Chem 321 Lecture 16 - Potentiometry

10/22/13

Student Learning Objectives

In lab you will use an ion-selective electrode to determine the amount of fluoride in an unknown solution. In this approach, as with pH measurements, the potential of an electrochemical cell is associated with the concentration (actually activity) of a particular ion in the solution being analyzed. In order to properly interpret the chemistry occurring in electrochemical cells, it is usually necessary to be able to assign oxidation numbers and to write balanced redox equations. These concepts are reviewed below.

Assigning Oxidation Numbers

Oxidation is an increase in oxidation number while **reduction** is a decrease in oxidation number. In order to recognize these processes, one must be able to assign proper oxidation numbers to the various elements associated with a particular chemical reaction. Remember that **oxidation number**, or **oxidation state**, is a bookkeeping device used to track electron transfer. The following guidelines will assist you in assigning oxidation numbers.

chemical species	oxidation number
elemental form (e.g., Cu or Br_2)	zero
monatomic ion (e.g., Na^+ or S^{2-})	charge on monatomic ion
chemically combined hydrogen	+1 (notable exception is in a metal hydride such as NaH where ox. no. = -1)
chemically combined oxygen	-2 (notable exception is in a peroxide such as H_2O_2 where ox. no. = -1)
The sum of the oxidation numbers of all atoms in a given chemical species is equal to the net charge on the species.	

Check for Understanding 11.1

Solutions

1. Assign oxidation numbers to all atoms in each of the following.

a) HClO b) $HClO_3$ c) SO_3^{2-} d) $Cr_2O_7^{2-}$ e) Hg_2Cl_2

Guidelines for Balancing Redox Equations

The method presented here is similar to the half-reaction method that is described in general chemistry textbooks. It is easy to apply to redox reactions which take place in aqueous solution, however, one must be careful to follow the sequence of steps exactly.

1. Assign oxidation numbers to all atoms in the equation and determine which substance is being oxidized and which is being reduced (from changes in oxidation numbers). Write separate half-reactions for each process.

2. Balance each half-reaction in the following way.

    a) By using appropriate coefficients, balance all atoms other than hydrogen and oxygen in the basic half-reaction. If hydrogen and/or oxygen are being oxidized or reduced, these atoms should be balanced as well. Keep in mind that atoms, except for hydrogen and oxygen as noted below, may appear in the half-reaction only in the form of substances indicated in the original equation.

    b) Add the necessary number of electrons (to account for the change in oxidation number) to the appropriate side of the equation; to the reactants' side if it is a reduction half-reaction, and to the products' side if it is an oxidation half-reaction.

    c) Balance charge by the addition of H^+ ions if the reaction is in acidic solution, or OH^- ions if the conditions are basic.

    d) Balance the hydrogen and oxygen atoms by the addition of water.

3. Combine the balanced half-reactions so that the electrons cancel exactly on each side of the final equation. This may necessitate multiplying one or both half-reactions by some integer to equalize the number of electrons involved in each half-reaction.

4. Cancel substances common to both sides of the equation.

5. Check to see if both atom and charge balance have been achieved.

Check for Understanding 11.2

Solutions

1. Balance each of the following redox equations and indicate which element is being oxidized and which is being reduced.

   a) $NO_3^-(aq) + Cu(s) \rightleftharpoons NO_2(g) + Cu^{2+}(aq)$ (acidic soln)

   b) $MnO_4^-(aq) + Br^-(aq) \rightleftharpoons MnO_2(s) + BrO_3^-(aq)$ (basic soln)

Electrochemical Cells

A shorthand **line notation** for the description of an electrochemical cell is often used in place of detailed cell diagrams. The general convention is to indicate the cell **anode** on the left and the cell **cathode** on the right. They are usually separated by a pair of vertical parallel lines that signify a **salt bridge**.

$$\text{Anode} \ \| \ \text{Cathode}$$

The anode is always the site of the oxidation half-reaction and the cathode is always the site of the reduction half-reaction. The salt bridge serves as an ion channel that permits charges to move from one electrode to another to maintain electrical neutrality in each half-cell while keeping the half-cell components separate.

The line notation for each half-cell indicates the oxidized and reduced forms of the electroactive substance in the half-cell, along with any special reagent conditions. The substance that serves as the electrical contact between the half cell and the external circuitry is always placed at the extreme left and the extreme right positions in the line notation. Substances that are in contact and in different physical phases are separated by a single vertical line. To illustrate this, consider a cell with an anode that consists of a Ag wire coated with AgCl and immersed in a saturated KCl aqueous solution and a cathode consisting of a platinum wire in contact with an aqueous solution containing Fe^{2+} and Fe^{3+}. The two electrodes are connected by a salt bridge. The line notation below describes this cell.

Anode Cathode

$$\mathrm{Ag(s)}\ \Big|\ \mathrm{AgCl(s)}\ \Big|\ \mathrm{KCl(sat'd)}\ \Big\|\ \mathrm{Fe^{2+}(aq),\ Fe^{3+}(aq)}\ \Big|\ \mathrm{Pt(s)}$$

Note that because neither of the forms of the substance (Fe) that is being reduced in the cathode compartment is a suitable electrical contact for an external circuit a non-reactive electrical conductor like Pt is used for the half-cell contact. Also note that since both Fe^{2+} and Fe^{3+} are in the same phase (aqueous solution) they are separated by a comma and not a vertical line.

This notation indicates that the anode involves the oxidation of Ag in the presence of chloride ion to form AgCl. The anode half reaction is:

anode: $\mathrm{Ag(s)} + \mathrm{Cl^-(aq)} \rightleftharpoons \mathrm{AgCl(s)} + e^-$

In this cell, the reaction at the cathode involves the reduction of Fe^{3+} to Fe^{2+}.

cathode: $\mathrm{Fe^{3+}(aq)} + e^- \rightleftharpoons \mathrm{Fe^{2+}(aq)}$

In this particular electrochemical cell the anode half-cell is a **reference electrode**. A reference electrode is a half-cell with a constant, and usually known, half-cell potential. To see how this is achieved for a reference electrode such as the one above, recall the **Nernst equation** that describes the cell or half-cell potential. For reaction $aA + bB \rightleftharpoons cC + dD$, the potential (E) is given by

$$E = E^0 - \frac{2.303RT}{nF}\log\frac{a_C{}^c a_D{}^d}{a_A{}^a a_B{}^b}$$

where E^0 is the standard cell (or half-cell) potential, R is the universal gas constant, T is the Kelvin temperature, n is the number of moles of electrons involved in the redox process, F is the Faraday and the log term involves the reaction quotient (Q) written using activities. At 25 °C the Nernst equation becomes:

$$E = E^0 - \frac{0.05916}{n}\log\frac{a_C{}^c a_D{}^d}{a_A{}^a a_B{}^b}$$

For the anode half-cell above, the Nernst equation is:

$$E_{ox} = E^{0}_{Ag/AgCl} - \frac{0.05916}{n} \log \frac{1}{a_{Cl^-}}$$

Recall that the **standard half-cell potential** is the electrode potential when all reactants and products are at unit activity (a=1). An extensive list of standard half-cell reduction potentials is posted at **https://www.csun.edu/~hcchm003/321/Ered.pdf**. To get a standard oxidation half-cell potential, reverse the reduction reaction and change the sign of the reduction potential.

Check for Understanding 11.3 **Solution**

1. What is the value for $E^0_{Ag/AgCl}$?

Substituting for E^0 and n in the anode Nernst equation above gives:

$$E_{ox} = -0.222\ V - \frac{0.05916}{1} \log \frac{1}{a_{Cl^-}}$$

This indicates that the half-cell potential depends only on the chloride ion activity present in the electrode compartment. A constant half-cell potential is achieved by constructing the electrode with a large concentration of chloride ion. When a KCl-saturated solution is used, the anode potential is -0.197 V.

Recall that $\Delta G = -nFE$. Thus, a negative potential is associated with a non-spontaneous process ($\Delta G > 0$), and a positive potential is associated with a spontaneous process ($\Delta G < 0$). A strong **oxidizing agent** (a substance that is easily reduced) will have a large, positive reduction half-cell potential (E_{red}). A strong **reducing agent** (a substance that is easily oxidized) will have a large, positive oxidation half-cell potential (E_{ox}).

Electrochemical cells, such as the one used in a pH meter, are often connected so that very little current flows in the cell. Consequently, very little reaction, which could alter the composition of the half-cell, occurs while the cell is being monitored.

In a similar way, the Nernst equation for the cathode is:

$$E_{red} = E^0_{Fe^{3+}/Fe^{2+}} - \frac{0.05916}{n}\log\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} = 0.771\ V - \frac{0.05916}{1}\log\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

The overall cell potential (E_{cell}) is the sum of the half-cell potentials.

$$E_{cell} = E_{ox} + E_{red}$$

For the cell above,

$$E_{cell} = E_{ox} + E_{red} = E_{ref} + 0.771\ V - 0.05916\log\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

Since the potential of the reference electrode (E_{ref}) is fixed, the overall cell potential depends only on the relative Fe^{2+} and Fe^{3+} activities in the anode compartment.

Check for Understanding 11.4

Solution

1. What is the potential expected for the cell when the cathode contains a solution with $[Fe^{2+}] = [Fe^{3+}] = 0.035$ M? Assume a KCl-saturated Ag/AgCl reference electrode and an ionic strength of 0.10 M for the cathode solution.

One analytical application of direct potentiometric measurements is in a potentiometric titration. In such an approach you construct an electrochemical cell that uses the titration solution as one of its electrodes. This is illustrated in the diagram below. In this case, the chloride in a dissolved sample is being titrated with a $AgNO_3$ solution. As the titration proceeds, the concentration (and activity) of Cl^- in solution decreases and this causes a change in the cell potential. By continuously monitoring the cell potential during the titration, it is possible to determine the equivalence point in the titration. In the cell shown in Figure 11.1, the titration solution containing chloride is serving as the cathode.

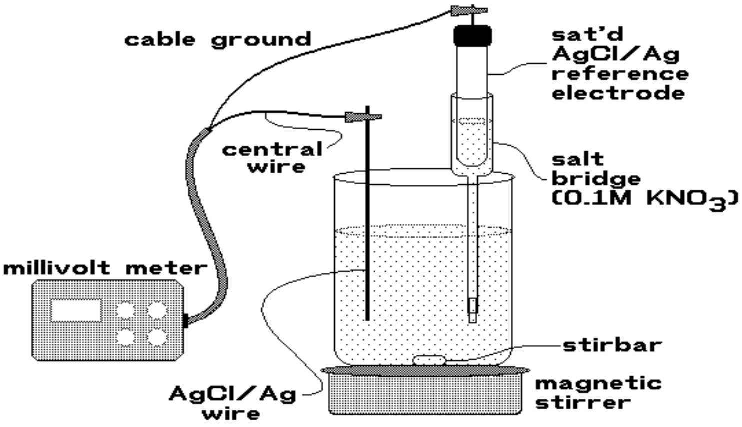

Figure 11.1 Diagram of an electrochemical cell for the potentiometric titration of chloride

Check for Understanding 11.5 **Solutions**

1. What is the line notation for the cell above?
2. What reaction is occurring at the anode? At the cathode?
3. Write the Nernst equation for the anode and cathode half cells and an expression for the overall cell potential.

The potentiometric chloride titration reaction is:

$$Cl^-(aq) \ + \ Ag^+(aq) \ \rightarrow \ AgCl(s)$$

As the titration proceeds, the concentration and activity of chloride ion in the titration solution decrease, which in turn causes E_{red} and E_{cell} to increase (remember that the anode is a reference electrode with a constant half-cell potential). Initially the potential changes only slightly with addition of titrant. However, around the equivalence point the cell potential increases significantly for even small additions of titrant, resulting in a characteristic S-shaped titration curve similar to that found for acid-base titrations (see Fig. 11.2).

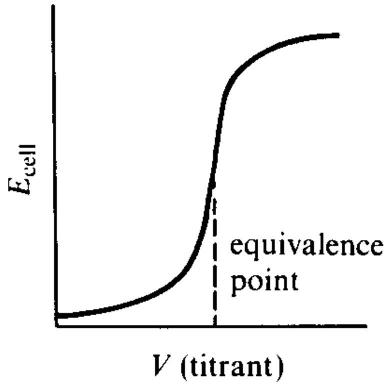

Figure 11.2 Characteristic curve for a potentiometric chloride titration

The equivalence point in a potentiometric chloride titration is at the inflection point in the steep portion of the curve and can be determined by various graphical methods. One can plot the rate of change in the potential per added titrant volume ($\Delta_{Ecell}/\Delta V$) vs. V_{AgNO3} (the average titrant volume) and use the peak center of this pseudo-derivative plot as the equivalence point in this titration (see Fig. 11.3).

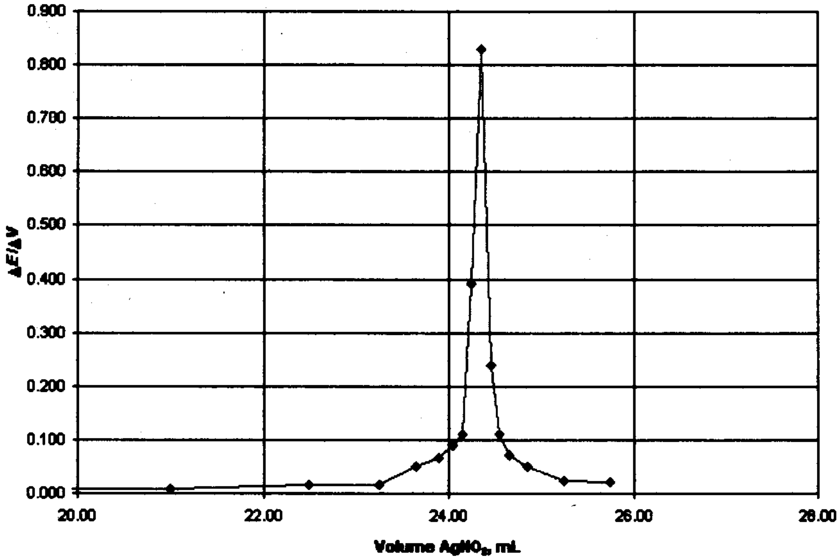

Figure 11.3 Pseudo-derivative plot for a potentiometric chloride titration

Potentiometric titrations such as this also provide a means to measure equilibrium constants. In this case, the K_{sp} for AgCl can be determined. At the equivalence point of the titration, equal amounts of silver ion and chloride ion must be present in the solution (i.e., $[Ag^+] = [Cl^-]$). Since the hydrated ion size is nearly the same for Ag^+ and Cl^-, the activity coefficients of these ions are essentially equal and $a_{Ag+} = a_{Cl-}$ at the equivalence point. The solubility product expression at the equivalence point then becomes:

$$K_{sp} = (a_{Ag+})(a_{Cl-}) = (a_{Cl-})^2$$

The value of a_{Cl-} at the equivalence point can be evaluated from

$$E_{cell} = E_{ref} + 0.222\ V - 0.05916 \log a_{Cl^-}$$

if the cell potential at the equivalence point and the reference half-cell potential are known.

The value of E_{ref} can be determined by measuring E_{cell} under the conditions where the cathode half-cell contains a solution of known potassium chloride concentration and known ionic strength. The chloride ion activity in the equation above is calculated from $a_{Cl}- = [Cl^-]\ \gamma_{Cl-}$, and the equation above is solved for E_{ref}.

Check for Understanding 11.6

Solutions

1. What is the chloride ion activity in a 0.100 M KCl solution?

2. What is the approximate potential expected for the cell when the cathode contains the 0.100 M KCl solution? Assume a KCl-saturated Ag/AgCl reference electrode.

3. What is the approximate cell potential expected at the equivalence point in the chloride titration?