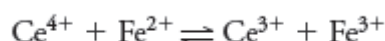# Oxidation reduction reaction in electrochemical cell

Oxidation reduction reaction:

In an **oxidation/reduction reaction** electrons are transferred from one reactant to another. An example is the oxidation of iron(II) ions by cerium(IV) ions. The reaction is described by the equation
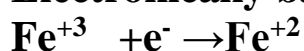
$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

In this reaction, an electron is transferred from Fe^2 to Ce^4 to form Ce^3 and Fe^3 ions. A substance that has a strong affinity for electrons, such as Ce^4, is called an **oxidizing agent**, or an **oxidant**. A **reducing agent**, or **reductant**, is a species, such as Fe^2, that donates electrons to another species. To describe the chemical behavior represented by, we say that Fe^2 is oxidized by Ce^4 ; similarly, Ce^4 is reduced by Fe^2. We can split any oxidation/reduction equation into two half-reactions that show which species gains electrons and which loses them

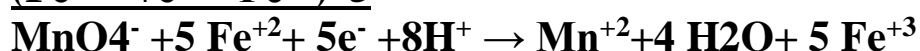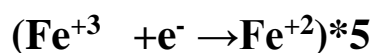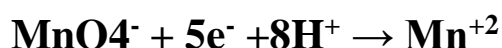$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad \text{(reduction of } Ce^{4+})$$
$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \qquad \text{(oxidation of } Fe^{2+})$$

Balancing oxidation reduction equation

1- Electronically balanced
$$Fe^{+3} + e^- \rightarrow Fe^{+2}$$

2- Charge balance
$$Fe^{+3} + e^- \rightarrow Fe^{+2}$$

3- Mass balance
$$MnO4^- + 5e^- \rightarrow Mn^{+2}$$

$$MnO4^- + 5e^- + 8H^+ \rightarrow Mn^{+2}$$

$$MnO4^- + 5e^- + 8H^+ \rightarrow Mn^{+2} + 4\ H2O$$

$$\underline{(Fe^{+3} + e^- \rightarrow Fe^{+2})*5}$$
$$MnO4^- + 5\ Fe^{+2} + 5e^- + 8H^+ \rightarrow Mn^{+2} + 4\ H2O + 5\ Fe^{+3}$$

Electrochemical cell :

An electrochemical cell consists of two conductors called **electrodes**, each of which is immersed in an electrolyte solution. In most of the cells that will be of interest to us, the solutions surrounding the two electrodes are different and must be separated to avoid direct reaction between the reactants. The most common way of avoiding mixing is to insert a salt bridge, between the solutions. Conduction of electricity from one electrolyte solution to the other then occurs by migration of potassium ions in the bridge in one direction and chloride ions in the other. However, direct contact between copper metal and silver ions is prevented.
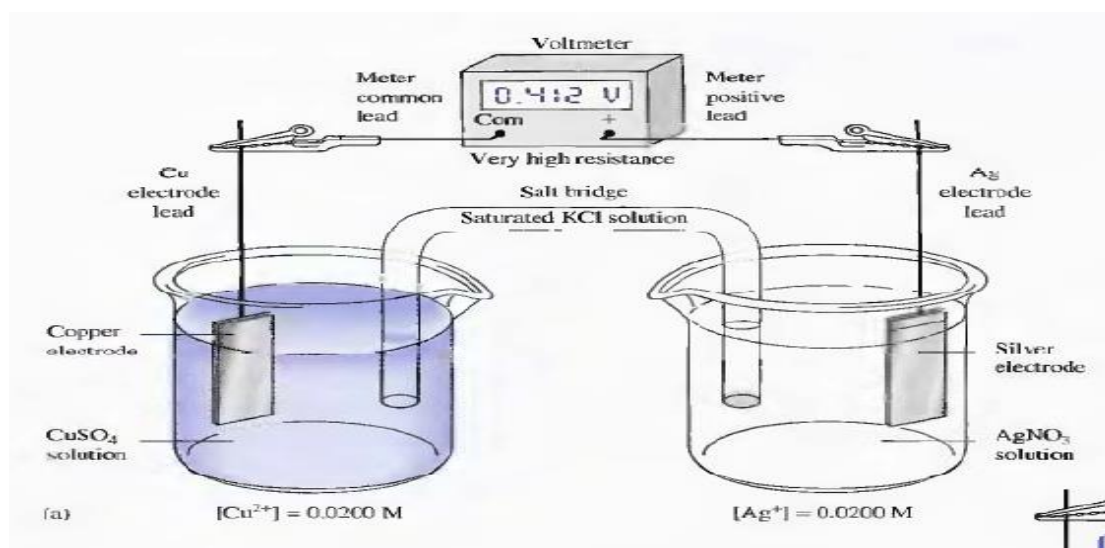

Salt bridge isolates the reactants but maintains electrical contact between the two halves of the cell

The voltmeter measures the potential difference, or **voltage** between two electrodes at any instant. The voltage is a measure of the tendency of the cell reaction to proceed toward equilibrium.

- The study of redox equiliberia by measuring the potentials of electrochemical cells (the two half-reactions are participant)
- Characteristics of electrochemical cells
1. Two conductors (ELECTRODES: a conductor at the surface of which electron transfer to or from surrounding solution take place).
2. Electrolyte soln. that each electrode immersed in it.
3. Solutions of electrode are different and must be separated.
4. The conduction of electricity from one electrolyte solution to the other by ions in the bridge.

Cathodes and Anodes

The **cathode** in an electrochemical cell is the electrode at which reduction occurs. The **anode** is the electrode at which an oxidation takes place.

$$Ag^+ + e^- \rightleftharpoons Ag(s)$$

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

$$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$$
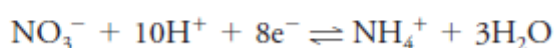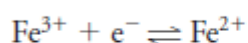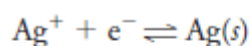
We can force a desired reaction to occur by applying a suitable potential to an electrode made of an unreactive material such as platinum. Note that the reduction of NO3 in the third reaction reveals that anions can migrate to a cathode and be reduced.

$$Cu(s) \rightleftharpoons Cu^{2+} + 2e^-$$

$$2Cl^- \rightleftharpoons Cl_2(g) + 2e^-$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$
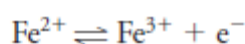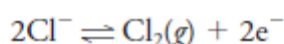
Types of electrochemical cell

1- Electrolytic cell

An electrolytic cell is an electrochemical cell that drives a non-pontaneous redox reaction through the application of electrical energy. They are often used to decompose chemical compounds, in a process called electrolysis—the Greek word lysis means *to break up*. An electrolytic cell has three component parts: an electrolyte and two electrodes (a cathode and an anode). The electrolyte is usually a solutionof water or other solvents in which ions are dissolved. Molten salts such as sodium chloride are also electrolytes.
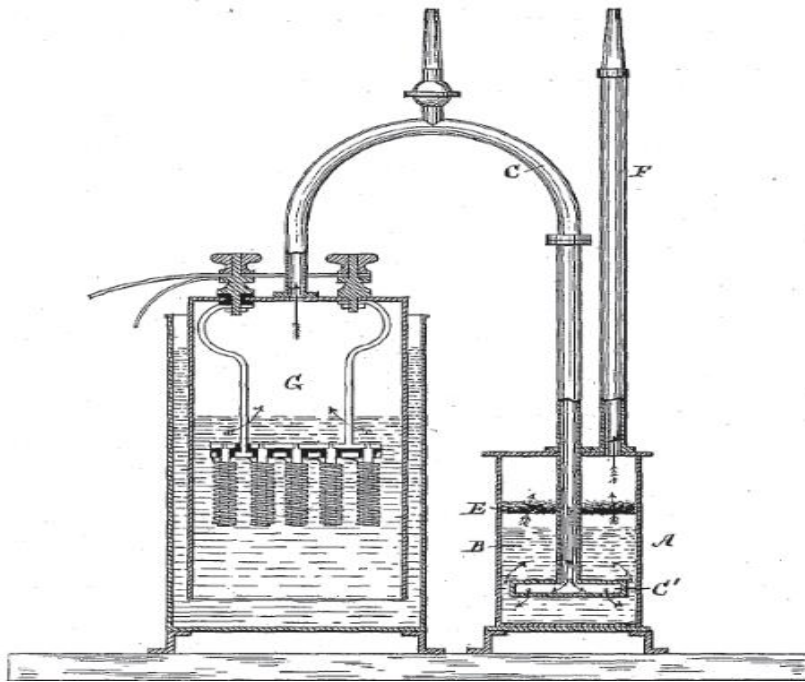
2- Galvanic cell

A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

Volta was the inventor of the voltaic pile, the first electrical battery. In common usage, the word "battery" has come to include a single galvanic cell, but a battery properly consists of multiple cells.

Representing cell:

(a) $[Cu^{2+}] = 0.0200\ M$ $[Ag^+] = 0.0200\ M$

$$Cu \mid Cu^{2+}(0.0200\ M) \parallel Ag^+(0.0200\ M) \mid Ag$$

$$Cu \mid CuSO_4(0.0200\ M) \parallel AgNO_3(0.0200\ M) \mid Ag$$
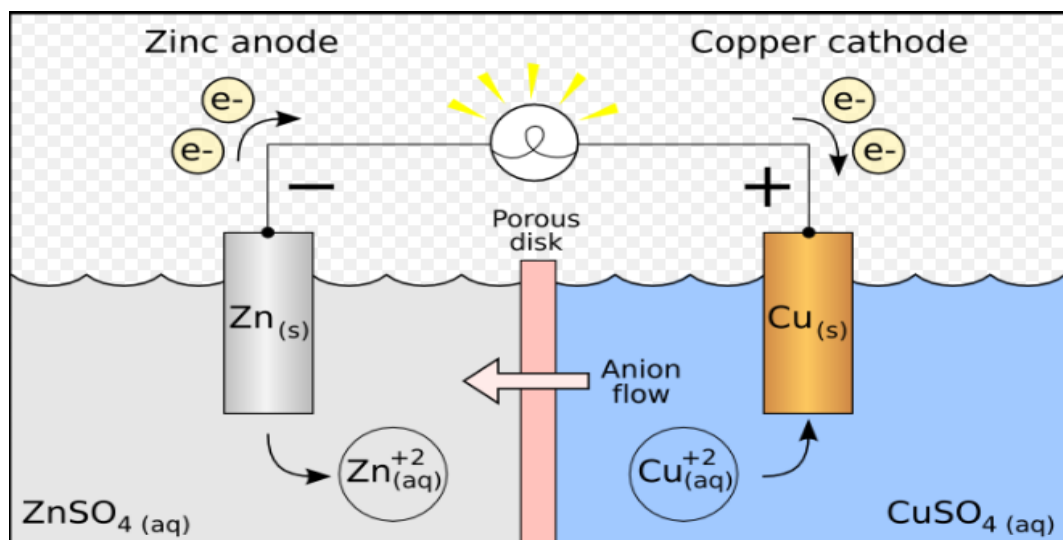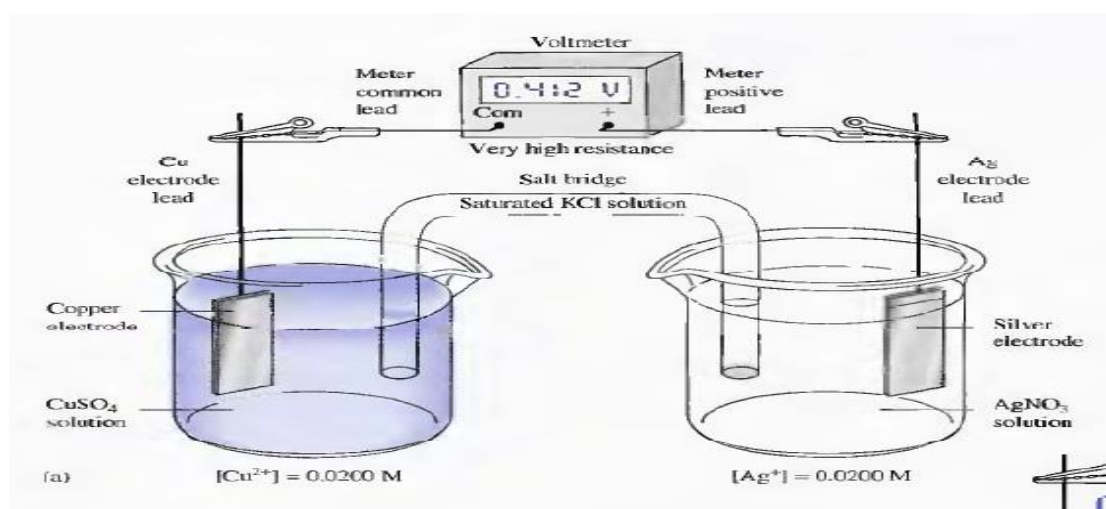
Interface: the phase boundary between an electrode and its solution

Danial cell

The Daniell gravity cell was one of the earliest galvanic cells to find widespread practical application. It was used in the mid-1800s to power telegraphic communication systems. As shown in **Figure** , the cathode was a piece of copper immersed in a saturated solution of copper sulfate.
A much less dense solution of dilute zinc sulfate was layered on top of the copper sulfate, and a massive zinc electrode was located in this solution. The electrode reactions were

$$Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$$
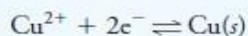
This cell develops an initial voltage of 1.18 V, which gradually decreases as the cell discharges.
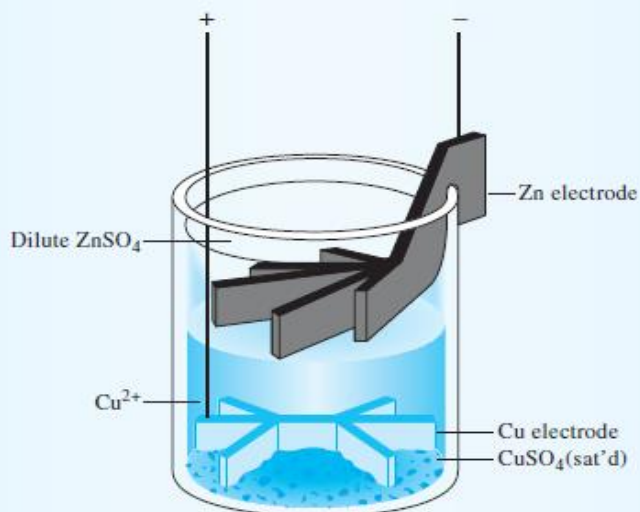
Currents in Electrochemical Cells

1. Electrons carry the charge within the electrodes as well as the external conductor. Notice that by convention, current, which is normally indicated by the symbol I, is opposite in direction to electron flow.
2. Anions and cations are the charge carriers within the cell. At the left-hand electrode, copper is oxidized to copper ions, giving up electrons to the electrode. As shown in Figure above, the copper ions formed move away from the copper electrode into the bulk of solution, while anions, such as sulfate and hydrogen sulfate ions, migrate toward the copper anode. Within the salt bridge, chloride ions migrate toward and into the copper compartment, and potassium ions move in the opposite direction. In the right-hand compartment, silver ions move toward the silver electrode where they are reduced to silver metal, and the nitrate ions move away from the electrode into the bulk of solution.
3. The ionic conduction of the solution is coupled to the electronic conduction in the electrodes by the reduction reaction at the cathode and the oxidation reaction at the anode.

Electrochemical potential

The potential difference between the electrodes of the cell in **Figure** is a measure of the tendency for the reaction

$$2Ag(s) + Cu^{2+} \rightleftharpoons 2Ag^+ + Cu(s)$$

potential E_{cell} is related to the free energy of the reaction ΔG by

$$\Delta G = -nFE_{cell}$$

If the reactants and products are in their **standard states**, the resulting cell potential is called the **standard cell potential**. This latter quantity is related to the standard free-energy change for the reaction and thus to the equilibrium constant by

$$\Delta G^0 = -nFE_{cell}^0 = -RT \ln K_{eq} \qquad (18\text{-}7)$$

Half-Cell Potentials

is the difference between two half-cell or single-electrode potentials, one associated with the half-reaction at the right-hand electrode (Eright) and the other associated with the half-reaction at the left-hand electrode (Eleft).
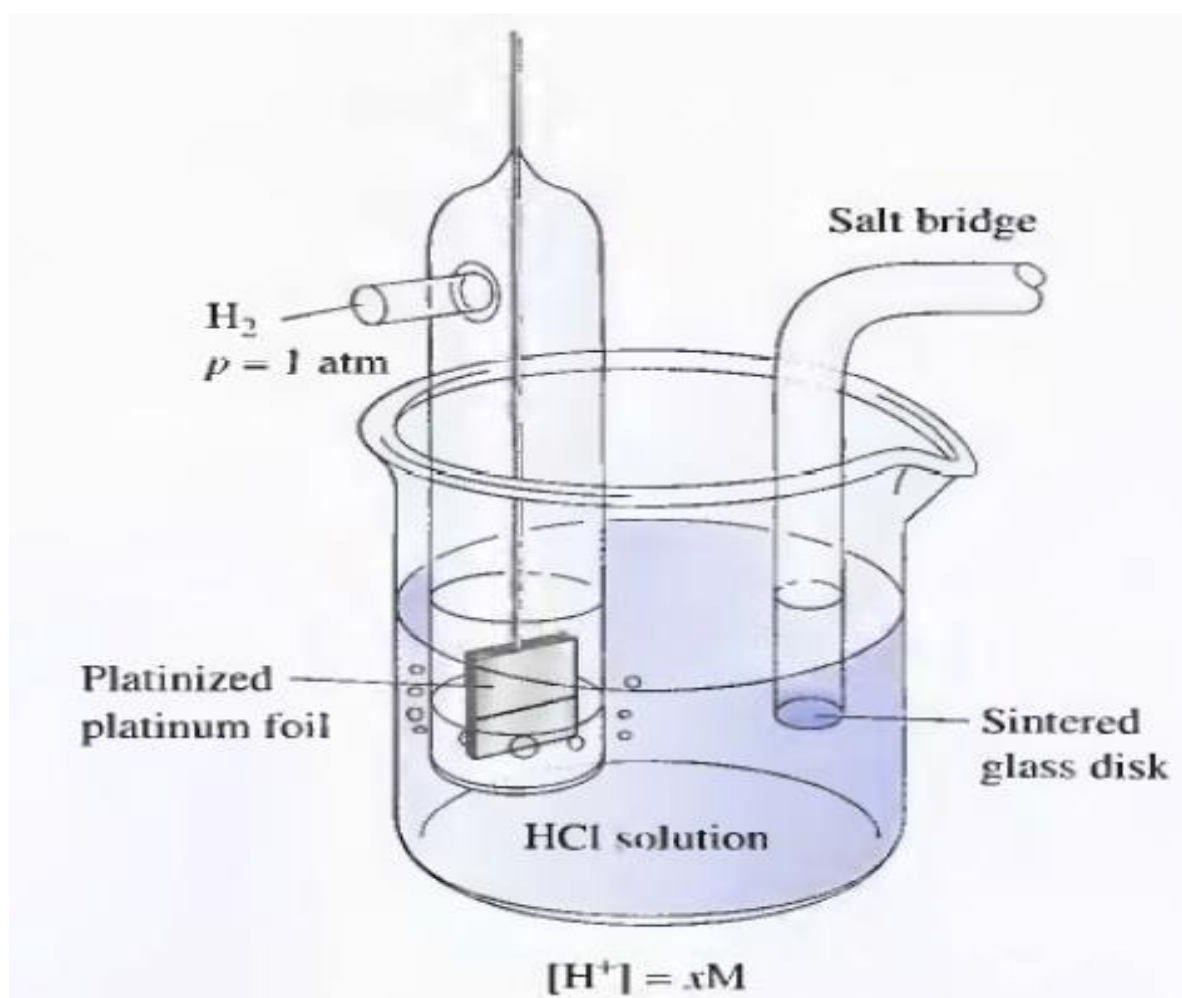
$$E_{cell} = E_{right} - E_{left}$$

reference electrode

 1- The Standard Hydrogen Reference Electrode

The **standard hydrogen electrode (SHE)** meets these specifications and has been used throughout the world for many years as a universal reference electrode. It is a typical **gas electrode**. shows the physical arrangement of a hydrogen electrode. Themetal conductor is a piece of platinum that has been coated, or **platinized**, with finely divided platinum (platinum black) to increase its specific surface area. This electrode is immersed in an aqueous acid solution of known, constant hydrogen ion activity. The solution is kept saturated with hydrogen by bubbling the gas

at constant pressure over the surface of the electrode. The platinum does not take part in the electrochemical reaction and serves only as the site where electrons are transferred. The half-reaction responsible for the potential that develops at this electrode is

The half-reaction responsible for the potential that develops at this electrode is

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \tag{18-9}$$

$$Pt, H_2(p = 1.00 \text{ atm}) \mid ([H^+] = x \text{ M}) \parallel$$

Salt bridge

H_2
$p = 1$ atm

Platinized platinum foil

Sintered glass disk

HCl solution

$[H^+] = x\text{M}$

2-Saturated calomel electrode (SCE)

is a reference electrode based on the reaction between elemental mercury and mercury(I) chloride. It has been widely replaced by the silver chloride electrode, however the calomel electrode has a reputation of being more robust. The aqueous phase in contact with the mercury and the mercury(I) chloride (Hg_2Cl_2, "calomel") is a saturated solution of potassium chloride in water. The electrode is normally linked via a porous frit to the solution in which the other electrode is immersed. This porousfrit is a salt bridge.
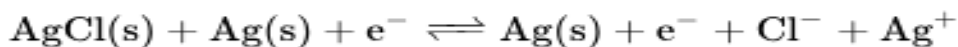
$$Cl^- (4\,M)|Hg_2Cl_2(s)|Hg(l)|Pt$$
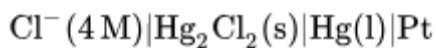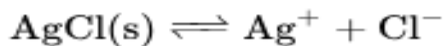
3- silver chloride electrode

is a type of reference electrode, commonly used in electrochemical measurements. For environmental reasons it has widely replaced the saturated calomel electrode. For example, it is usually the internal reference electrode in pH meters and it is often used as reference in reduction potential measurements. As an example of the latter, the silver chloride electrode is the most commonly used reference electrode for testing cathodic protectioncorrosion control systems in sea water environments.

$$Ag^+ + e^- \rightleftharpoons Ag(s)$$
$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$$
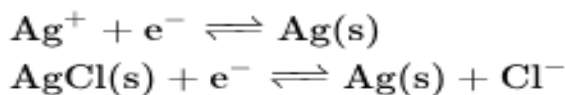
or can be written together:

$$AgCl(s) + Ag(s) + e^- \rightleftharpoons Ag(s) + e^- + Cl^- + Ag^+$$

which can be simplified:

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

Electrode potential :

An **electrode potential** is defined as the potential of a cell in which the electrode in question is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.

$$E_{cell} = E_{right} - E_{left}$$
$$= E_{Ag} - E_{SHE}$$
$$= E_{Ag} - 0.000$$
$$= E_{Ag}$$

Standared electrod potential

The **standard electrode potential**, E_0, of a half-reaction is defined as its electrode potential when the activities of the reactants and products are all unity

$$Pt, H_2(p = 1.00\ atm)\ |\ H^+(a_{H^-} = 1.00)\ ||\ Ag^+(a_{Ag^+} = 1.00)\ |\ Ag$$
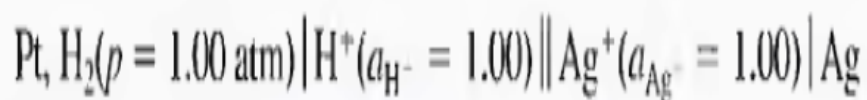
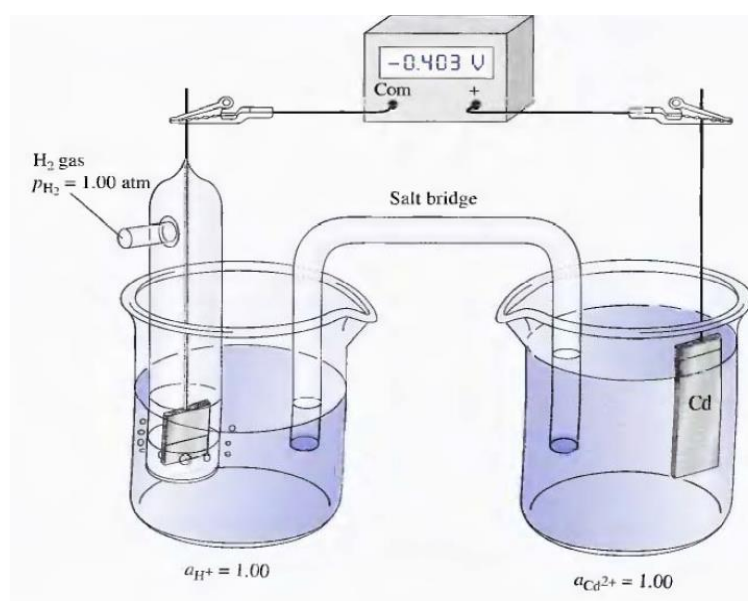| Half-Reaction	Standard Electrode Potential, V
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+ 0.799
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	− 0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	− 0.763

Figure 18-8 Measurement of the standard electrode potential for $Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$.

The Nernest equation

An electrode potential is a measure of the extent to which the concentrations of the species in a half-cell differ from their equilibrium values

$$Ag^+ + e^- \rightleftharpoons Ag(s)$$

$$aA + bB + \cdots + ne^- \rightleftharpoons cC + dD + \cdots$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d \cdots}{[A]^a[B]^b \cdots} \tag{18-11}$$

where

E^0 = the *standard electrode potential,* which is characteristic for each half-reaction
R = the ideal gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
T = temperature, K
n = number of moles of electrons that appears in the half-reaction for the electrode
    process as written
F = the faraday = 96,485 C (coulombs) per mole of electrons
ln = natural logarithm = 2.303 log

If we substitute numerical values for the constants, convert to base 10 logarithms, and specify 25°C for the temperature, we get

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d \cdots}{[A]^a[B]^b \cdots} \tag{18-12}$$

EXAMPLE 18-2

Typical half-cell reactions and their corresponding Nernst expressions follow.

(1) $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $E = E^0 - \dfrac{0.0592}{2} \log \dfrac{1}{[Zn^{2+}]}$

No term for elemental zinc is included in the logarithmic term because it is a pure second phase (solid). Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration.

(2) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}(s)$ $E = E^0 - \dfrac{0.0592}{1} \log \dfrac{[Fe^{2+}]}{[Fe^{3+}]}$

The potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species. The potential depends on the logarithm of the ratio between the molar concentrations of these ions.

(3) $2H^+ + 2e^- \rightleftharpoons H_2(g)$ $E = E^0 - \dfrac{0.0592}{2} \log \dfrac{p_{H_2}}{[H^+]^2}$

In this example, p_{H_2} is the partial pressure of hydrogen (in atmospheres) at the surface of the electrode. Usually, its value will be the same as atmospheric pressure.

(4) $MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$

$$E = E^0 - \dfrac{0.0592}{5} \log \dfrac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$
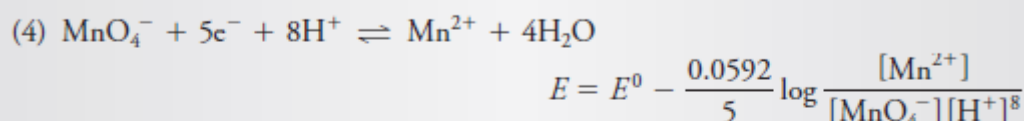
In this situation, the potential depends not only on the concentrations of the manganese species but also on the pH of the solution.

(5) $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$ $E = E^0 - \dfrac{0.0592}{1} \log [Cl^-]$
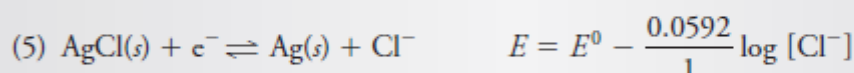
This half-reaction describes the behavior of a silver electrode immersed in a chloride solution that is *saturated* with AgCl. To ensure this condition, an excess of the solid AgCl must always be present. Note that this electrode reaction is the sum of the following two reactions:

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$
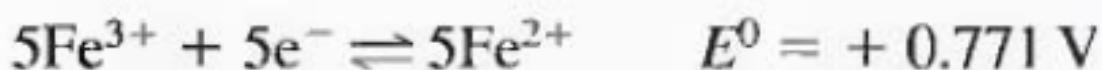$$Ag^+ + e^- \rightleftharpoons Ag(s)$$
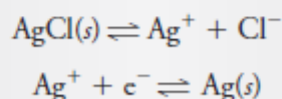
Note also that the electrode potential is independent of the amount of AgCl present as long as there is at least some present to keep the solution saturated.

The standard electrode potential

- **For a half- reaction, $E°$, is defined as the electrode potential when all reactants and products of a half reaction are at unit activity.**

- **$E°$ provides quantitative information regarding the driving force for a half-cell reaction.**

CARACTERISTICS OF THE STANDARD ELECTRODE POTENTIALS $E^\bullet$

1. **$E^\bullet$ is a relative quantity (it is E of an electrochemical cell in which reference electrode is SHE.**

2. **$E^\bullet$ for a half-reaction refers to reduction reaction.**

3. **$E^\bullet$ is independent of the number of moles of reactant and product.**

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = +0.771 \text{ V}$$

$$5Fe^{3+} + 5e^- \rightleftharpoons 5Fe^{2+} \qquad E^0 = +0.771 \text{ V}$$

4. $E°$ measure the relative force tending to derive the half-reaction from a state in which the reactants and products are at unit activity to their equilibrium one , relative to SHE.

5. the positive potential indicates that the half-reaction in question is spontaneous with respect to SHE half-reaction. And negative sign indicates just the opposite.

6. $E°$ for a half-reaction is temperature dependent.

Ex. Calculation of electrode potentials from standard potential :

1- Potential for a half-cell consisting of a cadmium electrode immersed in a solution that is 0.0100M Cd^{2+}
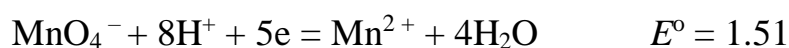
$$Cd^{2+} + 2e \rightarrow \quad Cd(s) \qquad E° = -0.402 \text{ V}$$

$$E = E° - (0.0592/2) \, log \, (1/[Cd^{2+}])$$
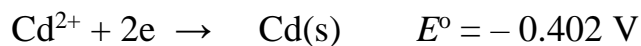
$$= -0.402 - (0.0592/2) \, log \, (1/0.0100)$$

$$= -0.461\text{V}$$

2- calculate the electrode potential of a half-cell containing 0.100M $KMnO_4$ and 0.0500M $MnCl_2$ in a solution whose pH is 1.00.

$$MnO_4{}^- + 8H^+ + 5e = Mn^{2+} + 4H_2O \qquad E° = 1.51$$

$$E = E° - (0.0592/5) \, log \, ([Mn^{2+}] \, /[MnO_4{}^-][H^+]^8)$$

$$= 1.51 - (0.0592/5) \, log \, \{0.0500 \, / \, \{0.100 \times (1.00 \times 10^{-1})^8\}$$

$$= 1.42 \text{ V}$$

Systems involving precipitates or complex ions

For silver there is several potentials :

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad\qquad E^0_{Ag^-/Ag} = +0.799 \text{ V}$$

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \qquad\qquad E^0_{AgCl/Ag} = +0.222 \text{ V}$$

$$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-} \qquad E^0_{Ag(S_2O_3)_2^{3-}/Ag} = +0.017 \text{ V}$$

The Nernst expression for the first half-reaction is

$$E = E^0_{Ag^+/Ag} - \frac{0.0592}{1} log \frac{1}{[Ag^+]}$$

If we replace $[Ag^+]$ with $K_{sp}/[Cl^-]$, we obtain

$$E = E^0_{Ag^+/Ag} - \frac{0.0592}{1} \log \frac{[Cl^-]}{K_{sp}} = E^0_{Ag^+/Ag} + 0.0592 \log K_{sp} - 0.0592 \log [Cl^-]$$

By definition, the standard potential for the second half-reaction is the potential where $[Cl^-] = 1.00$. That is, when $[Cl^-] = 1.00$, $E = E^0_{AgCl/Ag}$. Substituting these values gives

$$E^0_{AgCl/Ag} = E^0_{Ag^+/Ag} - 0.0592 \log 1.82 \times 10^{-10} - 0.0592 \log (1.00)$$
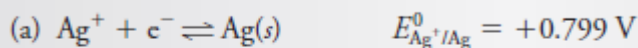$$= 0.799 + (-0.577) - 0.000 = 0.222 \text{ V}$$

$$E^0_{Ag(S_2O_3)_2^{3-}/Ag} = E^0_{Ag^+/Ag} - 0.0592 \log \beta_2$$

$$\beta_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag^+][S_2O_3^{2-}]^2}$$

EXAMPLE 18-3

Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^0_{Ag^+/Ag} = 0.799$ V and (b) $E^0_{AgCl/Ag} = 0.222$ V.

Solution

(a) $Ag^+ + e^- \rightleftharpoons Ag(s)$ $\qquad E^0_{Ag^+/Ag} = +0.799$ V

The Ag^+ concentration of this solution is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9} \text{ M}$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$

(b) We may write this last equation as

$$E = 0.222 - 0.0592 \log [Cl^-] = 0.222 - 0.0592 \log 0.0500$$
$$= 0.299$$

Limitations to the use of $E°$'s

- Use of concentrations instead of activities

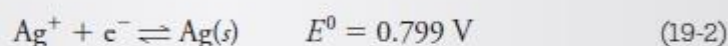- Effect of other equiliberia

- Formal potentials

EXAMPLE 19-1

Calculate the thermodynamic potential of the following cell and the free energy change associated with the cell reaction:

$$Cu|Cu^{2+}(0.0200\ M)\ ||\ Ag^+(0.0200\ M)|Ag$$

Note that this cell is the galvanic cell shown in Figure 18-2a.

Solution

The two half-reactions and standard potentials are

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^0 = 0.799\ V \qquad (19\text{-}2)$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \qquad E^0 = 0.337\ V \qquad (19\text{-}3)$$

The electrode potentials are

$$E_{Ag^+/Ag} = 0.799 - 0.0592 \log \frac{1}{0.0200} = 0.6984\ V$$

$$E_{Cu^{2+}/Cu} = 0.337 - \frac{0.0592}{2} \log \frac{1}{0.0200} = 0.2867\ V$$

We see from the cell diagram that the silver electrode is the right-hand electrode and the copper electrode is the left-hand electrode. Therefore, application of Equation 19-1 gives

$$E_{cell} = E_{right} - E_{left} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu} = 0.6984 - 0.2867 = +0.412\ V$$

The free energy change ΔG for the reaction $Cu(s) + 2Ag^+ \rightleftharpoons Cu^{2+} + Ag(s)$ is found from

$$\Delta G = -nFE_{cell} = -2 \times 96485\ C \times 0.412\ V = -79,503\ J\ (18.99\ kcal)$$

EXAMPLE 19-2

Calculate the potential for the cell

$$Ag|Ag^+(0.0200\ M)\ ||\ Cu^{2+}(0.0200\ M)|Cu$$

Solution

The electrode potentials for the two half-reactions are identical to the electrode potentials calculated in Example 19-1, that is,

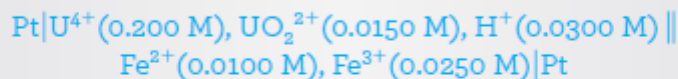$$E_{Ag^+/Ag} = 0.6984\ V \quad \text{and} \quad E_{Cu^{2+}/Cu} = 0.2867\ V$$

In contrast to the previous example, however, the silver electrode is on the left, and the copper electrode is on the right. Substituting these electrode potentials into Equation 19-1 gives

$$E_{cell} = E_{right} - E_{left} = E_{Cu^{2+}/Cu} - E_{Ag^+/Ag} = 0.2867 - 0.6984 = -0.412\ V$$
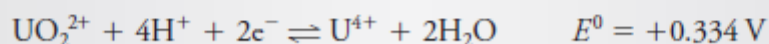

EXAMPLE 19-3

Calculate the potential of the following cell and indicate the reaction that would occur spontaneously if the cell were short-circuited (see Figure 19-1).

$$Pt|U^{4+}(0.200\ M), UO_2^{2+}(0.0150\ M), H^+(0.0300\ M)\ ||$$
$$Fe^{2+}(0.0100\ M), Fe^{3+}(0.0250\ M)|Pt$$

Solution

The two half-reactions are

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad\qquad E^0 = +0.771\ V$$

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^0 = +0.334\ V$$
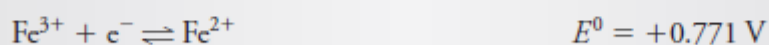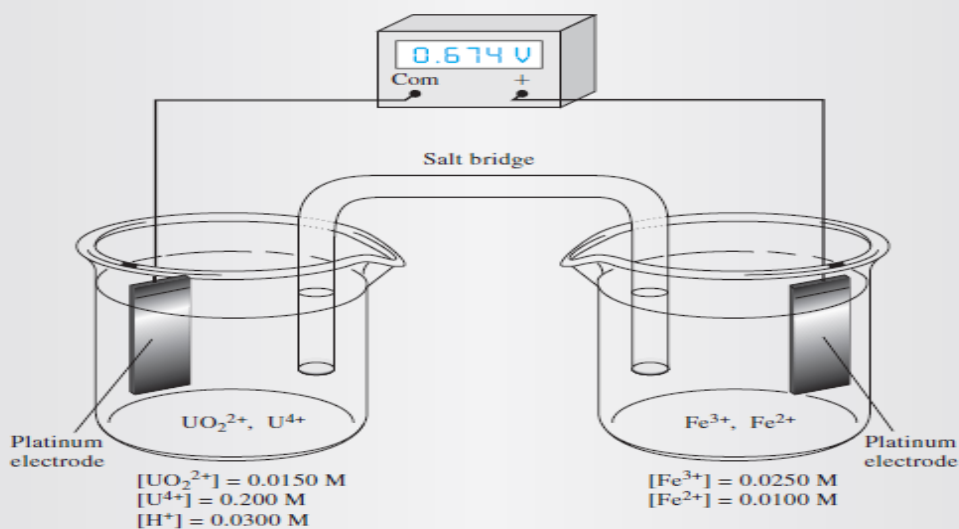
The electrode potential for the right-hand electrode is

$$E_{\text{right}} = 0.771 - 0.0592 \log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.771 - 0.0592 \log\frac{0.0100}{0.0250} = 0.771 - (-0.0236)$$

$$= 0.7946 \text{ V}$$

The electrode potential for the left-hand electrode is

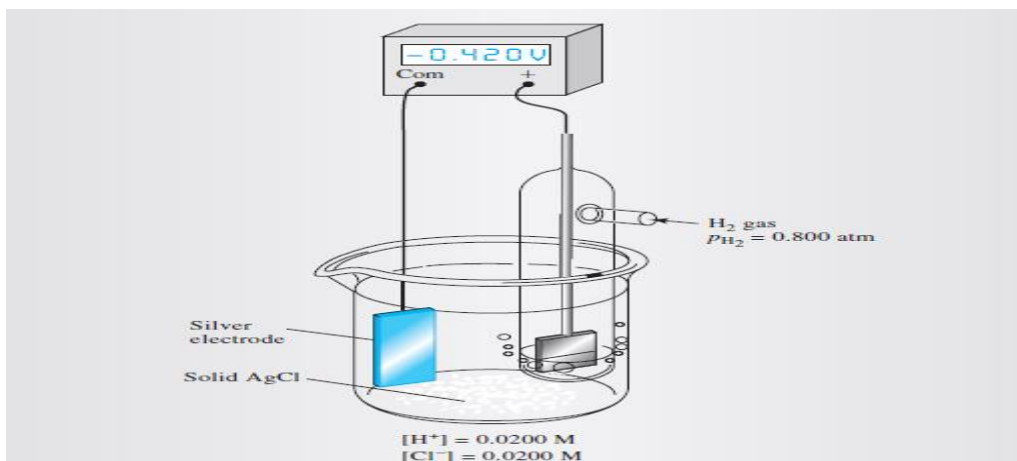$$E_{\text{left}} = 0.334 - \frac{0.0592}{2} \log\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

$$= 0.334 - \frac{0.0592}{2} \log\frac{0.200}{(0.0150)(0.0300)^4}$$

$$= 0.334 - 0.2136 = 0.1204 \text{ V}$$

and

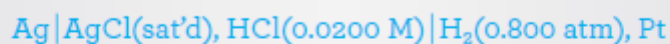$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.7946 - 0.1204 = 0.6742 \text{ V}$$

The positive sign means that the spontaneous reaction is the oxidation of U^{4+} on the left and the reduction of Fe^{3+} on the right, or
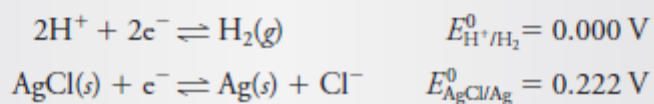
$$U^{4+} + 2Fe^{3+} + 2H_2O \rightarrow UO_2^{2+} + 2Fe^{2+} + 4H^+$$

Silver electrode

Solid AgCl

H₂ gas
P_{H_2} = 0.800 atm

$[H^+]$ = 0.0200 M
$[Cl^-]$ = 0.0200 M

EXAMPLE 19-4

Calculate the cell potential for

$$Ag\,|\,AgCl(sat'd), HCl(0.0200\ M)\,|\,H_2(0.800\ atm), Pt$$

Note that this cell does not require two compartments (nor a salt bridge) because molecular H_2 has little tendency to react directly with the low concentration of Ag^+ in the electrolyte solution. This is an example of a **cell without liquid junction** (see **Figure 19-2**).

Solution

The two half-reactions and their corresponding standard electrode potentials are (see Table 18-1).

$$2H^+ + 2e^- \rightleftharpoons H_2(g) \qquad E^0_{H^+/H_2} = 0.000\ V$$

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \qquad E^0_{AgCl/Ag} = 0.222\ V$$

The two electrode potentials are

$$E_{right} = 0.000 - \frac{0.0592}{2} \log \frac{p_{H_2}}{[H^+]^2} = -\frac{0.0592}{2} \log \frac{0.800}{(0.0200)^2}$$

$$= -0.0977 \text{ V}$$

$$E_{left} = 0.222 - 0.0592 \log[Cl^-] = 0.222 - 0.0592 \log 0.0200$$

$$= 0.3226 \text{ V}$$

The cell potential is thus

$$E_{cell} = E_{right} - E_{left} = -0.0977 - 0.3226 = -0.420 \text{ V}$$

The negative sign indicates that the cell reaction as considered

$$2H^+ + 2Ag(s) \rightarrow H_2(g) + 2AgCl(s)$$
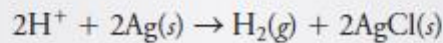
is nonspontaneous. In order to get this reaction to occur, we would have to apply an external voltage and construct an electrolytic cell.

Activity and activity coefficient

ionic Strength

Ionic strength calculates the degree to which charges on ions influence how far a solution deviates from ideal behavior. This a combination of concentration and unaltered charge and concentration of a given ion

$$\text{ionic strength} = \mu = \frac{1}{2}([A] Z_A^2 + [B] Z_B^2 + [C] Z_C^2 + \cdots) \qquad (10\text{-}1)$$

where [A], [B], [C], ... represent the species molar concentrations of ions A, B, C, ... and Z_A, Z_B, Z_C, ... are their charges.

EXAMPLE 10-1

Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4.

(a) For the KNO_3 solution, $[K^+]$ and $[NO_3^-]$ are 0.1 M and

$$\mu = \frac{1}{2}(0.1 \text{ M} \times 1^2 + 0.1 \text{ M} \times 1^2) = 0.1 \text{ M}$$

(b) For the Na_2SO_4 solution, $[Na^+] = 0.2$ M and $[SO_4^{2-}] = 0.1$ M. Therefore,

$$\mu = \frac{1}{2}(0.2 \text{ M} \times 1^2 + 0.1 \text{ M} \times 2^2) = 0.3 \text{ M}$$

$$a_X = [X] \gamma_X \qquad (10\text{-}2)$$

where a_X is the activity of the species X, $[X]$ is its molar concentration, and γ_X is a dimensionless quantity called the **activity coefficient.** The activity coefficient and

$$-\log \gamma_X = \frac{0.51 Z_X^2 \sqrt{\mu}}{1 + 3.3 \alpha_X \sqrt{\mu}} \qquad (10\text{-}5)$$

where

γ_X = activity coefficient of the species X
Z_X = charge on the species X
μ = ionic strength of the solution
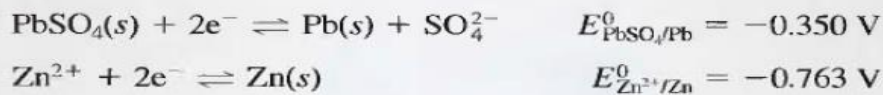α_X = effective diameter of the hydrated ion X in nanometers (10^{-9} m)

EXAMPLE 19-5

Calculate the potential for the following cell using (a) concentrations and (b) activities:

$$Zn \mid ZnSO_4(x \text{ M}), PbSO_4(\text{sat'd}) \mid Pb$$

where $x = 5.00 \times 10^{-4}, 2.00 \times 10^{-3}, 1.00 \times 10^{-2},$ and 5.00×10^{-2}.

The half-reactions and standard electrode potentials are (see Table 18-1)

$$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-} \qquad E^0_{PbSO_4/Pb} = -0.350 \text{ V}$$
$$Zn^{2+} + 2e^- \rightleftharpoons Zn(s) \qquad E^0_{Zn^{2+}/Zn} = -0.763 \text{ V}$$

The lead electrode potential is

$$E_{PbSO_4/Pb} = E^0_{PbSO_4/Pb} - \frac{0.0592}{2} \log[SO_4^{2-}]$$

$$= -0.350 - \frac{0.0592}{2} \log(5.00 \times 10^{-4}) = -0.252 \text{ V}$$

The zinc electrode potential is

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]}$$

$$= -0.763 - \frac{0.0592}{2} \log \frac{1}{5.00 \times 10^{-4}} = -0.860 \text{ V}$$

The cell potential is thus

$$E_{cell} = E_{right} - E_{left} = E_{PbSO_4/Pb} - E_{Zn^{2+}/Zn} = -0.252 - (-0.860) = 0.608 \text{ V}$$

Cell potentials at the other concentrations can be derived in the same way. Their values are given in Table 19-1.

(b) To calculate activity coefficients for Zn^{2+} and SO_4^{2-}, we must first find the ionic strength of the solution using Equation 10-1:

$$\mu = \frac{1}{2}[5.00 \times 10^{-4} \times (2)^2 + 5.00 \times 10^{-4} \times (2)^2] = 2.00 \times 10^{-3}$$

In Table 10-1, we find that $\alpha_{SO_4^{2-}} = 0.4$ nm and $\alpha_{Zn^{2+}} = 0.4$ nm. If we substitute these values into Equation 10-5, we find that

$$-\log\gamma_{SO_4^{2-}} = \frac{0.51 \times (2)^2\sqrt{2.00 \times 10^{-3}}}{1 + 3.3 \times 0.4\sqrt{2.00 \times 10^{-3}}} = 8.61 \times 10^{-2}$$

$$\gamma_{SO_4^{2-}} = 0.820$$

Repeating the calculations for Zn^{2+}, we find that

$$\gamma_{Zn^{2+}} = 0.825$$

The Nernst equation for the lead electrode is now

$$E_{PbSO_4/Pb} = E^0_{PbSO_4/Pb} - \frac{0.0592}{2}\log (\gamma_{SO_4^{2-}})(c_{SO_4^{2-}})$$

$$= -0.350 - \frac{0.0592}{2}\log (0.820 \times 5.00 \times 10^{-4}) = -0.250 \text{ V}$$

and for the zinc electrode, we have

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.0592}{2}\log \frac{1}{(\gamma_{Zn^{2+}})(c_{Zn^{2+}})}$$

$$= -0.763 - \frac{0.0592}{2}\log \frac{1}{0.825 \times 5.00 \times 10^{-4}} = -0.863 \text{ V}$$

Finally, we find the cell potential from

$$E_{cell} = E_{right} - E_{left} = E_{PbSO_4/Pb} - E_{Zn^{2+}/Zn} = -0.250 - (-0.863) = 0.613 \text{ V}$$

Values for other concentrations and experimentally determined potentials for the cell are found in Table 19-1.

EXAMPLE 19-5

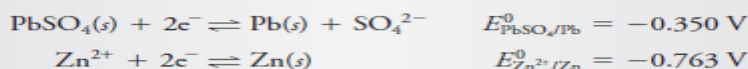Calculate the potential for the following cell using (a) concentrations and (b) activities:

$$Zn \mid ZnSO_4(x\ M),\ PbSO_4(sat'd) \mid Pb$$

where $x = 5.00 \times 10^{-4},\ 2.00 \times 10^{-3},\ 1.00 \times 10^{-2},\ 5.00 \times 10^{-2}$.

Solution

(a) In a neutral solution, little HSO_4^- is formed, and we can assume that

$$[SO_4^{2-}] = c_{ZnSO_4} = x = 5.00 \times 10^{-4}\ M$$

The half-reactions and standard electrode potentials are (see Table 18-1).

$$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-} \qquad E^0_{PbSO_4/Pb} = -0.350\ V$$
$$Zn^{2+} + 2e^- \rightleftharpoons Zn(s) \qquad E^0_{Zn^{2+}/Zn} = -0.763\ V$$

The lead electrode potential is

$$E_{PbSO_4/Pb} = E^0_{PbSO_4/Pb} - \frac{0.0592}{2} \log [SO_4^{2-}]$$

$$= -0.350 - \frac{0.0592}{2} \log(5.00 \times 10^{-4}) = -0.252\ V$$

The zinc electrode potential is

$$\frac{0.0592}{} \qquad 1$$

The zinc electrode potential is

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]}$$

$$= -0.763 - \frac{0.0592}{2} \log \frac{1}{5.00 \times 10^{-4}} = -0.860\ V$$

The cell potential is thus

$$E_{cell} = E_{right} - E_{left} = E_{PbSO_4/Pb} - E_{Zn^{2+}/Zn} = -0.252 - (-0.860) = 0.608\ V$$

Cell potentials at the other concentrations can be calculated in the same way. Their values are given in Table 19-1.

(b) To calculate activity coefficients for Zn^{2+} and $[SO_4^{2-}]$, we must first find the ionic strength of the solution using Equation 10-1:

$$\mu = \frac{1}{2}[5.00 \times 10^{-4} \times (2)^2 + 5.00 \times 10^{-4} \times (2)^2] = 2.00 \times 10^{-3}$$

In Table 10-2, we find and $\alpha_{SO_4^{2-}} = 0.4$ nm and $\alpha_{Zn^{2+}} = 0.6$ nm. If we substitute these values into Equation 10-5, we find that

$$-\log \gamma_{SO_4^{2-}} = \frac{0.51 \times (2)^2 \sqrt{2.00 \times 10^{-3}}}{1 + 3.3 \times 0.4\sqrt{2.00 \times 10^{-3}}} = 8.61 \times 10^{-2}$$

$$\gamma_{SO_4^{2-}} = 0.820$$

Repeating the calculations for Zn^{2+}, we find that

$$\gamma_{Zn^{2+}} = 0.825$$

The Nernst equation for the lead electrode is now

$$E_{PbSO_4/Pb} = E^0_{PbSO_4/Pb} - \frac{0.0592}{2} \log \gamma_{SO_4^{2-}} c_{SO_4^{2-}}$$

$$= -0.350 - \frac{0.0592}{2} \log(0.820 \times 5.00 \times 10^{-4}) = -0.250 \text{ V}$$

and for the zinc electrode, we have

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.0592}{2} \log \frac{1}{\gamma_{Zn^{2+}} c_{Zn^{2+}}}$$

$$= -0.763 - \frac{0.0592}{2} \log \frac{1}{0.825 \times 5.00 \times 10^{-4}} = -0.863 \text{ V}$$

Finally, we find the cell potential from
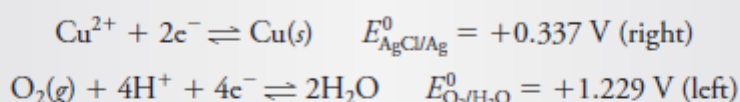
$$E_{cell} = E_{right} - E_{left} = E_{PbSO_4/Pb} - E_{Zn^{2+}/Zn} = -0.250 - (-0.863) = 0.613 \text{ V}$$

Calculate the potential required to initiate deposition of copper from a solution that is 0.010 M in $CuSO_4$ and contains sufficient H_2SO_4 to give a pH of 4.00.

Solution

The deposition of copper necessarily occurs at the cathode, which according to IUPAC convention is the right-hand-electrode. Since there is no more easily oxidizable species than water in the system, O_2 will evolve at the anode. The two half-reactions and their corresponding standard electrode potentials are (see Table 18-1):

$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \qquad E^0_{AgCl/Ag} = +0.337 \text{ V (right)}$$

$$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^0_{O_2/H_2O} = +1.229 \text{ V (left)}$$

The electrode potential for the Cu electrode is

$$E_{Cu^{2+}/Cu} = +0.337 - \frac{0.0592}{2} \log \frac{1}{0.010} = +0.278 \text{ V}$$

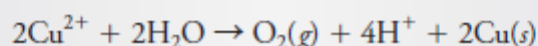If O_2 is evolved at 1.00 atm, the electrode potential for the oxygen electrode is

$$E_{O_2/H_2O} = +1.229 - \frac{0.0592}{4} \log \frac{1}{p_{O_2}[H^+]^4}$$

$$= +1.229 - \frac{0.0592}{4} \log \frac{1}{(1 \text{ atm})(1.00 \times 10^{-4})^4} = +0.992 \text{ V}$$

and the cell potential is thus

$$E_{cell} = E_{right} - E_{left} = E_{Cu^{2+}/Cu} - E_{O_2/H_2O} = +0.278 - 0.992 = -0.714 \text{ V}$$

The negative sign shows that the cell reaction

$$2Cu^{2+} + 2H_2O \rightarrow O_2(g) + 4H^+ + 2Cu(s)$$

is nonspontaneous and that, to cause copper to be deposited according to the following reaction, we must apply a negative potential slightly greater than -0.714 V.

Calculating Redox Equilibrium Constants

$$Cu(s) + 2Ag^+ \rightleftharpoons Cu^{2+} + 2Ag(s) \qquad (19\text{-}4)$$

The equilibrium constant for this reaction is

$$K_{eq} = \frac{[Cu^{2+}]}{[Ag^+]^2} \qquad (19\text{-}5)$$

$$E_{cell} = E_{right} - E_{left} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$$

$$E_{cell} = 0 = E_{right} - E_{left} = E_{Ag} - E_{Cu}$$

$$E_{right} = E_{left} = E_{Ag} = E_{Cu} \qquad (19\text{-}6)$$

$$E_{Ag}^0 - \frac{0.0592}{2} \log \frac{1}{[Ag^+]^2} = E_{Cu}^0 - \frac{0.0592}{2} \log \frac{1}{[Cu^{2+}]} \qquad (19\text{-}7)$$

$$E_{Ag}^0 - E_{Cu}^0 = \frac{0.0592}{2} \log \frac{1}{[Ag^+]^2} - \frac{0.0592}{2} \log \frac{1}{[Cu^{2+}]}$$

$$E_{Ag}^0 - E_{Cu}^0 = \frac{0.0592}{2} \log \frac{1}{[Ag^+]^2} + \frac{0.0592}{2} \log \frac{[Cu^{2+}]}{1}$$

$$\frac{2(E_{Ag}^0 - E_{Cu}^0)}{0.0592} = \log \frac{[Cu^{2+}]}{[Ag^+]^2} = \log K_{eq} \qquad (19\text{-}8)$$

We can also obtain Equation 19-8 from the free energy change for the reaction, as was given in Equation 18-7. Rearrangement of this equation gives

$$\ln K_{eq} = -\frac{\Delta G^0}{RT} = \frac{nFE_{cell}^0}{RT} \qquad (19\text{-}9)$$

At 25°C after conversion to base 10 logarithms, we can write

$$\log K_{eq} = \frac{nE_{cell}^0}{0.0592} = \frac{n(E_{right}^0 - E_{left}^0)}{0.0592}$$

EXAMPLE 19-8

Calculate the equilibrium constant for the reaction shown in Equation 19-4 at 25°C.

Substituting numerical values into Equation 19-8 yields

$$\log K_{eq} = \log \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{2(0.799 - 0.337)}{0.0592} = 15.61$$

$$K_{eq} = \text{antilog } 15.61 = 4.1 \times 10^{15}$$

EXAMPLE 19-10

Calculate the equilibrium constant for the reaction

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_2(s) + 4H^+$$

In Appendix 5, we find

$$2MnO_4^- + 8H^+ + 6e^- \rightleftharpoons MnO_2(s) + 4H_2O \qquad E^0 = +1.695 \text{ V}$$

$$3MnO_2(s) + 12H^+ + 6e^- \rightleftharpoons 3Mn^{2+} + 6H_2O \qquad E^0 = +1.23 \text{ V}$$

Again we have multiplied both equations by integers so that the numbers of electrons are equal. When this system is at equilibrium.

$$E_{MnO_4^-/MnO_2} = E_{MnO_2/Mn^{2+}}$$

$$1.695 - \frac{0.0592}{6} \log \frac{1}{[MnO_4^-]^2[H^+]^8} = 1.23 - \frac{0.0592}{6} \log \frac{[Mn^{2+}]^3}{[H^+]^{12}}$$

If we invert the logarithmic term on the right and rearrange, we obtain

$$\frac{6(1.695 - 1.23)}{0.0592} = \log \frac{1}{[MnO_4^-]^2[H^+]^8} + \log \frac{[H^+]^{12}}{[Mn^{2+}]^3}$$

Adding the two logarithmic terms gives

$$\frac{6(1.695 - 1.23)}{0.0592} = \log \frac{[H^+]^{12}}{[MnO_4^-]^2[Mn^{2+}]^3[H^+]^8}$$

$$47.1 = \log \frac{[H^+]^4}{[MnO_4^-]^2[Mn^{2+}]^3} = \log K_{eq}$$

$$K_{eq} = \text{antilog } 47.1 = 1 \times 10^{47}$$

CONSTRUCTING REDOX TITRATION CURVES

- When redox systems are at equilibrium, the electrode potentials of all half reactions are identical. whether the reaction take place directly in soln. or indirectly in galvanic cell

- Most end points in oxidation reduction titrations are based on the rapid changes in E $_{system}$ that occur at or near chemical equivalence.

- Before the equivalence point, E $_{system}$ calculations are done using Nernst equation for the analyte. After the equivalence point, the Nernst equation for the titrant are used.

EQUIVALENCE- POINT POTENTIALS

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0\prime} = 1.44 \text{ V (1 M } H_2SO_4)$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^{0\prime} = 0.68 \text{ V (1 M } H_2SO_4)$$

$$F_{eq} = F^0_{Ce^{4+}/Ce^{3+}} - \frac{0.0592}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_{eq} = E^0_{Fe^{3+}/Fe^{2+}} - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$2E_{eq} = E^0_{Fe^{3+}/Fe^{2+}} + E^0_{Ce^{4+}/Ce^{3+}} - \frac{0.0592}{1} \log \frac{[Ce^{3+}][Fe^{2+}]}{[Ce^{4+}][Fe^{3+}]}$$

The definition of equivalence point requires that

$$[Fe^{3+}] = [Ce^{3+}]$$

$$[Fe^{2+}] = [Ce^{4+}]$$

$$2E_{eq} = E^0_{Fe^{3+}/Fe^{2+}} + E^0_{Ce^{4+}/Ce^{3+}} - \frac{0.0592}{1} \log \frac{[Ce^{3+}][Ce^{4+}]}{[Ce^{4+}][Ce^{3+}]} = E^0_{Fe^{3+}/Fe^{2+}} + E^0_{Ce^{4+}/Ce^{3+}}$$

$$F_{eq} = \frac{E^0_{Fe^{3+}/Fe^{2+}} + E^0_{Ce^{4+}/Ce^{3+}}}{2} \qquad (19\text{-}12)$$

EXAMPLE 19-11

Obtain an expression for the equivalence-point potential in the titration of
0.0500 M U^{4+} with 0.1000 M Ce^{4+}. Assume both solutions are 1.0 M in H_2SO_4.

$$U^{4+} + 2Ce^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Ce^{3+} + 4H^+$$

In Appendix 5, we find

$$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O \qquad E^0 = 0.334 \text{ V}$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44 \text{ V}$$
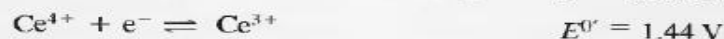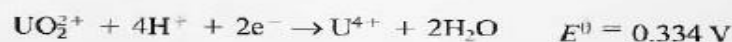
$$E_{eq} = E^0_{UO_2^{2+}/U^{4+}} - \frac{0.0592}{2} \log \frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

$$E_{eq} = E^{0'}_{Ce^{4+}/Ce^{3+}} - \frac{0.0592}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$2E_{eq} = 2E^0_{UO_2^{2+}/U^{4+}} - 0.0592 \log \frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

$$3E_{eq} = 2E^0_{UO_2^{2+}/U^{4+}} + E^{0'}_{Ce^{4+}/Ce^{3+}} - 0.0592 \log \frac{[U^{4+}][Ce^{3+}]}{[UO_2^{2+}][Ce^{4+}][H^+]^4}$$

But at equivalence

$$[U^{4+}] = [Ce^{4+}]/2$$

and

$$[UO_2^{2+}] = [Ce^{3+}]/2$$

$$E_{eq} = \frac{2E^0_{UO_2^{2+}/U^{4+}} + E^{0'}_{Ce^{4+}/Ce^{3+}}}{3} - \frac{0.0592}{3} \log \frac{2[Ce^{4+}][Ce^{3+}]}{2[Ce^{3+}][Ce^{4+}][H^+]^4}$$

$$= \frac{2E^0_{UO_2^{2+}/U^{4+}} + E^{0'}_{Ce^{4+}/Ce^{3+}}}{3} - \frac{0.0592}{3} \log \frac{1}{[H^+]^4}$$

THE TITRATION CURVE

The titration of 50.00ml of 0.0500 M Fe^{2+} with 0.1000M Ce^{4+} in a medium that is 1.0 M in H_2SO_4

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44 \text{ V (1 M } H_2SO_4)$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^{0'} = 0.68 \text{ V (1 M } H_2SO_4)$$

Initial potential

We do not have enough information to calculate an initial potential.

Potential after the addition of 5.00 ml of Cerium *(IV)*

$$[Fe^{3+}] - \frac{5.00 \times 0.1000}{50.00 + 5.00} - [Ce^{4+}] - \frac{0.500}{55.00} \quad [Ce^{4+}]$$

$$[Fe^{2+}] = \frac{50.00 \times 0.0500 - 5.00 \times 0.1000}{55.00} + [Ce^{4+}] = \frac{2.00}{55.00} + [Ce^{4+}]$$

$$[Fe^{3+}] = \frac{0.500}{55.00} \quad \text{and} \quad [Fe^{2+}] = \frac{2.00}{55.00}$$

$$E_{system} = +0.68 - \frac{0.0592}{1} \log \frac{2.00/55.00}{0.20/55.00} = 0.64 \text{ V}$$

EQUIVALENCE POINT POTENTIAL

$$E_{eq} = \frac{E^{0'}_{Ce^{4+}/Ce^{3+}} + E^{0'}_{Fe^{3+}/Fe^{2+}}}{2} = \frac{1.44 + 0.68}{2} = 1.06 \text{ V}$$

POTENTIAL AFTER ADDITION OF 25.10 Ml of Cerium *(IV)*

$$[Ce^{3+}] = \frac{25.00 \times 0.1000}{75.10} - [Fe^{2+}] \approx \frac{2.500}{75.10}$$

$$[Ce^{4+}] = \frac{25.10 \times 0.1000 - 50.00 \times 0.0500}{75.10} + [Fe^{2+}] \approx \frac{0.010}{75.10}$$

$$E = +1.44 - \frac{0.0592}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.44 - \frac{0.0592}{1} \log \frac{2.500/\cancel{75}+0}{0.010/\cancel{75}+0}$$
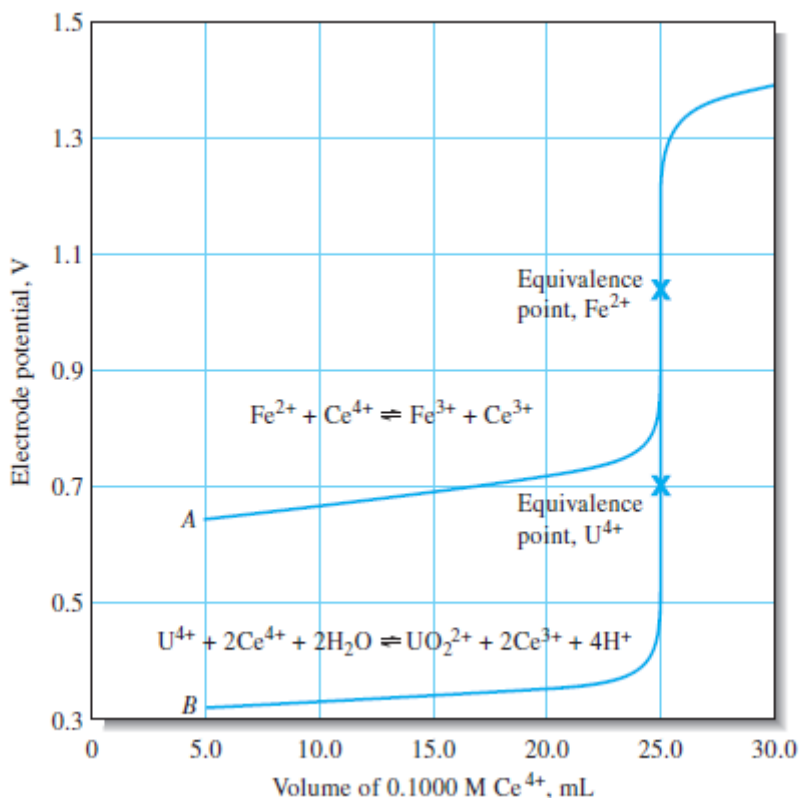
$$= +1.30 \text{ V}$$

TABLE 19-2

Electrode Potential Versus SHE in Titrations with 0.100 M Ce^{4+}

		Potential, V vs. SHE*		
Reagent Volume, mL	50.00 mL of 0.0500 M Fe^{2+}			50.00 mL of 0.02500 M U^{4+}
5.00	0.64			0.316
15.00	0.69			0.339
20.00	0.72			0.352
24.00	0.76			0.375
24.90	0.82			0.405
25.00	1.06	← Equivalence point →		0.703
25.10	1.30			1.30
26.00	1.36			1.36
30.00	1.40			1.40

*H_2SO_4 concentration is such that $[H^+] = 1.0$ throughout in both titrations.

The y-axis is labeled "Electrode potential, V" with values ranging from 0.3 to 1.5. The x-axis is labeled "Volume of 0.1000 M Ce^{4+}, mL" with values from 0 to 30.0.

Upper curve labeled: Equivalence point, Fe^{2+}

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

Point A

Lower curve labeled: Equivalence point, U^{4+}

$$U^{4+} + 2Ce^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Ce^{3+} + 4H^+$$
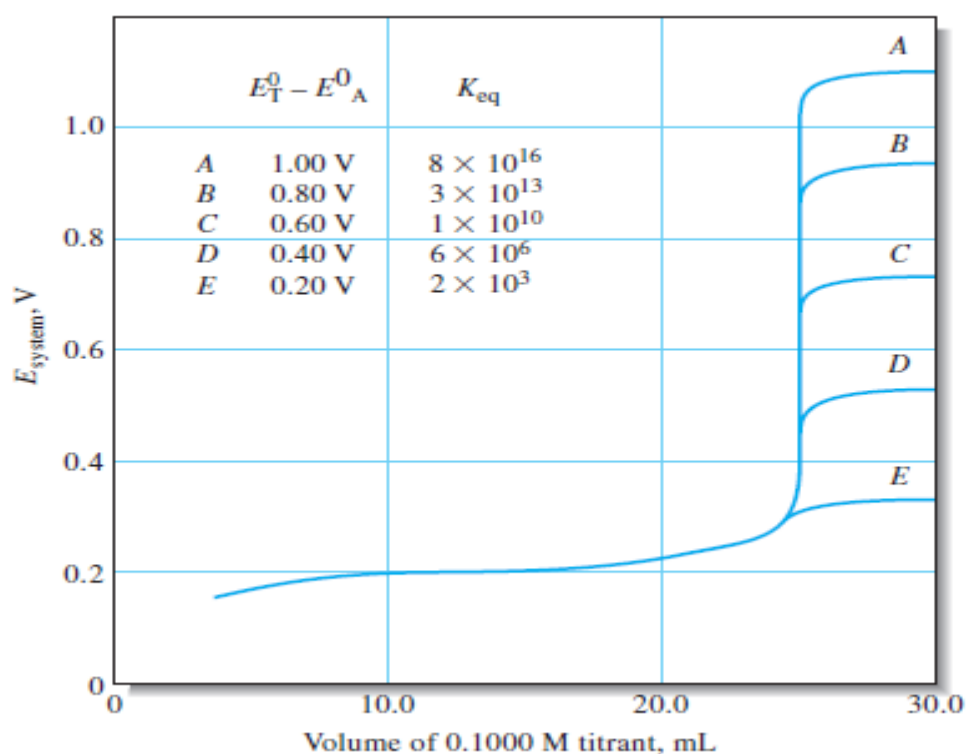
Point B

Effect of Variables on Redox Titration Curves

Reactant Concentration

As we have just seen, E system for an oxidation/reduction titration is usually independent of dilution. Consequently, titration curves for oxidation/reduction reactions are usually independent of analyte and reagent concentrations. This characteristic is in distinct contrast to that observed in the other types of titration curves we have encountered.

Completeness of the Reaction

The change in potential in the equivalence-point region of an oxidation/reduction titration becomes larger as the reaction becomes more complete. This effect is demonstrated by the two curves. The equilibrium constant for the reaction of cerium(IV) with iron(II) is $7 * 10^{12}$ while that for U(IV) is $2 * 10^{37}$.

	$E_T^0 - E_A^0$	K_{eq}
A	1.00 V	8×10^{16}
B	0.80 V	3×10^{13}
C	0.60 V	1×10^{10}
D	0.40 V	6×10^6
E	0.20 V	2×10^3

Volume of 0.1000 M titrant, mL

OXIDATION /REDUCTION INDICATORS

General oxidation/reduction indicators are substances that change color on being oxidized or reduced. In contrast to specific indicators, the color changes of true redox indicators are largely independent of the chemical nature of the analyte and titrant and depend instead on the changes in the electrode potential of the system that occur as the titration progresses. The half-reaction responsible for color change in a typical general oxidation/reduction indicator can be written as

$$In_{ox} + ne^- \rightleftharpoons In_{red}$$

$$E = E^0_{In_{ox}/In_{red}} - \frac{0.0592}{n} \log \frac{[In_{red}]}{[In_{ox}]}$$

Typically, a change from the color of the oxidized form of the indicator to the color of the reduced form requires a change of about 100 in the ratio of reactant concentrations, that is, a color change appears when

$$\frac{[In_{red}]}{[In_{ox}]} \leq \frac{1}{10}$$

$$\frac{[In_{red}]}{[In_{ox}]} \geq 10$$

$$E = E^0_{In} \pm \frac{0.0592}{n}$$

Example of oxidation reduction indicator

- Iron(II) complexes of orthophenontheroline
- Starch /iodine solution

THE CHOICE OF REDOX INDICATOR
SPECIFIC INDICATOR

- STARCH
- AND POTASIUM THIOCYNATE: IRON (III) with titanium (iii)sulfate

APPLICATION OF OXIDATION/REDUCTION TITRATIONS
- Auxiliary reagents
- Preparation of standard solutions of oxidants and reductants
- Applications of these solutions

Auxiliary oxidizing and reducing agents (preoxidant and prereductant)

- Purpose of use :
  the steps precede the titration (e.g. dissolving) convert analyte to a mixture of ox.st. but in redox titration, the analyte must be in single ox. St. at the outset.

- Conditions of use
1- a reagent must react quantitatively with analyte
2- excess reagent must be easily removed

Auxiliary reducing agent

- Metals like Zn, Al, Cd, Ni, Pb, …etc(sticks or coil)
- Reductor
- Jones reductor: column of amalgamated zinc
- Walden reductor: column of silver

Uses of the Walden Reductor and the Jones Reductor*

| Walden $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$	Jones $Zn(Hg)(s) \rightarrow Zn^{2+} + Hg + 2e^-$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
$Cu^{2+} + e^- \rightarrow Cu^+$	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$
$H_2MoO_4 + 2H^+ + e^- \rightarrow MoO_2^+ + 2H_2O$	$H_2MoO_4 + 6H^+ + 3e^- \rightleftharpoons Mo^{3+} + 3H_2O$
$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$	$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$
	$UO_2^{2+} + 4H^+ + 3e^- \rightleftharpoons U^{3+} + 2H_2O^\dagger$
$V(OH)_4^+ + 2H^+ + e^- \rightarrow VO^{2+} + 3H_2O$	$V(OH)_4^+ + 4H^+ + 3e^- \rightleftharpoons V^{2+} + 4H_2O$
TiO^{2+} not reduced	$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$
Cr^{3+} not reduced	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$

Auxiliary oxidizing reagents

- Sodium bismothate

Sodium bismuthate is a powerful oxidizing agent capable, for example, of converting manganese(II) quantitatively to permanganate ion. This bismuth salt is a sparingly soluble solid with a formula that is usually written as NaBiO3, although its exact composition is somewhat uncertain.

$$NaBiO_3(s) + 4H^+ + 2e^- \rightleftharpoons BiO^+ + Na^+ + 2H_2O$$
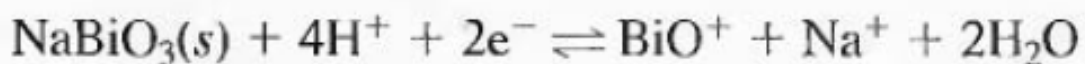
- Mn(II) to MnO_4^- Ammonium peroxysulfate
  Ammonium peroxydisulfate, (NH4)2S2O8, is also a powerful oxidizing agent. In acidic solution, it converts chromium(III) to dichromate, cerium(III) to cerium(IV), and manganese(II) to permanganate. The half-reaction is
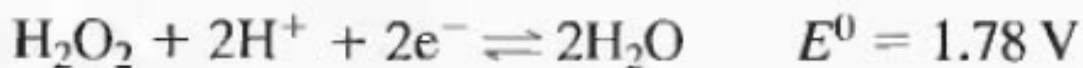
$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$$
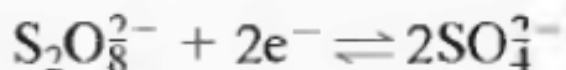
Cr(III) to CrO$_4^-$, Mn(II) to MnO$_4^-$, Ce(III) to Ce(IV) and decompose by boiling

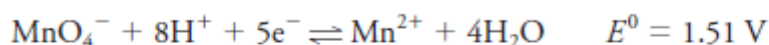$$2S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + O_2(g) + 4H^+$$
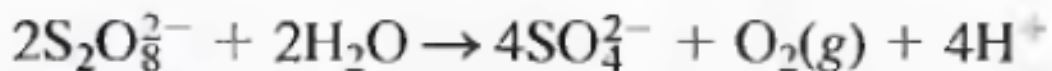
- Sodium peroxide and hydrogen peroxide

Peroxide is a convenient oxidizing agent either as the solid sodium salt or as a dilute solution of the acid. The half-reaction for hydrogen peroxide in acidic solution is

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^0 = 1.78 \text{ V}$$

Good oxidizing agent(potassium permanganate)

Solutions of permanganate ion and cerium(IV) ion are strong oxidizing reagents whose applications closely parallel one another. Half-reactions for the two are

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^0 = 1.51 \text{ V}$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44 \text{ V}(1 \text{ M H}_2SO_4)$$

The formal potential shown for the reduction of cerium(IV) is for solutions that are 1 M in sulfuric acid. In 1 M perchloric acid and 1 M nitric acid, the potentials are 1.70 V and 1.61 V, respectively. Solutions of cerium(IV) in the latter two acids are not very stable and thus find limited application. The half-reaction shown for permanganate ion occurs only in solutions that are 0.1 M or greater in strong acid. In less acidic media, the product may be Mn(III), Mn(IV), or Mn(VI), depending on conditions.

Some Common Oxidants Used as Standard Solutions

Reagent and Formula	Reduction Product	Standard Potential, V	Standardized With	Indicator*	Stability†
Potassium permanganate, $KMnO_4$	Mn^{2+}	$1.51^{\ddagger}$	$Na_2C_2O_4$, Fe, As_2O_3	MnO_4^-	(b)
Potassium bromate, $KBrO_3$	Br^-	$1.44^{\ddagger}$	$KBrO_3$	(1)	(a)
Cerium(IV), Ce^{4+}	Ce^{3+}	$1.44^{\ddagger}$	$Na_2C_2O_4$, Fe, As_2O_3	(2)	(a)
Potassium dichromate, $K_2Cr_2O_7$	Cr^{3+}	$1.33^{\ddagger}$	$K_2Cr_2O_7$, Fe	(3)	(a)
Iodine, I_2	I^-	$0.536^{\ddagger}$	$BaS_2O_3 \cdot H_2O$, $Na_2S_2O_3$	starch	(c)

Detecting the End Points

EXAMPLE 20-3

You wish to standardize the solution in Example 20-2 against primary $Na_2C_2O_4$ (134.00 g/mol). If you want to use between 30 and 45 mL of the reagent for the standardization, what range of masses of the primary standard should you weigh out?

(continued)

Solution

For a 30-mL titration,

$$\text{amount } KMnO_4 = 30 \text{ mL } KMnO_4 \times 0.010 \frac{\text{mmol } KMnO_4}{\text{mL } KMnO_4}$$

$$= 0.30 \text{ mmol } KMnO_4$$

$$\text{mass } Na_2C_2O_4 = 0.30 \text{ mmol } KMnO_4 \times \frac{5 \text{ mmol } Na_2C_2O_4}{2 \text{ mmol } KMnO_4}$$

$$\times 0.134 \frac{\text{g } Na_2C_2O_4}{\text{mmol } Na_2C_2O_4}$$

$$= 0.101 \text{ g } Na_2C_2O_4$$

Proceeding in the same way, we find for a 45-mL titration,

$$\text{mass } Na_2C_2O_4 = 45 \times 0.010 \times \frac{5}{2} \times 0.134 = 0.151 \text{ g } Na_2C_2O_4$$

Thus, you should weigh between 0.10 and 0.15 g samples of the primary standard.

EXAMPLE 20-4

A 0.1278-g sample of primary-standard $Na_2C_2O_4$ required exactly 33.31 mL of the permanganate solution in Example 20-2 to reach the end point. What was the molar concentration of the $KMnO_4$ reagent?

Solution

$$\text{amount } Na_2C_2O_4 = 0.1278 \text{ g } Na_2C_2O_4 \times \frac{1 \text{ mmol } Na_2C_2O_4}{0.13400 \text{ g } Na_2C_2O_4}$$

$$= 0.95373 \text{ mmol } Na_2C_2O_4$$

$$c_{KMnO_4} = 0.95373 \text{ mmol } Na_2C_2O_4 \times \frac{2 \text{ mmol } KMnO_4}{5 \text{ mmol } Na_2C_2O_4} \times \frac{1}{33.31 \text{ mL } KMnO_4}$$

$$= 0.01145 \text{ M}$$

EXAMPLE 20-5

Aqueous solutions containing approximately 3% (w/w) H_2O_2 are sold in drug stores as a disinfectant. Propose a method for determining the peroxide content of such a preparation using the standard solution described in Examples 20-3 and 20-4. Assume that you wish to use between 30 and 45 mL of the reagent for a titration. The reaction is

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$

Solution

The amount of $KMnO_4$ in 35 to 45 mL of the reagent is between

$$\text{amount } KMnO_4 = 35 \text{ mL } KMnO_4 \times 0.01145 \frac{\text{mmol } KMnO_4}{\text{mL } KMnO_4}$$

$$= 0.401 \text{ mmol } KMnO_4$$

and

$$\text{amount } KMnO_4 = 45 \times 0.01145 = 0.515 \text{ mmol } KMnO_4$$

The amount of H_2O_2 consumed by 0.401 mmol of $KMnO_4$ is

$$\text{amount } H_2O_2 = 0.401 \text{ mmol } KMnO_4 \times \frac{5 \text{ mmol } H_2O_2}{2 \text{ mmol } KMnO_4} = 1.00 \text{ mmol } H_2O_2$$

and

$$\text{amount } H_2O_2 = 0.515 \times \frac{5}{2} = 1.29 \text{ mmol } H_2O_2$$

We, therefore, need to take samples that contain from 1.00 to 1.29 mmol H_2O_2.

$$\text{mass sample} = 1.00 \text{ mmol } H_2O_2 \times 0.03401 \frac{g \text{ } H_2O_2}{\text{mmol } H_2O_2} \times \frac{100 \text{ g sample}}{3 \text{ g } H_2O_2}$$
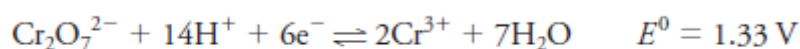
$$= 1.1 \text{ g sample}$$

to

$$\text{mass sample} = 1.29 \times 0.03401 \times \frac{100}{3} = 1.5 \text{ g sample}$$

Thus, our samples should weigh between 1.1 and 1.5 g. These should be diluted to perhaps 75 to 100 mL with water and made slightly acidic with dilute H_2SO_4 before titration.

Potassium Dichromate

In its analytical applications, dichromate ion is reduced to green chromium(III) ion:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^0 = 1.33 \text{ V}$$

Dichromate titrations are generally carried out in solutions that are about 1 M in hydrochloric or sulfuric acid. In these media, the formal potential for the half-reaction is 1.0 to 1.1 V.

Potassium dichromate solutions are indefinitely stable, can be boiled without decomposition, and do not react with hydrochloric acid. Moreover, primary-standard reagent is available commercially and at a modest cost. The disadvantages of potassium dichromate compared with cerium(IV) and permanganate ion are its lower electrode potential and the slowness of its reaction with certain reducing agents.

EXAMPLE 20-6

A 5.00-mL sample of brandy was diluted to 1.000 L in a volumetric flask. The ethanol (C_2H_5OH) in a 25.00-mL aliquot of the diluted solution was distilled into 50.00 mL of 0.02000 M $K_2Cr_2O_7$ and oxidized to acetic acid with heating:

$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$$

After cooling, 20.00 mL of 0.1253 M Fe^{2+} was pipetted into the flask. The excess Fe^{2+} was then titrated with 7.46 mL of the standard $K_2Cr_2O_7$ to a diphenylamine sulfonic acid end point. Calculate the percent (w/v) C_2H_5OH (46.07 g/mol) in the brandy.

Solution

total amount $K_2Cr_2O_7$

$$= (50.00 + 7.46)\ \text{mL } K_2Cr_2O_7 \times 0.02000\ \frac{\text{mmol } K_2Cr_2O_7}{\text{mL } K_2Cr_2O_7}$$

$$= 1.1492\ \text{mmol } K_2Cr_2O_7$$

amount $K_2Cr_2O_7$ consumed by Fe^{2+}

$$= 20.00\ \text{mL } Fe^{2+} \times 0.1253\ \frac{\text{mmol } Fe^{2+}}{\text{mL } Fe^{2+}} \times \frac{1\ \text{mmol } K_2Cr_2O_7}{6\ \text{mmol } Fe^{2+}}$$

$$= 0.41767\ \text{mmol } K_2Cr_2O_7$$

amount $K_2Cr_2O_7$ consumed by C_2H_5OH = $(1.1492 - 0.41767)$ mmol $K_2Cr_2O_7$

amount $K_2Cr_2O_7$ consumed by C_2H_5OH = $(1.1492 - 0.41767)$ mmol $K_2Cr_2O_7$

$$= 0.73153\ \text{mmol } K_2Cr_2O_7$$

mass C_2H_5OH

$$= 0.73153\ \text{mmol } K_2Cr_2O_7 \times \frac{3\ \text{mmol } C_2H_5OH}{2\ \text{mmol } K_2Cr_2O_7} \times 0.04607\ \frac{\text{g } C_2H_5OH}{\text{mmol } C_2H_5OH}$$

$$= 0.050552\ \text{g } C_2H_5OH$$

$$\text{percent } C_2H_5OH = \frac{0.050552\ \text{g } C_2H_5OH}{5.00\ \text{mL sample} \times 25.00\ \text{mL}/1000\ \text{mL}} \times 100\%$$

$$= 40.4\%\ C_2H_5OH$$