Faculty of science

Oxidation Reduction (**Redox**) Reactions

3rd -Year Students, General- Science
Course Code: 317 Chem.

Date: March 15, 2020

Oxidation Reduction (Redox) Reaction

•An oxidation-reduction (redox) reaction occur when the reactants undergo change in their oxidation numbers.

•Oxidation: describes increase in oxidation number, a process resulting from a loss of electrons.

•Reduction: describes a decrease in oxidation number, a process resulting from a gain of electrons.

•The substance causing the oxidation is called the oxidizing agent or oxidant

•The substance causing the reduction is called reducing agent or reductant.

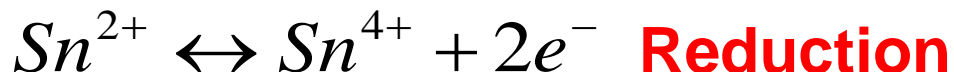# Example: The oxidation of Tin (II) by Fe(III)

$$2Fe^{3+} + Sn^{2+} \leftrightarrow Sn^{4+} + 2Fe^{2+}$$

**Oxidizing agent**

Reducing agent

- Sn^{2+} is oxidized by the oxidizing agent, Fe^{3+} and Fe^{3+} is reduced by the reducing agent Sn^{2+}

- A half-reaction is simply a representation of the oxidation or reduction process.

$$Fe^{3+} + e^- \leftrightarrow 2Fe^{2+}$$ **Oxidation**

$$Sn^{2+} \leftrightarrow Sn^{4+} + 2e^-$$ **Reduction**

Half-Reaction Method for Balancing Redox Reactions

- Divide the reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species.

- Balance the atoms and charges in each half-reaction.
  - First balance atoms other than O and H, then O, then H.
  - Balance the electrons at both sides of half reaction.

- If necessary, multiply one or both half-reactions by an integer so that
  - number of e^- gained in reduction = number of e^- lost in oxidation
- Add the balanced half-reactions, and include states of matter.

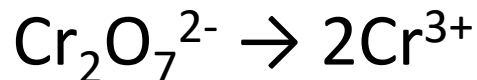# Example: Balancing Redox Reactions in Acidic Solution
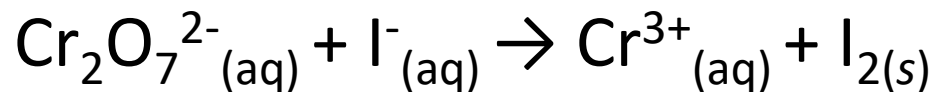
$$Cr_2O_7{}^{2-}{}_{(aq)} + I^-{}_{(aq)} \rightarrow Cr^{3+}{}_{(aq)} + I_{2(s)}$$

Step 1: Divide the reaction into half-reactions.
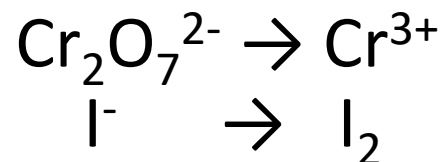
$$Cr_2O_7{}^{2-} \rightarrow Cr^{3+}$$
$$I^- \rightarrow I_2$$

Step 2: Balance the atoms and charges in each half-reaction.

For the $Cr_2O_7{}^{2-}/Cr^{3+}$ half-reaction:

Balance atoms other than O and H:
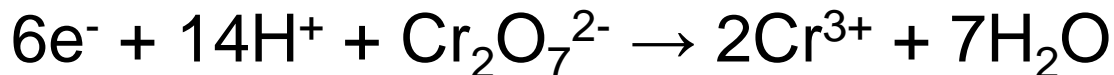
$$Cr_2O_7{}^{2-} \rightarrow 2Cr^{3+}$$

Balance O atoms by adding H_2O molecules:

$$Cr_2O_7{}^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

Balance H atoms by adding H^+ ions:

$$14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

Balance charges by adding electrons:

$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
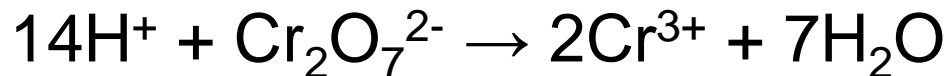
This is the *reduction* half-reaction. $Cr_2O_7^{2-}$ is reduced, and is the oxidizing agent. The O.N. of Cr decreases from +6 to +3.

For the I^-/I_2 half-reaction:

Balance atoms other than O and H:

$$2I^- \rightarrow I_2$$

Balance the electrons
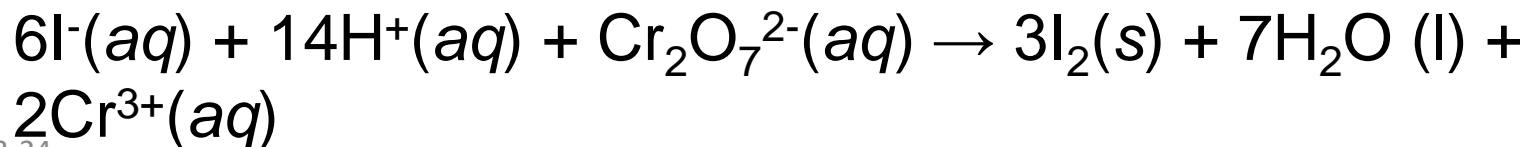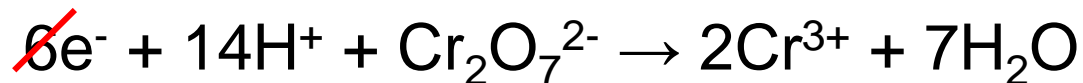
$$2I^- \rightarrow I_2 + 2e^-$$
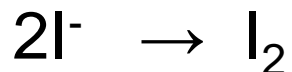
This is the *oxidation* half-reaction. I^- is oxidized, and is the reducing agent. The O.N. of I increases from -1 to 0.

Step 3: Multiply each half-reaction, by an integer so that the number of e⁻ lost in the oxidation equals the number of e⁻ gained in the reduction.

The reduction half-reaction shows that 6e⁻ are gained; the oxidation half-reaction shows only 2e⁻ being lost and must be multiplied by 3:

$$3(2I^- \rightarrow I_2 + 2e^-)$$

$$6I^- \rightarrow 3I_2 + 6e^-$$
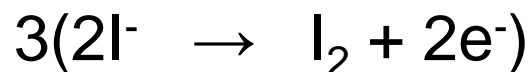
Step 4: Add the half-reactions, canceling substances that appear on both sides, and include states of matter. Electrons must always cancel.

$$\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
$$6I^- \rightarrow 3I_2 + \cancel{6e^-}$$

$$6I^-(aq) + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3I_2(s) + 7H_2O\ (l) + 2Cr^{3+}(aq)$$

Balancing Redox Reactions in Basic Solution

An acidic solution contains H^+ ions and H_2O. We use H^+ ions to balance H atoms.

A basic solution contains OH^- ions and H_2O. To balance H atoms, we proceed as if in acidic solution, and then add one OH^- ion to *both* sides of the equation.

For every OH^- ion and H^+ ion that appear on the *same* side of the equation we form an H_2O molecule.

Excess H_2O molecules are canceled in the final step, when we cancel electrons and other common species.

Problem: Permanganate ion reacts in basic solution with oxalate ion to form carbonate ion and solid manganese dioxide. Balance the ionic equation for the reaction between $NaMnO_4$ and $Na_2C_2O_4$ in basic solution:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow MnO_2(s) + CO_3^{2-}(aq) \text{ [basic solution]}$$
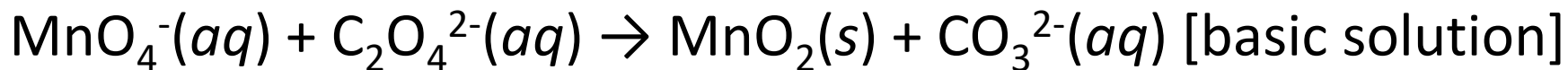
Solution

Step 1: Divide the reaction into half-reactions.
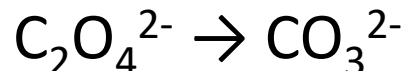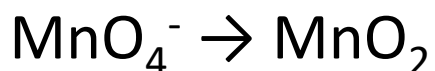
$MnO_4^- \rightarrow MnO_2$ $\qquad\qquad\qquad$ $C_2O_4^{2-} \rightarrow CO_3^{2-}$

Step 2: Balance the atoms and charges in each half-reaction.

Balance atoms other than O and H:

$MnO_4^- \rightarrow MnO_2$ $\qquad\qquad\qquad$ $C_2O_4^{2-} \rightarrow 2CO_3^{2-}$

Balance O atoms by adding H_2O molecules:

$$MnO_4^- \rightarrow MnO_2 + 2H_2O \qquad\qquad 2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-}$$

Balance H atoms by adding H^+ ions:

$$4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O \quad 2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+$$

Balance charges by adding electrons:

$$3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O \qquad \text{[reduction]}$$

$$2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+ + 2e^- \qquad \text{[oxidation]}$$

Step 3: Multiply each half-reaction, if necessary, by an integer so that the number of e⁻ lost in the oxidation equals the number of e⁻ gained in the reduction.

x 2 $6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O$

x 3 $6H_2O + 3C_2O_4^{2-} \rightarrow 6CO_3^{2-} + 12H^+ + 6e^-$

Step 4: Add the half-reactions, canceling substances that appear on both sides.

$6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O_4$

$2\ 6H_2O + 3C_2O_4^{2-} \rightarrow 6CO_3^{2-} + 12H^+ + 6e^-$

$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+$

Basic. Add OH⁻ to both sides of the equation to neutralize H⁺, and cancel H₂O.

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + [4H^+ + 4OH^-]$$

$$2MnO_4^- + 2\cancel{H_2O} + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + \cancel{2}4\cancel{H_2O}$$
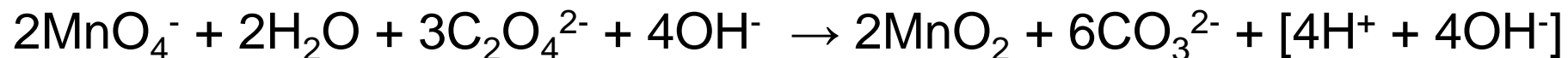
Including states of matter gives the final balanced equation:

$$2MnO_4^-(aq) + 3C_2O_4^{2-}(aq) + 4OH^-(aq) \rightarrow 2MnO_2(s) + 6CO_3^{2-}(aq) + 2H_2O(l)$$
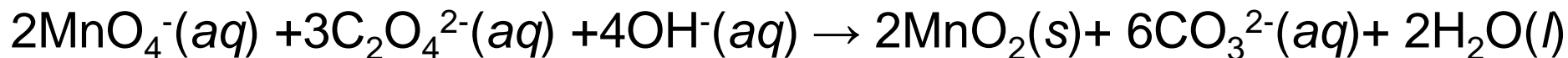
Problem: Balance the following Redox reactions

$(1)\ VO_2^+ + Zn \rightarrow VO^{2+} + Zn^{2+}$ (in acid solution)

$(2)\ MnO_4^- + H_2C_2O_4 \rightarrow Mn^{2+} + CO_2$ (in acidic solution)

$(3)\ MnO_4^- + HCOO^- \rightarrow MnO_2 + CO_3^{2-}$ [basic solution]

$(4)\ Cu^0_{(s)} + Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Ag^0_{(s)}$
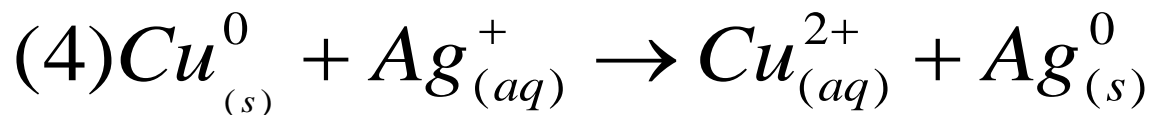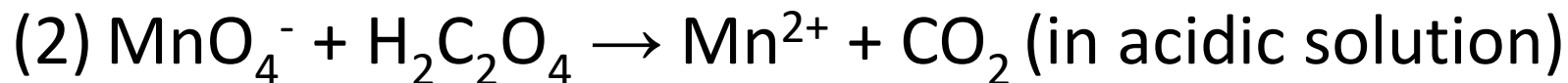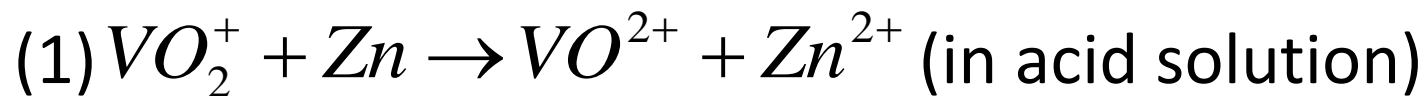
Spontaneous Redox Reactions

A strip of zinc metal in a solution of Cu^{2+} ions will react spontaneously:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ [reduction]

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ [oxidation]

$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
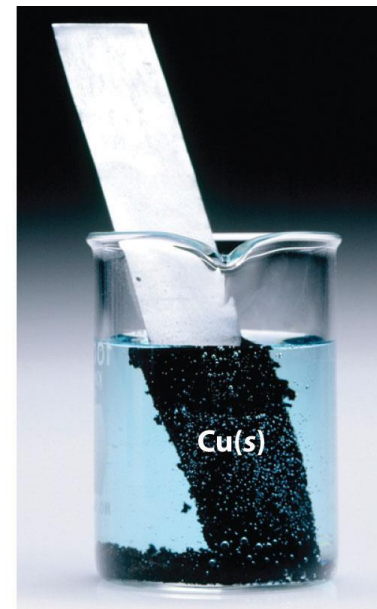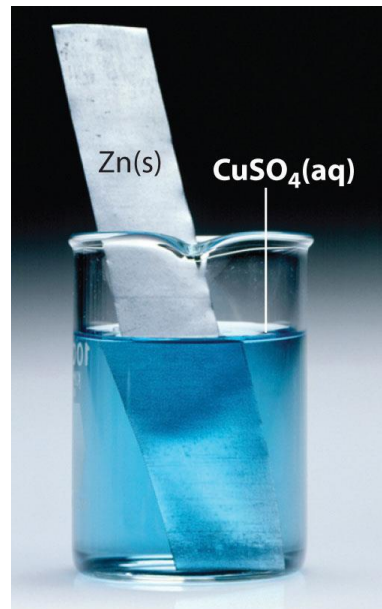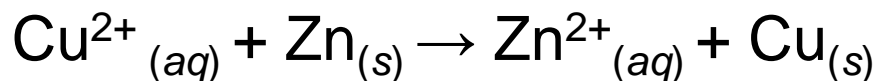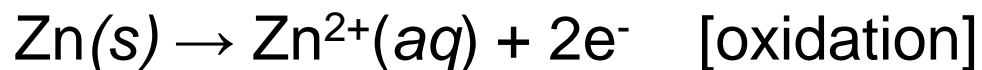
Zn is oxidized and loses electrons to Cu^{2+}.
To measure the <u>generated electrical energy</u>, we should separate the oxidation from the reduction.

Redox Potential

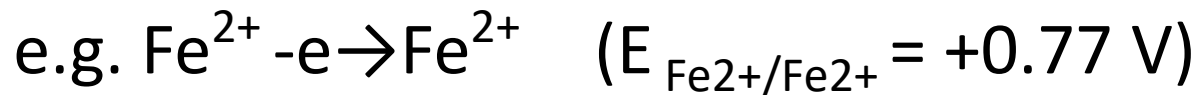$$Ox_1 + \mathrm{Re}\,d_2 \rightarrow Ox_2 + \mathrm{Re}\,d_1$$
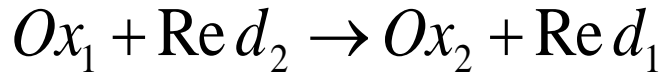
•The **affinity** of an atom to electrons is measured a s **potential**, (E) which is the driving force (e.m.f) to drive elections from the atom.

•The easier the metal, ion or molecule to loose electrons (little affinity to electrons), and the required E is smaller, the more it acts as strong reducing agent.

e.g. $Fe^{2+} - e \rightarrow Fe^{2+}$ $(E_{Fe2+/Fe2+} = +0.77$ V$)$

while Ti^{4+}/Ti^{3+} couple has a E= 0.1 volt, it acts as a strong reducing agent (Ti^{3+} is stronger reductant than Fe^{2+}).

The higher the voltage required to drive electrons from an ion, the more it acts as a strong oxidant.

e.g. MnO_4^-/Mn^{2-} has a $E_{MnO4-/Mn2-} = 1.2$, ($E_{Fe3+/Fe2+} = 0.77$ V)

So, MnO_4^- has a high affinity to the electrons of Fe^{2+} and Fe^{3+} have a low affinity to electrons.

MnO_4^- will gain electrons from Fe^{2+} and the oxidation reduction process takes place.

To understand the redox potentials: electrochemical cells are discussed.

Electrochemical Cell

•A galvanic (voltaic) cell uses a <u>spontaneous</u> redox reaction (ΔG < 0) to generate electrical energy.
•The system does work on the surroundings.

•A electrolytic cell uses electrical energy to drive a <u>nonspontaneous</u> reaction (ΔG > 0).
•The surroundings do work on the system.

•Both cell types are fabricated using two electrodes placed in an electrolyte solution.

•The <u>anode</u> is the electrode at which <u>oxidation</u> occurs.
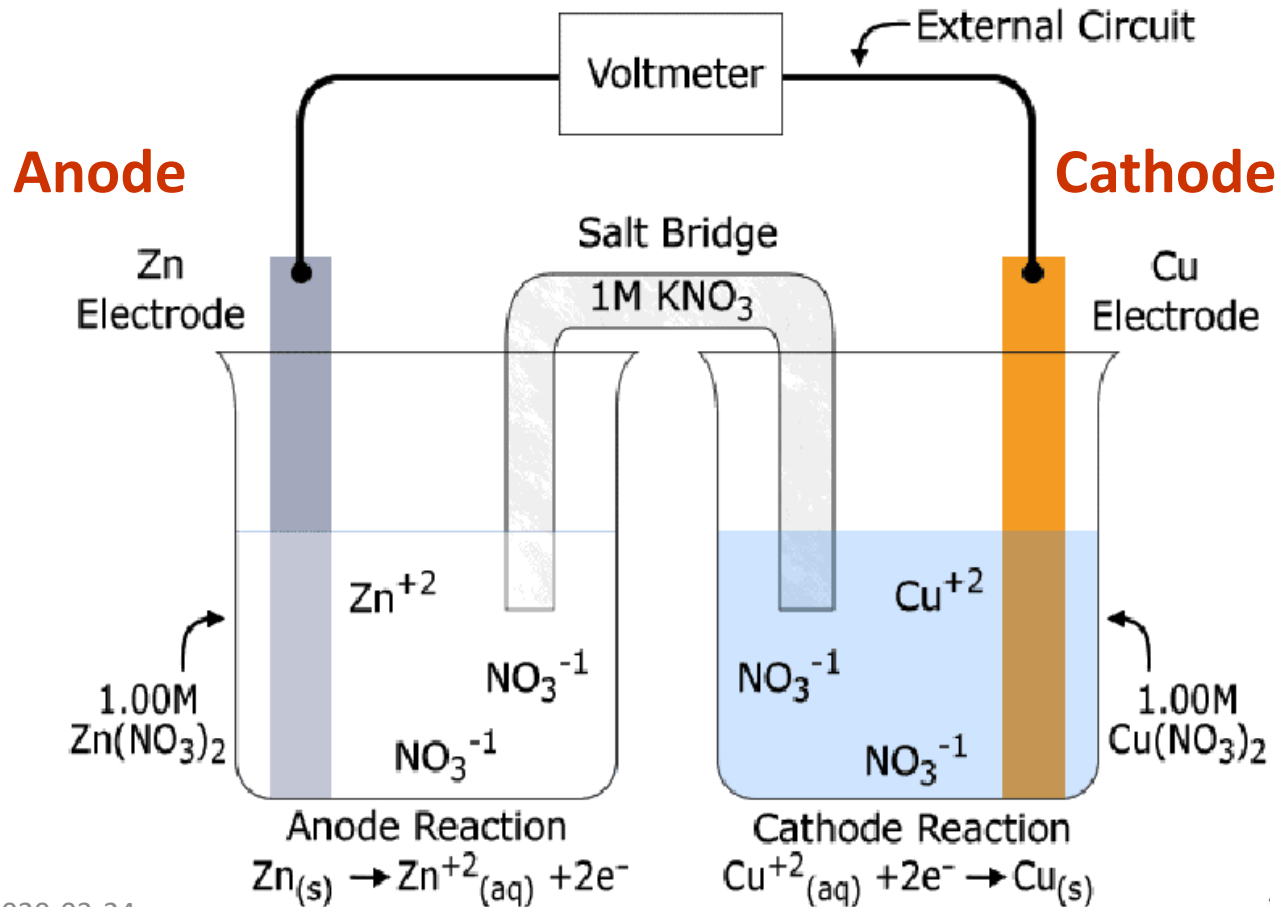•The <u>cathode</u> is the electrode at which <u>reduction</u> occurs.

Construction of a Galvanic (Voltaic) Cell

- The two half-cell reactions are physically separate.

- Each half-cell consists of an electrode in an electrolyte solution.

- The half-cells are connected by the external circuit.

- A *salt bridge* completes the electrical circuit.

Galvanic Cell

Consists of 2 electrodes dipping into solution with electrical contact between electrodes and the solution (salt bridge or a membrane).
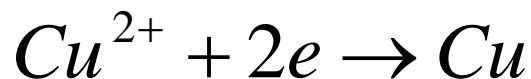
Daniel Cell

Anode

Cathode

External Circuit

Voltmeter

Zn Electrode

Salt Bridge

1M KNO$_3$

Cu Electrode

Zn^{+2}

Cu^{+2}

NO$_3^{-1}$

NO$_3^{-1}$

1.00M Zn(NO$_3$)$_2$

NO$_3^{-1}$

NO$_3^{-1}$

1.00M Cu(NO$_3$)$_2$

Anode Reaction
$$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$$

Cathode Reaction
$$Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

Electrode Reactions

- Zn has a greater tendency to lose electrons than Cu.

$$Zn \rightarrow Zn^{2+} + 2e$$

- The elections pass through the external circuit to the Cu electrode.

- The Cu^{2+} gains these e⁻s to form Cu metal and deposits on the Cu electrode.

$$Cu^{2+} + 2e \rightarrow Cu$$

- At the boundary of each electrode and its surrounding solution, a potential develops which is called electrode potential.

- Zn electrode (**anode**), is **negative**
- Cu electrode (**cathode**) is **positive**.

Daniell Cell Reactions

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

- The *anode* produces e$^-$ by the oxidation of Zn(*s*), the anode is the *negative* electrode.
- Electrons flow through the external wire *from the anode to the cathode*, to reduce Cu^{2+} ions, the cathode is the *positive* electrode.

Oxidation half-reaction
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

After several hours, the Zn anode weighs less as Zn is oxidized to Zn^{2+}.

Reduction half-reaction
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The Cu cathode gains mass over time as Cu^{2+} ions are reduced to Cu.

Salt Bridge

What is the role of the salt bridge?

- Makes cell construction and operation easier.

- Completes the electrical circuit and allows *ions* to flow through both half-cells and maintains electrical neutrality
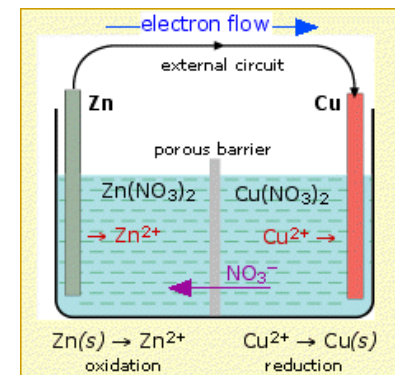
Fill a tube with a viscous aqueous solution of KCl or KNO_3 (using hot agar). The viscosity prevents mixing with the electrolytes. The ions permit exchange of charge.

Heat a mixture (3 g agar +30 g of KCl or KNO_3 in 100 mL of H_2O)
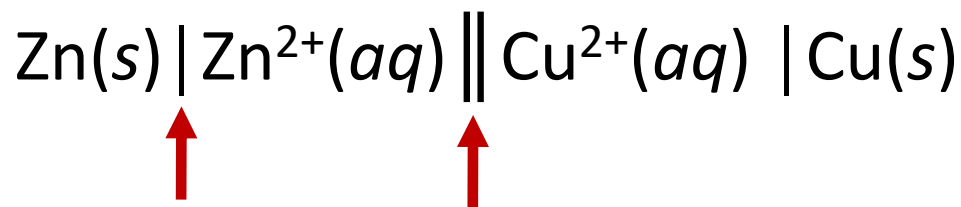
Cell notation

The components of each half-cell are written in the same order as in their half-reactions.

The anode components are written on the *left*.

The cathode components are written on the *right*.

$$Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$$

The single vertical line shows a **phase boundary** between the components of a half-cell.

The double line shows that the two half-cells are physically separated by **salt bridge.**

- Write components in sequence
- Separate phases with a single vertical line "|"
- A salt bridge or membrane is represented by a double vertical line "‖"
- Include a specification of the species concentration

Electrode Convention

• The electrode at which oxidation is occurring is called the anode.

• The electrode at which reduction is occurring is called the cathode.

• **Write the anode on the left and the cathode on the right.**

• Connect the <u>positive electrode (cathode)</u> to the positive terminal of the voltmeter. If it reads a positive potential, you have correctly identified all the terminals.

• If you read a negative potential, then you have misidentified the reactions in the cells, and you have reverse them.

• In a galvanic cell **the cathode is +ve**

• In an electrolytic cell the **cathode is -ve**.

Example: Draw a diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is <u>negative</u> relative to the Ag electrode.
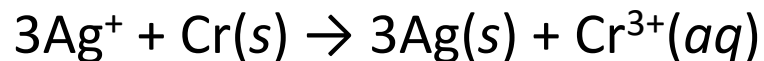
Solution

First, we write the half-reactions.
Electrons are released into the anode during oxidation, so it has a negative charge. Since Cr is negative, it must be the anode, and Ag is the cathode.
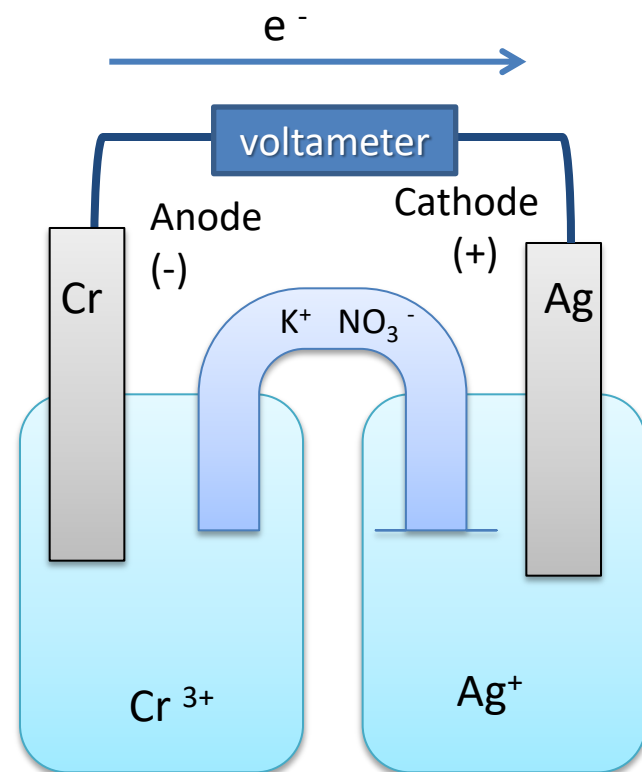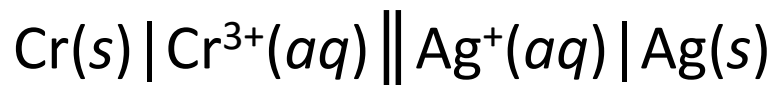
The half-reactions are:

$Ag^+(aq) + e^- \rightarrow Ag(s)$ [reduction; cathode]

$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$ [oxidation; anode]

The balanced overall equation is:

$3Ag^+ + Cr(s) \rightarrow 3Ag(s) + Cr^{3+}(aq)$

The cell notation is given by:

$Cr(s) \,|\, Cr^{3+}(aq) \,\|\, Ag^+(aq) \,|\, Ag(s)$

e $^-$

voltameter

Anode (-)

Cathode (+)

Cr

K$^+$ NO$_3^-$

Ag

Cr $^{3+}$

Ag$^+$

The cell diagram shows the anode on the left and the cathode on the right.

Single Electrode Potential

When a strip of metal e.g. Zn is placed in 1 M solution of its ions, an equilibrium reaction develops between the metal and its ions

$$Zn \rightarrow Zn^{2+} + 2e$$

- A potential develops at the electrode can not be measured

- Only the E of a cell, resulting from combination of 2 electrodes is measured.

- To measure and evaluate potential difference between various electrodes (half cells).

- It is necessary to use an **Electrode as Reference**.

Measuring Standard Electrode Potential

- Use a cell consisting of the <u>H_2 electrode and the electrode whose potential is unknown</u> (standard state, unit activity).

- Connect the 2 half cells by a salt bridge containing a concentrated solution of KCl with an agar plug at the end.

- The potential of the reference electrode is subtracted from the e.m.f. of the cell to get the E^o value of the half cell under test.

- The H_2 electrode may serve as an anode or cathode.

Reference electrode

Requirements for reference electrodes

- Easy to construct
- Show a reversible behavior
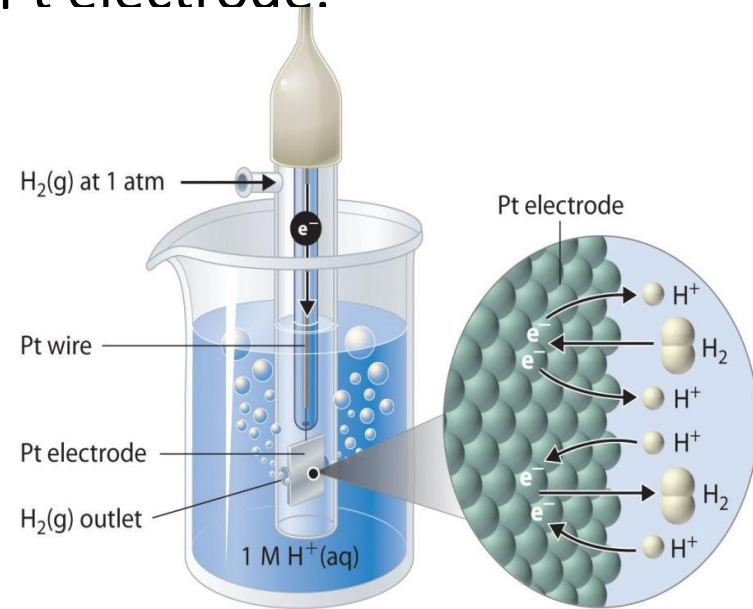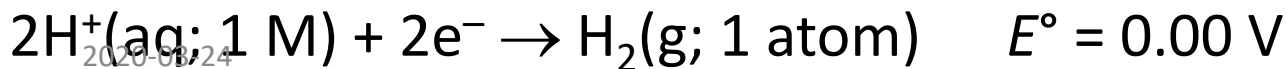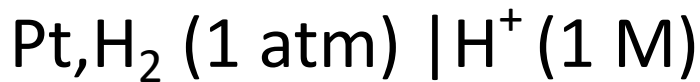- Give constant and reproducible potentials for a given set of conditions.

For example: Standard Hydrogen Electrode (SHE)

Standard Hydrogen Electrode

- It is assigned a potential of zero. $E° = 0.00$ V
- The electrode consists of a piece of Pt connected with a wire and immersed in a solution of H^+ ions (1M).

- The Pt electrode is covered with finely divided platinum.

- H_2 (1 atm) is bubbled over the platinized Pt electrode.

The finely divided platinum adsorbs H_2 exists in equilibrium with H^+ ions

The half reaction for the electrode.

Pt, H_2 (1 atm) $| H^+$ (1 M)

H_2(g) at 1 atm

Pt electrode

Pt wire

Pt electrode

H_2(g) outlet

1 M H⁺(aq)

H⁺ H_2 H⁺ H⁺ H_2 H⁺

half-reaction at Pt surface:
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

$2H^+(aq; 1 M) + 2e^- \rightarrow H_2(g; 1 atom)$ $E° = 0.00$ V

Application of Standard Electrode Potential

- The standard electrode potentials of various system are arranged in a table.

- The table gives a E^o values and indicates the relative tendencies for substances at the standard sate to lose or gain electrons.

- The substance at the top of the table (higher E^o) have high tendency to gain elections (i.e. strong oxidizing agents)

Standard Potential Tables

At equilibrium, electrochemical data is presented in **Standard Reduction Potential** tables (electrochemical series).

$F_2 + 2e^- \rightarrow 2F^-$	+2.87	$2H^+ + 2e^- \rightarrow H_2$	0.000
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^+ + e^- \rightarrow Au$	+1.69	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$In^{3+} + 3e^- \rightarrow In$	-0.34
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	$V^{2+} + 2e^- \rightarrow V$	-1.19
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22	$Cs^+ + e^- \rightarrow Cs$	-2.92
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15	$Li^+ + e^- \rightarrow Li$	-3.05

# **Calculating a Cell Potential**

Because we tabulate <u>Reduction Potentials</u>, the cell potential is calculated (from those tabulated numbers) as

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

The minus sign is present only because we are using reduction potential tables and, by definition, an anode is where oxidation occurs.

Using Half-Reactions to write a Spontaneous Redox Reaction

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \qquad E°_{tin} = -0.14 \text{ V}$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E°_{silver} = 0.80 \text{ V}$$
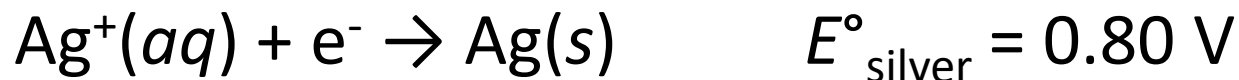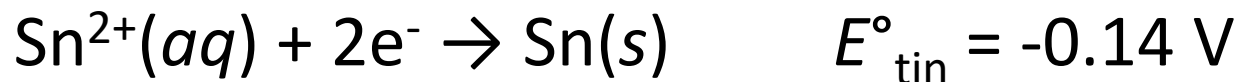
Step 1: *Reverse one of the half-reactions into an oxidation step so that the difference between the* **E° *values will be positive.***

Here the Ag⁺/Ag half-reaction has the more positive $E°$ value, so it must be oxidizing agent (the reduction). This half-reaction remains as written.

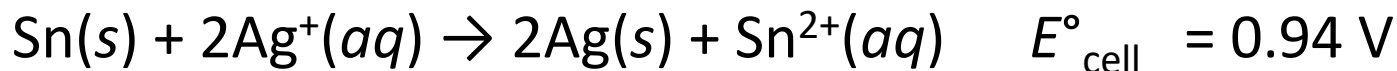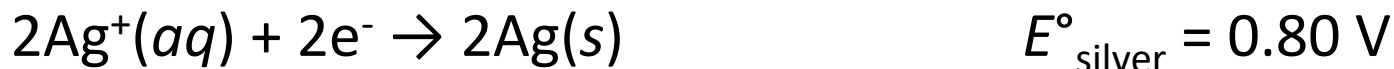We reverse the Sn^{2+}/Sn half-reaction, but we do *not* reverse the sign:

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \qquad E°_{tin} = -0.14 \text{ V}$$
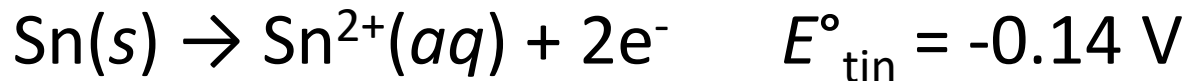
Step 2: Multiply the half-reactions if necessary so that the number of e⁻ lost is equal to the number or e⁻ gained.

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s) \quad E°_{silver} = 0.80 \text{ V}$$

Note that we multiply the equation but *not* the value for $E°$.

Step 3: Add the reactions together, cancelling common species. Calculate $E°_{cell} = E°_{cathode} - E°_{anode}$

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \qquad\qquad E°_{tin} \;= -0.14 \text{ V}$$
$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s) \qquad\qquad E°_{silver} = 0.80 \text{ V}$$
$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$
$$Sn(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Sn^{2+}(aq) \qquad E°_{cell} \;= 0.94 \text{ V}$$

$$E°_{cell} = E°_{silver} - E°_{tin} = 0.80 - (-0.14) = 0.94 \text{ V}$$

Example 1

Consider the following two half-reactions

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad\qquad E= -0.44\ V$$
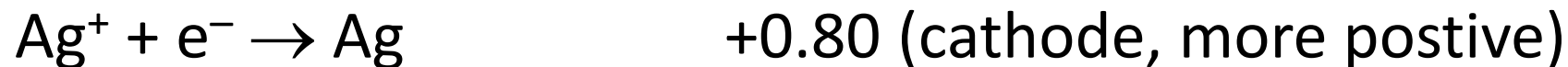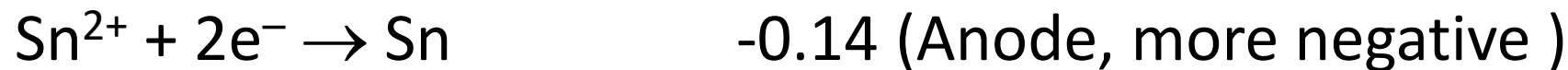$$V^{2+} + 2e^- \rightarrow V \qquad\qquad E= -1.19\ V$$

1. Let the more negative (least positive) reaction be that for the anode. That means that its direction will be reversed.

2. Balance the number of electrons but scaling the reactions appropriately, but DO NOT modify their cell potentials.

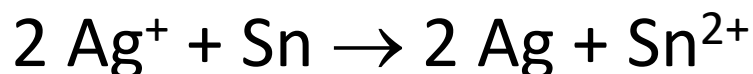To get a final positive cell potential, consider the more negative half-reaction (V) as the anode.

$$Fe^{2+} + V \rightarrow Fe\ + V^{2+}$$
$$E_{cell} = -0.44 - (-1.19) = +0.75\ V$$

Example 2

$Sn^{2+} + 2e^- \rightarrow Sn$ -0.14 (Anode, more negative)

$Ag^+ + e^- \rightarrow Ag$ +0.80 (cathode, more postive)

Consider the more negative potential reaction as the anode (Sn^{2+}).

Multiply the Ag reaction by 2, but don't modify the cell potential.

$2\ Ag^+ + Sn \rightarrow 2\ Ag + Sn^{2+}$

$E_{cell} = +0.80 - (-0.14) = +0.94\ V$

Problems

1) For each pair of species, choose the best reducing agent?
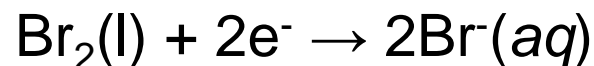(a) Ag(s) or Sn(s) , given:

Ag+(aq) + e⁻ → Ag(s) $\qquad$ E°red = 0.799 V
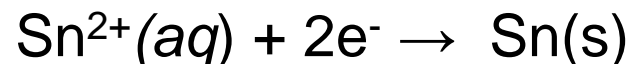
Sn^{2+}(aq) + 2e⁻ → Sn(s) $\qquad$ E°red = -0.136 V

(b) Br⁻(aq) or Cl⁻(aq), given:

Br_2(l) + 2e⁻ → 2Br⁻(aq) $\qquad$ E°red = 1.065 V
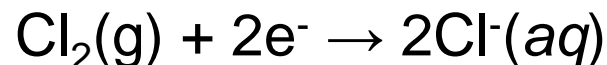
Cl_2(g) + 2e⁻ → 2Cl⁻(aq) $\qquad$ E°red = 1.359 V

(c) Au(s) or I⁻(aq), given:

Au^{3+} (aq) + 3e⁻ → Au(s) $\qquad$ E°red = 1.420 V
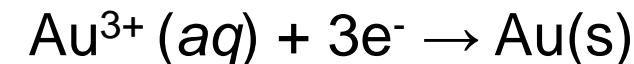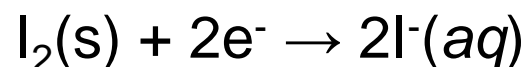
I_2(s) + 2e⁻ → 2I⁻(aq) $\qquad$ E°red = 0.540 V

2) Calculate the cell potential for the following half-reactions?

(a) Sn^{2+} + 2e⁻ → Sn $\quad$ $E°$ = -0.14

$\qquad$ Ag⁺ + e⁻ → Ag $\quad$ $E°$ = +0.80

(b) Li⁺ + e⁻ → Li $\qquad$ $E°$ = -3.05 V

$\qquad$ Co^{3+} + e⁻ → Co^{2+} $\quad$ $E°$ =+1.81
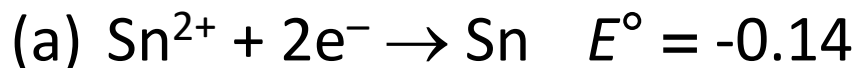
Active and Inactive Electrodes

Consider the Redox reaction:

$$MnO_4^-(aq) + I^-(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(s) + H_2O\ (l)$$
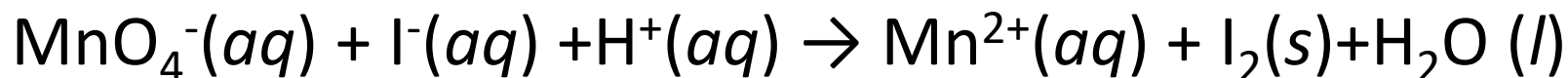
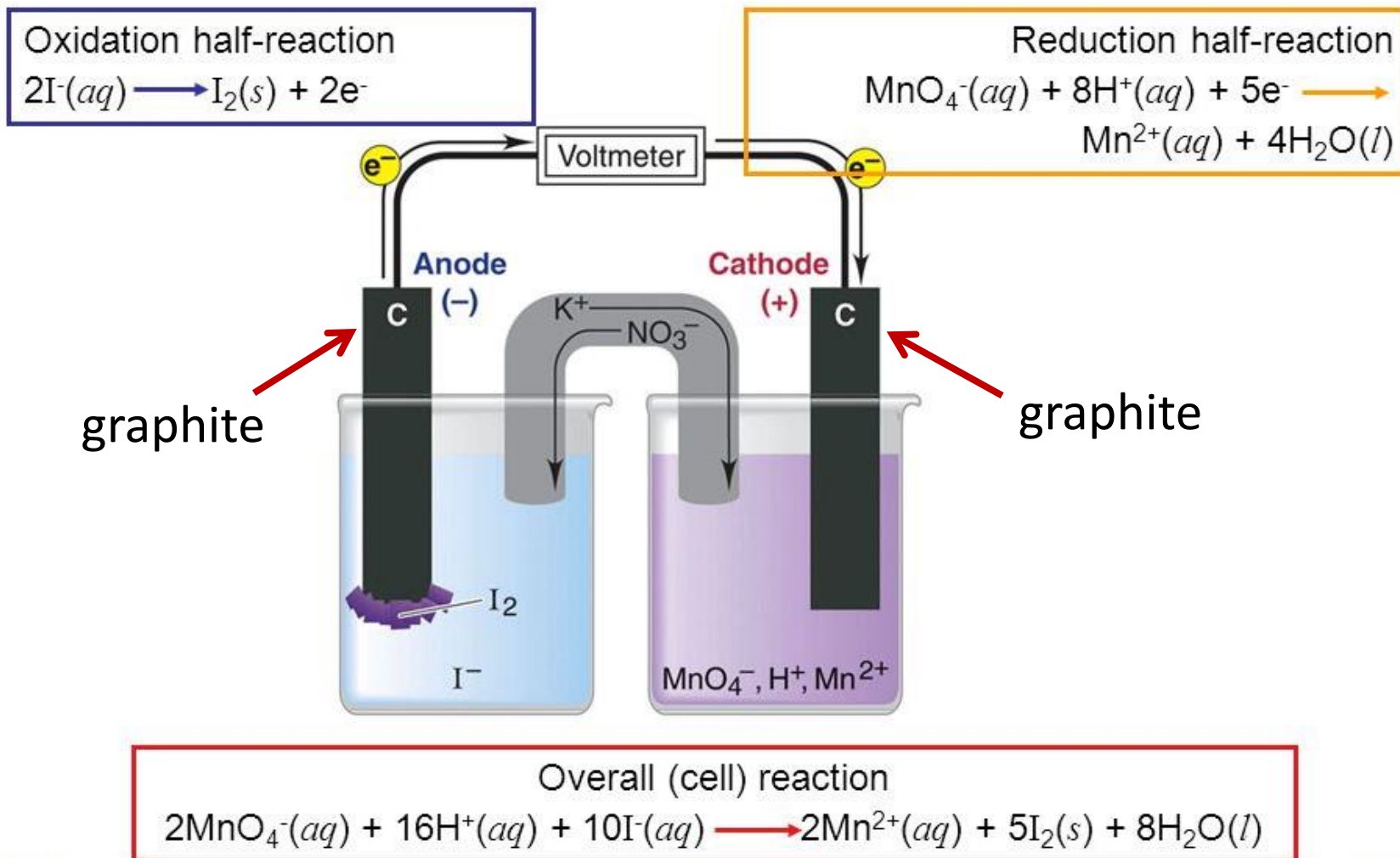Is it possible to construct a voltaic cell using this reaction?

Yes, use an inactive electrode!!

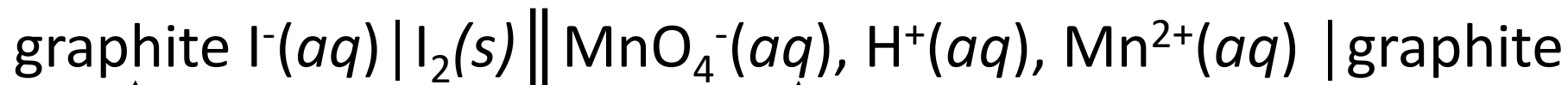An active electrode is an active component in its half-cell and is a reactant or product in the overall reaction.

An inactive electrode provides a surface for the reaction and completes the circuit. It does not participate actively in the overall reaction.

Inactive electrodes are inert substances such as *graphite, gold or platinum.*

A galvanic cell using inactive electrodes

Oxidation half-reaction
$2I^-(aq) \longrightarrow I_2(s) + 2e^-$

Reduction half-reaction
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

Voltmeter

Anode (−)

Cathode (+)

K^+

NO_3^-

graphite

graphite

I_2

I^-

MnO_4^-, H^+, Mn^{2+}

Overall (cell) reaction
$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

A galvanic cell using inactive electrodes, _{continued}

graphite I$^-$(*aq*) | I$_2$(*s*) ‖ MnO$_4^-$(*aq*), H$^+$(*aq*), Mn^{2+}(*aq*) | graphite

↑

The inert electrode is specified.

A comma is used to show components that are in the same phase.

Problem:

For the following Redox reaction:

Sn$^{2+}_{(aq)}$ + Fe$^{3+}_{(aq)}$ ---> Sn$^{4+}_{(aq)}$ + Fe$^{2+}_{(aq)}$

(a) Draw the diagram for a voltaic cell using a Pt electrode?
(b) Write the cell shorthand notation as well as the balanced half-cell reactions?

Standard Reference States

All thermodynamic measurements are of differences between states.
Therefore, to quantify thermodynamics, we use
a reference state.

Reference States
Temperature = 298 K (25 ˚C)
Pressure = 1 atm
Concentration = 1 molal (mol of solute/kg of solvent)
BUT…
Volume is easier to measure so, 1 M is **used reference state**

Reference states are indicated by superscript ˚
C˚   or   P˚

Activity Coefficients

Activity, a is the propensity for a given material to contribute to a reaction.

$$a = \gamma \frac{C}{C^\circ}$$

$$a = \gamma \frac{P}{P^\circ}$$

activity is unitless!

- Activity coefficients close to 1 for dilute solutions and low partial pressures.

- it changes with concentration& temperature.

- For simplicity, we ignore activity coefficients.

- In the case of pressure, the coefficient used is called "fugacity"

- SOLID: reference is itself
- PURE LIQUID: reference is itself
- SOLVENT: reference is itself

Activity = 1

Nernst Equation

Use the expression for the Gibbs dependence on activity and convert it to an expression in terms of the cell potential.

$$\Delta G = \Delta G^\circ + R\,T \ln Q$$

The relation between cell potential E and free energy gives

$$-nFE = -nFE^0 + RT \ln Q$$

Rearrange and obtain the Nernst Equation.

$$\boxed{E = E^\circ - \frac{R\,T}{n\,F} \ln Q}$$

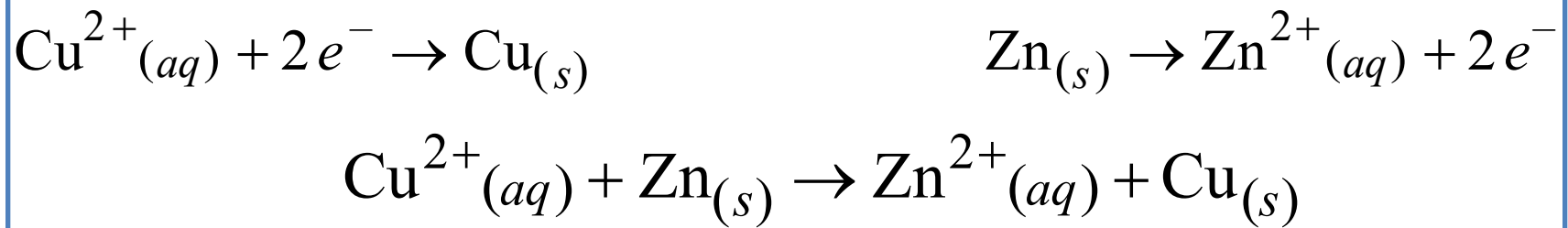This expression relates the dependence of the cell potential on the reaction quotient.

Nernst Equation continued

At T = 25 °C and plug in the values for the constants, R and F.

$$E = E° - \frac{0.0592}{n} \log Q$$

"n" – the number of moles of electrons transferred in the process according to the stoichiometry chosen.

Example: Daniell Cell

Cu is cathode (it is reduced). Zn is anode (it is oxidized).

$$Cu^{2+}{}_{(aq)} + 2\,e^- \rightarrow Cu_{(s)} \qquad\qquad Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2\,e^-$$

$$Cu^{2+}{}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

Note that n=2 for this reaction

$$=1$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{Cu}\, a_{Zn^{2+}}}{a_{Cu^{2+}}\, a_{Zn}}$$

$$=1$$

$$= \gamma \frac{[Zn^{2+}]}{[\ ]^\circ}$$

Activity for solid materials is 1; replace activities with concentrations.

$$E = E^0 - \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.10 - \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$
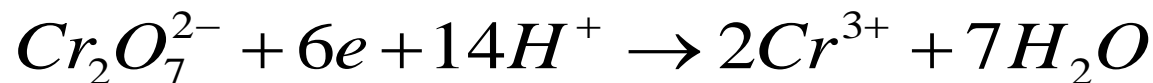
Example continued

What is the potential in the cell if $[Cu^{2+}] = 0.01$ M and $[Zn^{2+}] = 1.00$ M?

$$E = 1.10 - 0.0296 \log \frac{1.00}{0.01} = 1.10 - 0.0296 \log 100$$

$$= 1.10 - 0.0296(2) = 1.041 \text{ V}$$

Factors Affecting the Electrode Potential

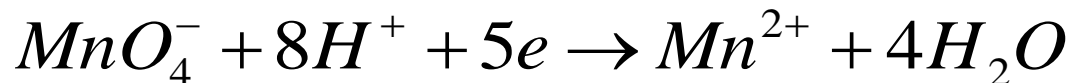## 1. H$^+$ ion concentration

If H$^+$ ion is involved in the half reaction, it must be included in Nernst equation (e.g. $Cr_2O_7{}^{2-}/Cr^{3+}$ and MnO_4^-/Mn^{2+} system):

$$Cr_2O_7^{2-} + 6e + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

$$E = 1.33 - \frac{0.059}{6}\log\frac{(Cr^{3+})^2}{(Cr_2O_7^{2-})(H^+)^{14}}$$

$$E^o = +1.33V$$

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

$$E = 1.51 - \frac{0.059}{5}\log\frac{Mn^{2+}}{(MnO_4^-)(H^+)^8}$$

$$E^o = +1.51V$$

2. Effect of other equilibria on potentials

The occurrence of association, precipitation, **complex formation** and other reactions involving the species entering into a redox reaction, cause complication to standard reduction potentials.

Complex formation

Example: Fe^{3+}/Fe^{2+} system, the addition of F^- or PO_4^{3-} ions forms slightly ionized ferric complex (FeF_6^-) and <u>decrease the potential through shifting the half reaction to the left</u>:
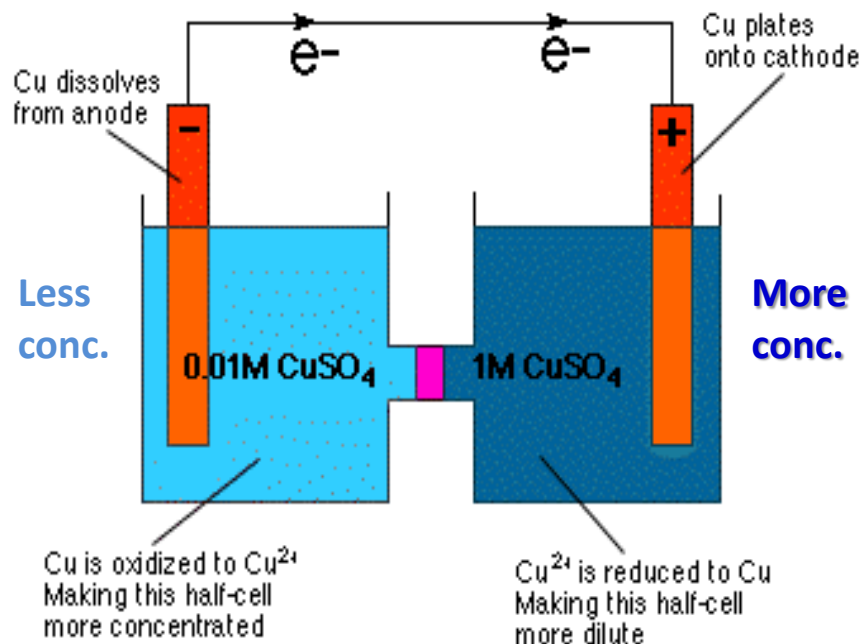
$$Fe^{3+} + e \rightarrow Fe^{2+}$$
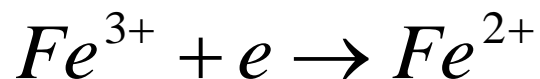
Concentration Cells

A cell made of the <u>same materials</u>, but with <u>different concentrations</u>, will produce a potential difference.

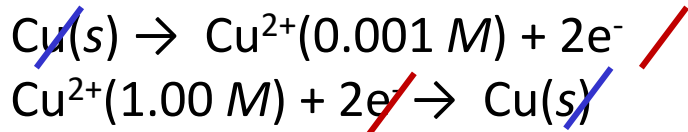$$Cu(s)|Cu^{2+} (0.001\ M)||Cu^{2+} (1.00\ M)|\ Cu(s)$$

As the concentrations of the solutions are different, the cell potential is > 0 and the cell can do work.

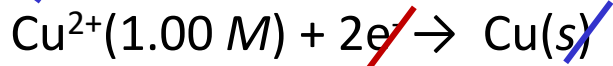What is standard cell potential E˚ for this cell? What is the cell potential E?

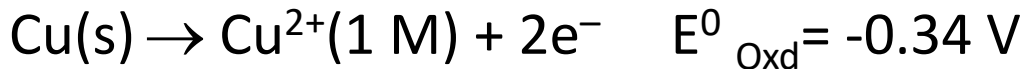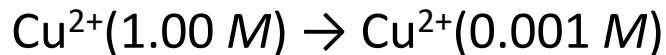What is the value of the cell potential at equal half-cell concentrations?

Cu dissolves from anode

e-

e-

Cu plates onto cathode

−

+

Less conc.

More conc.

0.01M CuSO₄

1M CuSO₄

Cu is oxidized to Cu²⁺ Making this half-cell more concentrated

Cu²⁺ is reduced to Cu Making this half-cell more dilute

Concentration Cells, continued

Cu(s)|Cu²⁺ (0.001 M)||Cu²⁺ (1.00 M)| Cu(s)

$Cu(s) \rightarrow Cu^{2+}(0.001\ M) + 2e^-$ [anode; oxidation]

$Cu^{2+}(1.00\ M) + 2e^- \rightarrow Cu(s)$ [cathode; reduction]

_____

$Cu^{2+}(1.00\ M) \rightarrow Cu^{2+}(0.001\ M)$

$Cu^{2+}(1\ M) + 2e^- \rightarrow Cu(s)$ $E^0_{Red} = +0.34\ V$

$Cu(s) \rightarrow Cu^{2+}(1\ M) + 2e^-$ $E^0_{Oxd} = -0.34\ V$

_____

$E^0_{Cell} = 0.0\ V$

The standard cell potential in this cell must be 0 for the two electrodes, at standard conditions.

$$E = E^0 - \frac{0.0592}{n}\log\left(\frac{\left[Cu^{2+}\right]_{anode}}{\left[Cu^{2+}\right]_{cathode}}\right)$$

$$= 0 - \frac{0.0592}{2}\log\left(\frac{0.001}{1.00}\right) = +0.089V$$

A concentration cell of Cu/Cu²⁺ half-reaction
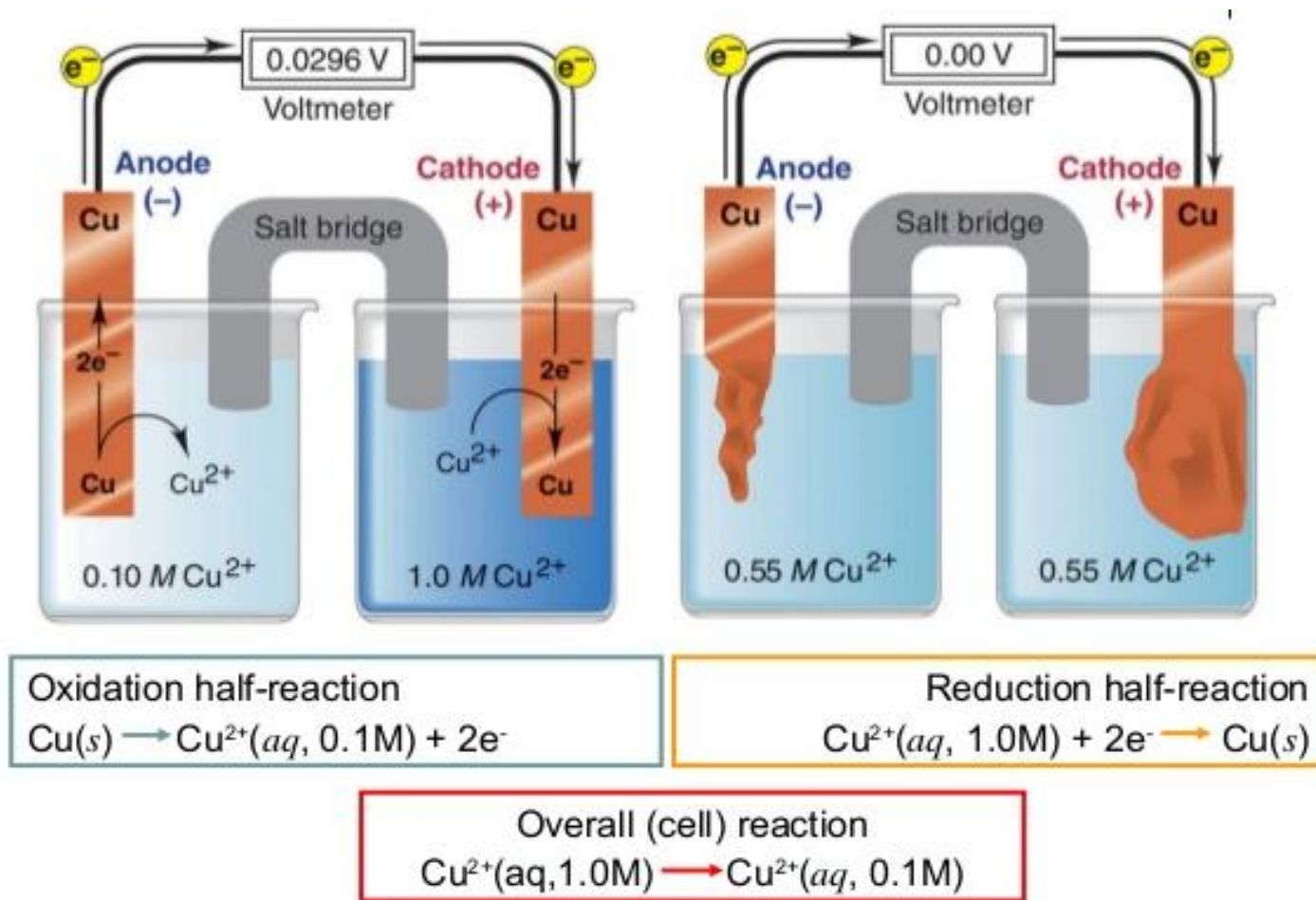
$E_{cell} > 0$ as long as the half-cell concentrations are different.
Once the concentrations are equal, the cell is no longer able to do work

Titration of curves in redox reactions

- Plot of cell potential containing two reactants against the volume of the titrant added (the variable is E cell).

- The cell potential can be measured potentiometrically by constructing a cell consisting of an indicator electrode (e.g. Platinum), dipped into a beaker containing the system being titrated and a reference electrode (calomel).

- The calomel half cell maintains a constant potential

- Any change in the indicator electrode potential is reflected in the value of E cell which is measured by the potentiometer.

- The titration reaction system is not considered as a cell, but a half cell and the calomel electrode is the other half cell.
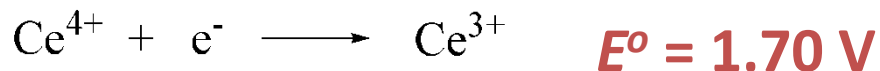
Redox Titrations

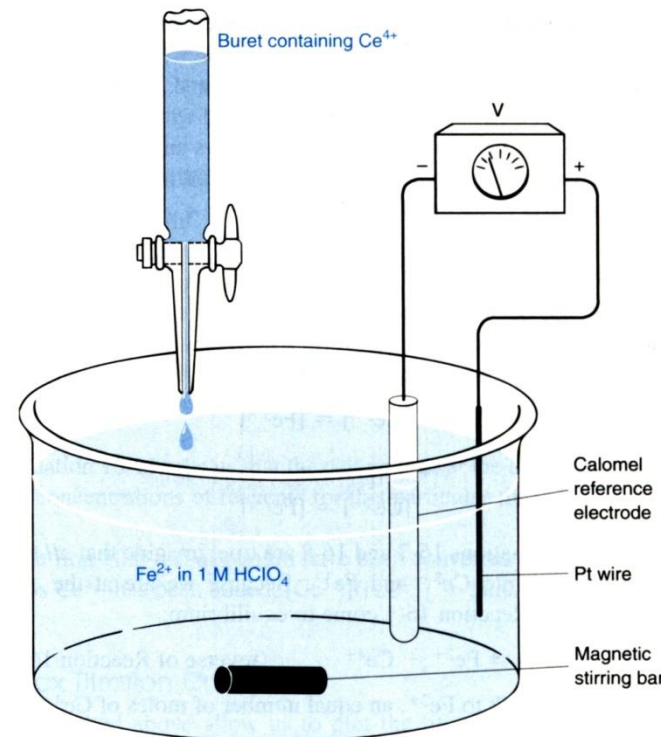**Potential Change as a Function of Added Titrant**

For the titration Reaction

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$
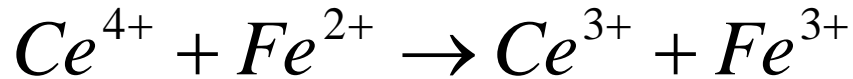
• Ce^{4+} is added from a buret to a solution of Fe^{2+}

• Pt electrode responds to relative concentration of Fe^{3+}/Fe^{2+} & Ce^{4+}/Ce^{3+}

• Calomel electrode used as reference

Indicator half-reactions at Pt electrode:

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad \textbf{\textit{E}^{o} = 0.771 V}$$

$$Ce^{4+} + e^- \longrightarrow Ce^{3+} \quad \textbf{\textit{E}^{o} = 1.70 V}$$

Buret containing Ce^{4+}

Calomel reference electrode

Pt wire

Fe^{2+} in 1 M $HClO_4$

Magnetic stirring bar

Redox Titrations

Problem: Plot the titration curve for 50 mL of 0.05 M Fe^{2+} with 0.10 M Ce^{4+}

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

Titration Curve has four Regions

- Initial point
- Before the Equivalence Point
- At the Equivalence Point
- After the Equivalence Point

- At the end point when equilibrium is established E (Fe^{3+}/Fe^{2+}), will be identical to that of E (Ce^{4+} /Ce^{3+}) system.
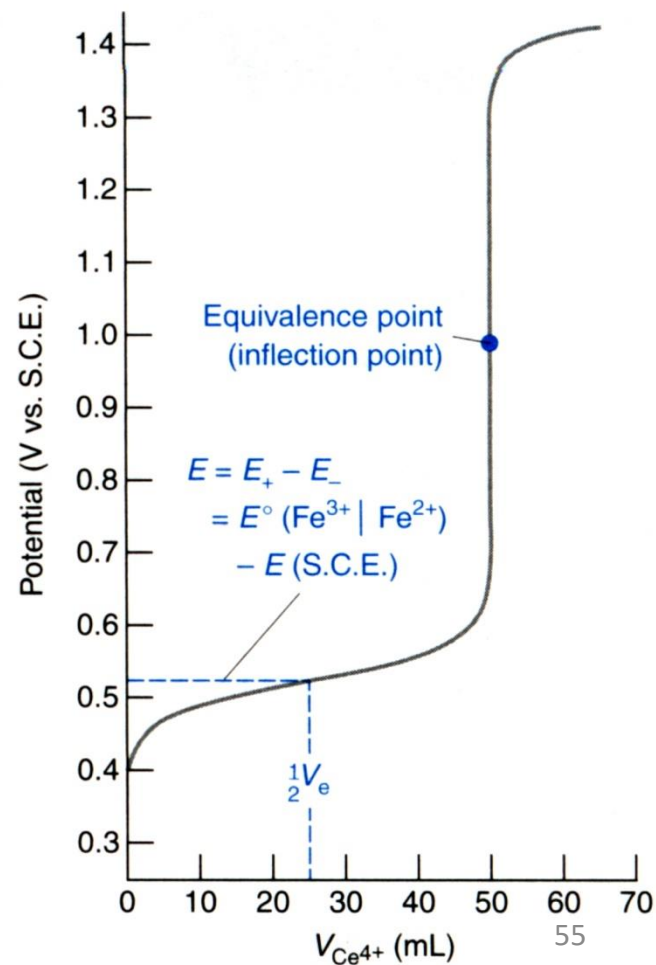
Detection of End Point in Redox Titration

- Redox titration curves shows that the potential change abruptly in the region of the equivalence point.

- The more sharp the change in the region of the equivalence pint, the more accurate the end point is located

Redox Indicators

Varies as a function of E_{cell}

Rely on a color change with Ind_{ox} and Ind_{red} being different colors.

Ind_{ox} + ne⁻ $\Leftrightarrow$ Ind_{red}

$$E = E^o_{ind} - \frac{0.0592V}{n} \log \frac{[Ind_{red}]}{[Ind_{ox}]} \qquad \frac{[Ind_{red}]}{[Ind_{ox}]} \leq \frac{1}{10} \ or \geq \frac{10}{1} \qquad E = E^o_{ind} \pm \frac{0.0592V}{n}$$

To see a color change, you need approximately a 10% conversion from one form to another.

Methods location of the end point

1. Miscellaneous indicators :

a) **Specific indicators:** substance which react specially with one of the reagents in the titration to produce a color e.g. starch gives blue color with iodine, SCN^- in gives red color with Fe^{3+}

b) **Colored titrtant**: which acts as self indicators e.g. MnO_4^- ion

2. External indicators:

- $[Fe(CN)_6]^{3-}$ ion is used an external indicator for titration of Fe^{2+} against a standard oxidant.
- It gives a blue as long as Fe^{2+} is still present in solution.

Specific indicators

Starch

Starch + I_3^- ⇔ blue complex
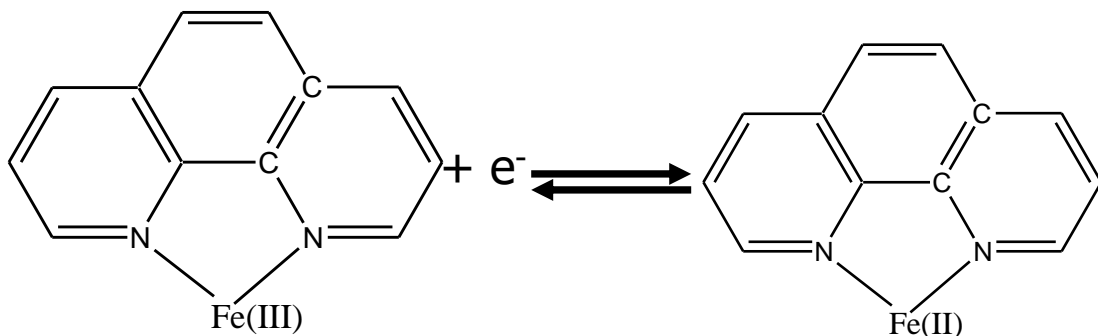
It is easy to detect and color change is rapid!!
This interaction explains why we use iodine as a titrant even though it is a very weak oxidant.

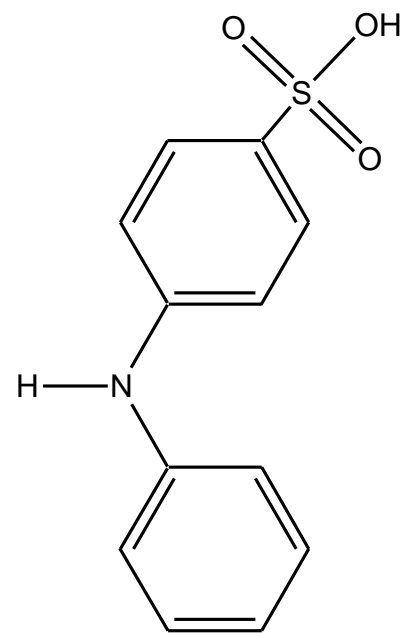# Examples

1,10 phenanthrolene-Fe

Diphenylamine sulphonic acid

$+ e^-$ ⇌

BLUE   RED

$E^o = 1.06$ V

$E^o = 0.80V$

Common Titrants

Oxidizing agents

- $Cr_2O_7^{2-}$
need an indicator
Very stable
E=1.44 V

- Ce^{4+}

- MnO_4^-
Solutions must be standardized
Reagent slowly degrades
No indicator needed excess
reagent is pink
E=1.51 V

Reducing Titrants
Fe^{2+}

Usually $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 1M H_2SO_4
Solution must be standardized each day

I^-
Indirect method
Your lab was an excellent
example

Common Titrant: Oxidizing Agents

**Potassium permanganate** MnO_4^- $\qquad$ E=+1.51 V

- The most widely used oxidizing agent
- Solutions must be standardized
- It is a powerful oxidizer.
- It serves as self indicator
- Reagent slowly degrades
- Its tendency to oxidize Cl^- ion represents a serous limitation for MnO_4^- because HCl is usually a desirable solvent

Reactions of MnO_4^-

The oxidation # of Mn in MnO_4^- is +7

It can be reduced to **+2, +3, +4, +6,** states according to the conditions. These reaction are the basis for many volumetric determinations

a) Reduction to +2 state: Solutions of 0.1 N H$^+$ or more

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

$$(E^0 = 1.51V)$$
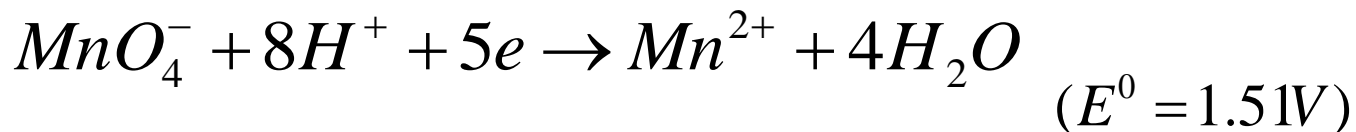
- This is the most widely used of MnO_4^- titrations. Oxidation proceeds rapidly in an acid medium.
- Exception are oxalic acid require 50°C
- The Mn^{2+} ion formed during reaction has a catalyst effect .

b) Reduction to +4 state:

In solutions of **weakly acidic/neutral or weakly alkaline** MnO_2 is the reduction product.

$$MnO_4^- + 4H^+ + 3e \Leftrightarrow MnO_2 + 2H_2O \qquad (E^0 = 1.69V)$$
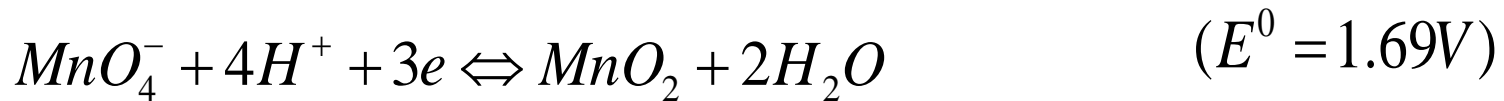
It used to determine substances which can not be titrated in acid medium

$$CN^- \rightarrow CNO^- \qquad S^{2-}, SO_3^{2-}, S_2O_3^{2-} \rightarrow SO_4^{2-}$$
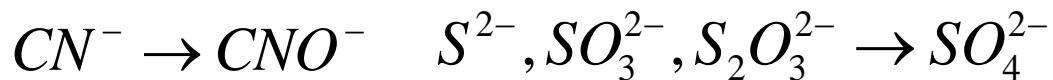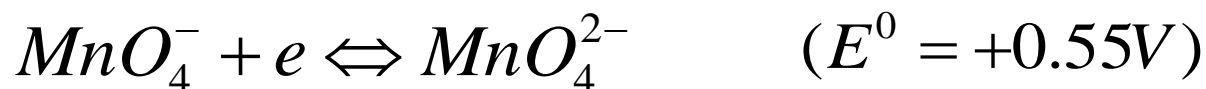
Formation of MnO_2 interfere the end point
Allow the solid to settle down before the first excess of MnO_4 can be detected

c) Reduction to +6 state:

MnO$_4^-$ is reduced to **manganate state in strong alkaline medium** (1 M or more).

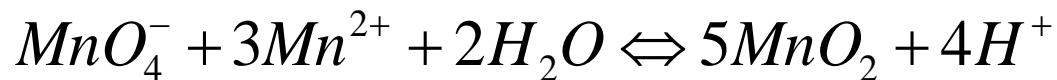$$MnO_4^- + e \Leftrightarrow MnO_4^{2-} \qquad (E^0 = +0.55V)$$

•Used to determine organic compounds such as the oxidation HCHO to CO$_3^{2-}$, CN$^-$ to CNO$^-$ and other organic compounds.

Detection of end point

**Self indicator**, in case of dilute solution redox indicator maybe used.

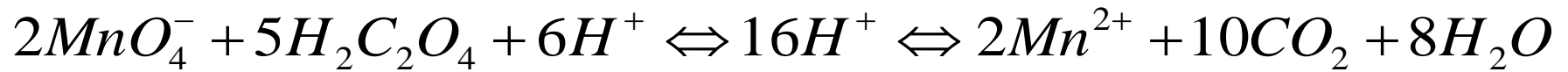The MnO_4^- end point is not permanent. It gradually fades away due to the reaction.

$$MnO_4^- + 3Mn^{2+} + 2H_2O \Leftrightarrow 5MnO_2 + 4H^+$$

• The stability of MnO_4^- solutions: MnO_4^- solutions are stable if placed in diffused light and away of dust.

Standardization of permanganate solutions

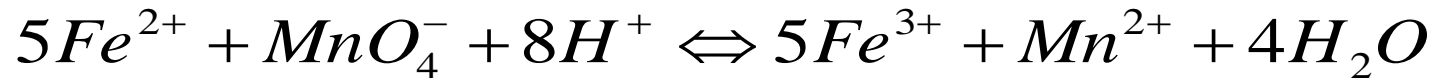**1. Against reducing agent of H$_3$As$_2$O$_3$**

$$5H_3AsO_3 + 2MnO_4^- + 6H^+ \Leftrightarrow 5H_3AsO_4 + 2Mn^{2+} + 3H_2O$$
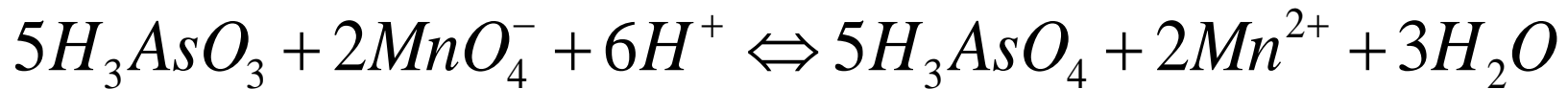
2. Against sodium oxalate

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \Leftrightarrow 16H^+ \Leftrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In hot, acid medium. The reaction is first slow, then the formed Mn^{2+} catalyzes the reaction

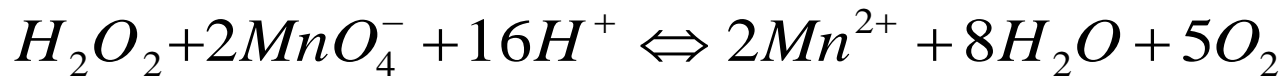# Application of MnO_4^- titrations in acidic solution

1. Determination of Iron

$$5Fe^{2+} + MnO_4^- + 8H^+ \Leftrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

- Direct titration in sulfuric acid medium.

- H_3PO_4 is added to decolorize Fe^{3+}, complexing it as colorless complex $Fe(HPO_4)^+$.

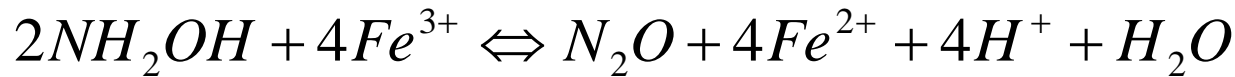- HCl is not suitable acidic medium due to the oxidation of Cl^- to Cl_2 by MnO_4^-.

$$2MnO_4^- + 10Cl^- + 16H^+ \Leftrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$
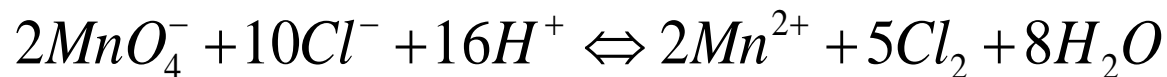
2. Some pharmaceutical applications

a) ZnO$_2$ (Zinc peroxide)

$$ZnO_2 + 2H^+ \Leftrightarrow Zn^{2+} + H_2O_2$$

$$H_2O_2 + 2MnO_4^- + 16H^+ \Leftrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

b) Hydroxylamine

$$2NH_2OH + 4Fe^{3+} \Leftrightarrow N_2O + 4Fe^{2+} + 4H^+ + H_2O$$

$$5Fe^{2+} + MnO_4^- + 8H^+ \Leftrightarrow Mn^{2+} + 5Fe^{3+} + 8H_2O$$

Application of MnO_4^- titration in alkaline medium

- MnO_4^- in alkaline medium is an important reagent for determination of organic compounds which contain –C-C, OH group (alcoholic or phenolic), NH_2, -CHO, or –C=O group.

- In strongly alkaline medium, MnO_4^- is changed to MnO_4^{2-} and organic compound is oxidized to CO_3^{2-}.

- In weakly alkaline medium, MnO_4^- is changed to MnO_2 and the organic compound is oxidized to a mixture of oxalate and carbonate.

- In both cases oxidation is a slow process accordingly back titration processes are adopted

Analysis a mixture of CH₃COOH& HCOOH

1. Total acids: acid base titration

2. Formic acid: a measured excess of standard MnO_4^- is added to the mixture and the mixture is made strongly alkaline, only HCOOH is oxidized, then the excess MnO_4^- is determined

3. After acidifying the medium and titrating the excess of MnO_4^-.

4. HAC is determined by difference

$$2MnO_4^- + HCOO^- + 3OH^- \Leftrightarrow 2MnO_4^{-} + CO_3^{2-} + 2H_2O$$
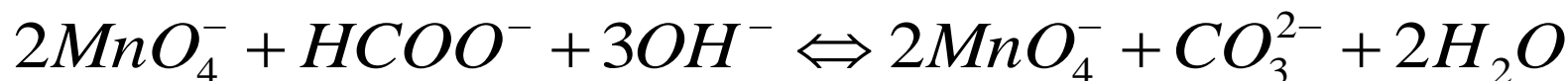
Potassium Dichromate, $K_2Cr_2O_7$

- It is limited to use than $KMnO_4$.
- Due to the stability of its solution and being obtainable in high purity (primary standard)
- $K_2Cr_2O_7$ does not oxidize HCl.

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \quad (E^o = +1.36V)$$
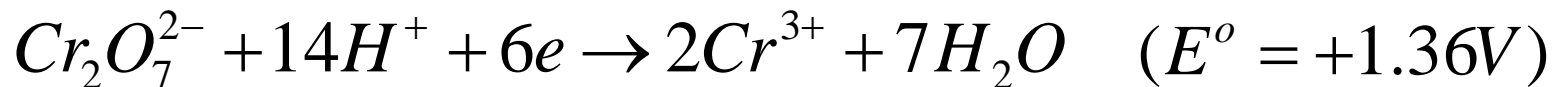
- It can not oxidize oxalic acid or ferricyanide.
- It's main application is the direct and indirect determination of Fe^{2-} ion.

- It can not serve as a self indicator reagent: $Cr_2O_7^{2-}$ is orange and Cr^{3+} is green colored. A redox indicator is used.
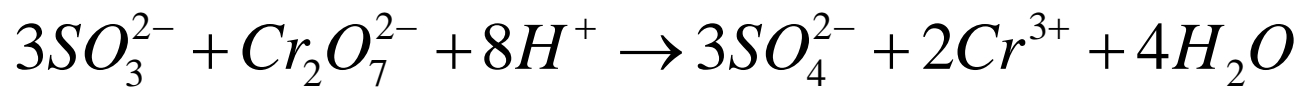
The indicators usually used are:

1) Diphenyl amine sulphonic acid
2) 4-7 dimethyl 1,10 phenoanthroline ferrous

On using $Cr_2O_7^{2-}$ as standard titrant for Fe^{2+}, H_3PO_4 or F^- are added to depress the Fe^{3+}/Fe^{2+} system potential

Applications

(1) Determination of reducing agents.

e.g.Na_2SO_3 measured excess of $Cr_2O_7^{2-}$ in presence of H_2SO_4

$$3SO_3^{2-} + Cr_2O_7^{2-} + 8H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

The excess dichromate is titrated **iodometrically**

(2) Organic compounds e.g. glycerol

Glycerol is treated with an excess of $Cr_2O_7^{2-}$ in presence of H_2SO_4 when glycerol is oxidized to CO_2 and water.

$$3C_3H_8O_3 + 7Cr_2O_7^{2-} + 56H^+ \rightarrow 14Cr^{3+} + 9CO_2 + 40H_2O$$
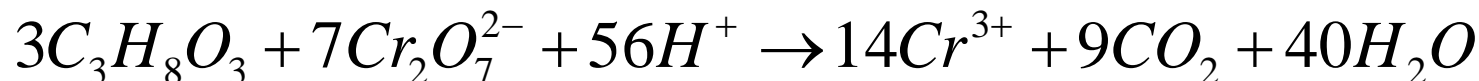
The excess dichromate is determined **iodometrically**.

Iodine as oxidant

$$I_2(solid) + 2e \rightarrow 2I^- \quad (E^o = +0.535V)$$

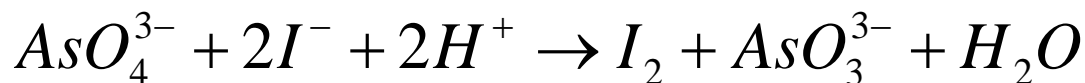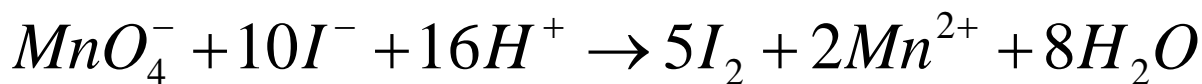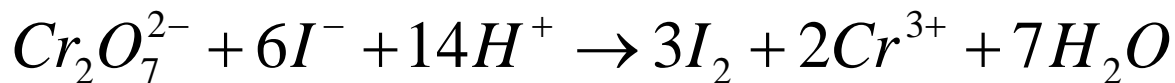- I_2 is a weak oxidant.
- Iodine/iodide system is used in quantitative analysis for direct and indirect titrimetirc methods.

1. Direct titrations (iodimetric methods)

Here I_2 is the standard, Iodine is used to determine easily oxidisable substance e.g

$$2S_2O_3^{2-} + I_2 \rightarrow 2S_4O_6^{2-} + 2I^-$$
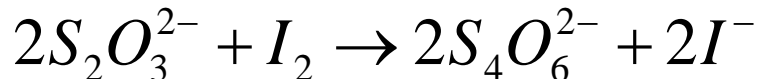
2. Indirect titrations (iodometric methods) oxidizing agents are determined by treating with an excess of iodide ion, and the librated I_2 is determined by titration with $Na_2S_2O_3$ solution

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$$

$$MnO_4^- + 10I^- + 16H^+ \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O$$

$$AsO_4^{3-} + 2I^- + 2H^+ \rightarrow I_2 + AsO_3^{3-} + H_2O$$

Preparation of solution of I$_2$

Its solubility in water is limited, but in presence of I$^-$ ion, iodine dissolves forming the soluble tri iodide complex:

$$I_2 + I^- \rightarrow I_3^-$$

Detection of the End Point in Iodine Titrations

1. **The use of starch:** the I_3^- gives a soluble deep blue adsorption complex with starch

In strong acid medium starch hydrolyses giving products which give with iodine non reversible reddish color which masks the end point change.

2. **Use of organic solvent (chloform of CCl_4)**

- These solvents give intensely colored purple solution, and the end point will be the appearance of disappearance of the purple color in the organic solvent layer.
- This method is useful in case of very dilute solutions and in case of high acidity.

Sources of Error In Iodimetry

1) I_2 is volatile (high vapor pressure) especially at high temperature and at a low concentration of I^- ion.

2) I_2 concentration is changed if the solution gets in contact with rubber, organic matter, dust, SO_2 , H_2S.

Reference

Daniel Harris,(2007), "Quantitative Chemical Analysis" 7th Edition, New York, Chapters 10& 11.