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Chapter 6. Oxidation and reduction
Oxidation Reduction Chemistry
The simplest possible chemical reaction involves the transfer of one or more electrons between two atoms.
In the simple reaction:

\[ 2 \text{Na} + \text{Cl}_2 \rightarrow 2 \text{NaCl} \]

we assume that sodium transfers an electron to chlorine creating the sodium ion and the chloride ion. We can write the two steps of this reaction as:

\[ \text{Na} \rightarrow \text{Na}^{+1} + e^{-1} \]

and

\[ \text{Cl}_2 + 2 e^{-1} \rightarrow 2 \text{Cl}^{-1} \]

The first of these steps involves the loss of an electron and is called an oxidation reaction, while the second step involves the gain of an electron and is called a reduction reaction.
The simple nemonic "Leo goes Ger" or Loss of electrons - oxidation; Gain of electrons - reduction has been used by several generations of students to remember these definitions. (OK! This is Simba, my apologies to Lion King aficionados.)

Oxidation and reduction reactions (usually called redox reactions) are important in biochemistry and important families of enzymes are called reductases or oxidases based on their reduction or oxidation catalysis.

We recognize ethanol as common drinking alcohol, but most people don't realize that ethanol is generated by fermentation reactions that naturally take place in the intestines. The body always has a small amount of ethanol being transported across the intestine walls. As a result, the body has an enzyme to metabolize ethanol called ethanol oxidase. (You might want to think about this. The body didn't invent ethanol to compensate for the consumption of fermented beverages like beer and wine since there are relatively recent on an evolutionary time scale. Ethanol oxidase is present in the body because it had to be there to compensate for the background ethanol. I would suspect that all mammals have this enzyme, not just people. Other things that are ingested by people for their psychotropic effects do not necessarily have enzymes for their detoxification, thus they stay in the tissues longer and have a greater potential for doing damage. If you follow my dictum of not consuming anything for which you don't have an enzyme, you'll be relatively safe.)

Redox chemistry also forms the basis of corrosion chemistry and battery chemistry (electrochemistry).

**Simple electrochemical reactions**

If we take a piece of zinc metal and put it into a beaker of HCl, we will quickly notice the formation of bubbles on the surface of the zinc. Were we to leave the zinc in the acid for several minutes, we'd easily observe that the zinc is being dissolved while a gas is being liberated. This process is illustrated below:
The reaction taking place here is obviously:

\[ \text{Zn} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \]

In this reaction, the hydrogen ions are being reduced while the zinc is being oxidized.

A similar reaction may be observed if we place a zinc bar into a solution containing copper sulfate.

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Zn}^{2+} \]

Again the zinc is being oxidized while the copper is being reduced. Unlike the case of zinc in acid, the reaction will only continue until the copper has formed a film on the surface of the zinc, at which point the reaction stops since zinc ions are no longer able to escape to the solution.

**Rules for assigning oxidation numbers:**

1. The oxidation number of a free element = 0.
2. The oxidation number of a monatomic ion = charge on the ion.
3. The oxidation number of hydrogen = +1 and rarely -1.
4. The oxidation number of oxygen = -2 and in peroxides -1.
5. The sum of the oxidation numbers in a polyatomic ion = charge on the ion.

Elements in group 1, 2, and aluminum are always as indicated on the periodic table.

**K\textsubscript{2}CO\textsubscript{3}**

The sum of all the oxidation numbers in this formula equal 0. Multiply the subscript by the oxidation number for each element.
To calculate O.N. of C
\[ K = (2) \cdot (1) = +2 \]
\[ O = (3) \cdot (-2) = -6 \]
therefore, \( C = (1) \cdot (4) = +4 \)

\[ \text{HSO}_4^- \]

To calculate O.N. of S
The sum of all the oxidation numbers in this formula equal -1. Multiply the subscript by the oxidation number for each element.
\[ H = (1) \cdot (1) = +1 \]
\[ O = (4) \cdot (-2) = -8 \]
therefore, \( S = (1) \cdot (6) = +6 \)

Calculate O.N. in following compounds:
1. Sb in \( \text{Sb}_2\text{O}_5 \)
2. N in \( \text{Al(NO}_3\text{)}_3 \)
3. P in \( \text{Mg}_3(\text{PO}_4)\text{)}_2 \)
4. S in \( (\text{NH}_4\text{)}_2\text{SO}_4 \)
5. Cr in \( \text{CrO}_4^{2-} \)
6. Hg in \( \text{Hg(ClO}_3\text{)}_2 \)
7. B in \( \text{NaBO}_3 \)
8. Si in \( \text{MgSiF}_6 \)
9. I in \( \text{IO}_3^- \)
10. N in \( (\text{NH}_2\text{)}_2\text{S} \)
11. Mn in \( \text{MnO}_4^- \)
12. Br in \( \text{BrO}_3^- \)
13. Cl in \( \text{ClO}^- \)
14. Cr in \( \text{Cr}_2\text{O}_7^{2-} \)
15. Se in \( \text{H}_2\text{SeO}_3 \)

Reducing Agents and Oxidizing Agents

- **Reducing agent** - the reactant that gives up electrons.
- The reducing agent contains the element that is oxidized (looses electrons).
- If a substance gives up electrons easily, it is said to be a **strong reducing agent**.

- **Oxidizing agent** - the reactant that gains electrons.
- The oxidizing agent contains the element that is reduced (gains electrons).
- If a substance gains electrons easily, it is said to be a **strong oxidizing agent**.

\[
\begin{align*}
\text{MnO}_4^- & + \text{H}_2\text{SO}_3 & \rightarrow & \text{Mn}^{2+} + \text{HSO}_4^- \\
+7 & \text{to} & +2 & \text{gain } 5 \text{e}^- \\
+4 & \text{to} & +6 & \text{lose } 2 \text{e}^-
\end{align*}
\]

**Example:** \( \text{Fe}_2\text{O}_3(\text{cr}) + 3\text{CO}_2(\text{g}) \rightarrow 2\text{Fe}(\text{l}) + 3\text{CO}_2(\text{g}) \)

- Notice that the oxidation number of C goes from +2 on the left to +4 on the right.
- The reducing agent is CO, because it contains C, which loses e⁻.
Practice Problems: In any Redox equation, **at least** one particle will gain electrons and **at least** one particle will lose electrons. This is indicated by a change in the particle's oxidation number from one side of the equation to the other. For each reaction below, draw arrows and show electron numbers as in the example here. The top arrow indicates the element that gains electrons, **reduction**, and the bottom arrow indicates the element that loses electrons, **oxidation**. An arrow shows what **one atom** of each of these elements gains or loses.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Check</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg + O(_2) → MgO</td>
<td>check</td>
</tr>
<tr>
<td>Cl(_2) + I → Cl(^-) + I(_2)</td>
<td>check</td>
</tr>
<tr>
<td>MnO(_4)(^-) + C(_2)O(_4) → Mn(^{2+}) + CO(_2)</td>
<td>check</td>
</tr>
<tr>
<td>Cr + NO(_2) → CrO(_2)(^-) + N(_2)O(_2)</td>
<td>check</td>
</tr>
<tr>
<td>BrO(_3)(^-) + MnO(_2) → Br(^-) + MnO(_4)</td>
<td>check</td>
</tr>
<tr>
<td>Fe(^{2+}) + MnO(_4) → Mn(^{2+}) + Fe(^{3+})</td>
<td>check</td>
</tr>
<tr>
<td>Cl(_2) + I → Cl(^-) + I(_2)</td>
<td>check</td>
</tr>
<tr>
<td>NO(_3)(^-) + S → NO(_2) + H(_2)SO(_4)</td>
<td>check</td>
</tr>
<tr>
<td>IO(_4)(^-) + I → I(_2)</td>
<td>check</td>
</tr>
<tr>
<td>NO(_2) + ClO → NO(_3) + Cl(^-)</td>
<td>check</td>
</tr>
</tbody>
</table>

### Balancing Redox Equations by the Half-reaction Method

1. **Decide what is reduced** (oxidizing agent) and **what is oxidized** (reducing agent).

   - Do this by drawing arrows as in the practice problems.

2. **Write the reduction half-reaction.**
   - The top arrow in step #1 indicates the reduction half-reaction.
   - Show the electrons gained on the reactant side.
   - Balance with respect to atoms / ions.
   - To balance oxygen, add H\(_2\)O to the side with the least amount of oxygen. THEN: add H\(^+\) to the other side to balance hydrogen.

3. **Write the oxidation half-reaction.**
   - The bottom arrow in step #1 indicates the oxidation half-reaction.
   - Show the electrons lost on the product side.
   - Balance with respect to atoms / ions.
   - To balance oxygen, add H\(_2\)O to the side with the least amount of oxygen. THEN: add H\(^+\) to the other side to balance hydrogen.

4. **The number of electrons gained must equal the number of electrons lost.**
   - Find the least common multiple of the electrons gained and lost.
   - In each half-reaction, multiply the electron coefficient by a number to reach the common multiple.
   - Multiply all of the coefficients in the half-reaction by this same number.

5. **Add the two half-reactions.**
   - Write one equation with all the reactants from the half-reactions on the left and all the products on the right.
   - The order in which you write the particles in the combined equation does not matter.

6. **Simplify the equation.**
   - Cancel things that are found on both sides of the equation as you did in net ionic equations.
   - Rewrite the final balanced equation.

Check to see that electrons, elements, and total charge are balanced.
Practice Problems:

1. Identify the oxidizing agent and reducing agent in each equation:
   - \( \text{H}_2\text{SO}_4 + 8\text{HI} \rightarrow \text{H}_2\text{S} + 4\text{I}_2 + 4\text{H}_2\text{O} \)
   - \( \text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca(OH)}_2 \)
   - \( \text{Au}_2\text{S}_3 + 3\text{H}_2 \rightarrow 2\text{Au} + 3\text{H}_2\text{S} \)
   - \( \text{Zn} + 2\text{HCl} \rightarrow \text{H}_2 + \text{ZnCl}_2 \)

2. To make working with redox equations easier, we will omit all physical state symbols. However, remember that they should be there. An unbalanced redox equation looks like this:
   \[
   \text{MnO}_4^- + \text{H}_2\text{SO}_4 + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{HSO}_4^- + \text{H}_2\text{O}
   \]
   **Study how this equation is balanced using the half-reaction method.**
   ➡️ It is important that you understand what happens in each step.
   ➡️ Be prepared to ask questions about this process in class tomorrow.

Extraction of Elements

Electrolysis

6.1 Elements extracted by reduction (Metal Extraction)

Practical applications of electrolysis include the extraction of metals (e.g., sodium), the manufacture of compounds (e.g., sodium hydroxide), and both the electroplating and purification of metals (e.g., copper). These applications make use, indirectly, of two laws of electrolysis determined by Michael Faraday (1791 - 1867). His First Law states 'that the mass of a substance produced at an electrode during electrolysis is proportional to the quantity of electricity passed'. And his Second Law states 'that the quantity of electricity required to produce one mole of a substance from its ions is proportional to the charge on those ions'. Together, these two laws are summarized by two nifty equations, \( Q = I \times t \) and \( Q = n \times z \times F \)

where: \( Q \), measured in coulombs (C), is the quantity of electricity; \( I \), measured in amps (A), is the current; \( t \), measured in seconds (s), is the time; \( n \) is the number of moles of substance produced at the electrode; \( z \) is the charge on the ion; and, \( F \) is a constant, with a value of 96500 C mol\(^{-1}\).

This diagram shows a circuit, which includes three electrolytic cells connected in series, through which a current of 0.75 A was passed for 45 minutes; so, the quantity of electricity \( Q \) which passed through this circuit was: \( Q = I \times t = 0.75 \times 45 \times 60 = 2025 \) C. And the results of this experiment are summarized in the Table below; its careful study should prove rewarding.
Electrolysis of Molten salt

Molten salt electrolysis is the electrolytic decomposition of a compound dissolved in an ionic melt. The prime example of this process can be found in the production of aluminum. The compound, alumina (Al2O3), derived from the mineral bauxite, is dissolved in an ionic melt comprising a multicomponent solution of cryolite (Na3AlF6), aluminum fluoride (AlF3), and calcium fluoride (CaF2). The products of electrolysis are molten aluminum and carbon dioxide, the latter due to the attendant consumption of the carbon anode. Primary aluminum is produced in a reactor known as the Hall cell. Alternatively, the compound undergoing electrolytic decomposition can be derived from waste. Processing in molten salts, with their capacity to dissolve materials to very high concentrations compared to those attainable in aqueous solutions, can be rather advantageous.

Aluminum compounds, primarily the oxide in forms of various purity and hydration, are fairly widely distributed in nature. The feldspars, the most common rock-forming silicates, make up nearly 54% of the earth's crust; in these, aluminum has replaced up to half the silicon atoms in SiO2. The major ore of aluminum is bauxite, a hydrated aluminum (III) oxide (Al2O3.xH2O).

In the industrial Bayer process, bauxite is concentrated to produce aluminum hydroxide. When this concentrate is calcined at temperatures in excess of 1000°C, anhydrous aluminum oxide, Al2O3, is formed. Anhydrous aluminum oxide melts at over 2000°C. This is too high to permit its use as a molten medium for electrolytic formation of free aluminum. The electrolytic process commercially used to produce aluminum is known as the Hall process, named after its inventor, Charles M. Hall. The purified Al2O3 is dissolved in molten cryolite, Na3AlF6, which has a melting point of 1012°C and is an effective conductor of electric current. In the following schematic diagram of the electrolysis cell graphite rods are employed as anodes and are consumed in the electrolysis process. The cell electrolytic reaction is:

$$2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al}(l) + 3\text{CO}_2(g)$$
Typical Hall process electrolysis cell used to reduce aluminum. Because molten aluminum is more dense than the molten mixture of Na₃AlF₆ and Al₂O₃, the metal collects at the bottom of the cell. (reference)

The cells are designed to use 8,000 A and upwards, and a given cell requires about 5 V although only 2.1 V are theoretically required to decompose aluminum oxide. The excess 2.9 V, plus the heat of combustion of carbon, is used as heat to keep the cell warm. The production of one ton of aluminum requires about 65-70 GJ (18-20 MWh) and about half a ton of carbon. The process is generally nonpolluting but is a heavy consumer of electricity with approximately 36% of the electricity used in the Faradaic process, the rest being lost as heat.

**Copper**

**The Extraction of Copper**

Copper is extracted from its ore by two principal methods:

1. Pyrometallurgical method
2. Hydrometallurgical method

**Pyrometallurgical Method**

This technique is often used in the extraction of sulphide ores. There are four main stages:

- **Mining and Milling**
  The ore is crushed and ground into a powder usually containing less than 1% copper. Minerals are concentrated into a slurry that is about 15% copper.
  Copper minerals are separated from useless material by flotation using froth forming solutions.
- **Smelting**
  Smelting of the copper concentrate and extraction by heat, flux and addition of oxygen. Sulphur, iron and other undesirable elements are removed and the product is called blister copper.
- **Refining**
  This is the final stage in the process for obtaining high grade copper. Fire and electro-refining methods are the techniques used. The latter produces high purity copper fit for electrical uses.

**Hydrometallurgical Method -SX/EW**

Solvent Extraction / Electrowinning is the most dominant leaching process used today in the recovery of copper from chemical solutions. As the name suggests the method involves two major stages:
Solvent Extraction - the process by which copper ions are leached or otherwise extracted from the raw ore using chemical agents.

Electrowinning - electrolysis of a metal ion containing solution such that Cu ions within it are plated onto the cathode and thereafter removed in elemental form.

The process takes place in the following steps:

- A lixivant (leaching solution) is selected for use in leaching Cu ions from the ore. Common reagents are weak acids e.g. H$_2$SO$_4$, H$_2$SO$_4$ + Fe$_2$(SO$_4$)$_3$, acidic chloride solutions e.g. FeCl$_2$, ammonium chloride and ammonium salt compositions.
- When applied to the ore the chosen lixivant dissolves the copper ions present to give a lixivant product called a "pregnant leach solution".
- An organic extractant is then selected to remove Cu ions from the aqueous solution. Preferred organic extractants consist of hydroxyphenyl oximes having the basic chemical formula: C$_6$H$_3$(R)(OH)CNOHR*, R= C$_9$H$_{19}$ or C$_{12}$H$_{25}$ and R*= H, CH$_3$, or C$_6$H$_5$

Examples of such extractants are 5-nonyl salicylaldoxime and a mixture of this compound and 2-hydroxy-5-nonyl-acetophenone oxime. The commercially available reagents usually contain 5%-10% of the oxime in a 90-95% petroleum dilutant such as kerosene.

Prior to mixing with lixivant product the extractant will contain little or no copper and is at this stage called the "barren organic extractant".

- Copper ions are transferred from the leaching solution to the organic extractant upon mixing of the two reagents. A phase separation takes place to give an aqueous and an organic phase termed the first aqueous and first organic phases respectively. The first aqueous phase, the "raffinate", is the lixivant stripped of its copper ions while the first organic phase is the "loaded organic extractant" i.e. extractant with copper ions present.
- The raffinate is recycled to the leaching pad while the loaded organic extractant is mixed with an electrolyte solution called the "lean electrolyte" (i.e. containing no copper). Typical electrolytes are acidic solutions such as sulphuric acid, H$_2$SO$_4$. The copper ions that were present in the organic extractant thus dissolve in the electrolyte solution to give a copper containing "rich electrolyte." Here again there is a phase separation. The second organic phase is the barren organic extractant while the second aqueous phase is the "rich electrolyte". The barren organic extractant is then recycled for reuse in application to lixivant product.

The final stage of the process is the electrolysis of the acidic metal ion solution. As a result dissolved copper ions become plated onto the cathode and elemental copper is removed. The recovery process is thus complete.

**Alkali Metals**

These elements are too reactive to be found free in nature. Sodium occurs mainly as NaCl (salt) in sea-water and dried-up sea beds. Potassium is more widely distributed in minerals such as sylvite, KCl, but is also extracted from sea-water. The alkali metals are so reactive they cannot be displaced by another element, so are isolated by electrolysis of their molten salts.

**Iron**

**Extraction of Iron in a Blast Furnace**

The significant reactions occurring within the Blast Furnace can be described via the following steps:

1. Iron is extracted from its ores by the chemical reduction of iron
oxides with carbon in a furnace at a temperature of about 800°C; overall, the processes can be summarized by these equations:

\[
\begin{align*}
2Fe_2O_3(s) + 3C(s) & \xrightarrow{\Delta} 4Fe(l) + 3CO_2(g) \\
Fe_3O_4(s) + 2C(s) & \xrightarrow{\Delta} 3Fe(l) + 2CO_2(g)
\end{align*}
\]

Coke, the source of chemical energy in the blast furnace, is burnt both to release heat energy and to provide the main reducing agent:

\[
\begin{align*}
C(s) + O_2(g) & \xrightarrow{\Delta} CO_2(g) \quad \Delta H = -394 \text{ kJ mol}^{-1} \\
2C(s) + O_2(g) & \xrightarrow{\Delta} 2CO(g)
\end{align*}
\]

Calcium oxide, formed by thermal decomposition of limestone, reacts with the silicon oxide present in sand, a major impurity in iron ores, to form slag (which is less dense than molten iron):

\[
\begin{align*}
CaCO_3(s) & \xrightarrow{\Delta} CaO(s) + CO_2(g) \\
CaO(s) + SiO_2(s) & \xrightarrow{\Delta} CaSiO_3(l)
\end{align*}
\]

(a) Label this diagram of an iron blast furnace with: Blast of hot air; Molten iron; Molten slag; Outlet for iron; Outlet for slag; Reactants (iron ore, coke, and limestone); and, Waste gas outlet.

### The Blast Furnace

- **At 500°C**
  - \(3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2\)
  - \(Fe_2O_3 + CO \rightarrow 2FeO + CO_2\)

- **At 850°C**
  - \(Fe_3O_4 + CO \rightarrow 3FeO + CO_2\)

- **At 1000°C**
  - \(FeO + CO \rightarrow Fe + CO_2\)

- **At 1300°C**
  - \(CO_2 + C \rightarrow 2CO\)

- **At 1900°C**
  - \(C + O_2 \rightarrow CO_2\)
  - \(FeO + C \rightarrow Fe + CO\)

---

### Introduction to Metal Deposition

The application of a plate, or coat, of metal to a surface for decoration, reflection of light, protection against corrosion, or increased wearing quality. The practice is of ancient origin. Romans soldered silver plates to articles of baser metals and in the 5th century iron weapons were coated with copper by dipping them in a copper solution. During the 18th century, plating of copper or brass with silver by fusion started in England.
Plating by electrolysis, or electroplating, is quite commonly used mostly because it permits the control of the thickness of the plating. Cadmium, zinc, silver, gold, tin, copper, nickel, and chromium are the most frequently used plating metals.

Any of the common metals and some nonmetals, e.g., plastics, with suitably prepared surfaces can be used as a base.

In electroforming, a mold made of specially prepared wax is electroplated. The wax is then melted and the plating itself constitutes the finished product. The part to be plated may be dipped in molten metal:

- molten zinc is used in galvanizing
- lead-tin alloy, in terneplating
- tin, in tinning.

Without electricity, some metals can be precipitated from chemical solutions onto the surface of plastics or metals. A powdered, liquid, or gaseous plating metal can be made to diffuse into a heated base-metal surface.

Sherardizing is the diffusion coating of zinc on steel
Chromizing, chromium on steel
Calorizing, aluminum on steel.

The application by welding or brazing of a sheet or plate to the base metal is called cladding.

Decorative metal coatings are applied to plastic by vapor deposition. The metal, usually aluminum, and the plastic parts are put in a vacuum chamber. When aluminum is vaporized by a surge of electricity, the particles settle on exposed surfaces. Worn parts can be sprayed with molten metal to build them up to their original dimensions.

Silvering of mirrors is a type of plating in which silver is precipitated chemically on glass.

6.2 Elements extracted by oxidation

Reduction potentials
6.3 Redox half-reactions
6.4 Kinetic factors

Redox stability in water
6.5 Reactions with water
6.6 Disproportionation
6.7 Oxidation by atmospheric oxygen

The diagrammatic presentation of potential data

Ellingham diagram

It is possible to use plots of the free energy of formation of metal oxides vs. temperature to predict the temperatures at which a metal is stable and the temperatures at which it will spontaneously oxidize. For temperatures at which the free energy of formation of the oxide is positive, the reverse reaction is favored and the oxide will spontaneously decompose to the metal.
From evaluation of the thermodynamic data presented in this figure, it can be seen that at 1100°C, Al will oxidize in an environment that has an oxygen partial pressure of $10^{-32}$ atm or greater, while chromium will oxidize in an oxygen partial pressure of $10^{-19}$ atm or higher. In general, a vacuum environment will be oxidizing to these elements unless a reducing species such as hydrogen is present. If inadequate oxygen is present, a non-protective oxide film may be formed which could promote alloy depletion and loss of strength.

6.8 Latimer diagrams

A Latimer diagram provides us a concise way of presenting a great deal of information about the various oxidation states of the elements. Below is a Latimer diagram for chlorine in acid solution. The potentials that are given are the reduction potential for going from the species at the left of a line to the one at the right of the line.

![Latimer Diagram](image)

The arrow connecting $\text{ClO}_4^-$ and $\text{ClO}_3^-$ represents the half-reaction

$$\text{ClO}_4^- + 1.20 \rightarrow \text{ClO}_3^- + 1.18$$

$$\text{ClO}_2 + 1.70 \rightarrow \text{HClO} + 1.63$$

$$\text{Cl}_2 + 1.36 \rightarrow \text{Cl}^-$$

You can easily use a Latimer diagram to determine the reduction potential for half-reactions between non-adjacent species. This procedure is different from what you are accustomed to doing when you add two half-reactions in order to generate an overall reaction with no excess electrons. In that case, you simply add the $E^0$'s for the two half reactions. In the case of making a new half-reaction, a reaction that has electrons on one side or the other, you need to remember that the relation between free energy and $E^0$ is $\Delta G^0 = -nF E^0$. Therefore when you add two half-reactions where the electrons do not cancel, the potential of the resultant reaction is given by
As an example, to go from HClO to Cl\(^-\) the potential would be given by
\[ E^0 = \frac{n_1 E^{0_1} + n_2 E^{0_2}}{n_1 + n_2} \]

You can also use Latimer diagrams to predict whether or not a particular form of an element will be stable in solution, or will undergo a disproportionation reaction. Look at a species in a Latimer diagram. If the potential going to the right is more positive than that going to the left, the species is unstable and will undergo, slowly or quickly, a disproportionation reaction. For example, looking at the diagram above you can see that ClO\(_2\) will disproportionate to HClO and ClO\(_3^-\). The Latimer diagram will not tell us if the disproportionation will be fast or slow, that is kinetics.

Here is a Latimer diagram for manganese in acidic solution.

\[
\begin{align*}
\text{MnO}_4^- & \rightarrow \text{MnO}_4^{2-} \quad 0.65 \\
\text{MnO}_4^{2-} & \rightarrow \text{MnO}_2^- \quad 0.27 \\
\text{MnO}_2^- & \rightarrow \text{MnO}_2 \quad 4.27 \\
\text{MnO}_2 & \rightarrow \text{Mn}^{2+} \quad 0.56 \\
\text{Mn}^{2+} & \rightarrow \text{Mn} \quad 1.10
\end{align*}
\]

Answer the following based on this diagram:

1. Write the full half-reaction for each step in the diagram.
2. Calculate the potential for going from MnO\(_4^-\) to Mn\(^{2+}\).
3. Which species, if any, will undergo disproportionation in solution?
   The potential given here are for reactions in the standard state, which means that [H\(^+\)] = 1M, among other things. Recalculate the Latimer diagram at pH=3.

### 6.9 Frost diagrams

**Frost Diagrams**

Frost or oxidation state diagrams plot the relative free energy of a species versus oxidation state. These diagrams visually show quite a bit about the properties of the different oxidation states of a species. Frost diagrams can be constructed from Latimer diagrams. The values to be plotted on the y-axis are obtained by multiplying the number of electrons transferred during an oxidation state change by the standard reduction potential for that change.

![The Frost Diagram for Manganese](image)

**What You Can and Cannot Learn From a Frost Diagram:**
- Thermodynamic stability is found at the bottom of the diagram. Thus, the lower a species is positioned on the diagram, the more thermodynamically stable it is (from an oxidation-reduction perspective). Mn (II) is the most stable species.

- A species located on a convex curve can undergo disproportionation. MnO$_4^-$ and Mn (III) tends to disproportionate.

- Those species on a concave curve do not typically disproportionate. MnO$_2$ does not disproportionate.

- Any species located on the upper left side of the diagram will be a strong oxidizing agent. MnO$_4^-$ is a strong oxidizer.

- Any species located on the upper right side of the diagram will be a reducing agent. Manganese metal is a moderate reducing agent.

- These diagrams describe the thermodynamic stability of the various species. Although a given species might be thermodynamically unstable toward reduction, the kinetics of such a reaction might be very slow. Although it is thermodynamically favorable for permanganate ion to be reduced to Mn (II) ion, the reaction is slow except in the presence of a catalyst. Thus, solutions of permanganate can be stored and used in the laboratory.

- The information obtained from a Frost diagram is for species under standard conditions (pH=0 for acidic solution and pH=14 for basic solution). Changes in pH may change the relative stabilities of the species. The potential of any process involving the hydrogen ion will change with pH because the concentration of this species is changing. Under basic conditions aqueous Mn$^{2+}$ does not exist. Instead Insoluble Mn(OH)$_2$ forms.

### Pourbaix Diagrams

Pourbaix or eh-pH diagrams depict the thermodynamically form of an element as a function of potential and pH. The Pourbaix diagram is a type of predominance diagram – it shows the predominate form in an element will exist under a given set of environmental conditions. These diagrams give a visual representation of the oxidizing and reducing abilities of the major stable compounds of an element and are
used frequently in geochemical, environmental and corrosion applications. Like Frost diagrams, Pourbaix diagrams display thermodynamically preferred species. Kinetics is not incorporated.

**How to Read a Pourbaix Diagram**

- Vertical lines separate species that are in acid-base equilibrium.
- Non vertical lines separate species related by redox equilibria.
  - Horizontal lines separate species in redox equilibria not involving hydrogen or hydroxide ions.
  - Diagonal boundaries separate species in redox equilibria in which hydroxide or hydrogen ions are involved.
- Dashed lines enclose the practical region of stability of the water solvent to oxidation or reduction.

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**Pourbaix Diagram for Manganese**

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**What You Can Learn From a Pourbaix Diagram**

- Any point on the diagram will give the thermodynamically most stable (and theoretically most abundant) form of that element at a given potential and pH condition.
- Strong oxidizing agents and oxidizing conditions are found only at the top of Pourbaix diagrams. Strong oxidizing agents have lower boundaries that are also high on the diagram. Permanganate is an oxidizing agent over all pH ranges. It is very strongly oxidizing at low pH.
- Reducing agents and reducing conditions are found at the bottom of a diagram and not elsewhere. Strong reducing agents have low upper boundaries on the diagram. Manganese metal is a reducing agent over all pH ranges and is strongest in basic conditions.
- When the predominance area for a given oxidation state disappears completely above or below a given pH and the element is in an intermediate oxidation state, the element will undergo disproportionation. MnO$_4$ is tends to disproportionate. A species that ranges from the top to the bottom of the diagram at a given pH will have no oxidizing or reducing properties at that pH.
6.10 pH dependence
The effect of complex formation on potentials

**STANDARD REDUCTION POTENTIALS (in Volts), 25°C**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E^o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_2 + 2e^- \rightarrow 2F^-)</td>
<td>+2.87</td>
</tr>
<tr>
<td>(Co^{3+} + e^- \rightarrow Co^{2+})</td>
<td>+1.80</td>
</tr>
<tr>
<td>(PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4(s) + 2H_2O)</td>
<td>+1.69</td>
</tr>
<tr>
<td>(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)</td>
<td>+1.49</td>
</tr>
<tr>
<td>(PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{3+} + 2H_2O)</td>
<td>+1.46</td>
</tr>
<tr>
<td>(Cl_2 + 2e^- \rightarrow 2Cl^-)</td>
<td>+1.36</td>
</tr>
<tr>
<td>(Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O)</td>
<td>+1.33</td>
</tr>
<tr>
<td>(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O)</td>
<td>+1.23</td>
</tr>
<tr>
<td>(Br_2 + 2e^- \rightarrow 2Br^-)</td>
<td>+1.07</td>
</tr>
<tr>
<td>(NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O)</td>
<td>+0.96</td>
</tr>
<tr>
<td>(Hg^{2+} + 2e^- \rightarrow Hg)</td>
<td>+0.85</td>
</tr>
<tr>
<td>(Ag^+ + e^- \rightarrow Ag)</td>
<td>+0.80</td>
</tr>
<tr>
<td>(Ag^+ + e^- \rightarrow Ag)</td>
<td>+0.80</td>
</tr>
<tr>
<td>(Fe^{3+} + e^- \rightarrow Fe^{2+})</td>
<td>+0.77</td>
</tr>
<tr>
<td>(I_2 + 2e^- \rightarrow 2I^-)</td>
<td>+0.54</td>
</tr>
<tr>
<td>(Cu^+ + e^- \rightarrow Cu)</td>
<td>+0.52</td>
</tr>
<tr>
<td>(Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-})</td>
<td>+0.36</td>
</tr>
<tr>
<td>(Cu^{2+} + 2e^- \rightarrow Cu)</td>
<td>+0.34</td>
</tr>
<tr>
<td>(Cu^{2+} + e^- \rightarrow Cu^+)</td>
<td>+0.15</td>
</tr>
<tr>
<td>(Sn^{4+} + 2e^- \rightarrow Sn^{3+})</td>
<td>+0.15</td>
</tr>
<tr>
<td>(2H^+ + 2e^- \rightarrow H_2)</td>
<td>0.00</td>
</tr>
<tr>
<td>(Fe^{3+} + 3e^- \rightarrow Fe)</td>
<td>-0.04</td>
</tr>
<tr>
<td>(Pb^{2+} + 2e^- \rightarrow Pb)</td>
<td>-0.13</td>
</tr>
<tr>
<td>(Sn^{4+} + 2e^- \rightarrow Sn)</td>
<td>-0.14</td>
</tr>
<tr>
<td>(Ni^{2+} + 2e^- \rightarrow Ni)</td>
<td>-0.25</td>
</tr>
<tr>
<td>(Co^{2+})</td>
<td></td>
</tr>
</tbody>
</table>
### Electrochemical Cell Potentials

This topic would be covered in much more detail in a course on electrochemistry/analytical chemistry. Suffice it to say:

\[ \Delta G^\circ = -nF\Delta E^\circ \]

where \( \Delta E^\circ \) is the potential difference between two electrodes, \( n \) is the number of electrons in the redox process and \( F \) is the faraday, 96 486.7 C mol\(^{-1}\)

**Oxidation number answers:**

1. Sb\(^{+5}\)  
2. N\(^{+5}\)  
3. P\(^{+5}\)  
4. S\(^{+6}\)  
5. Cr\(^{+6}\)  
6. Cl\(^{+6}\)  
7. B\(^{+5}\)  
8. Si\(^{+4}\)  
9. I\(^{+5}\)  
10. N\(^{-3}\)  
11. Mn\(^{+7}\)  
12. Br\(^{+5}\)  
13. Cl\(^{+1}\)  
14. Cr\(^{+6}\)  
15. Se\(^{+4}\)

**Oxidizing and reducing agents:**

a. oxidizing agent - H\(_2\)SO\(_4\) || reducing agent - HI

b. oxidizing agent - H\(_2\)O || reducing agent - CaC\(_2\)

c. oxidizing agent - Au\(_2\)S\(_3\) || reducing agent - H\(_2\)  
   oxidizing agent - HCl || reducing agent - Zn

**Balanced Redox Equations:**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(^{2+}) + 2e(^-) → Co</td>
<td>-0.29</td>
</tr>
<tr>
<td>PbSO(_4) + 2e(^-) → Pb + SO(_4^{2-})</td>
<td>-0.359</td>
</tr>
<tr>
<td>PbI(_2) + 2e(^-) → Pb + 2I(^-)</td>
<td>-0.365</td>
</tr>
<tr>
<td>Cr(^{3+}) + e(^-) → Cr(^{2+})</td>
<td>-0.40</td>
</tr>
<tr>
<td>Cd(^{2+}) + 2e(^-) → Cd</td>
<td>-0.40</td>
</tr>
<tr>
<td>Fe(^{2+}) + 2e(^-) → Fe</td>
<td>-0.41</td>
</tr>
<tr>
<td>Cr(^{3+}) + 3e(^-) → Cr</td>
<td>-0.74</td>
</tr>
<tr>
<td>Zn(^{2+}) + 2e(^-) → Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>2H(_2)O + 2e(^-) → H(_2)(g) + 2OH(^-)</td>
<td>-0.83</td>
</tr>
<tr>
<td>V(^{2+}) + 2e(^-) → V</td>
<td>-1.18</td>
</tr>
<tr>
<td>Mn(^{3+}) + 2e(^-) → Mn</td>
<td>-1.18</td>
</tr>
<tr>
<td>Al(^{3+}) + 3e(^-) → Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Mg(^{2+}) + 2e(^-) → Mg</td>
<td>-2.37</td>
</tr>
</tbody>
</table>
1. Define the following in your own words: oxidation, reduction, oxidising agent, reducing agent, oxidant, reductant, redox, ionic half equation, oxidation number, complex ion, systematic nomenclature, aqua complex, ligand, deprotonation, hydrated cation, ligand exchange, transition metal, chelation
2. Classify ionic half equations as involving oxidation or reduction.
3. Write balanced chemical equations for redox reactions from half equations.
4. Recall rules for working out oxidation number.
5. Work out the oxidation number of an element in an ion or a molecule.
6. Write electronic configurations of elements Ti to Cu given a periodic table.
7. Write electronic configurations for ions of Ti to Cu given a periodic table.
8. List typical properties of transition and non-transition metals.
   * List properties caused by incomplete d orbitals.
9. Draw the bonding in some common complex ions.
10. Name the colours of common aqua complexes.
11. Write equations for the reactions of transition metal ions with NaOH(aq) or NH₃(aq).
12. Describe the colours of hydroxides of common transition metals.
13. Classify reactions as involving deprotonation or ligand exchange.
14. List the colours of vanadium ions.
15. Describe an experiment to interconvert vanadium ions.
16. Describe an experiment to make anhydrous FeCl₂ and FeCl₃.
17. List industrial processes which use transition metal catalysts.
18. List some common ionic half equations.
19. Name positive complex ions of transition metals given formulae.
20. Work out formulae of positive complex ions of transition metals from the name.
21. Identify solutions from their reactions with NaOH(aq) or NH₃(aq).
22. Write equations to show the redox reactions of vanadium when used as a catalyst.
23. Identify stable electronic configurations of transition metals and ions.
24. Describe the effect of oxygen on aqueous iron II ions.