Reduction & Oxidation

Unit 9

Reactivity, Electrolytic Cells,
Electrode Potentials

Writing RedOx Equations using 1/2 Reactions

Summary of steps in writing redox equations.

1. Assign oxidation states to determine which atoms are being oxidized and which are being reduced.
2. Write half-equations for oxidation and reduction as follows:
   (a) balance the atoms other than H and O;
   (b) balance each half-equation for O by adding H_2O as needed;
   (c) balance each half-equation for H by adding H^+ as needed;
   (d) balance each half-equation for charge by adding electrons to the sides with the more positive charge.
   (e) check that each half-equation is balanced for atoms and for charge.
3. Equalize the number of electrons in the two half-equations by multiplying each appropriately.
4. Add the two half-equations together, cancelling out anything that is the same on both sides.

Page 413 for Worked Example.

Example to start the day!

- Balance the following reactions which occur in acidic solutions:
  - $I_{2(aq)} + OCl^-_{(aq)} \rightarrow IO_3^-{}_{(aq)} + Cl^-_{(aq)}$
  - $MnO_4^-{}_{(aq)} + H_2SO_{3(aq)} \rightarrow Mn^{+2}{}_{(aq)} + SO_4^{-2}{}_{(aq)}$

RedOx Titrations

- Equivalence point = stoichiometric reaction between species by transferring electrons.

Acid-base titration	RedOx titration
Neutralization reaction between acid and base	redox reaction between Ox Agent & Red Agent
protons are transferred from acid to base	electrons are transferred from RA to OA.

- Commonly used in food & beverage, pharmaceutical and environmental industries.

Analysis of iron with manganate (VII)

- $KMnO_4$ in an acidic solution

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

Purple Colorless

Equivalence indicated by purple to colorless…internal indicator

Example

- All the iron in a 2.000 g tablet was dissolved in an acidic solution and converted to Fe^{2+}. This was then titrated with $KMnO_4$. The titration required 27.50 cm^3 of 0.100 mol dm^{-3} $KMnO_4$. Calculate the total mass of iron in the tablet and its percentage by mass. Describe what would be observed during the reaction, and how the equivalence point can be detected.

Iodine-thiosulfate reaction

- $2I^-_{(aq)}$ + oxidizing agent --> $I_{2(aq)}$ + reduced product
- Oxidizing agents include $KMnO_4$, KIO_3, $K_2Cr_2O_7$ and NaOCl
- Liberated I_2 titrated with $Na_2S_2O_3$ using starch as indicator

Oxidation: $2S_2O_3^{2-}{}_{(aq)} \rightarrow S_4O_6^{2-} + 2e^-$

Reduction: $I_2 + 2e^- \rightarrow 2I^-$

$$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow 2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

Deep blue in presence of starch

Example #2

- Household bleach is an oxidizing agent that contains sodium hypochlorite, NaOCl, as the active ingredient. It reacts with iodide ions in acidic solutions as follows:
- $OCl^{-}_{(aq)} + 2I^{-}_{(aq)} + 2H^{+}_{(aq)} \text{-->} I_{2(aq)} + Cl^{-}_{(aq)} + H_2O_{(l)}$
- A 10.00 cm^3 sample of bleach was reacted with a solution of excess iodide ions, and the liberated iodine was then titrated with $Na_2S_2O_3$. The titration required 38.65 cm^3 of 0.0200 mol dm^{-3} $Na_2S_2O_3$. Determine the concentration of OCl^- in the bleach.

Winkler method for calculating dissolved oxygen

- Dissolved O_2 an indicator of water quality.
- As pollutants increase, available O_2 decreases, hurting aquatic life.
- BOD (biological oxygen demand) measures degree of pollution.
- Oxygen used to decompose organic matter in water per unit time (high BOD is bad).

Winkler Method

1. Dissolved oxygen 'fixed' by addition of $MnSO_4$. This causes oxidation of Mn.

- $2Mn^{2+}_{(aq)} + O_{2(g)} + 4OH^-_{(aq)}$ --> $2MnO_{2(aq)} + 2H_2O_{(l)}$

2. Acidified I^- added and oxidized by the Mn(IV)

- $MnO_{2(aq)} + 2I^-_{(aq)} + 4H^+_{(aq)}$ --> $Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$

3. Iodine titrated with $Na_2S_2O_3$.

- $2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)}$ --> $2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

- Overall, for every 1 mole of O_2 in the water, 4 mol of $S_2O_3^{2-}$ are used.

Example #3

- A 500 cm^3 sample of water was collected and tested for dissolved oxygen by the addition of $MnSO_4$ in basic solution, followed by the titration of acidified KI. It was found that 12.50 cm^3 of 0.0500 mol dm^{-3} $Na_2S_2O_{3(aq)}$ was required to react with iodine produced. Calculate the dissolved oxygen content of the water in g dm^{-3}.

Reactivity: Metals and NM

- When looking at a reaction, you can tell if it will occur by looking at an activity series (TABLE J from last year) (pushing electrons)
- For example:
  - Mg, Al, Zn, Fe, Pb, Cu, Ag
  - Mg - strongest reducing agent (oxidizes most readily)
  - Ag - weakest reducing agent (oxidizes least readily)

Reactivity: Metals and NM

- Example:
  - Predict whether the following reaction will occur:
    - $ZnCl_{2(aq)} + 2Ag_{(s)} \rightarrow 2AgCl_{(aq)} + Zn_{(s)}$ Nope
    - $2FeCl_{3(aq)} + 3Mg_{(s)} \rightarrow 3MgCl_{2(aq)} + 2Fe_{(s)}$ Yup

- **IF the ATOM is above the ION in Table 25, the reaction will be spontaneous.**

Reactivity: Metals and NM

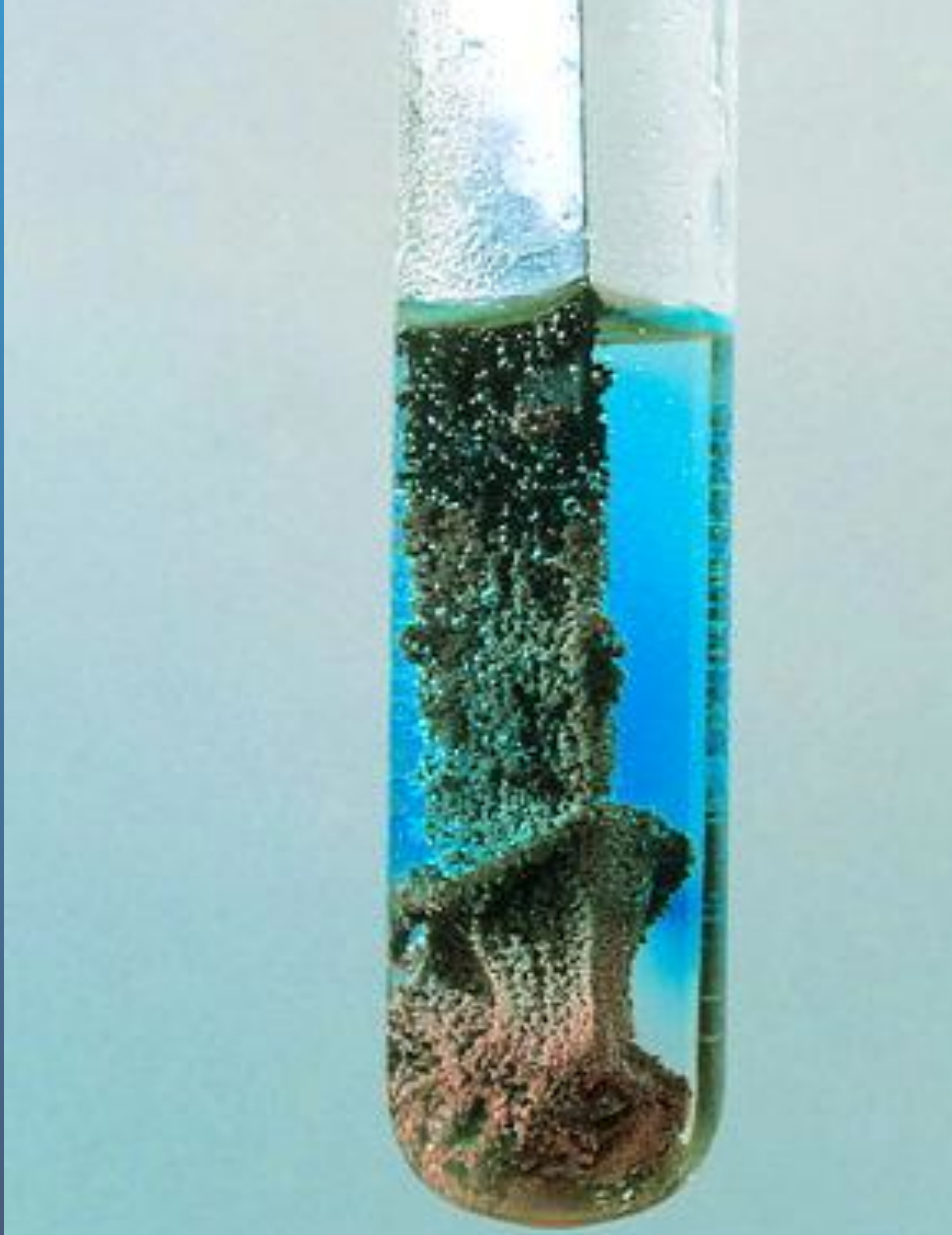
- For non-metals, the halogens are the most common group of oxidizing agents:
  - F_2, Cl_2, Br_2, I_2
  - Flourine - strongest oxidizing agent
  - Iodine - weakest oxidizing agent
    - $Cl_{2(aq)} + 2KI_{(aq)} \rightarrow 2KCl_{(aq)} + I_{2(aq)}$ K^+ is a spectator
    - $Cl_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + I_{2(aq)}$

Why does this reaction occur?

Voltaic Cells

- Example:
  - $Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$
  - A spontaneous reaction

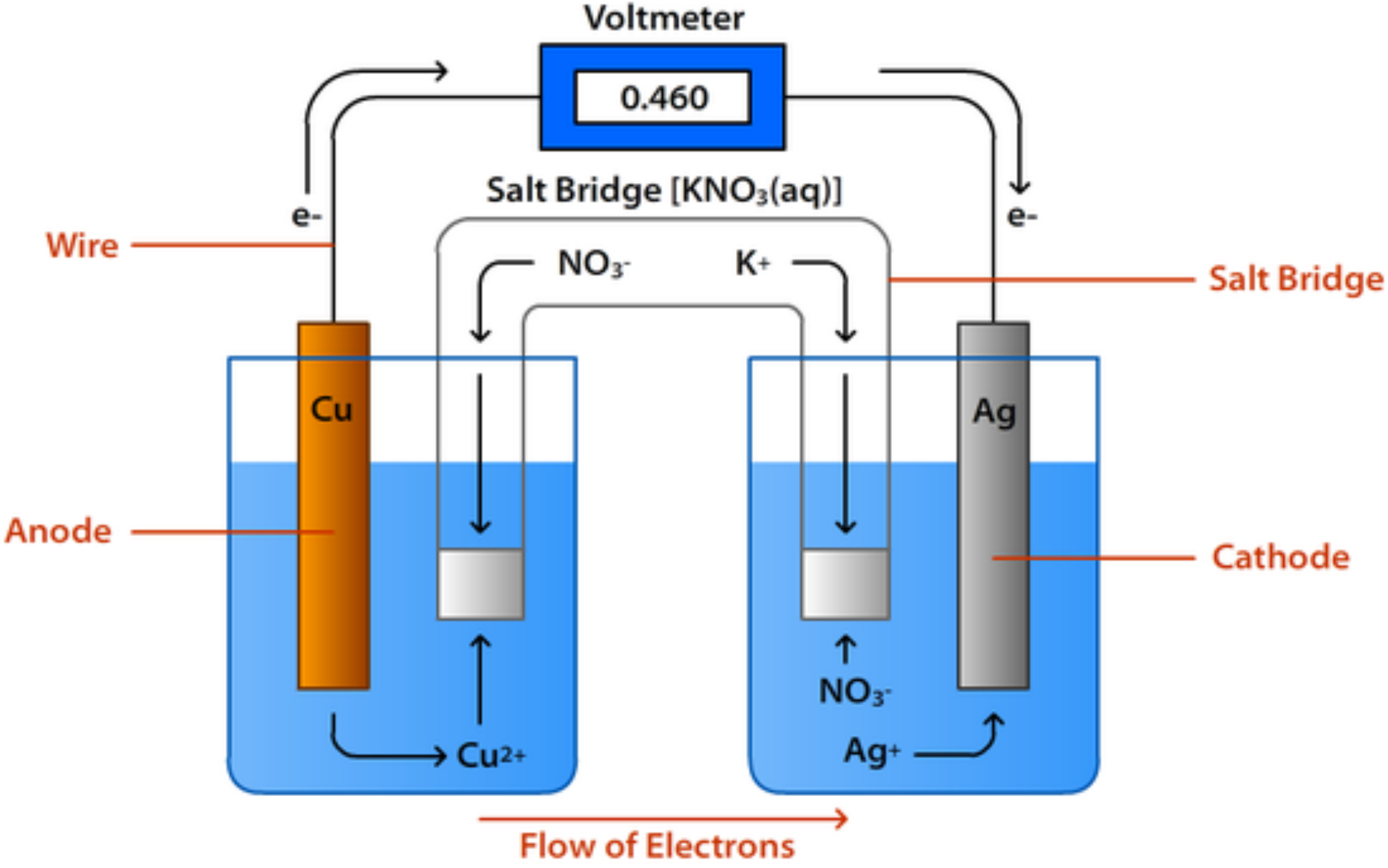
If this takes place in a voltaic cell…what can happen?



Voltaic Cells

- $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ oxidation half cell
- $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ reduction half cell

- These half cells will generate electrical potentials
  - Chemical Energy converted to Electrical Energy

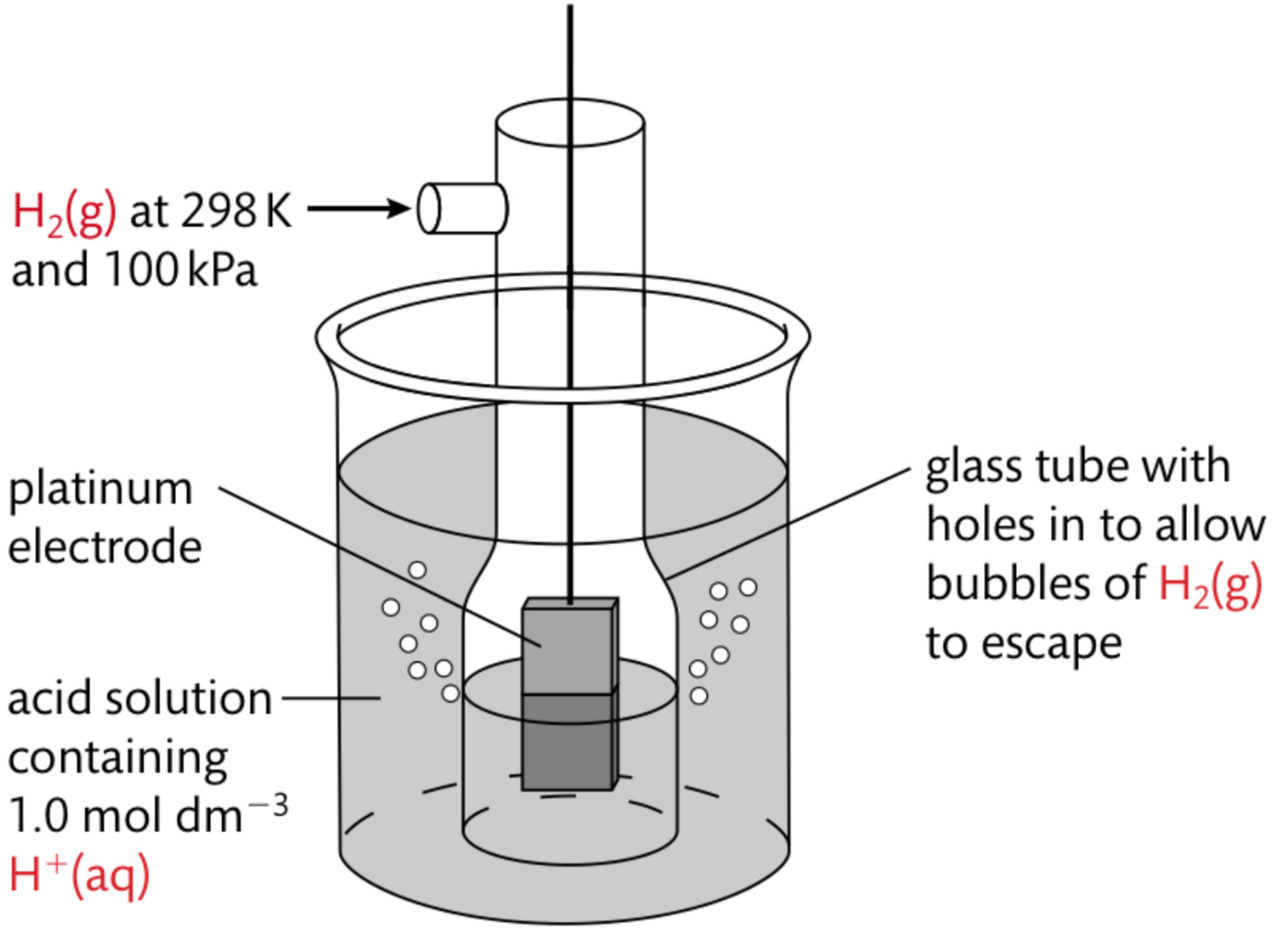

Voltmeter
0.460
Salt Bridge [KNO3(aq)]
e-
e-
Wire
NO3-
K+
Salt Bridge
Cu
Ag
Anode
Cathode
Cu2+
NO3-
Ag+
Flow of Electrons

Standard Electrode Potentials

- Electrodes cannot be isolated to measure a standard electrode potential - must be measured in tandem
- Must be a way to have a standard:
  - Standard Hydrogen Electrode (SHE) - provides baseline for measuring and comparing other half-cells

Standard H_2 Electrode (SHE)

- Platinum electrode used
  - In an acidic solution (H^+) and $H_{2(g)}$ to form an equilibrium
  - This half cell is assigned an arbitrary value of zero volts (0.00 V)

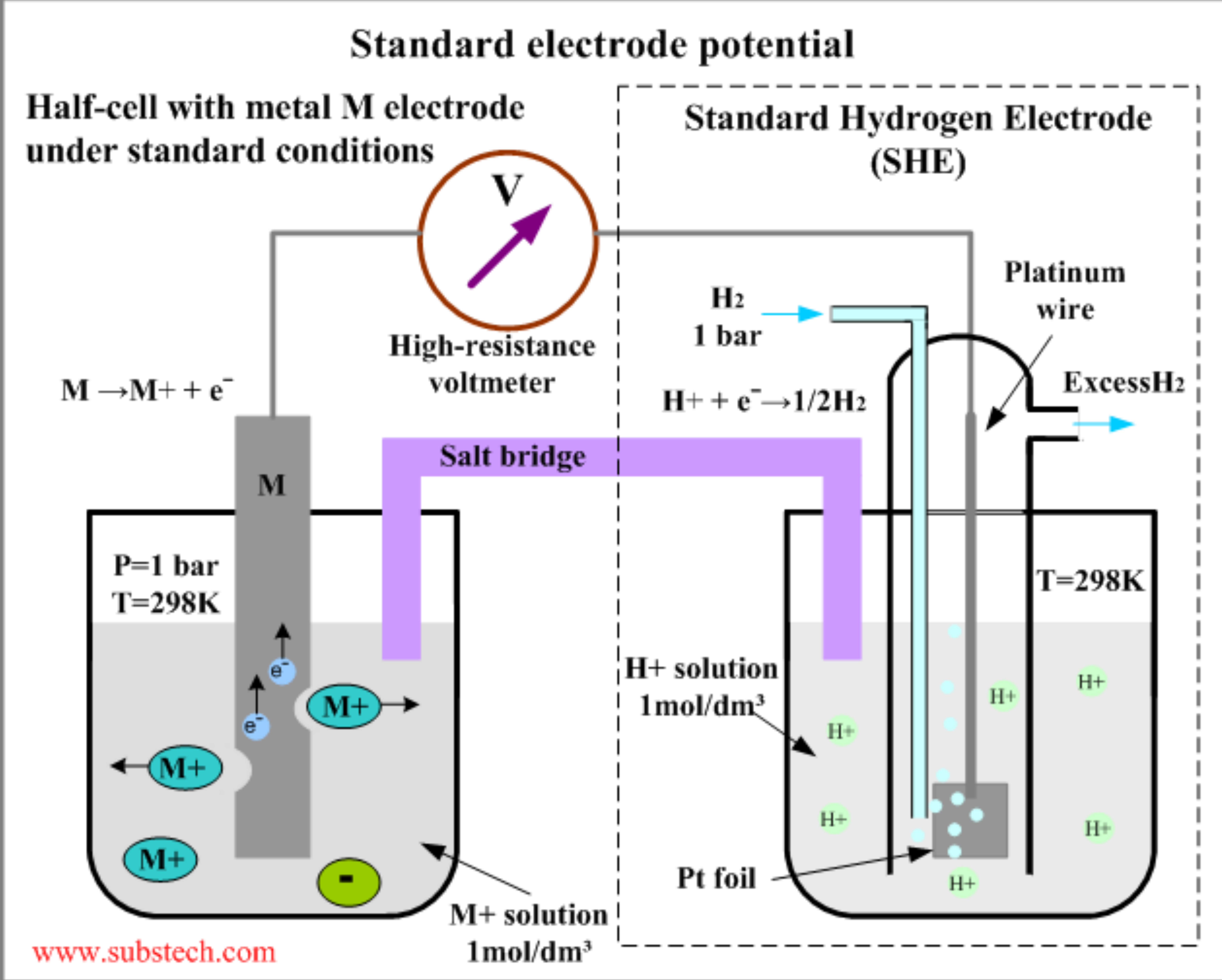

$H_2(g)$ at 298 K and 100 kPa
platinum electrode
glass tube with holes in to allow bubbles of $H_2(g)$ to escape
acid solution containing 1.0 mol dm^{-3} $H^+(aq)$

Measuring Electrode Potentials

- Standard Conditions:
  - Concentration of solutions = 1 mol dm^{-3}
  - Pressure of gases = 100 kPa
  - Substances must be pure
  - Temperature = 298K or 25°C
  - If the half-cell doesn't include a solid metal, Pt is used as the electrode
- Cells that exist under these conditions are <u>standard half-cells</u>

If M = Cu,
E° = +0.34V

The positive E° value means Cu half-cell is more likely to be reduced than the H_2 half cell



Standard Electrode Potentials

- Since half-reactions can either be oxidation or reduction, we need to standardize which electrode the potential (voltage) represents
- The *standard electrode potential* is always given for the **reduction** reaction
- ∴ E° (standard electrode potential) is often called the *standard reduction potential*
- Table 24 in your IB Data Booklet!

Table 24: Standard Electrode Potentials

- All for the reduction reaction
- E° → reduction potential
- If you switch the sign on the value --> Oxidation
- Do not need to be scaled for stoichiometry (# of e^-)
- The more positive the value, the more readily it is reduced

Example:

- Calculate the emf (electromotive force) for a voltaic cell constructed from a zinc half-cell and a copper half-cell. Identify the anode and cathode.
  - (HINT! - figure out who is more likely to oxidize, find the half reactions and calculate)
  - $E^0_{cell} = E^0_{\text{half-cell where reduction occurs}} - E^0_{\text{half-cell where oxidation occurs}}$
  - DO NOT INVERT any values from Table 24

Example

- Use E° values to deduce the reaction that occurs when $Cu_{(s)}$ and $Ag_{(s)}$ are added to a solution that contains $Cu^{+2}_{(aq)}$ and $Ag^{+}_{(aq)}$. Write the equation for this reaction.

Determining Spontaneity

- $E°_{cell}$: positive - the reaction will occur spontaneously
- $E°_{cell}$: negative - the reaction will not occur
  - If $E°_{cell}$ is negative, the reverse reaction will be spontaneous

Example

- Use E° values to determine whether the reaction:
  - $Ni_{(s)} + Mn^{+2}_{(aq)} \rightarrow Ni^{+2}_{(aq)} + Mn_{(s)}$
- Spontaneous under standard conditions?

Electrode Potential & Free Energy

$$\Delta G^{o} = -nFE^{\circ}$$

- n = # of moles of electrons transferred in the reaction
- F = the charge carried by 1 mole of electrons, known as the Faraday constant.

- When E_{cell} is positive, ΔG is negative => spontaneous
- When E_{cell} is negative, ΔG is positive => non-spontaneous

Example

$$\Delta G^{o} = -nFE^{\circ}$$

Calculate the free energy change at 298 K for the zinc - copper voltaic cell, which has a standard cell potential of +1.10 V

Summary

$\Delta G^{\circ} = -nFE^{\circ}$

Type of Cell	E_{cell}	ΔG	Type of Rxn
voltaic	>0	<0	spontaneous
electrolytic	<0	>0	non-spontaneous
equilibrium	0	0	dead battery

Electrolytic Cells

- uses an external source of voltage to bring about a redox reaction that would have otherwise been non-spontaneous
- page 443 for picture of electrolytic cells

	Voltaic Cell		*Electrolytic Cell*	
Anode	oxidation	negative	oxidation	positive
Cathode	reduction	positive	reduction	negative

Electrolysis

- The break down of a molten ionic substance through the use of electricity
- $NaCl_{(l)} \rightarrow Na^+_{(l)} + Cl^-_{(l)}$
- Na^+ to the cathode (negative electrode)
- Cl^- to the anode (positive electrode)

Predicting the Products in Electrolytic Cells

- Identify the ions and determine which electrode they will migrate to
- Balance the electrons lost and gained & write the equation for the reaction
  - (Remember - # of e^- lost = # of e^- gained)
- Consider what changes you might **<u>see</u>** at each electrode

Example

- Describe the reactions that occur at the two electrodes during the electrolysis of molten lead (II) bromide. Write an equation for the overall reaction and comment on any likely changes you will observe.

A Potential Problem

- What do we know about melting ionic compounds? Why is this significant?
- NaCl (MP = 801°C)
- If we add molten $CaCl_2$, this temperature drops to about 580°C for the mixture of the two
- What could go wrong in an electrolytic cell with both Ca^{+2} and Na^{+} in the system?
- Continued…

Electrolytic cell with multiple cations…

- Draw electrolytic cell…
- $Ca^{+2}_{(aq)} + 2e^{-} \rightarrow Ca_{(s)}$
- $Na^{+}_{(aq)} + e^{-} \rightarrow Na_{(s)}$
- Find the E° for each
  - Which is more likely to be reduced?
    - Since Na^{+} is more likely to be reduced, adding Ca will not change the outcome

In Groups…Add to your notes…

- Read 447-450 CAREFULLY!!
- Electrolysis of Water page 448 (12-15 minutes)
- Electrolysis of NaCl page 449 (12-15 minutes)
  - (Check out Purple ! on page 449 margin)
- Discussion on Electrolysis of Copper Sulfate to assess understanding

Factors Affecting the Amount of Product

- $NaCl_{(l)}$ electrolyte — At cathode:
  - $Na^{+}_{(l)} + e^{-} \rightarrow Na_{(l)}$
- $PbBr_{2(l)}$ electrolyte — At cathode:
  - $Pb^{+2}_{(l)} + 2e^{-} \rightarrow Pb_{(s)}$
- What is the difference between the two?
- What does that mean?

Factors Affecting the Amount of Product

- The charge, depends on the current (how much electricity is flowing) and the amount of time the current flows for
  - Charge = Current x Time (seconds)
    - Page 452!

Example Problem

- A) How many grams of Cu are deposited on the cathode of an electrolytic cell containing $CuCl_{2(aq)}$ if a current of 2.00 A is run for 15 min?
- B) How would the amount differ if the same conditions were applied using $CuCl_{(aq)}$?

Example Problem

- If a current of 2.00 A is passed through a solution of $AgNO_3$ for 10 minutes it is found that 0.0124 moles of Ag are formed.

(a) How much would form if a current of 1.00 A is passed through the same solution for 30 minutes?

(b) What amount of Cu would form if the quantity of electricity in (a) was passed through a solution of $CuSO_4$?

Factors that might influence voltage of a Cell

- Size of the electrodes
- Distance between the electrodes
- Type of electrode (which metals)
- Nature of solutions (which solutions)
- Concentration of solutions

Electroplating

- An Electrolytic Cell used for electroplating has the following features:
  - An electrolyte containing the metal ions to be deposited
  - A cathode made of the object to be plated
  - sometimes the anode is made of the same metal which is to be coated (replenish an oxidized metal)

Purposes

- Decorative
- Corrosion control - layer of zinc - galvanized iron
  - (sacrificial protection)
- Improvement of function - chromium
  - improves wear on some parts - tools