

# Electrochemical Analysis



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# Electrochemical Analysis



- References
- Analytical Chemistry, Gary Christian( ch.12,13,14,15)
- الكيمياء التحليلية- التحليل الآليو الدكتور ابراهيم الزامل
- مسائل وحلول في الكيمياء التحليلية و الدكتور حسن السويدان

## Chapter 12: Electrochemical Cell and Electrode Potentials

- At the end of this Chapter (12), the student is expected to be able to :
- 1- Understand the concepts of oxidation and reduction .
- 2- Distinguish between oxidizing and reducing agents in a redox reaction .
- 3- Understand the electrochemical Cells.
- 4- Write and Balance redox reaction equations .
- 5- Realize the role of standard potential in expecting the completeness and the direction of a redox reaction .
- 6- Understand and write the symbol for a galvanic cell reaction .
- 7- Calculate the electrode potential .
- 8- Understand the Nernst Equation and effects of concentrations on potentials.

### 12.1 What Are Redox Reaction

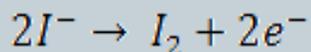
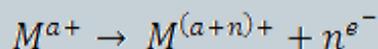
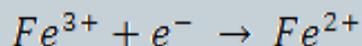
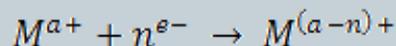
Redox reactions, or oxidation - reduction reactions , are a family of reactions that are concerned with the transfer of electrons between species. There is no oxidation reaction without a reduction reaction happening at the same time. Oxidation refers to the loss of electrons, while reduction refers to the gain of electrons. Each reaction by itself is called a "half-reaction", simply because we need two (2) half-reactions to form a whole redox reaction.



## 12.1 What Are Redox Reaction



An Oxidizing substance will tend to take on an electron or electrons and be reduced to a lower oxidation state:



## 12.2 Electrochemical Cell- What Electroanalytical Chemists Use



There are two kind of electrochemical cells:

- Voltaic (galvanic), spontaneous, ex. Battery
- Electrolytic, non spontaneous, ex. The electrolysis of water

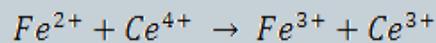
In both type of these cells, the electrode at which oxidation occurs is the **anode**, and that at which reduction occur is **cathode**.

## what is the cell potential

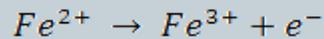


**Consider the following redox reaction in Voltaic cell:**

redox reaction

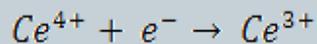


half- reaction



anode( electron donor, reducing agent)

half- reaction



cathode (electron acceptor, oxidizing agent)

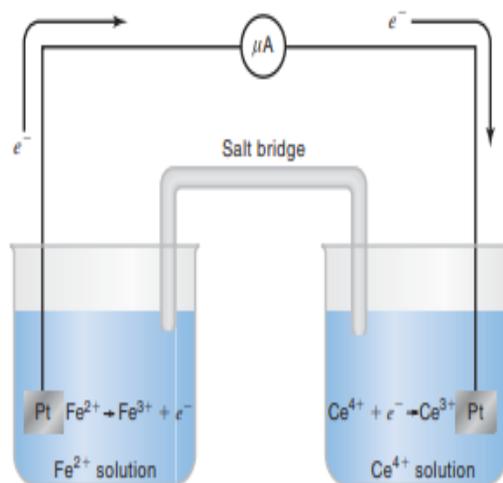


Fig. 12.1. Voltaic cell.

## Half- reaction potentials-they are measured relative to each other:

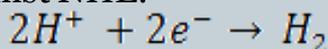


Standard electrode potential is given the symbol  $E^\circ$  and it is an electrode potential measured under standard conditions; a room temperature ( $25^\circ\text{C}$ ), 1 atmosphere pressure and at 1 mole of the activity of redox participants of the half-reaction (i.e the Ox and the Red forms) Ox means the oxidized form and Red means the reduced form of a redox couple

The Standard electrode potential of a redox couple cannot be measured alone ( because free electrons do not exist in solution) unless is coupled to another electrode usually a standard hydrogen electrode (NHE ).



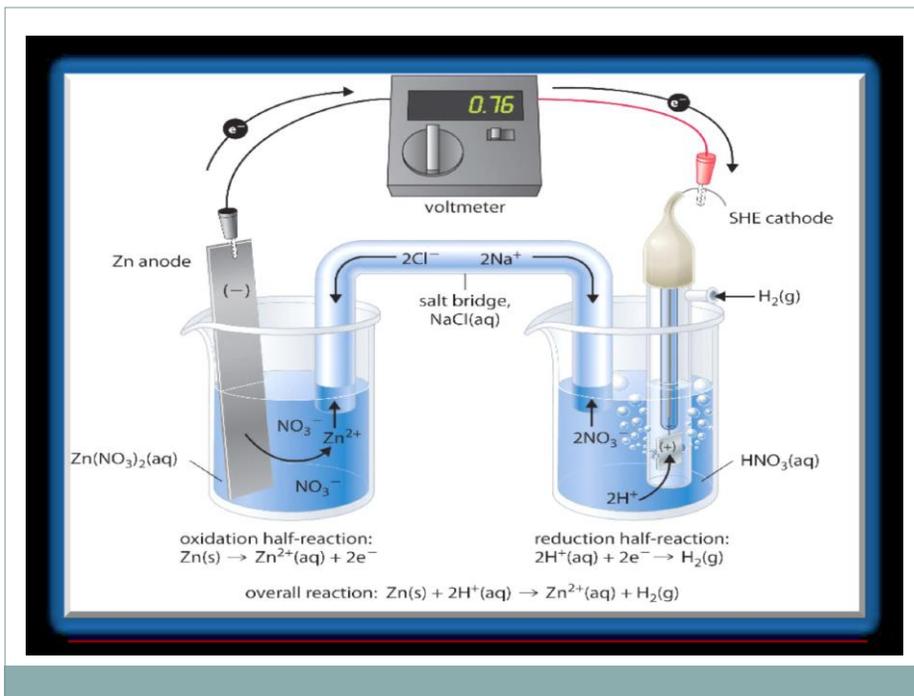
Both unknown and NHE electrodes are under standard conditions. The following graph shows the way that standard potential of the zinc couple is measured against NHE.



The  $E^\circ$  values for the common redox couples are measured by the same above way .This is how we established the electrochemical series, some of which are shown in the following table .It is assumed that the  $E^\circ$  for NHE under the standard conditions is equal to 0.00



1. The Ox form of a couple will oxidize the Red form of the couple under it in series but will not oxidize the Red form of the couple over it in the series e.g.  $\text{Fe}^{3+}$  will oxidize  $\text{Sn}^{2+}$  but not  $\text{Ag}^0$ .
2. All half reactions are written as reduction whatever the direction of the reaction.
3. The more negative the  $E^\circ$  value, the more readily the element loses electrons and becomes a reducing agent i.e the stronger its Red form and the weaker its Ox form.
4. The more positive (or less negative) the  $E^\circ$  value, the more readily the element gains electrons and becomes an oxidizing agent. I.e the stronger its Ox form and the weaker its Red form.





5. Therefore, for the two half reactions of the redox reaction, the one with the more positive  $E^\circ$  value is the oxidizing agent.
- 6- The – sign of  $E^\circ$  value indicates that this couple when joint with NHE under standard conditions will become reducing agent and its half reaction will proceed in the opposite direction (from right to left). In other words, the standard potential is a measure of the tendency of the oxidizing agent to be reduced. Its value is zero for  $H^+ + e^- \rightarrow \frac{1}{2} H_2$  by definition, positive for oxidizing agents stronger than  $H^+$  (e.g., +1.44 V for Ce ) and negative for oxidizing agents that are weaker than  $H^+$  (e.g., –0.76 V for  $Zn^{2+}$ ).



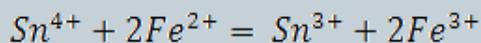
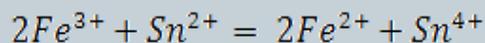
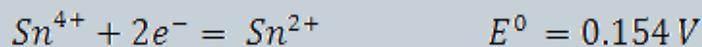
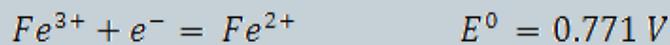
- 7- It is possible for a redox couple to be an oxidizing agent in a reaction and to be a reducing agent in another reaction e.g.  $Fe^{3+}$  will oxidize  $Sn^{2+}$  but  $Fe^{2+}$  will reduce  $Ag^+$  . However principal oxidising agents are: Potassium permanganate, potassium dichromate, iodine , cerium(IV) salt and potassium iodate . Also frequently used Reducing Agents are: iron (ii), tin (ii) compounds, sodium thiosulphate .
- 3- The oxidizing agent represents the cathode while the reducing agent represents the anode in a galvanic cell.

Table 12.1

## Some Standard Potentials

Half-Reaction	$E^0$ (V)
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1.77
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	1.695
$\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}$	1.61
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$2\text{IO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightleftharpoons \text{I}_2 + 6\text{H}_2\text{O}$	1.20
$\text{H}_2\text{O}_2 + 2\text{e}^- \rightleftharpoons 2\text{OH}^-$	0.88
$\text{Cu}^2 + \text{I}^- + \text{e}^- \rightleftharpoons \text{CuI}$	0.86
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	0.771
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$	0.682
$\text{I}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	0.6197
$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$	0.559
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	0.5355
$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$	0.154
$\text{S}_4\text{O}_6^{2-} + 2\text{e}^- \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$	0.08
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.000
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.763
$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	-0.828

## What substances react



## Example 12.1

For the following substances, list the oxidizing agents in decreasing order of oxidizing capability, and the reducing agents in decreasing order of reducing capability:  $\text{MnO}_4^-$ ,  $\text{Ce}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{IO}_3^-$ ,  $\text{Fe}^{3+}$ ,  $\text{I}^-$ ,  $\text{H}^+$ ,  $\text{Zn}^{2+}$ .

### Solution

Looking at Table 12.1, the following must be oxidizing agents (are in the oxidized forms) and are listed from the most positive  $E^0$  to the least positive:  $\text{MnO}_4^-$ ,  $\text{IO}_3^-$ ,  $\text{Fe}^{3+}$ ,  $\text{H}^+$ ,  $\text{Zn}^{2+}$ .  $\text{MnO}_4^-$  is a very good oxidizing agent,  $\text{Zn}^{2+}$  is very poor. The remainder are in the reduced form, and their reducing power is in the order  $\text{I}^-$ ,  $\text{Cr}^{3+}$ , and  $\text{Ce}^{3+}$ .  $\text{I}^-$  is a reasonably good reducing agent;  $\text{Ce}^{3+}$  is poor. ■

## Cell voltage and free energy:



The spontaneous cell reaction is the one that gives a positive cell voltage when subtracting one half-reaction from the other

$$\Delta G^\circ = -nF\Delta E^\circ$$

## Which is the anode and cathode

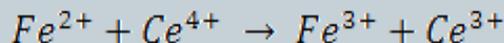


### drawing a cell

Instead of drawing a cell diagram chemists have devised a shorthand way of completely describing a cell called symbol or line notation. This notation scheme places the constituents of the cathode on the right of the salt bridge [which is shown in the notation as a double line (||)] and the anode components on the left.

The phases of all reactive species are listed and their concentrations or pressures are given if those species are not in their standard states. All phase interfaces are noted with a single line (|) and multiple species in a single phase are separated by commas. For example, the previous iron – zinc cell would be written as:

## Which is the anode and cathode



### Anode/ solution/ cathode



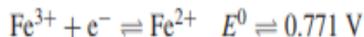
The potential of the voltaic cell is given by:

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} - E_{\text{anode}} = E_{+} - E_{-}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{Fe^{3+}, Fe^{2+}} - E^{\circ}_{Sn^{4+}, Sn^{2+}} = 0.771 - 0.154 = 0.617 \text{ V}$$

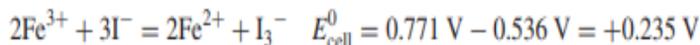
## Example 12.2

From the potentials listed in Table 12.1, determine the reaction between the following half-reactions, and calculate the corresponding cell voltage:



### Solution

Since the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  potential is the more positive,  $\text{Fe}^{3+}$  is a better oxidizing agent than  $\text{I}_3^{-}$ . Hence,  $\text{Fe}^{3+}$  will oxidize  $\text{I}^{-}$  and  $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^{\circ} - E_{\text{I}_3^{-}, \text{I}^{-}}^{\circ}$ . In the same fashion, the second half-reaction must be subtracted from the first (multiplied by 2) to give the overall cell reaction:

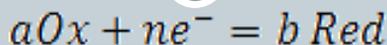


Note again that multiplying a half-reaction by any number does not change its potential. ■

## 12.3 Nernst Equation—Effects of Concentrations on Potentials



- 1- The potentials listed in Table 12.1 were determined for the case when the concentrations both the oxidized and reduced forms (and all other species) were at unit activity.
- 2- They are called the standard potentials, designated by  $E^{\circ}$ .
- 3- One of the more useful calculations in redox reactions is the Nernst Equation. This equation allows us to calculate the electric potential of a redox reaction in "non-standard" situations
- 4- The electrode potential is dependent on temperature, the concentrations of the Ox and the Red form of the electrode couple and the number of electrons transferred during half reaction.



$$E = E^{\circ} - \frac{2.302RT}{nF} \log \frac{[Red]^b}{[Ox]^a}$$

$$E = E^{\circ} - \frac{0.059}{n} \log \frac{[Red]^b}{[Ox]^a}$$

**where** a and b are the numbers of Ox and Red species in the half-reaction, E is the reduction potential at the specific concentrations, n is the number of electrons involved in the half-reaction (equivalents per mole),

- R is the gas constant (8.3143 V coul deg<sup>-1</sup> mol<sup>-1</sup>) or J/K.mol
- T is the absolute temperature in Kelvin,
- F is the Faraday constant (96,487 coul eq<sup>-1</sup>) or J/V.
- At 25°C (298.16 K), the value of 2.3026 RT/F is 0.05916 V
- The concentration of pure substances such as precipitates and liquids (H<sub>2</sub>O) is taken as unity.



**Note:** Activities should be used in the Nernst equation. We will use concentrations here because we are primarily concerned here with titrations.

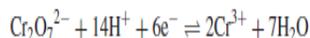
Titration end points involve large potential changes, and the errors are small by doing so.

**Note :** That the log term of the reduction half-reaction is the ratio of the concentrations of the right-side product(s) over the left-side reactants(s).

### Example 12.3

A solution is  $10^{-3} M$  in  $\text{Cr}_2\text{O}_7^{2-}$  and  $10^{-2} M$  in  $\text{Cr}^{3+}$ . If the pH is 2.0, what is the potential of the half-reaction at 298K?

#### Solution



$$\begin{aligned} E &= E_{\text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+}}^0 - \frac{0.05916}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}} \\ &= 1.33 - \frac{0.05916}{6} \log \frac{(10^{-2})^2}{(10^{-3})(10^{-2})^{14}} \\ &= 1.33 - \frac{0.05916}{6} \log 10^{27} = 1.33 - 27 \left( \frac{0.05916}{6} \right) \\ &= 1.06 \text{ V} \end{aligned}$$

### EQUILIBRIUM POTENTIAL—AFTER THE REACTION HAS OCCURRED



- 1- When the equilibrium is reached,  $E_c$  will be equal to  $E_a$  i.e the electrical current will stop and the battery will be dead ( $E_{\text{cell}} = 0$ ).
- 2- Suppose you have two water tanks connected through pipe, one is filled with water the other is half full. The water will flow from the filled one to the half filled till the level of water in both tanks are equal, then the water flow will stop. This is what happens in galvanic cell.
- 3- The potential of an inert electrode in a solution containing the ions of two half-reactions at equilibrium can be calculated relative to the NHE using the Nernst equation for either half-reaction.

$$E_{\text{cell}} = E_c - E_a = 0$$

$$E_c = E_a$$

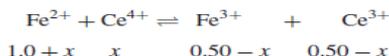
### Example 12.4

A 5.0 mL portion of 0.10 M  $\text{Ce}^{4+}$  solution is added to 5.0 mL of 0.30 M  $\text{Fe}^{2+}$  solution. Calculate the potential at 298K of a platinum electrode dipping in the solution (relative to the NHE).

#### Solution

We start with  $0.30 \text{ mmol mL}^{-1} \times 5.0 \text{ mL} = 1.5 \text{ mmol Fe}^{2+}$  and add  $0.10 \text{ mmol mL}^{-1} \times 5.0 \text{ mL} = 0.50 \text{ mmol Ce}^{4+}$ . So we form 0.50 mmol each of  $\text{Fe}^{3+}$  and  $\text{Ce}^{3+}$  and have 1.0 mmol  $\text{Fe}^{2+}$  remaining. The reaction lies far to the right at equilibrium if there is at least 0.2 V difference between the standard electrode potentials of two

half-reactions. But a small amount of  $\text{Ce}^{4+}$  ( $= x$ ) will exist at equilibrium, and an equal amount of  $\text{Fe}^{2+}$  will be formed:



where the numbers and  $x$  represent millimoles. To calculate the concentration of each species, the amounts in millimoles will need to be divided by the total volume of 10 mL, but since this same divisor appears in both the numerator and denominator, it cancels out when calculating concentration ratios. At equilibrium, the potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-reaction must be the same as that of the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  half-reaction:

$$0.771 - 0.059 \log \frac{(1.0 + x)}{(0.50 - x)} = 1.61 - 0.059 \log \frac{(0.50 - x)}{x}$$

$$1.61 - 0.771 = 0.839 = 0.059 \log \frac{(0.50 - x)^2}{x(0.10 + x)}$$

$$\frac{0.839}{0.059} = 14.22 = \log \frac{(0.50 - x)^2}{x(0.10 + x)}$$

A solution to this quadratic equation that is also readily solved by Goal Seek will result in  $x = 1.51 \times 10^{-15} \text{ M}$ . Putting this value of  $x$  in either half reaction will produce  $E = 0.753 \text{ V}$ .

We could do this, however, a lot simpler. Consider that this reaction is analogous to “ionization” of the product in precipitation or acid–base reactions written as association reactions; a slight shift of the equilibrium here to the left would be the “ionization.” The quantity  $x$  is very small compared with 0.50 or 1.0 and can be neglected. Either half-reaction can be used to calculate the potential. Since the concentrations of both species in the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple are known, we will use this:

$$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$$

$$0.50 \quad 1.0$$

$$E = 0.771 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E = 0.771 - 0.05916 \log \frac{1.0 \text{ mmol}/10 \text{ mL}}{0.50 \text{ mmol}/10 \text{ mL}} = 0.771 - 0.05916 \log 2.0$$

$$= 0.771 - 0.05916(0.30)$$

$$= 0.753 \text{ V}$$

Note that this approach can only succeed where the standard potentials of the two half-reaction are sufficiently far apart such that the addition of  $\text{Ce}^{4+}$  will result in essentially quantitative conversion of a corresponding amount of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (assuming sufficient  $\text{Fe}^{2+}$  was present). ■

## CELL VOLTAGE—BEFORE REACTION

The voltage of a cell can be calculated by taking the difference in potentials of the two half-reactions, to give a positive potential, calculated using the Nernst equation,

$$E_{\text{cell}} = E_c - E_a$$

In Example 12.2 for  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$  at 298K,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{Fe}^{3+}, \text{Fe}^{2+}} - E_{\text{I}_3^-, \text{I}^-} \\ &= \left( E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 - \frac{0.05916}{2} \log \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} \right) - \left( E_{\text{I}_3^-, \text{I}^-}^0 - \frac{0.05916}{2} \log \frac{[\text{I}^-]^3}{[\text{I}_3^-]} \right) \\ &= E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 - E_{\text{I}_3^-, \text{I}^-}^0 - \frac{0.05916}{2} \log \frac{[\text{Fe}^{2+}]^2 [\text{I}_3^-]}{[\text{Fe}^{3+}]^2 [\text{I}^-]^3} \quad (12.24) \end{aligned}$$

Note that the log term for the cell potential of a spontaneous reaction is always the ratio of the product concentration(s) over the reactant concentration(s), that is, right side over left side (as for a reduction half-reaction). Notice it was necessary to multiply the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-reaction by 2 (as when subtracting the two half-reactions) in order to combine the two log terms (with  $n = 2$ ), and the final equation is the same as we would have written from the cell reaction. Note also that  $E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 - E_{\text{I}_3^-, \text{I}^-}^0$  is the cell standard potential,  $E_{\text{cell}}^0$ .

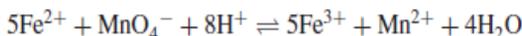
The term on the right of the log sign is the equilibrium constant expression for the reaction:

## Example 12.5

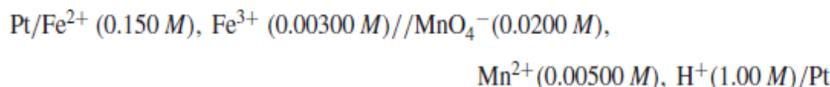
One beaker contains a solution of  $0.0200\text{ M KMnO}_4$ ,  $0.00500\text{ M MnSO}_4$ , and  $0.5\text{ M H}_2\text{SO}_4$ ; and a second beaker contains  $0.150\text{ M FeSO}_4$  and  $0.003\text{ M Fe}_2(\text{SO}_4)_3$ . The two beakers are connected by a salt bridge, and platinum electrodes are placed in each. The electrodes are connected via a wire with a voltmeter in between. What would be the potential of each half-cell (a) before reaction and (b) after reaction? What would be the measured cell voltage (c) at the start of the reaction and (d) after the reaction reaches equilibrium? Assume  $\text{H}_2\text{SO}_4$  to be completely ionized and in equal volumes in each beaker.

### Solution

The cell reaction is



and the cell is



$$\begin{aligned} \text{(a)} \quad E_{\text{Fe}} &= E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \\ &= 0.771 - 0.05916 \log \frac{0.150}{0.00300} = 0.671\text{ V} \\ E_{\text{Mn}} &= E_{\text{MnO}_4^- - \text{Mn}^{2+}}^0 - \frac{0.05916}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8} \\ &= 1.51 - \frac{0.05916}{5} \log \frac{0.00500}{(0.0200)(1.00)^8} = 1.52\text{ V} \end{aligned}$$

- (b) At equilibrium,  $E_{\text{Fe}} = E_{\text{Mn}}$ . We can calculate  $E$  from either half-reaction. First, calculate the equilibrium concentrations. Five moles of  $\text{Fe}^{2+}$  will react with each mole of  $\text{MnO}_4^-$ . The  $\text{Fe}^{2+}$  is in excess. It will be decreased by  $5 \times 0.0200 = 0.100\text{ M}$ , so  $0.050\text{ M Fe}^{2+}$  remains and  $0.100\text{ M Fe}^{3+}$  is formed (total now is  $0.100 + 0.003 = 0.103\text{ M}$ ). Virtually all the  $\text{MnO}_4^-$  is converted to  $\text{Mn}^{2+}$  ( $0.0200\text{ M}$ ) to give a total of  $0.0250\text{ M}$ . A small unknown amount of  $\text{MnO}_4^-$  remains at equilibrium, and we would need the equilibrium constant to calculate it; this can be obtained from  $E_{\text{cell}} = 0$  at equilibrium—as in Equation 12.24—and as carried out in Example 12.4, this is treated in more detail in Chapter 14. But we need not go to this trouble since  $[\text{Fe}^{2+}]$  and  $[\text{Fe}^{3+}]$  are known:

$$E_{\text{Mn}} = E_{\text{Fe}} = 0.771 - 0.05916 \log \frac{0.050}{0.103} = 0.790\text{ V}$$

Note that the half-cell potentials at equilibrium are in between the values for the two half-cells before reaction.

- (c)  $E_{\text{cell}} = E_{\text{Mn}} - E_{\text{Fe}} = 1.52 - 0.671 = 0.85\text{ V}$   
 (d) At equilibrium,  $E_{\text{Mn}} = E_{\text{Fe}}$ , and so  $E_{\text{cell}}$  is zero volts.

Note that if one of the species had not been initially present in a half-reaction, we could not have calculated an initial potential for that half-reaction. ■

## 12.4 Formal Potential—Use It for Defined Nonstandard Solution Conditions



- 1- The  $E^\circ$  values listed in Table 12.1 refer to standard conditions, all species are at an activity of 1 M.
- 2- The potential of a half-reaction may depend on the conditions of the solution.  
example, the  $E^\circ$  value for  $\text{Ce}^{4+} + e^- = \text{Ce}^{3+}$  is 1.61 V.
- 3- we can change this potential by changing the acid used to acidify the solution. (See Table C.5 in Appendix C.)
- 4- The change in potential happens because the anions of the different acids differ in their ability to form complexes with one form of the cerium relative to the other, and the concentration ratio of the two forms of the free cerium ion is thereby affected.
- 5- If we know the form of the complex, we could write a new half-reaction involving the acid anion and determine an  $E^\circ$  value for this reaction, keeping the acid and all other species at unit activity.

## 12.4 Formal Potential—Use It for Defined Nonstandard Solution Conditions



- 5- the complexes are frequently of unknown composition. So we define the formal potential and designate this as  $E^{\circ'}$ .
- 6- This is the standard potential of a redox couple with the oxidized and reduced forms at 1 M concentrations and with the solution conditions specified.  
example, the formal potential of the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  couple in 1 M HCl is 1.28 V.

**The formal potential is used when not all species are known. In a sense, the formal potential provides the same convenience as available with the use of conditional complexation constants or solubility products.**

## DEPENDENCE OF POTENTIAL ON pH



Hydrogen or hydroxyl ions are involved in many redox half-reactions. We can change the potential of these redox couples by changing the pH of the solution.

Consider the As(V)/As(III) couple:



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

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

$$E = E^\circ - 0.059 \log \text{pH} - \frac{0.059}{2} \log \frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_3\text{AsO}_4]}$$



The term  $E^\circ - 0.05916 \text{ pH}$ , where  $E^\circ$  is the standard potential for the half-reaction, can be considered as equal to a formal potential  $E^{\circ'}$ , which can be calculated from the pH of the solution.

In 0.1 M HCl (pH 1),  $E^{\circ'} = E^\circ - 0.05916$ . In neutral condition,

$$E^{\circ'} - 0.05916(7) = E^\circ - 0.41.$$

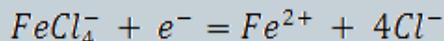
In strongly acid solution,  $\text{H}_3\text{AsO}_4$  will oxidize  $\text{I}^-$  to  $\text{I}_2$ . But in neutral solution, the potential of the As(V)/As(III) couple ( $E^{\circ'} = 0.146 \text{ V}$ ) is less than that for  $\text{I}_2/\text{I}^-$ , and the reaction goes in the reverse; that is,  $\text{I}_2$  will oxidize  $\text{H}_3\text{AsO}_3$ .

## DEPENDENCE OF POTENTIAL ON COMPLEXATION



In HCl (1M), the formal potential ( $E^0$ ) is 0.70 V.

If we assume that the complex is  $FeCl_4^-$ , then the half-reaction would be:



(assume that [HCl] is constant at 1 M),

$$E = E^0 - \frac{0.059}{n} \log \frac{[Fe^{2+}]}{[FeCl_4^-]}$$

In effect, we have stabilized the  $Fe^{3+}$  by complexing it, making it more difficult to reduce.

So the reduction potential is decreased. If we complexed the  $Fe^{2+}$ , the reverse effect would be observed. So the presence of complexing agents that have different

Complexing one ion reduces its effective concentration, which changes the potential.

## 12.5 Limitations of Electrode Potentials



Electrode potentials ( $E^0$  or  $E^0'$ ) predict whether a reaction can occur. They say nothing about the **kinetics** or **rate** of the reaction.