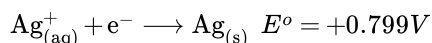
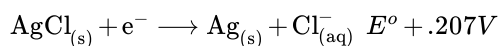
$$\frac{K_1}{K_2} = \exp\left(\frac{nFE^\circ}{RT}\right) = \exp[(1 \text{ equiv/mol})(96,500 \text{ C/equiv})(0.35 \text{ J/C})(8.314 \text{ J/molK})(298)] = \exp(13.63) = 8 \times 10^5$$

Thus we find that  $Fe(CN)_6^{3-}$  is about a million times more stable as a complex than  $Fe(CN)_6^{4-}$ .

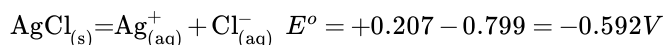
### Solubility Equilibria

We can use a similar procedure to measure  $K_{sp}$  values electrochemically.

For example, the silver halides ( $AgCl$ ,  $AgBr$ ,  $AgI$ ) are sparingly soluble. We can calculate the  $K_{sp}$  of  $AgCl$  by measuring the standard potential of the  $AgCl/Ag$  couple. This can be done very simply by measuring the potential of a silver wire, which is in contact with solid  $AgCl$  and 1 M  $Cl^-(aq)$ , against a hydrogen reference electrode. That value is then compared to the standard potential of the  $Ag^+/Ag$  couple:



Subtracting the second reaction from the first one we obtain:



and again using  $nFE^\circ = RT \ln K$ , we obtain  $K = K_{sp} = 9.7 \times 10^{-11} \text{ M}^2$ .



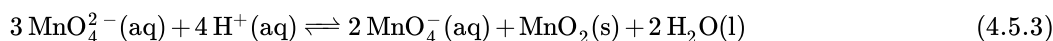
Because the solubility of the silver halides is so low, this would be a very difficult number to measure by other methods, e.g., by measuring the concentration of  $\text{Ag}^+$  spectroscopically, or by gravimetry. In practice almost all  $K_{sp}$  values involving electroactive substances are measured potentiometrically.

## Acid-Base Equilibria

Many electrochemical reactions involve  $\text{H}^+$  or  $\text{OH}^-$ . For these reactions, the half-cell potentials are **pH-dependent**.

**Example:** Recall that the disproportionation reaction  $3 \text{MnO}_4^{2-}_{(aq)} \longrightarrow 2 \text{MnO}_4^-_{(aq)} + \text{MnO}_2_{(s)}$  is **spontaneous** at  $\text{pH}=0$  ( $[\text{H}^+] = 1\text{M}$ ), from the Latimer diagram or Frost plot.

However, when we properly balance this half reaction we see that it involves **protons as a reactant**:



By Le Chatelier's principle, it follows that **removing protons** (increasing the pH) should **stabilize** the reactant,  $\text{MnO}_4^{2-}$ . Thus we would expect the +6 oxidation state of Mn, which is unstable in acid, to be stabilized in basic media. We will examine these proton-coupled redox equilibria more thoroughly in the context of Pourbaix diagrams below.



Acid mine drainage occurs when sulfide rocks such as pyrite ( $\text{FeS}_2$ ) are exposed to the air and oxidized. The reaction produces aqueous  $\text{Fe}^{3+}$  and  $\text{H}_2\text{SO}_4$ . When the acidic effluent of the mine meets a stream or lake at higher pH, solid  $\text{Fe}(\text{OH})_3$  precipitates, resulting in the characteristic orange muddy color downstream of the mine. The acidic effluent is toxic to plants and animals.

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