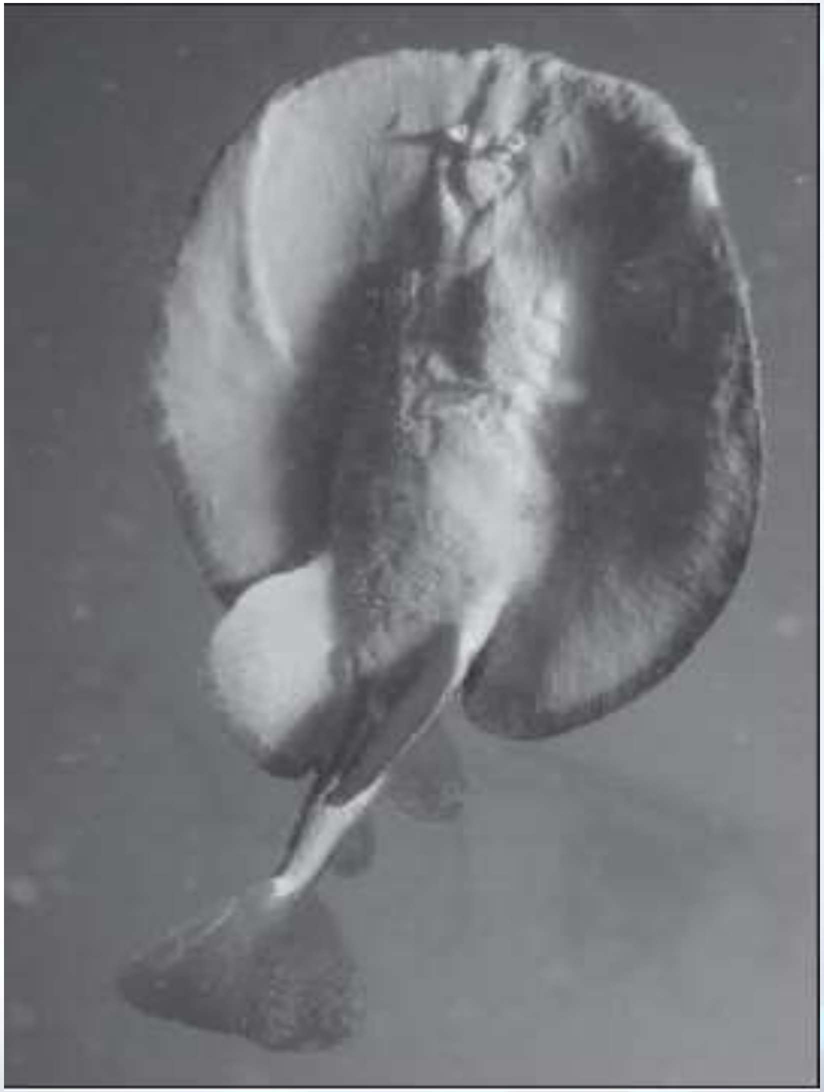
Lecture № 8

Analytical chemistry

Redox Equilibrium



Redox Reactions

- How do we identify redox pairs?
- How do we write balanced equations for redox processes?
- How do potentials govern energy?
- How do concentrations govern potentials?
- Application of redox reaction

Oxidation-reduction reaction (or redox reaction) is a reaction in which electrons are transferred between species or in which atoms change oxidation number.

$$\boxed{Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2}$$

Ox_1 is reduced to Red_1, and Red_2 is oxidized to Ox_2. Ox_1 is the oxidizing agent, and Red_2 is the reducing agent.

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

This equation is the sum of the two half-reactions

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

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

Ce^{4+}, is called an **oxidizing agent,** or an **oxidant.** A **reducing agent, or reductant** is Fe^{2+}, that *donates electrons* to another species. To describe the chemical behavior, we say that Fe^{2+} is oxidized by Ce^{4+}; similarly, Ce^{4+} is reduced by Fe^{2+}

Oxidation is the part of a redox reaction in which there is a loss of electrons by a species or an increase in the oxidation number of atom. **Reduction** is the part of a redox reaction in which there is a gain of electrons by a species or a decrease in the oxidation number of atom.

Oxidation number (or oxidation state) is the charge an atom in a substance would have it the pairs of electrons in each bond belonged to the more electronegative atom.

Types of Redox Reactions

1. The reaction in which electrons are transferred between a free element and a monatomic ion - ***displacement reactions***:

$Cu + 2AgNO_3 \leftrightarrow 2Ag\downarrow + Cu(NO_3)_2$

2. ***Disproportionation*** is a reaction in which a species is both oxidised and reduced:

$Hg_2(NO_3)_2 + 2NH_4OH \leftrightarrow Hg\downarrow + NH_2HgNO_3 + NH_4NO_3 + 2H_2O$

3. Redox reaction involving ***oxoanions***. Source of oxoanions are chemical combination with oxygen:

$10KBr + 2KMnO_4 + 16HCl \leftrightarrow 5Br_2 + 2MnCl_2 + 12KCl + 8H_2O$

4. ***Autocatalytic*** – in run of redox reaction forms species that is catalyst (catalyses) this reaction:

$2H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \leftrightarrow 10CO_2\uparrow + 2MnSO_4 + 2K_2SO_4 + 8H_2O$

Formed in reaction Mn^{2+} ion accelerates oxidation of oxalic acid.

6. ***Conjugated redox reactions*** called such two reactions, one of that runs spontaneously (primary (or initial) reaction), and second – only in case the first reaction running in same solution (secondary reaction).

A species, which take parts in both reactions, called actor, a species that takes part only in primary reaction is inductor, and a species that takes part only in secondary reaction is acceptor:

$KMnO_4 + 5FeCl_2 + 8HCl \leftrightarrow 5FeCl_3 + MnCl_2 + KCl + 4H_2O$ – primary (initial) reaction
actor inductor

$2KMnO_4 + 16HCl \leftrightarrow 2MnCl_2 + 5Cl_2 + 2KCl + 8H_2O$ – secondary (inducted) reaction
actor acceptor

Balancing Redox Equations

$$MnO_4^- + NO_2^- \rightleftharpoons Mn^{2+} + NO_3^-$$

First, we write and balance the two half-reactions. For MnO_4^-, we write

$$MnO_4^- \rightleftharpoons Mn^{2+}$$

To account for the 4 oxygen atoms on the left-hand side of the equation, we add $4H_2O$ on the right-hand side. Then, to balance the hydrogen atoms, we must provide $8H^+$ on the left

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

$$NO_2^- \rightleftharpoons NO_3^-$$

we add one H_2O to the left side of the equation to supply the needed oxygen and $2H^+$ on the right to balance hydrogen

$$NO_2^- + H_2O \rightleftharpoons NO_3^- + 2H^+ + 2e^-$$

Before combining the two equations, we must multiply the first by 2 and the second by 5 so that the number of electrons lost will be equal to the number of electrons gained. We then add the two half reactions to obtain

$$2MnO_4^- + 16H^+ + 10e^- + 5NO_2^- + 5H_2O \rightleftharpoons$$
$$2Mn^{2+} + 8H_2O + 5NO_3^- + 10H^+ + 10e^-$$

This equation rearranges to the balanced equation

$$2MnO_4^- + 6H^+ + 5NO_2^- \rightleftharpoons 2Mn^{2+} + 5NO_3^- + 3H_2O$$

Photograph of a “silver tree” created by immersing a coil of copper wire in a solution of silver nitrate. The result is the deposition of silver on the copper in the form of a “silver tree.”

Many oxidation/reduction reactions can be carried out in either of two ways that are physically quite different. In one, the reaction is performed by bringing the oxidant and the reductant into direct contact in a suitable container.

A spectacular example of direct contact is the famous “silver tree” experiment in which a piece of copper is immersed in a silver nitrate solution. Silver ions migrate to the metal and are reduced:

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

At the same time, an equivalent quantity of copper is oxidized:

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

By multiplying the silver half-reaction by two and adding the reactions, we obtain a net ionic equation for the overall process:

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

A unique aspect of oxidation/reduction reactions is that the transfer of electrons and thus an identical net reaction—can often be brought about in an **electrochemical cell** in which the oxidizing agent and the reducing agent are physically separated from one another.

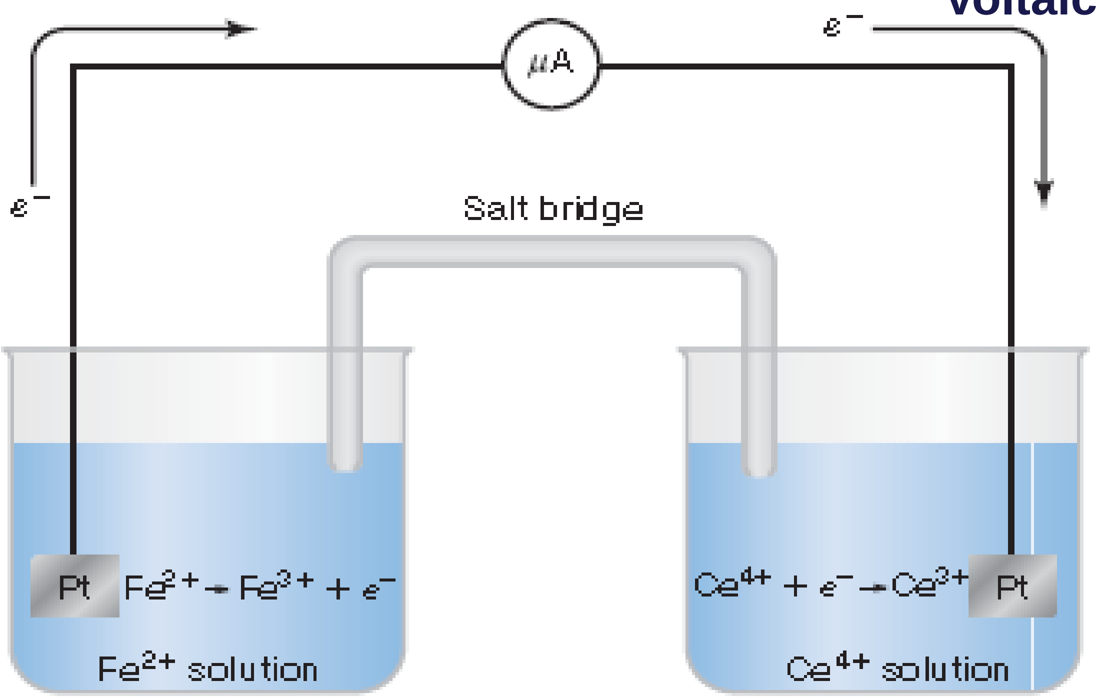
The reaction is carried out in an ***electrochemical cell*** in which the reactants do not come in direct contact with one another.

There are two kinds of electrochemical cells, **voltaic (galvanic) and electrolytic.** In **voltaic cells**, a chemical reaction spontaneously occurs to *produce electrical energy.* In **electrolytic cells**, on the other hand, *electrical energy is used to force* a nonspontaneous chemical reaction to occur, that is, to go in the reverse direction it would in a voltaic cell.

Voltaic cell

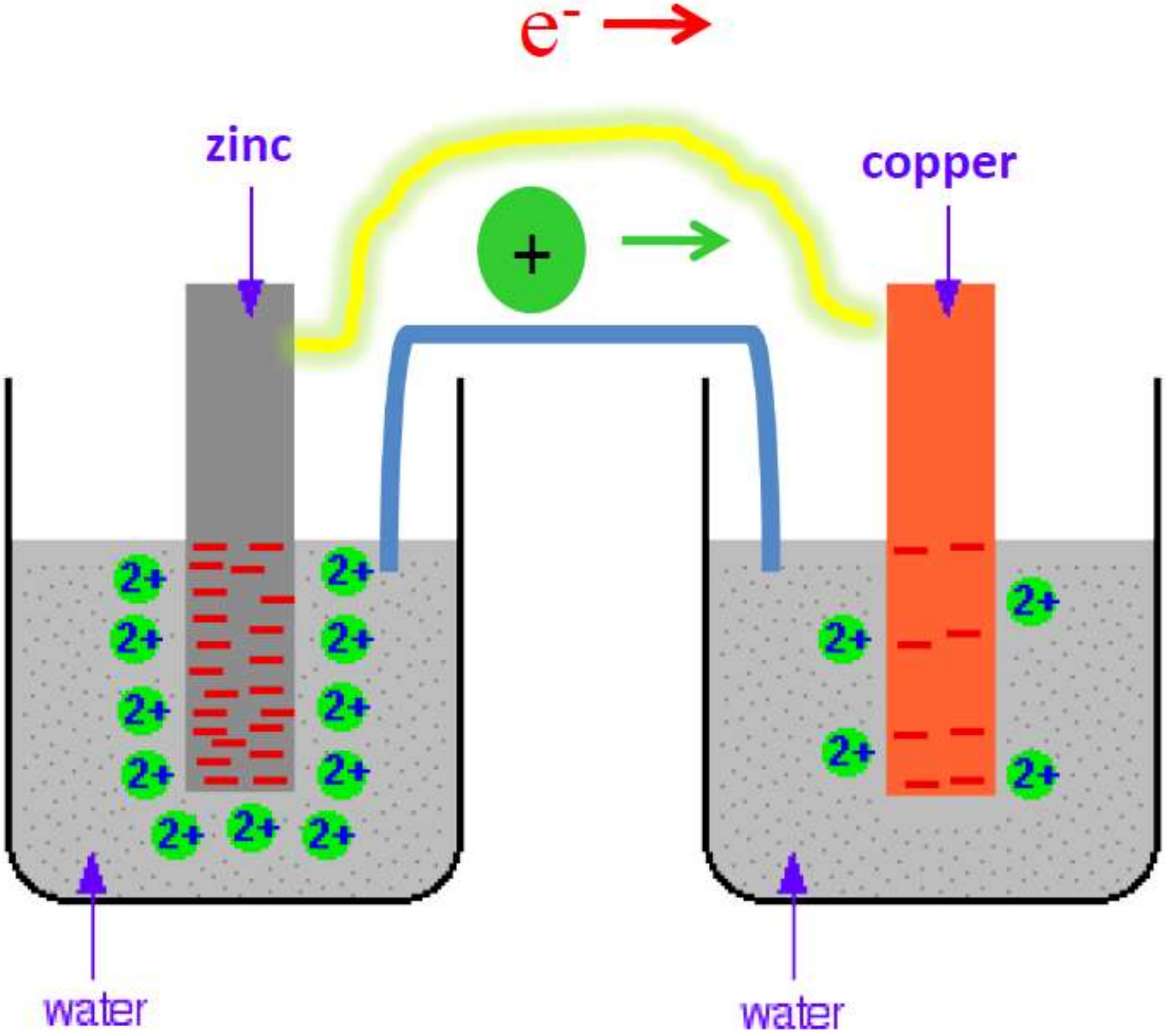
$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

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



In both types of these cells, the electrode at which oxidation occurs is the **anode,** and that at which reduction occurs is the **cathode.**

If we place two strips of metal in water then we can see the reactivity as indicated below. If we were to connect the two strips with a wire, then electrons could flow from the more negative to the the less negative strip.



However, the electrochemical cell shown below does not make a complete circuit so the current would lead to a small net transfer of charge, and then it would stop.

If we added a tube that connects the two solutions, then ions can flow between the two half-cells. This makes a complete circuit. The tube is a “salt bridge”.

Understanding the differing reactivities of metals

When metals react, they give away electrons and form positive ions. The oxidation potential gives an ordering of how easy or difficult it is to remove the electron and generate the hydrated ions.

We turn to the example of Zn and Cu. Zn is also “more reactive” than Cu meaning that it more readily gives up its electrons. This can be seen in the redox reaction:

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

We can obtain a number value for the potential of this reaction from the standard reduction potentials for each half reaction.

$$Cu^{2+} + 2e^{-} \rightarrow Cu \qquad E^{o} = +0.340\ V$$

$$Zn^{2+} + 2e^{-} \rightarrow Zn \qquad E^{o} = -0.763\ V$$

The positive sign means that the process is spontaneous in the direction it is written. Thus, copper readily forms the metal and Zu readily forms ions.

Currents in Electrochemical Cells

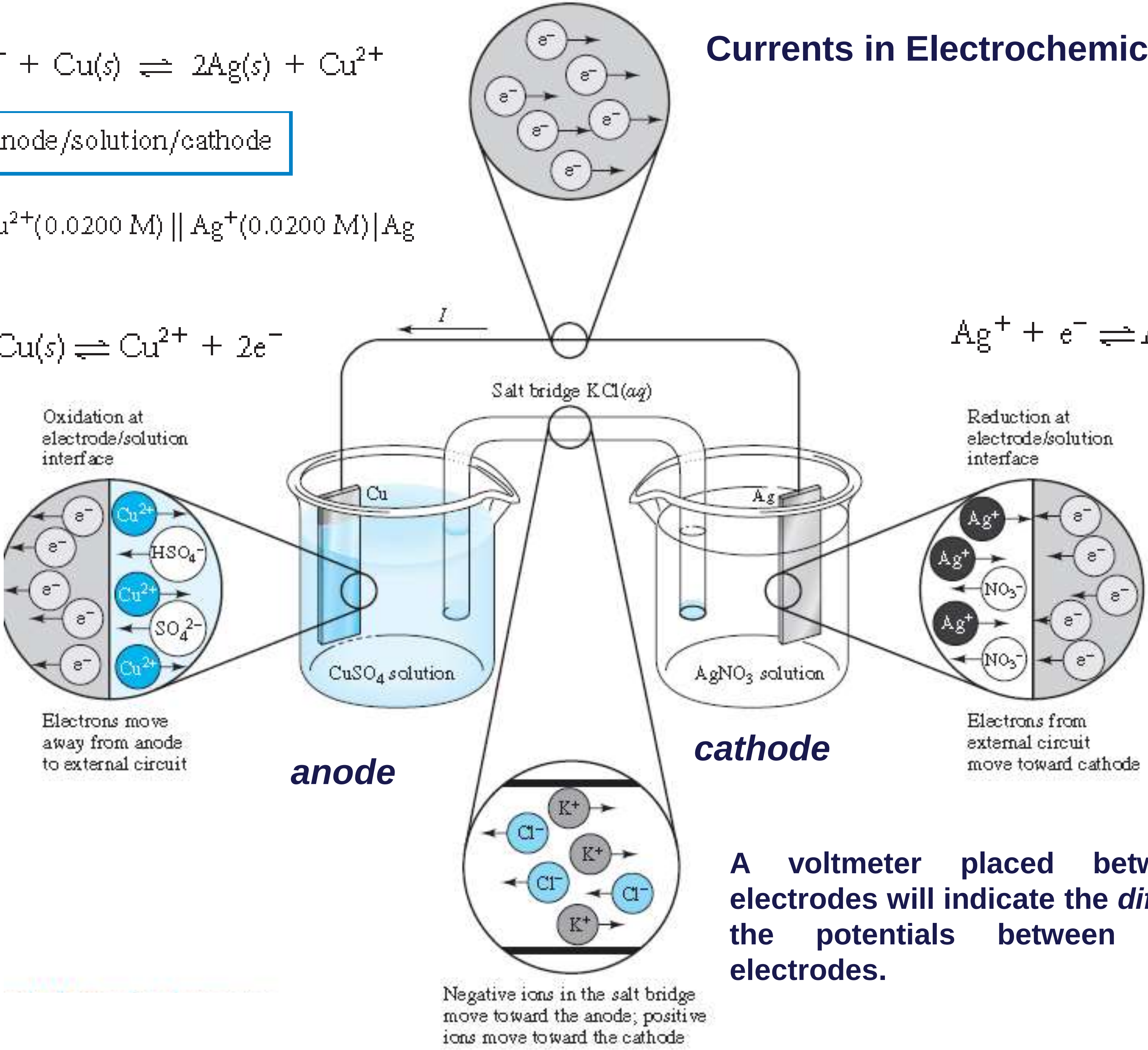
$$2Ag^{+} + Cu(s) \rightleftharpoons 2Ag(s) + Cu^{2+}$$

anode/solution/cathode

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

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

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



anode

cathode

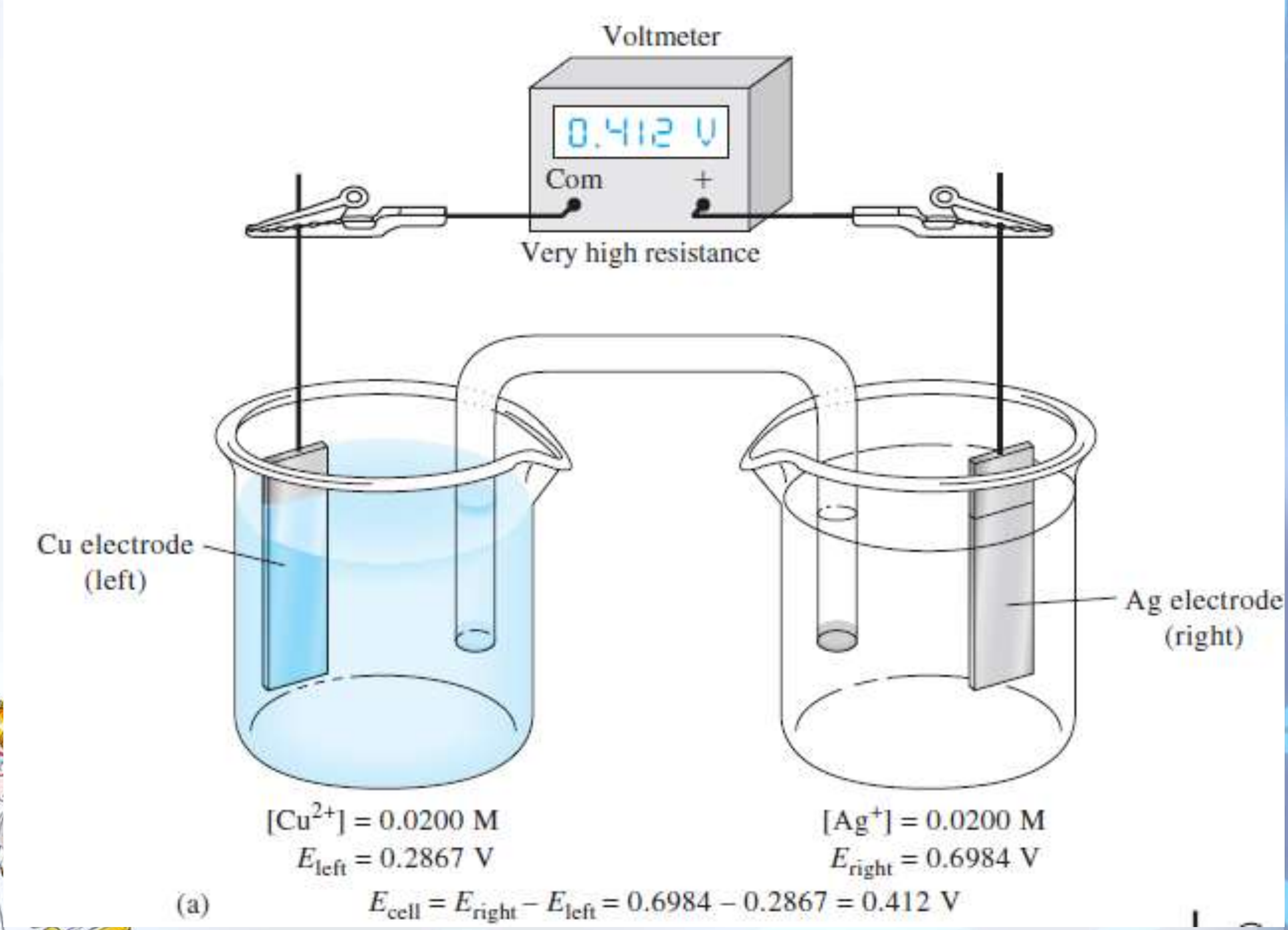
A voltmeter placed between the electrodes will indicate the *difference in* the potentials between the two electrodes.

1. Electrons carry the charge within the electrodes as well as the external conductor. Notice that by convention, current, which is normally indicated by the symbol *I,* is opposite in direction to electron flow.

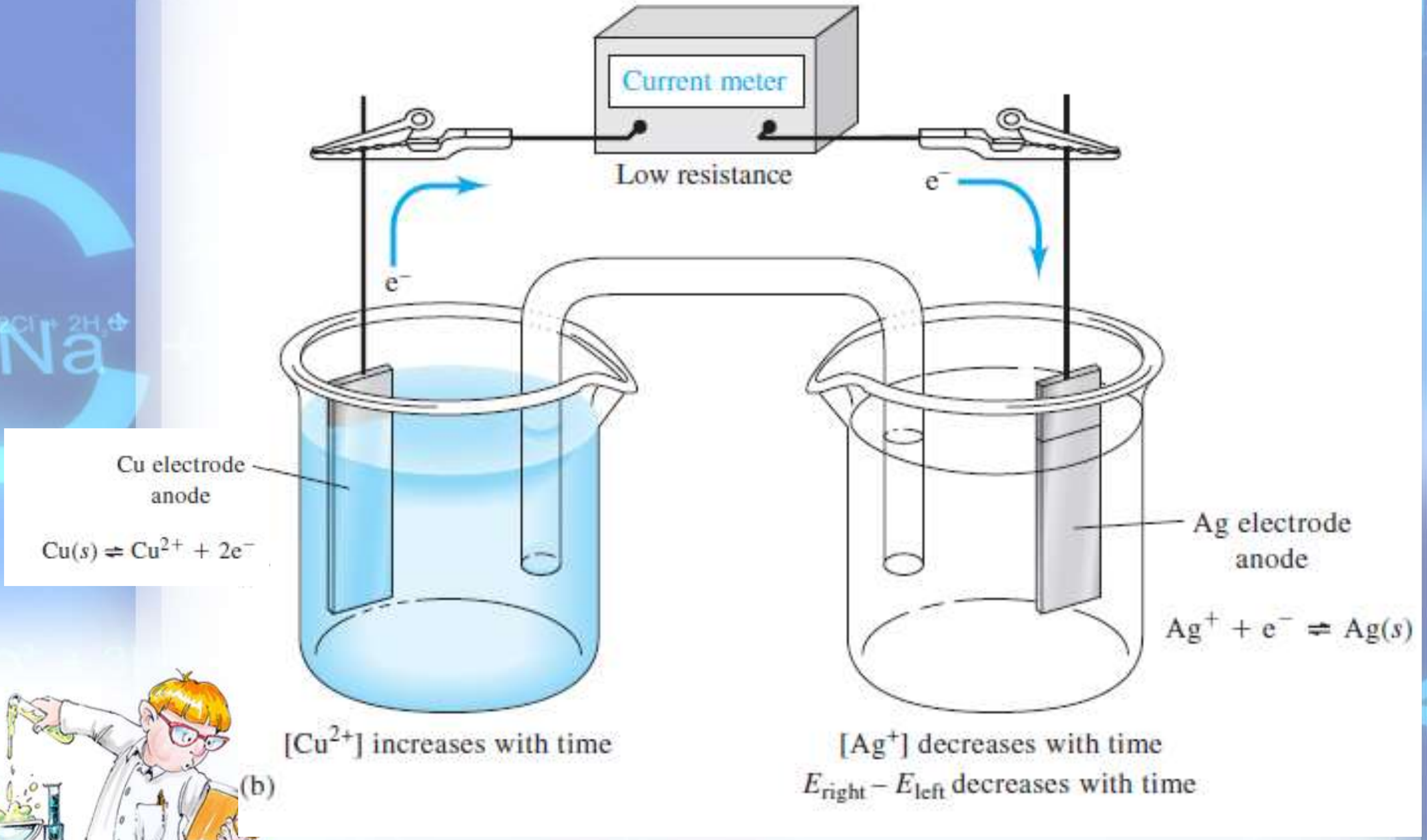
2. Anions and cations are the charge carriers within the cell. At the left-hand electrode, copper is oxidized to copper ions, giving up electrons to the electrode. As shown in Figure, the copper ions formed move away from the copper electrode into the bulk of solution, while anions, such as sulfate and hydrogen sulfate ions, migrate toward the copper anode. Within the salt bridge, chloride ions migrate toward and into the copper compartment, and potassium ions move in the opposite direction. In the right-hand compartment, silver ions move toward the silver electrode where they are reduced to silver metal, and the nitrate ions move away from the electrode into the bulk of solution.

3. The ionic conduction of the solution is coupled to the electronic conduction in the electrodes by the reduction reaction at the cathode and the oxidation reaction at the anode.

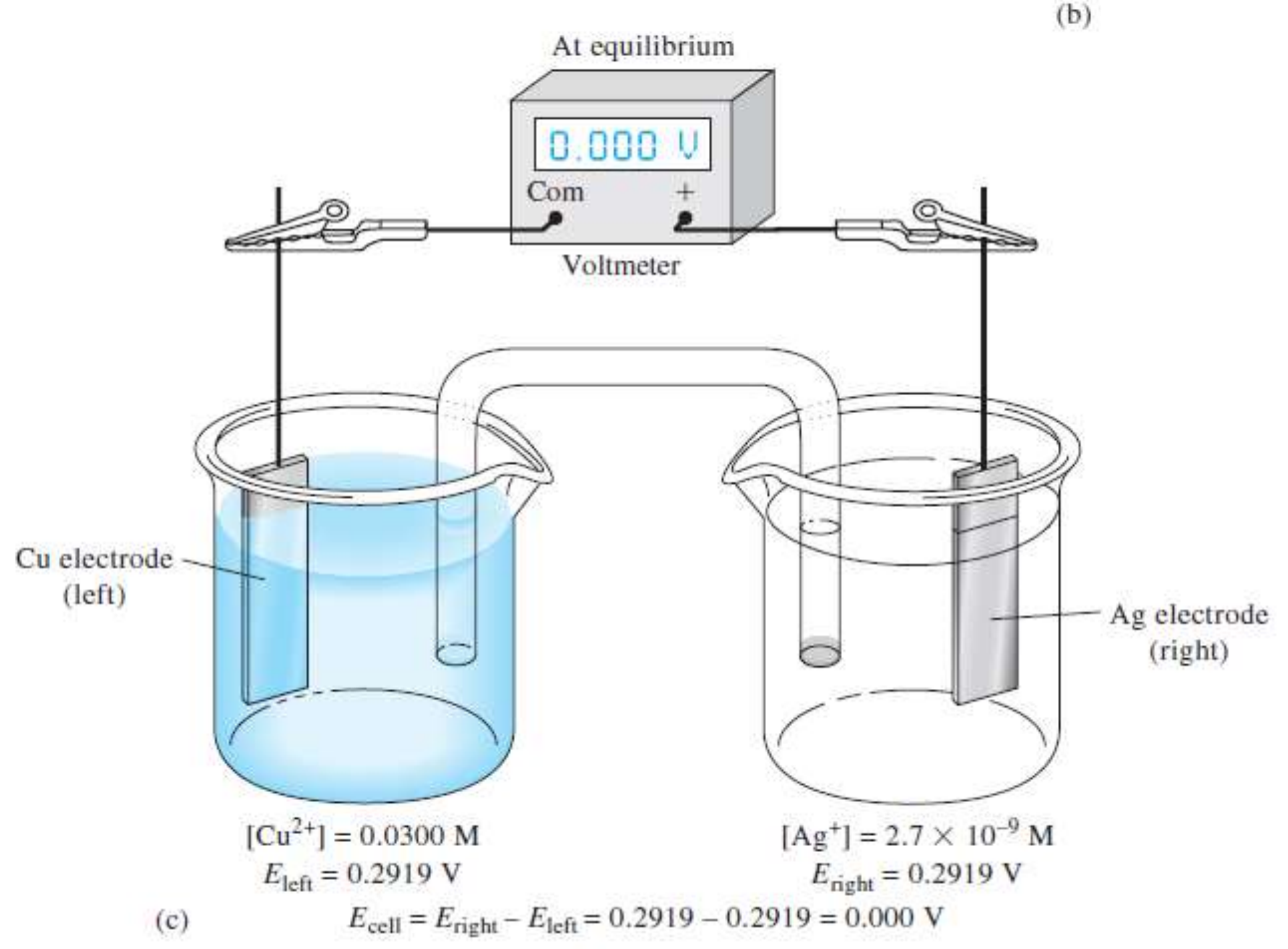
Change in cell potential after passage of current until equilibrium is reached. In (a), the high-resistance voltmeter prevents any significant electron flow, and the full open-circuit cell potential is measured. For the concentrations shown, this potential is 0.412 V.



Change in cell potential after passage of current until equilibrium is reached. In (b), the voltmeter is replaced with a low-resistance current meter, and the cell discharges with time until eventually equilibrium is reached.



Change in cell potential after passage of current until equilibrium is reached. In (c), after equilibrium is reached, the cell potential is again measured with a voltmeter and found to be 0.000 V. The concentrations in the cell are now those at equilibrium as shown.



Representing Cells Schematically

By convention, a single vertical line indicates a phase boundary, or interface, at which a potential develops. For example, the first vertical line in this schematic indicates that a potential develops at the phase boundary between the copper electrode and the copper sulfate solution. The double vertical lines represent two-phase boundaries, one at each end of the salt bridge. There is a **liquid-junction potential** at each of these interfaces. The junction potential results from differences in the rates at which the ions in the cell compartments and the salt bridge migrate across the interfaces. A liquid-junction potential can amount to as much as several hundredths of a volt but can be negligibly small if the electrolyte in the salt bridge has an anion and a cation that migrate at nearly the same rate. A saturated solution of potassium chloride, KCl, is the electrolyte that is most widely used. This electrolyte can reduce the junction potential to a few millivolts or less. For our purposes, we will neglect the contribution of liquid-junction potentials to the total potential of the cell. There are also several examples of cells that are without liquid junction and therefore do not require a salt bridge.

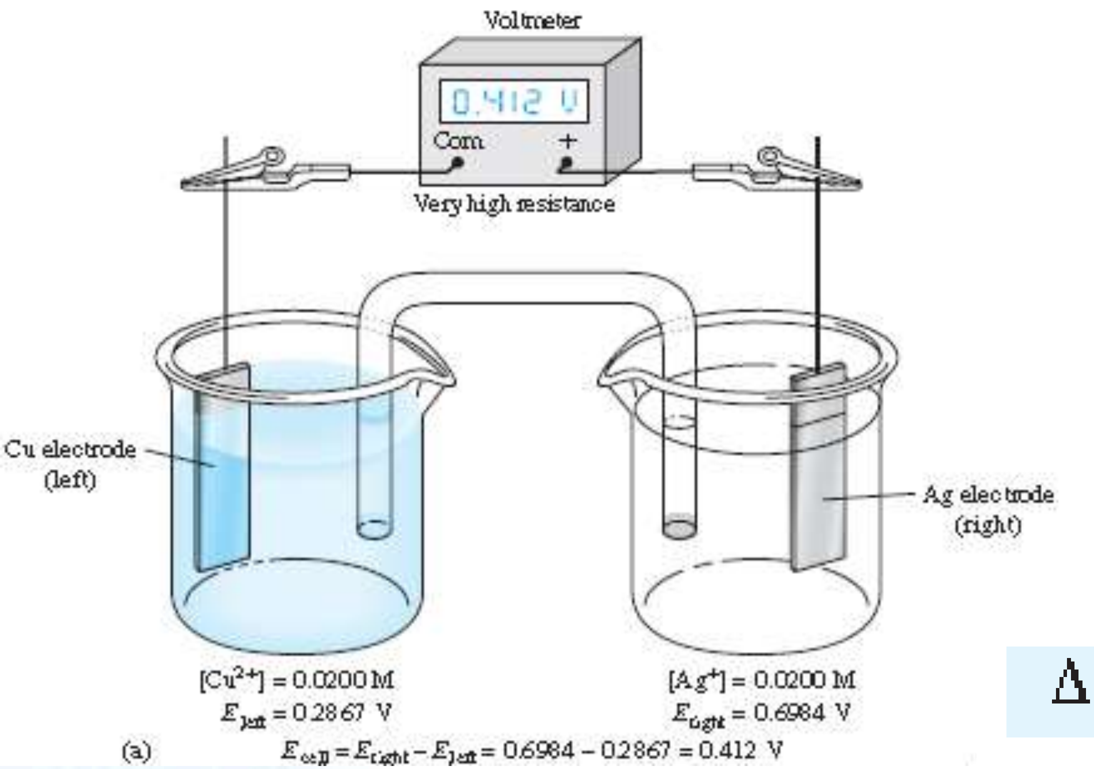
anode/solution/cathode

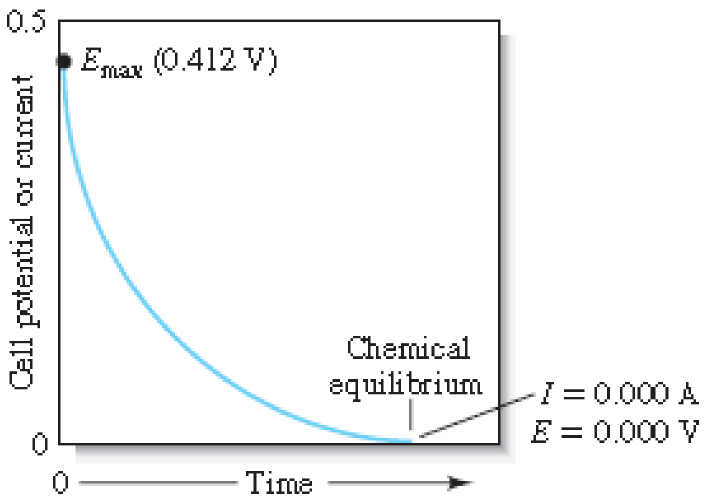
$$\mathrm{Cu} \mid \mathrm{CuSO_4}(0.0200\ \mathrm{M}) \parallel \mathrm{AgNO_3}(0.0200\ \mathrm{M}) \mid \mathrm{Ag}$$

$$\mathrm{Pt}\ |\mathrm{Red}_2(a_{\mathrm{red2i}}), \mathrm{Ox}_2(a_{\mathrm{ox2i}})|\mathrm{Red}_1(a_{\mathrm{red1i}}), \mathrm{Ox}_1(a_{\mathrm{ox1i}})|\mathrm{Pt},$$

If the reactants and products are in their **standard states, the resulting cell potential** is called the **standard cell potential**.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} - E_{\text{anode}} = E_{+} - E_{-}$$





$$\Delta G^0 = -nFE^0_{\text{cell}} = -RT \ln K_{\text{eq}}$$

if E_{cell} *is positive*, the free energy change for the reaction in the direction being considered is negative. Hence, the reaction in the direction being considered would occur spontaneously. On the other hand, if E_{cell} *is negative*, the free energy change is positive, and the reaction in the direction considered is *not the spontaneous cell reaction*

If the potentials of all half-reactions could be measured, then we could determine which oxidizing and reducing agents will react. There is no way to measure individual electrode potentials. But, as we just saw, the *difference between* two electrode potentials can be measured. Therefore, an arbitrary standard is chosen.

The electrode potential of the half-reaction:

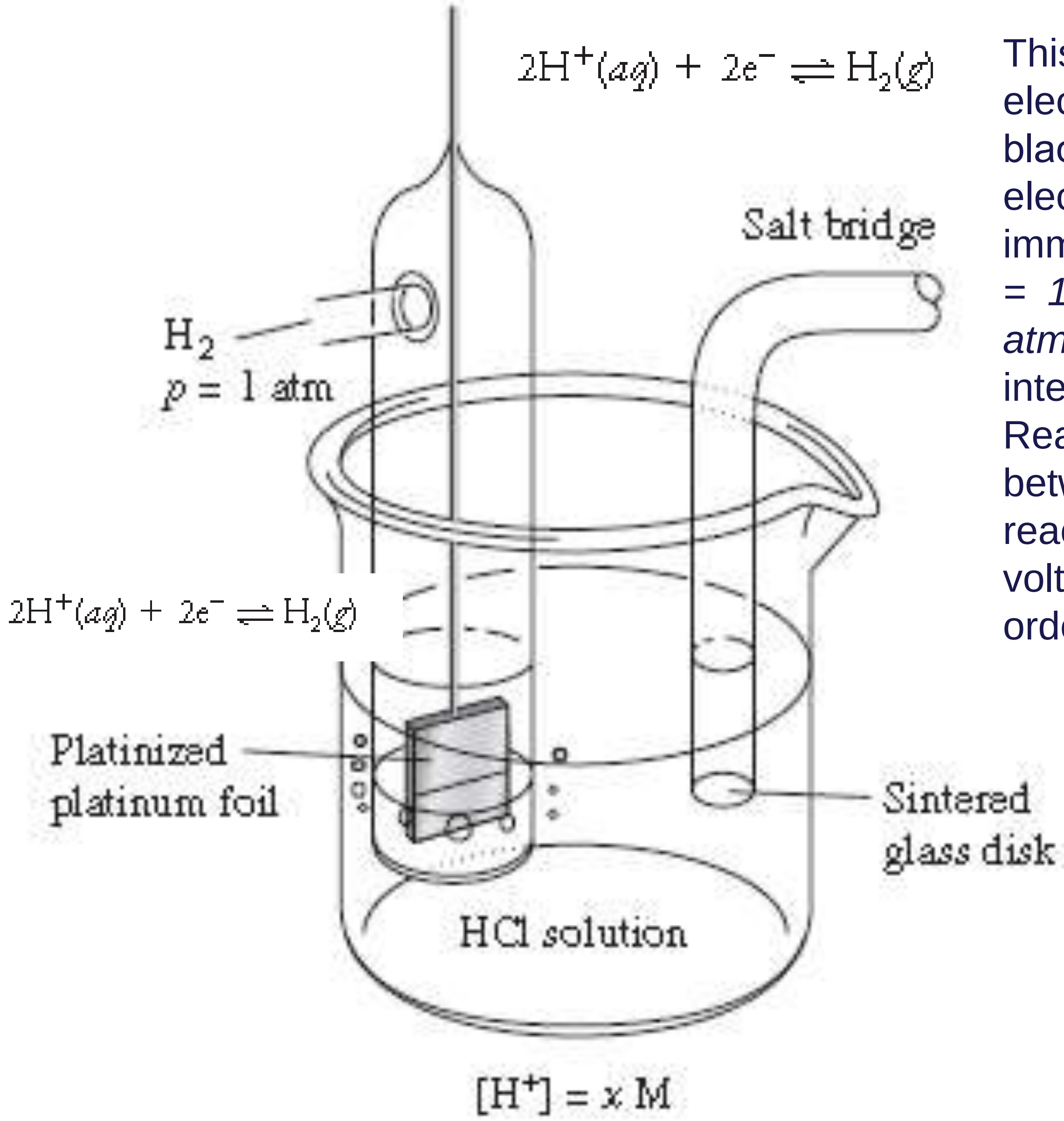
$$\boxed{2H^+ + 2e^- \rightleftharpoons H_2}$$

$$\mathrm{Pt},\ H_2(p = 1.00\ \mathrm{atm})\,|\,(H^+ = x\,\mathrm{M})\,||$$

has arbitrarily been assigned a value of 0.000 V. This is called the **normal hydrogen electrode (NHE), or the standard hydrogen electrode (SHE).**

This has an arbitrary **standard potential (at standard conditions [H_2] = 1 atm. and 25^{0}C) E^0 = 0.00 volts.** The symbol E^0 specifically denotes standard potential, whereas E would denote a potential at other than standard conditions.

Such an electrode must be easy to construct, reversible, and highly reproducible in its behavior.

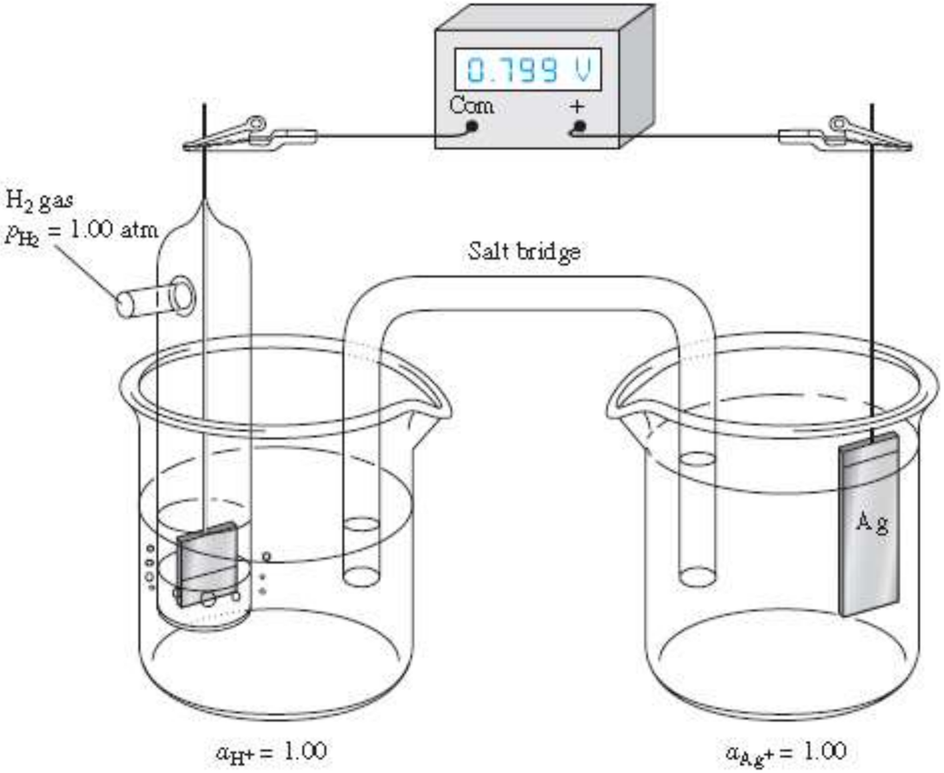


This consists of aplatinized platinum electrode (one coated with fine “platinum black” by electroplating platinum on the electrode) contained in a glass tube, immersed in an acid solution in which a_{H^+} *= 1 and where hydrogen gas (*P_{H2} *= 1 atm) is bubbled at the electrode/*solution interface. The platinum black catalyzes Reaction. The potential differences between this half-reaction and other half-reactions have been measured using voltaic cells and arranged in decreasing order.

An ***electrode potential*** is the potential of a cell that has a standard hydrogen electrode as the left electrode (reference).

The **standard electrode potential, *E^0, of a half-reaction*** is defined as its electrode potential when the activities of the reactants and products are all unity

$$2Ag^+ + H_2(g) \rightleftharpoons 2Ag(s) + 2H^+ \qquad E^0_{Ag^+/Ag} = +0.799\ V$$



The potentials are for the half-reaction written as a *reduction, and so they* represent **reduction potentials.** We will use the Gibbs–Stockholm electrode potential convention, adopted at the 17th Conference of the International Union of Pure and Applied Chemistry in Stockholm, 1953. In this convention, the half-reaction is written as a ***reduction***, and the potential increases as the tendency for reduction (of the oxidized form to be reduced) increases.

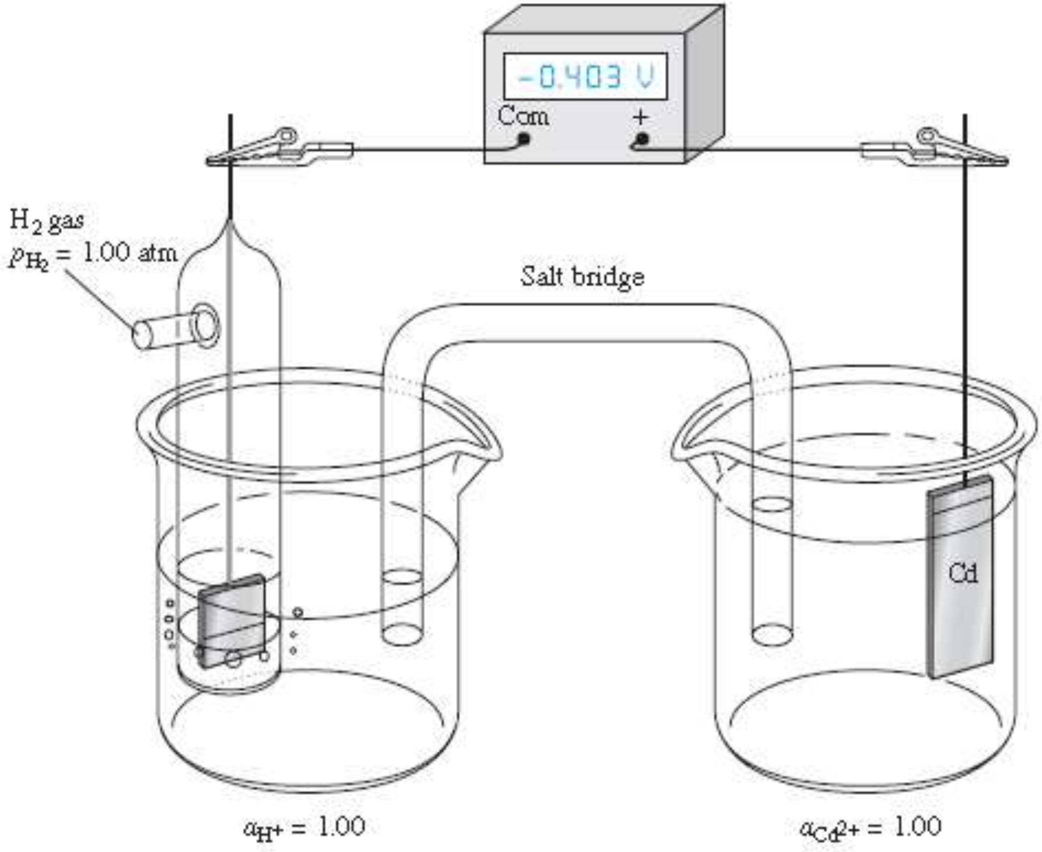
$$SHE \,||\, Ag^+(a_{Ag^+} = 1.00)|Ag \qquad Ag^+ + e^- \rightleftharpoons Ag(s)$$

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

$$E^0_{Cd^{2+}/Cd} = -0.403\ V$$

In contrast to the silver electrode, the cadmium electrode is negative with respect to the standard hydrogen electrode.

Because the cell potential is negative, the spontaneous cell reaction is not the reaction as written (that is, oxidation on the left and reduction on the right). Rather, the spontaneous reaction is in the opposite direction.

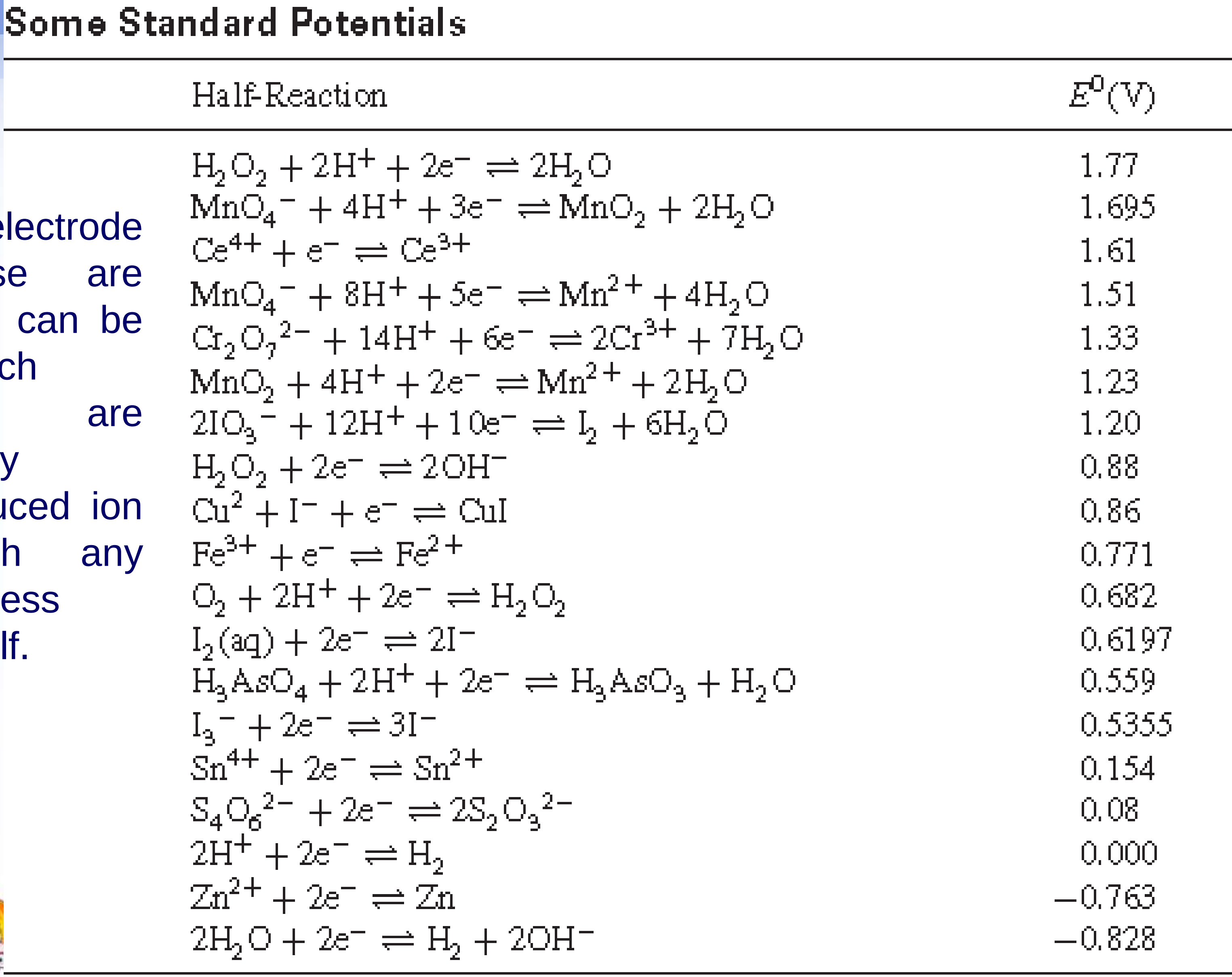


the more positive the electrode potential, the stronger an oxidizing agent the oxidized form is and the weaker a reducing agent the reduced form is.

the more negative the reduction potential, the weaker an oxidizing agent is the oxidized form is and the stronger a reducing agent the reduced form is.

$$Cd(s) + 2H^+ \rightleftharpoons Cd^{2+} + H_2(g)$$

A table of electrode potentials (these are readily available) can be used to judge which reactions are thermodynamically favorable. A reduced ion will react with any oxidized species less negative than itself.

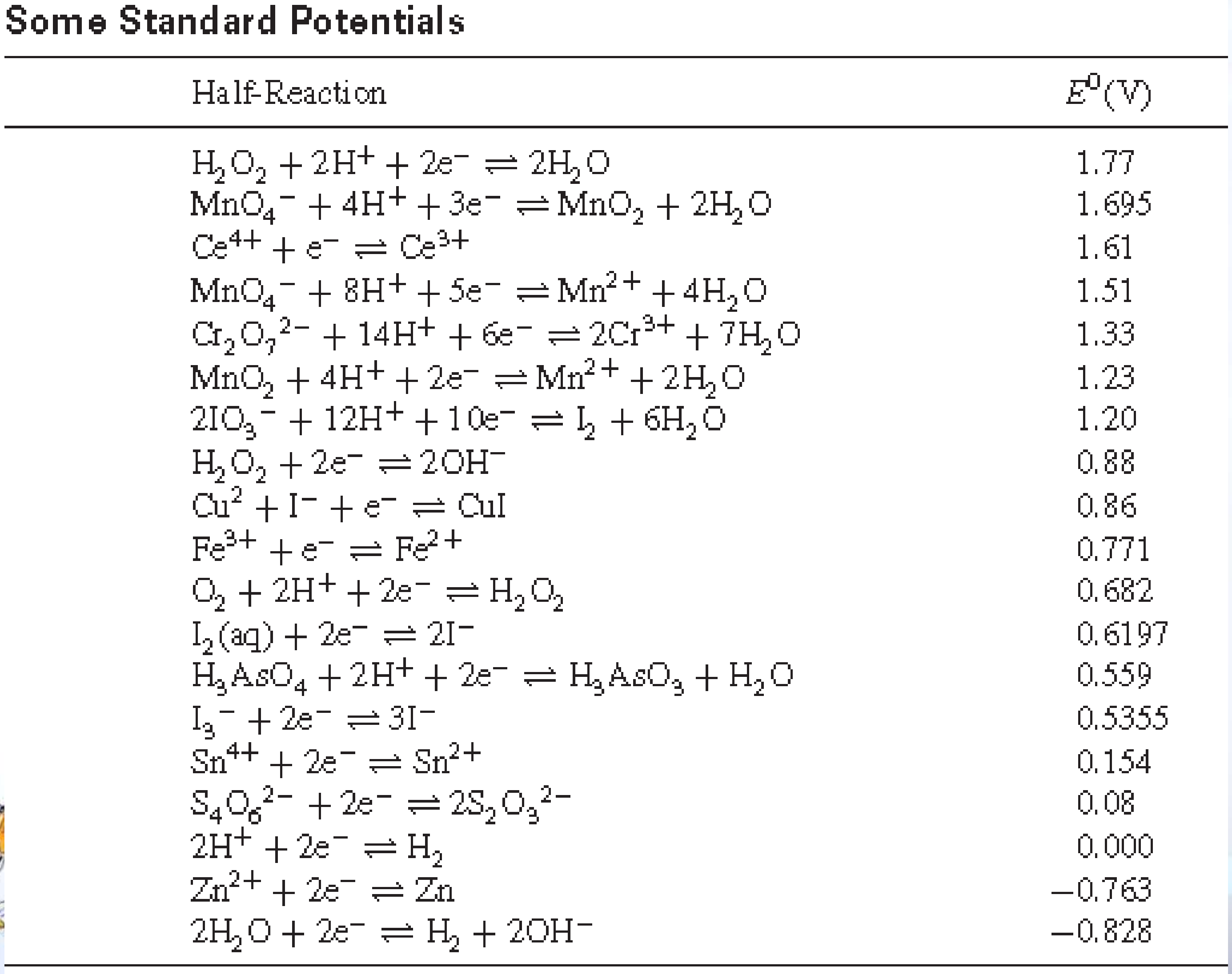


Some Standard Potentials

Half-Reaction	E^0(V)
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	1.695
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.61
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.51
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	1.33
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	1.23
$2IO_3^- + 12H^+ + 10e^- \rightleftharpoons I_2 + 6H_2O$	1.20
$H_2O_2 + 2e^- \rightleftharpoons 2OH^-$	0.88
$Cu^{2} + I^- + e^- \rightleftharpoons CuI$	0.86
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.771
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.682
$I_2(aq) + 2e^- \rightleftharpoons 2I^-$	0.6197
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O$	0.559
$I_3^- + 2e^- \rightleftharpoons 3I^-$	0.5355
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.154
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	0.08
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.763
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	−0.828

For the following substances, list the oxidizing agents in decreasing order of oxidizing capability, and the reducing agents in decreasing order of reducing capability: MnO_4^-, Ce^{3+}, Cr^{3+}, IO_3^-, Fe^{3+}, I^-, H^+, Zn^{2+}.

Looking at Table, the following must be oxidizing agents (are in the oxidized forms) and are listed from the most positive E^0 *to the least positive:* MnO_4^-, IO_3^-, Fe^{3+}, H^+, Zn^{2+}. MnO_4^- is a very good oxidizing agent, Zn^{2+} is very poor. The remainder are in the reduced form, and their reducing power is in the order I^-, Cr^{3+}, and Ce^{3+}. I^- is a reasonably good reducing agent; Ce^{3+} is poor.



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What substances react?

The oxidized form of a species in a half-reaction is capable of oxidizing the reduced form of a species in a half-reaction whose reduction potential is more *negative than its own, and vice versa: The reduced form in a half-reaction is* capable of reducing the oxidized form in a half-reaction with a more *positive* potential.

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

$$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+} \qquad E^0 = 0.154\ V$$

There are two combinations for possible reaction between an oxidizing and a reducing agent

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

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

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

$$I_3^- + 2e^- \rightleftharpoons 3I^- \qquad E^0 \rightleftharpoons 0.5355\ V$$

$$2Fe^{3+} + 3I^- = 2Fe^{2+} + I_3^-$$

$$E^0_{cell} = 0.771\ V - 0.536\ V = +0.235\ V$$

There is no possibility of reaction between Fe^{3+} and Sn^{4+} (both oxidizing agents) or between Fe^{2+} and Sn^{2+} (both reducing agents).

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

$$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^- \qquad E^0 \rightleftharpoons -0.154\ V$$

$$\overline{2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+} \qquad E^0 \rightleftharpoons 0.617\ V}$$

the reaction will proceed from left to right, if the summed E^0 value is positive.

The potential for a reaction may be related to the free energy of the reaction through the equation:

$$\Delta G^0 = -nFE^0_{\mathrm{cell}} = -RT\ln K_{\mathrm{eq}}$$

$$\ln K_{\mathrm{eq}} = -\frac{\Delta G^0}{RT} = \frac{nFE^0_{\mathrm{cell}}}{RT}$$

$$\log K_{\mathrm{eq}} = \frac{nE^0_{\mathrm{cell}}}{0.0592} = \frac{n(E^0_{\mathrm{right}} - E^0_{\mathrm{left}})}{0.0592}$$

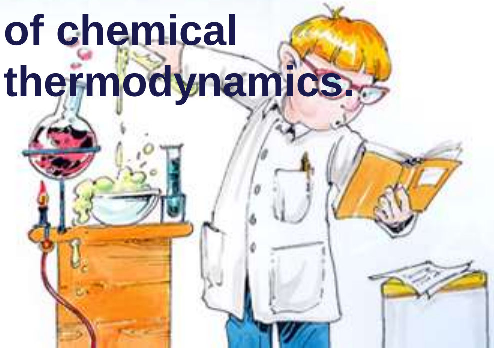
Calculate the equilibrium constant for the reaction

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

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

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

Walther Nernst (1864–1941) received the 1920 Nobel Prize in chemistry for his numerous contributions to the field of chemical thermodynamics.



Effect of Concentration on Electrode Potentials: The Nernst Equation

$$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{a_{ox}}{a_{re}} \qquad E = E^0 + \frac{0{,}059}{n} \cdot \ln \frac{a_{ox}}{a_{re}}$$

•E – potential of half-reaction;
•E^0 – standard redox potential (standard electrode potential), which are measured by activity of components of half-reaction, which is equal to 1;
•R – gas constant;
T – absolute temperature
n – number of electrons, which take part in half-reaction;
F – number of Faraday (96500);
ln – natural logarithm (2,303);
a_{ox} – activity of oxidized form;
a_{re} – activity of redused form

The real potential of redox reaction depends on:
1) concentration of oxidation and reducing agents;
2) temperature;
3) the pH value;
4) formation of insoluble compounds;
5) formation of complex compounds.

$$a\mathrm{Ox} + ne^- \rightleftharpoons b\mathrm{Red}$$

$$E = E^0 - \frac{2.3026RT}{nF} \log \frac{[\mathrm{Red}]^b}{[\mathrm{Ox}]^a}$$

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

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

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

(3) $2\mathrm{H}^+ + 2e^- \rightleftharpoons \mathrm{H}_2(g)$ $\qquad E = \frac{2.303RT}{F}\log\frac{1}{a_{\mathrm{H}+}} = -\frac{2.303RT}{F}\mathrm{pH}$

(4) $\mathrm{MnO}_4^- + 5e^- + 8\mathrm{H}^+ \rightleftharpoons \mathrm{Mn}^{2+} + 4\mathrm{H}_2\mathrm{O}$

$$E = E^0 - \frac{0.0592}{5}\log\frac{[\mathrm{Mn}^{2+}]}{[\mathrm{MnO}_4^-][\mathrm{H}^+]^8}$$

(5) $\mathrm{AgCl}(s) + e^- \rightleftharpoons \mathrm{Ag}(s) + \mathrm{Cl}^-$ $\qquad E = E^0 - \frac{0.0592}{1}\log[\mathrm{Cl}^-]$

The Standard Electrode Potential, E^0

1. The standard electrode potential is a relative quantity in the sense that it is the potential of an electrochemical cell in which the reference electrode (left-hand electrode) is the standard hydrogen electrode, whose potential has been assigned a value of 0.000 V.

2. The standard electrode potential for a half-reaction refers exclusively to a reduction reaction, that is, it is a relative reduction potential.

3. The standard electrode potential measures the relative force tending to drive the half-reaction from a state in which the reactants and products are at unit activity to a state in which the reactants and products are at their equilibrium activities relative to the standard hydrogen electrode.

4. The standard electrode potential is independent of the number of moles of reactant and product shown in the balanced half-reaction.

5. A positive electrode potential indicates that the half-reaction in question is spontaneous

with respect to the standard hydrogen electrode half-reaction. In other words, the oxidant in the half-reaction is a stronger oxidant than is hydrogen ion. A negative sign indicates just the opposite.

6. The standard electrode potential for a half-reaction is temperature dependent.

Systems Involving Precipitates or Complex Ions

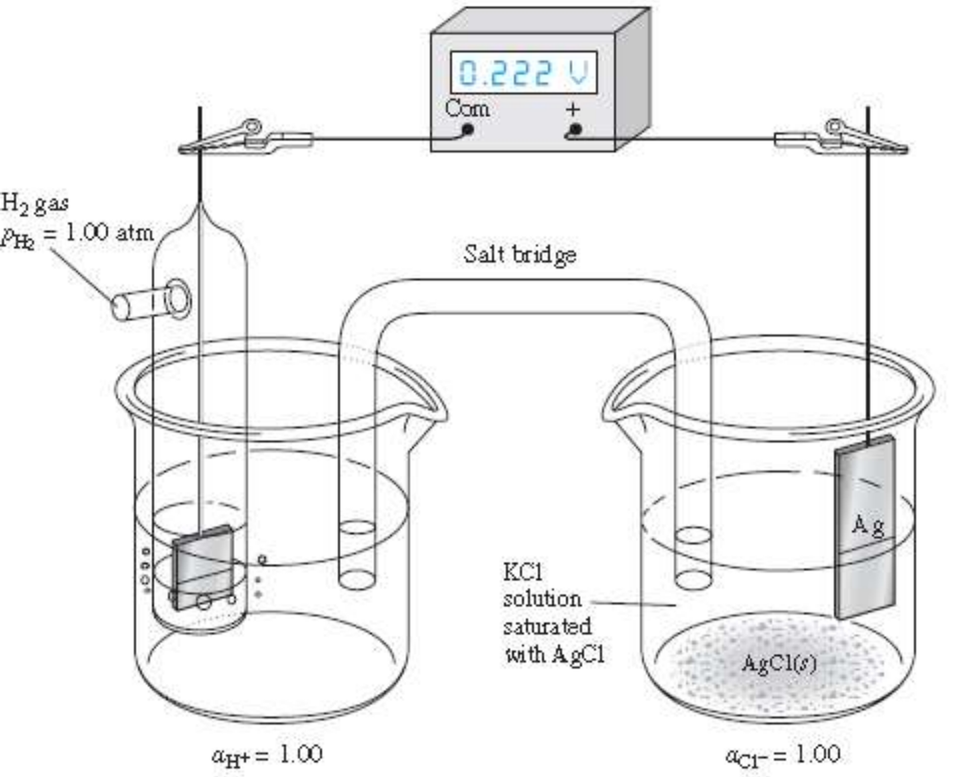
$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^0_{Ag^+/Ag} = +0.799\ V$$

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

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

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

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



$$E^0_{AgCl/Ag} = E^0_{Ag^+/Ag} - 0.0592\log 1.82 \times 10^{-10} - 0.0592\log(1.00)$$

$$= 0.799 + (-0.577) - 0.000 = 0.222\ V$$

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

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

Formation of insoluble compounds decrease the real potential (emf) of the system:

1) if oxidised form is insoluble compound:

$$\mathrm{OxA}\downarrow + ne \leftrightarrow \mathrm{Red} + \mathrm{A} \qquad \mathrm{E} = \mathrm{E}^\circ + \frac{0{,}0592}{\mathrm{n}} \cdot \lg K_{s\,\mathrm{Ox}}^{T};$$

2) if reduced form is insoluble compound:

$$\mathrm{Ox} + \mathrm{A} + ne \leftrightarrow \mathrm{RedA}\downarrow \qquad \mathrm{E} = \mathrm{E}^\circ - \frac{0{,}0592}{\mathrm{n}} \cdot \lg K_{s\,\mathrm{Red}}^{T}$$

Formation of complex compounds also decreases the emf of system:

1) if oxidised form is complex compound:

$$\mathrm{OxL} + ne \leftrightarrow \mathrm{Red} + \mathrm{L} \qquad \mathrm{E} = \mathrm{E}^\circ + \frac{0{,}0592}{\mathrm{n}} \cdot \lg \frac{1}{\beta};$$

2) if reduced form is complex compound:

$$\mathrm{Ox} + \mathrm{L}\, ne \leftrightarrow \mathrm{Red} + \mathrm{L} \qquad \mathrm{E} = \mathrm{E}^\circ + \frac{0{,}0592}{\mathrm{n}} \cdot \lg \beta$$

The formal potential

$E^{0'}$ of a system is the potential of the half-cell with respect to the standard hydrogen electrode measured under conditions such that the ratio of analytical concentrations of reactants and products as they appear in the Nernst equation is exactly unity and the concentrations of other species in the system are all carefully specified. For example, the formal potential for the half-reaction

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^{0'} = 0.792\ \text{V in } 1\ M\ HClO_4$$

This is the standard potential of a redox couple with the oxidized and reduced forms at 1 *M* concentrations and *with the solution conditions specified. For example, the formal* potential of the Ce^{4+}*/Ce^{3+} couple in 1 M HCl is 1.28 V. E^0 value for Ce^{4+} + e− Ce^{3+} is 1.61 V.*

Formal potentials are empirical potentials that compensate for the types of activity and competing equilibria effects that we have just described.

The real potential of redox reaction depends on:
1) concentration of oxidation and reducing agents;
2) temperature;
3) the pH value;
4) formation of insoluble compounds;
5) formation of complex compounds.

Using Redox Reactions in Analysis

1. Calculation equilibrium concentrations of all substances, which take part in redox process.
2. Development kinetics method of analysis.
3. Detecting of cations and anions:

$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \leftrightarrow 2HMnO_4 + 5\ Pb(NO_3)_2 + 6H_2O$;

$HgCl_2 + H_2[SnCl_4] \leftrightarrow Hg\downarrow + H_2[SnCl_6]$

4. Dissolving of insoluble sediments:

$As_2S_3 + 28HNO_3 \leftrightarrow 2H_3AsO_4 + 3H_2SO_4 + 28NO_2 + 8H_2O$

5. Separation in systematic analysis of cation mixes:

$2CrCl_3 + 10KOH + 3H_2O_2 \leftrightarrow 2K_2CrO_4 + 6KCl + 8H_2O$