OXIDATION/REDUCTION REACTIONS

An oxidation/reduction reaction is one in which electrons are transferred from one reactant to another. An example is the oxidation of iron(II) ions by cerium(IV) ions:

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

Here, Ce^{4+} ion extracts an electron from Fe^{2+} to form Ce^{3+} and Fe^{3+} ions.

Oxidation: is a process that results in the loss of one or more electrons by the susbtances (atoms, ions or molecules). $\rightarrow$ its oxidation state changes to more positive values.

Reduction: is a process that results in the gain of one or more electrons by the susbtances (atoms, ions or molecules). $\rightarrow$ its oxidation state changes to more negative values (or less positive).

Oxidizing agent or oxidant: a substance that has a strong affinity for electrons, and thus tends to remove them from other species.

Reducing agent or reductant: a substance that readily donates electrons to another species.

Reduction and oxidation always occur simultaneously.

Half-reactions

We can split any oxidation/reduction equation in 2 half-reactions:

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ reduction of Ce^{4+}

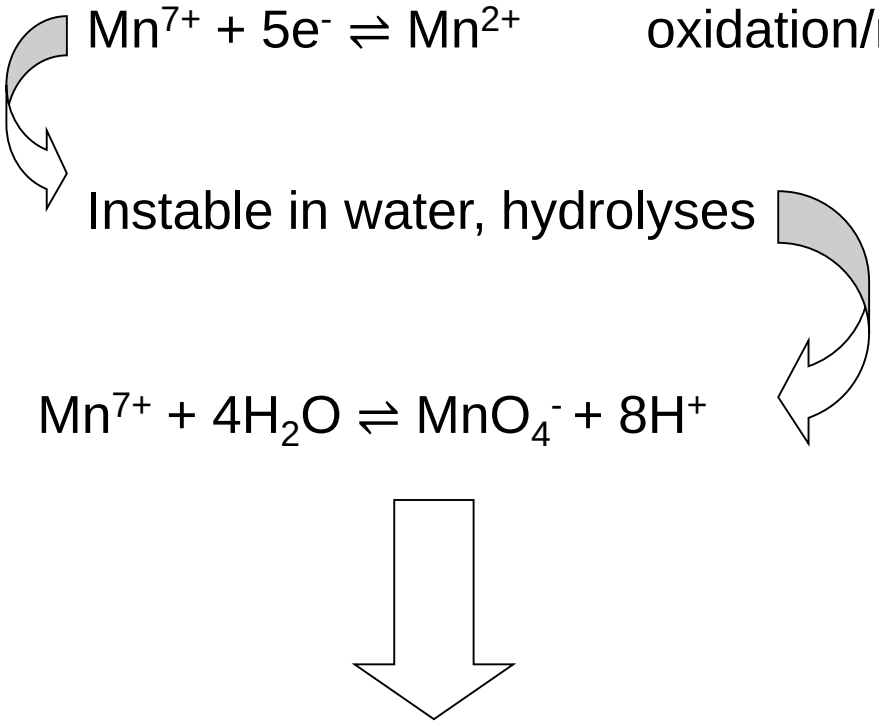
$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ oxidation of Fe^{2+}

The rules for balancing half-reactions are the same as those for the other reaction types; the number of atoms of each elemento as well as the net charge on each side of the equation must be the same.

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\qquad$ $Sn^{2+} \rightleftharpoons Sn^{4+} + \mathbf{2}e^-$

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

Combined redox and acid-base systems: involve not only the exchange of electrons, but also protons are transferred, as in any acid-base system.



Molecules

dehydroascorbic acid

$$C_6H_6O_6 + 2H^+ + 2e^- \rightleftharpoons C_6H_8O_6$$

ascorbic acid

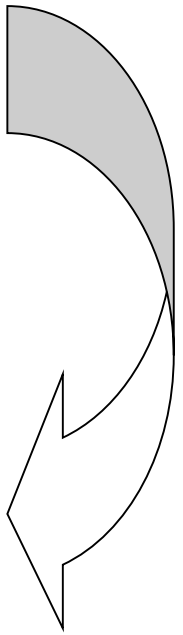
BALANCING

$2MnO_4^- + H_2O_2 + 6H^+ \dashrightarrow 2Mn^{2+} + 3O_2 + 4H_2O$

$2MnO_4^- + 3H_2O_2 + 6H^+ \dashrightarrow 2Mn^{2+} + 4O_2 + 6H_2O$

$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

$2MnO_4^- + 7H_2O_2 + 6H^+ \dashrightarrow 2Mn^{2+} + 6O_2 + 10H_2O$



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

$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^-$

Quantity of electrons released by reducing agent

=

Quantity of electrons captured by the oxidizing agent

EXAMPLES

Fe^{3+} and Sn^{2+}

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

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

BrO_3^- and I^-

$$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$$
$$2I^- \rightarrow I_2 + 2e^-$$

$$BrO_3^- + 6H^+ + 6I^- \rightarrow Br^- + 3I_2 + 3H_2O$$

CdS dissolved in hot HNO_3

$$HNO_3 + 3H^+ + 3e^- \rightarrow NO\uparrow + 2\,H_2O$$
$$CdS\downarrow \rightleftharpoons Cd^{2+} + S^{2-}$$
$$S^{2-} \rightarrow S\downarrow + 2e\text{-}$$

$$2HNO_3 + 6H^+ + 3CdS\downarrow \rightarrow$$
$$2NO\uparrow + 3Cd^{2+} + 3S\downarrow + 4H_2O$$

MnO_4^- and Mn^{2+}

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2\downarrow + 2H_2O$$
$$Mn^{2+} + 2H_2O \rightarrow MnO_2\downarrow + 4H^+ + 2e^-$$

?

$C_3H_8O_3$ (glycerin) and $Cr_2O_7^{2-}$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2\uparrow + 14H^+ + 14e^-$$

?

PRACTICING

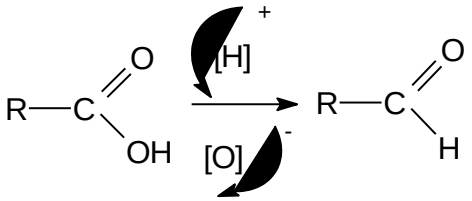
Oxidation of citrate base by $KMnO_4$ in alkaline solution

Oxidation of cobalt hexanitrite(II) by $KMnO_4$ in acid solution

$Co(NO_2)_6^{3-} + H_2O \rightleftharpoons Co^{2+} + NO_3^- + H^+ + e^-$

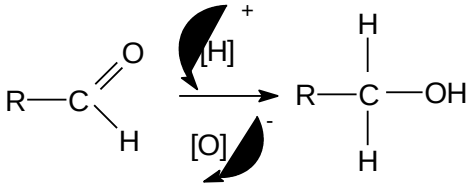
FOR ORGANIC COMPOUNDS

REDUCTION of an organic molecule usually corresponds to the **increase of its hydrogen content** and **the decrease of its content in oxygen**.



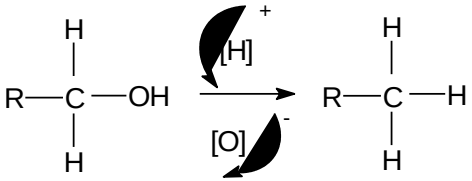
DECREASE OF ITS CONTENT IN OXYGEN

The above example is generic and shows the transformation of carboxylic acid into aldehyde.



INCREASE OF ITS HYDROGEN CONTENT

Aldehyde to alcohol



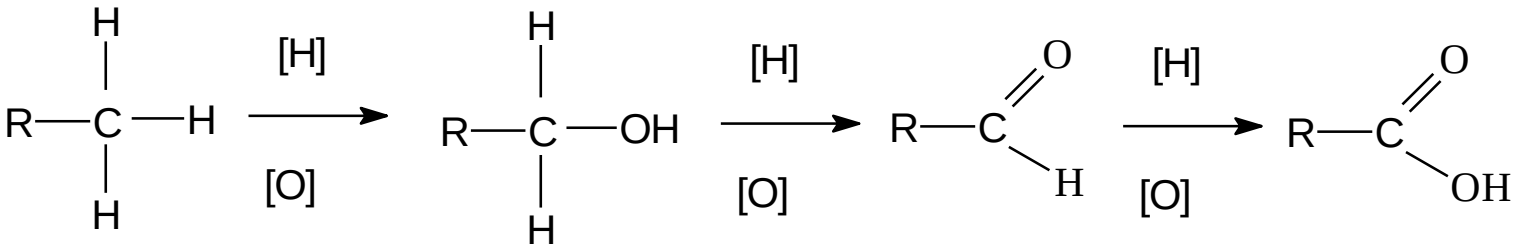
DECREASE OF ITS CONTENT IN OXYGEN

Alcohol to alkane

FOR ORGANIC COMPOUNDS

OXIDATION of an organic molecule usually corresponds to the **increase of its oxygen content** and **the decrease of its content in hydrogen**.

More generally, the oxidation of an organic compound is a reaction in which the contente of any element is more electronegative than carbon:



Oxidation state:

LOWER

Oxidation state:

HIGHER

OXIDATION/REDUCTION REACTIONS IN ELECTROCHEMICAL CELLS

Many oxidation/reduction reactions can be carried out in either of two ways that physically quite different.

1 – The reaction is performed by direct contact between the oxidant and the reductant in a suitable container.

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

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

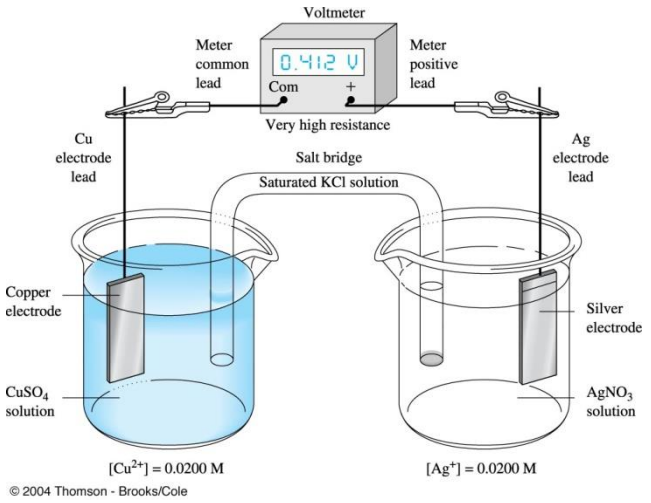
ELECTROCHEMICAL CELLS

An electrochemical cell consists of two conductors called ELECTRODES, each of which is immersed in an electrolyte solution.

In most of the cells that will be of interest to us, the solutions surrounding the two electrodes are different and must be separated to avoid direct reaction between the reactants.

The most common way of avoiding mixing is to insert a SALT BRIDGE, between the solutions.

Conduction of electricity from one electrolyte solution to the other then occurs by migration of potassium ions in the bridge in one direction and chloride ions in the other.



TYPES OF ELECTROCHEMICAL CELLS

Galvanic or voltaic: Store electrical energy. The reactions at the two electrodes in such cells to proceed spontaneously and produce a flow of electrons from the anode to the cathode via an external conductor.

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

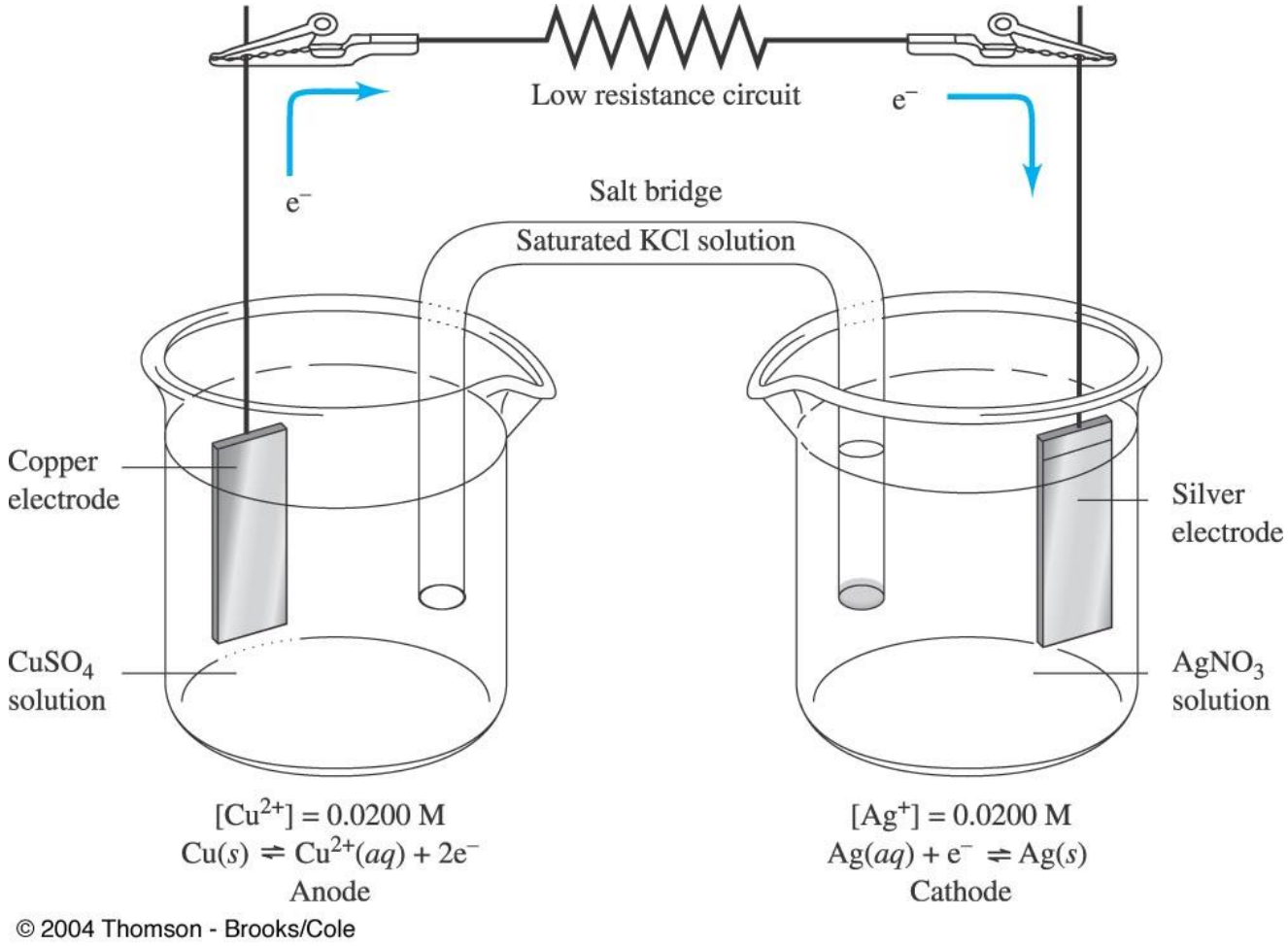
Cathode: the electrode at which a reduction reaction occurs.

Anode: the electrode at which an oxidation takes place.

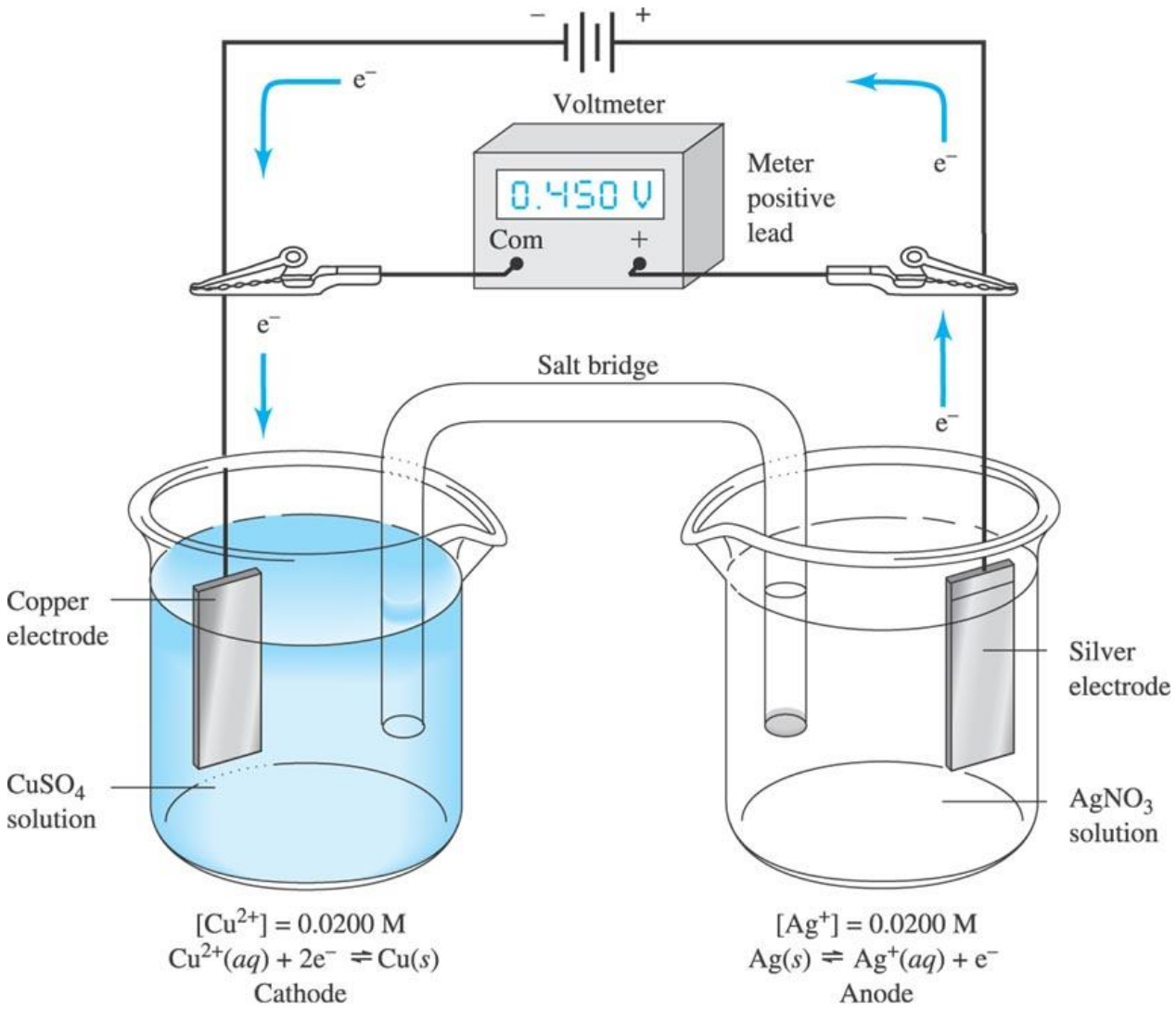
Electrolytic: requires an external source of electrical energy for operation.

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

A GALVANIC CELL



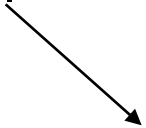
A ELECTROLYTIC CELL



SCHEMATIC REPRESENTATION OF CELLS

double vertical: represents two phase boundaries, one at each end of the salt bridge

$$Cu \mid Cu^{2+}\ (0.0200\ mol\ L^{-1}) \parallel Ag^{+}\ (0.0200\ mol\ L^{-1}) \mid Ag$$



vertical line: phase boundary, or interface, at which a potential develops

By convention, the anode is always displayed on the left in these representations.

LIQUID-JUNCTION POTENTIAL

Liquid-junction potential: results from differences in rates with 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 the junction potentials at the two ends of a salt bridge tend to cancel each other.

CURRENTS IN ELECTROCHEMICAL CELLS

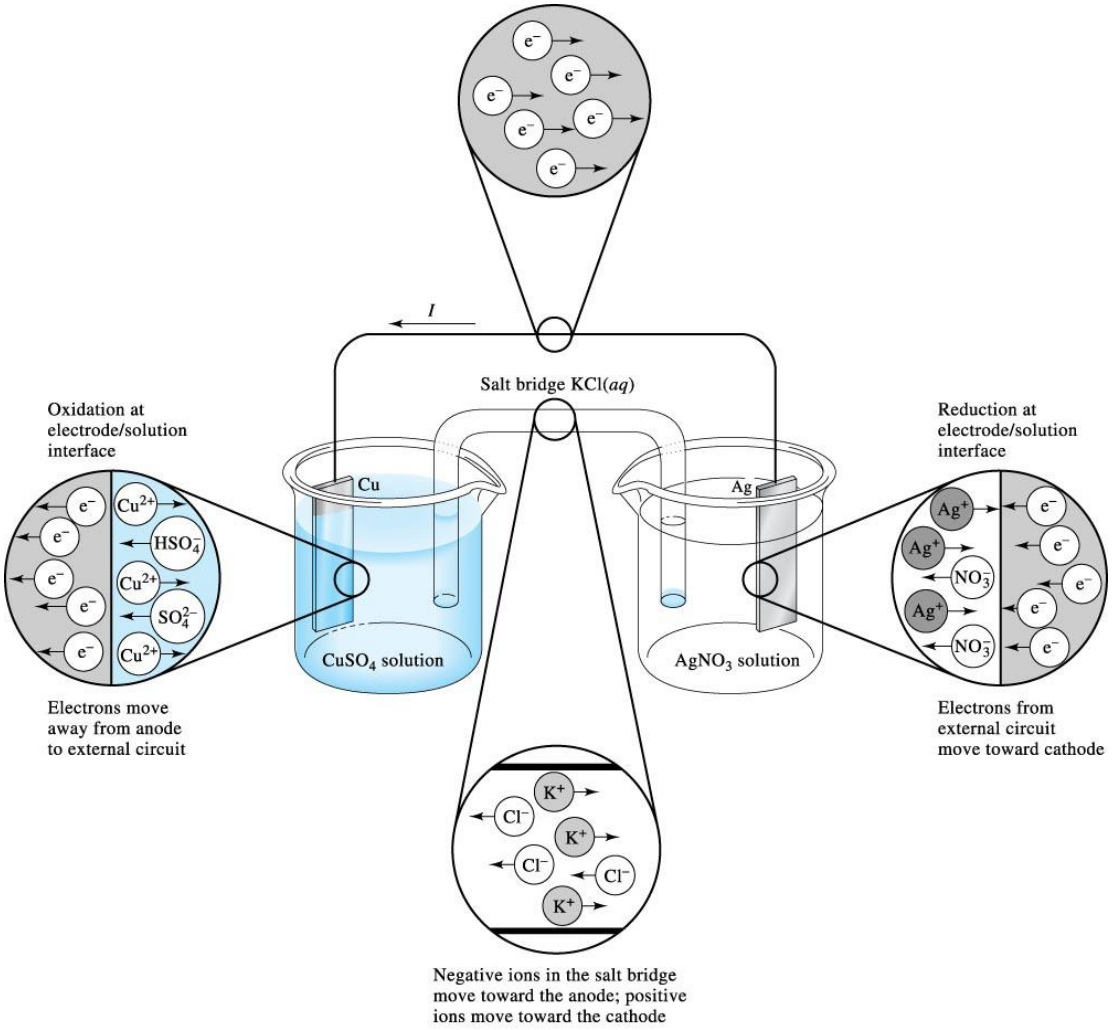
Electricity is transported through an electrochemical cell by three mechanisms:

1-Electrons carry electricity within the electrodes as well as the external conductor.

2-Anions and cations carry electricity within the cell.

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

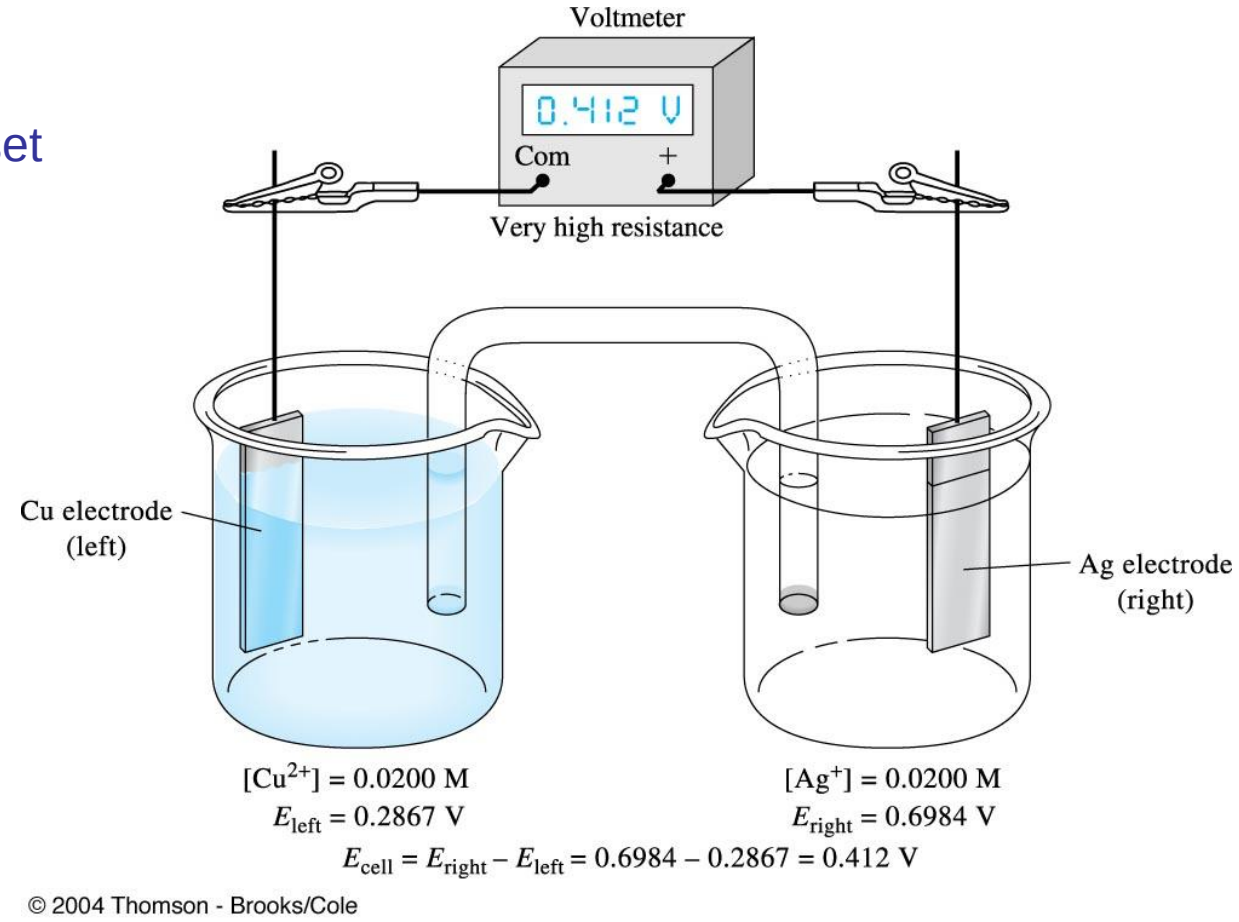
MOVEMENT OF CHARGE IN A GALVANIC CELL



ELECTRODE POTENTIALS

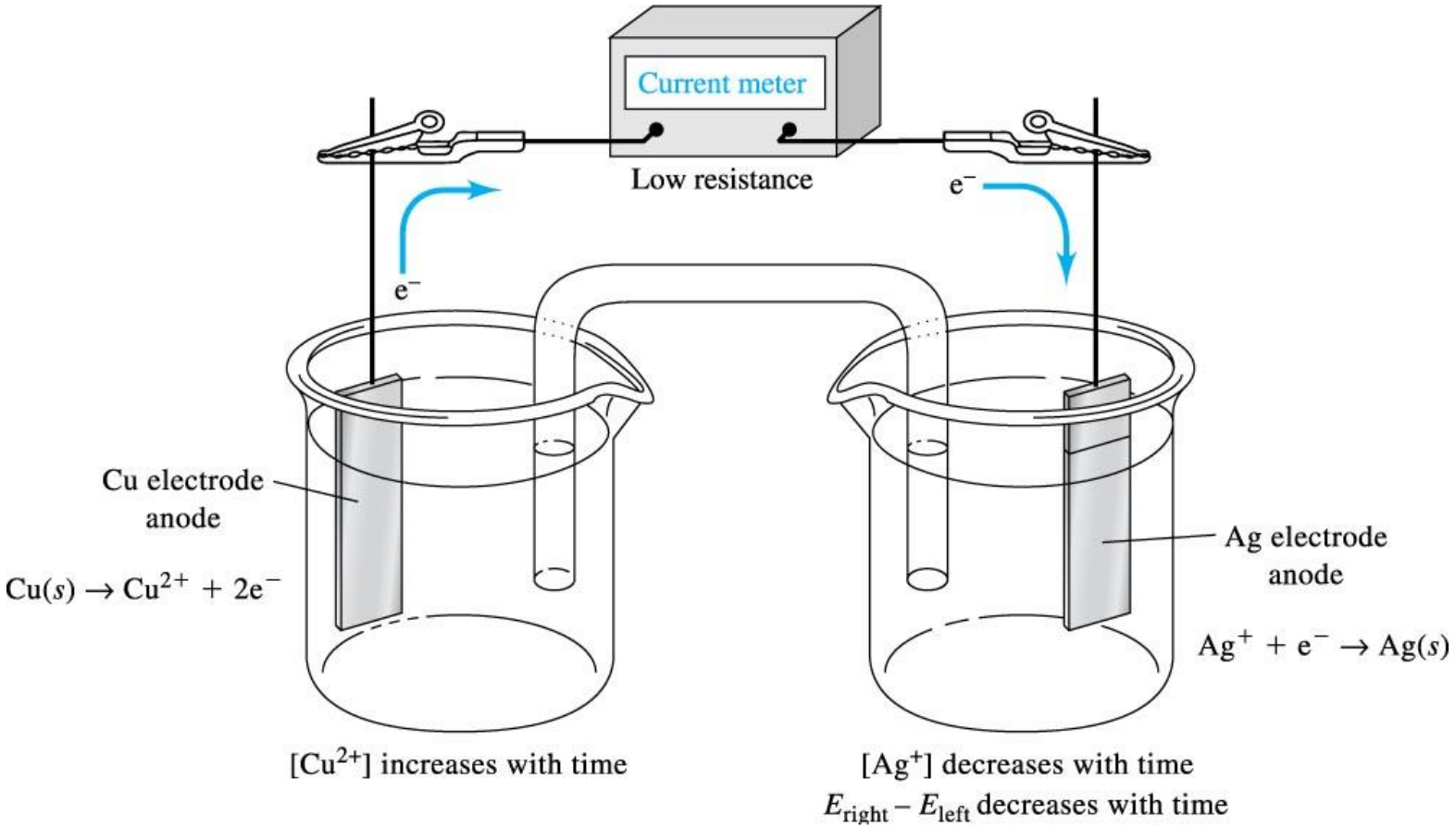
The potential difference that develops between the cathode and the anode of the cell is a measure of the tendency for the reaction to proceed from a nonequilibrium state to the condition of equilibrium.

At the outset

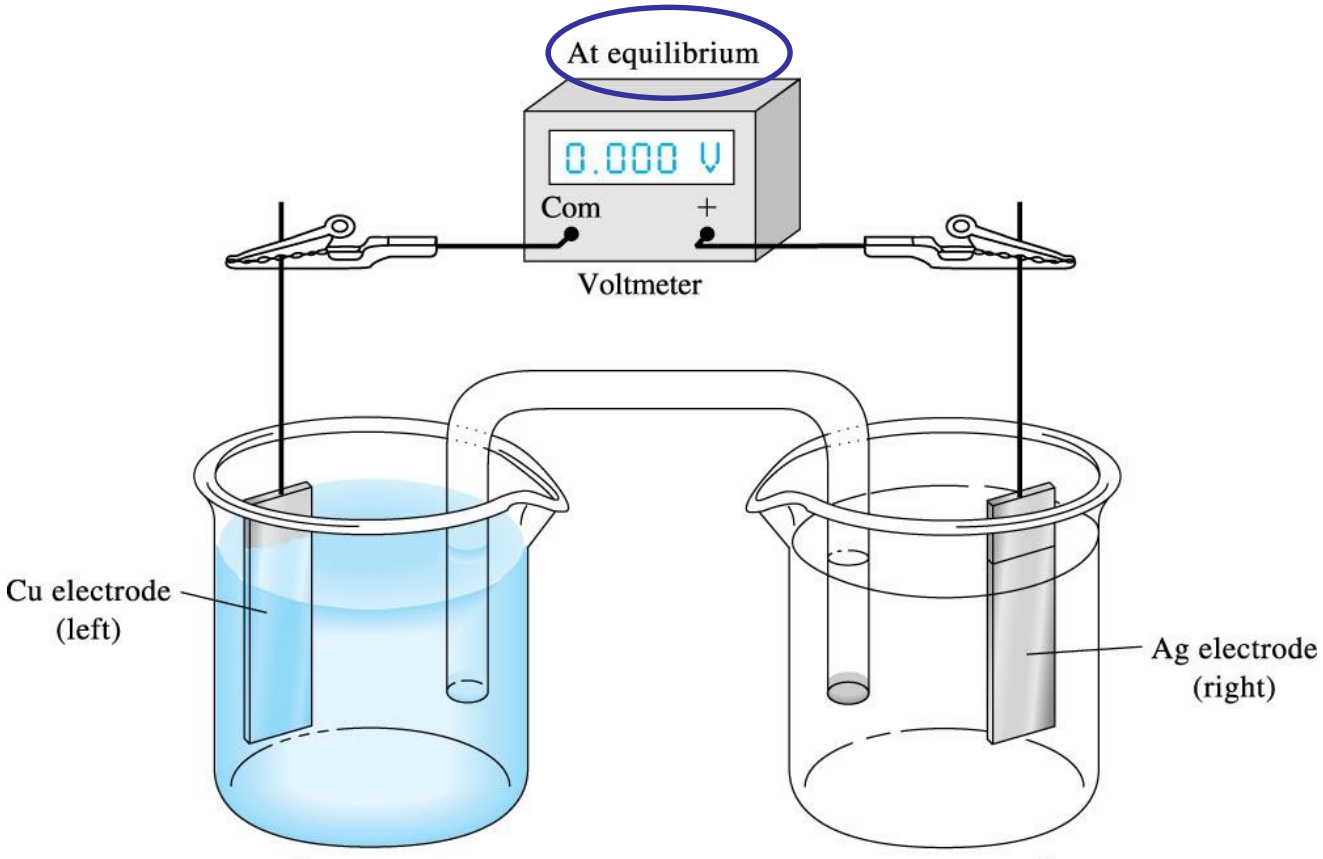


ELECTRODE POTENTIALS

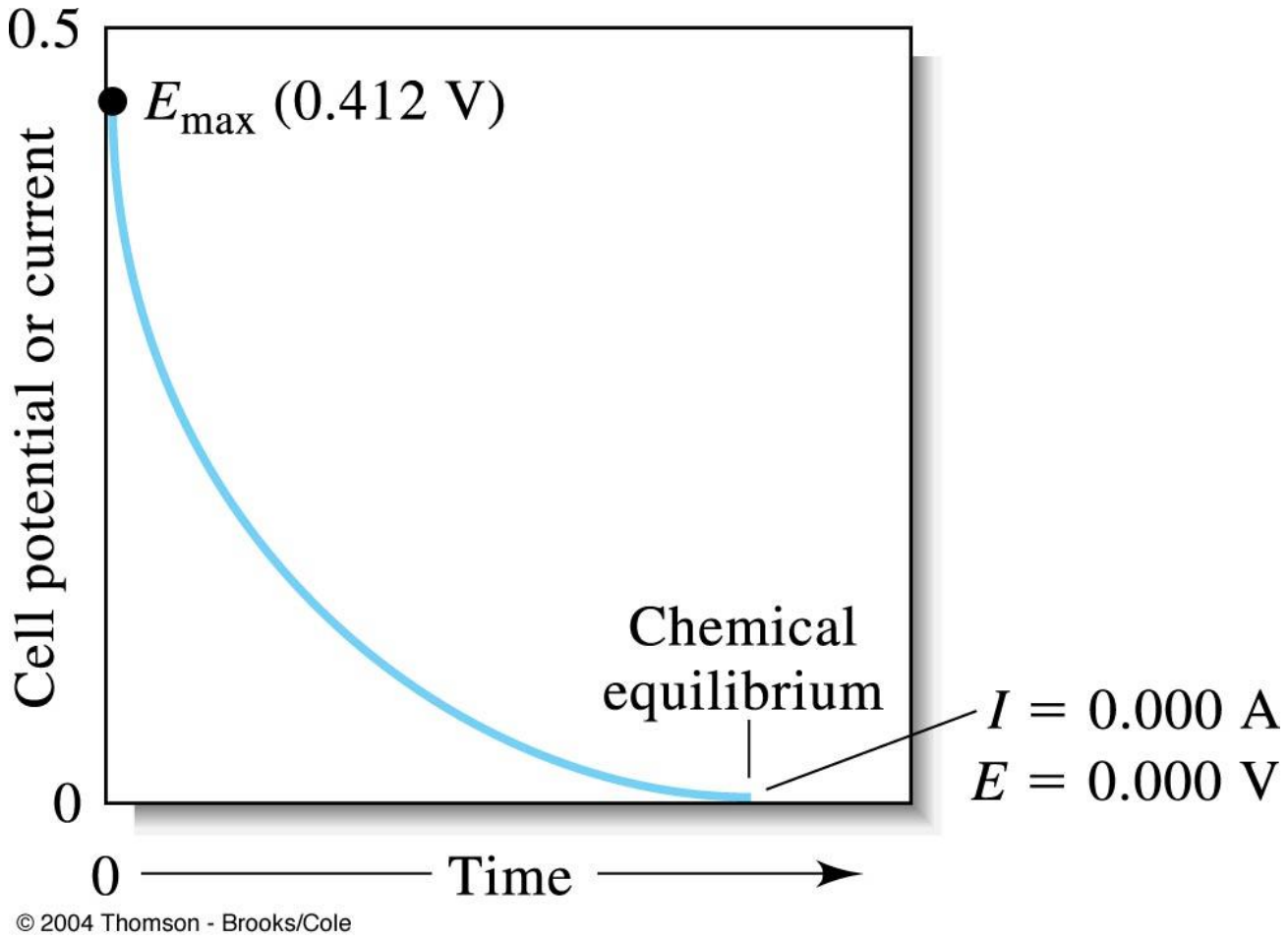
Cell discharging over time to reach equilibrium



ELECTRODE POTENTIALS



POTENTIAL OF CELL AS A FUNCTION OF TIME

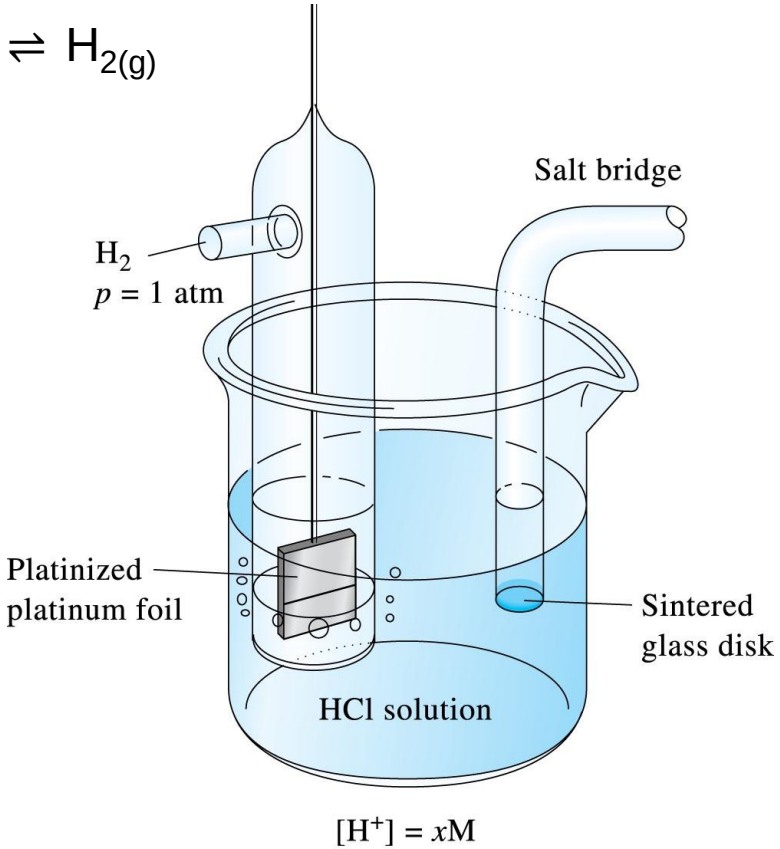


THE STANDARD HYDROGEN ELECTRODE

By convention, the potential of the standard hydrogen electrode is assigned a value of 0.000V at all temperatures.

$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$

$Pt, H_2 (p = 1.00 \text{ atm}) \mid ([H^+] = x \text{ mol } L^{-1}) \mid$

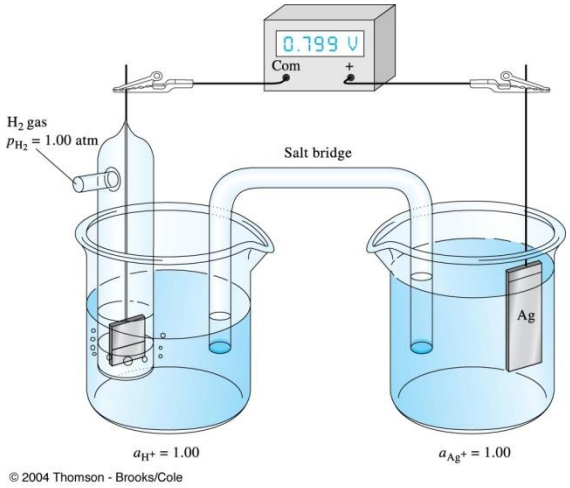


ELECTRODE POTENTIAL AND STANDARD ELECTRODE POTENTIAL

An electrode potential is defined as the potential of a cell consisting of the electrode in question acting as a cathode and the standard hydrogen electrode acting as an anode.

It should be emphasized that, despite its name, *an electrode potential is in fact the potential of an electrochemical cell involving a carefully defined reference electrode.*

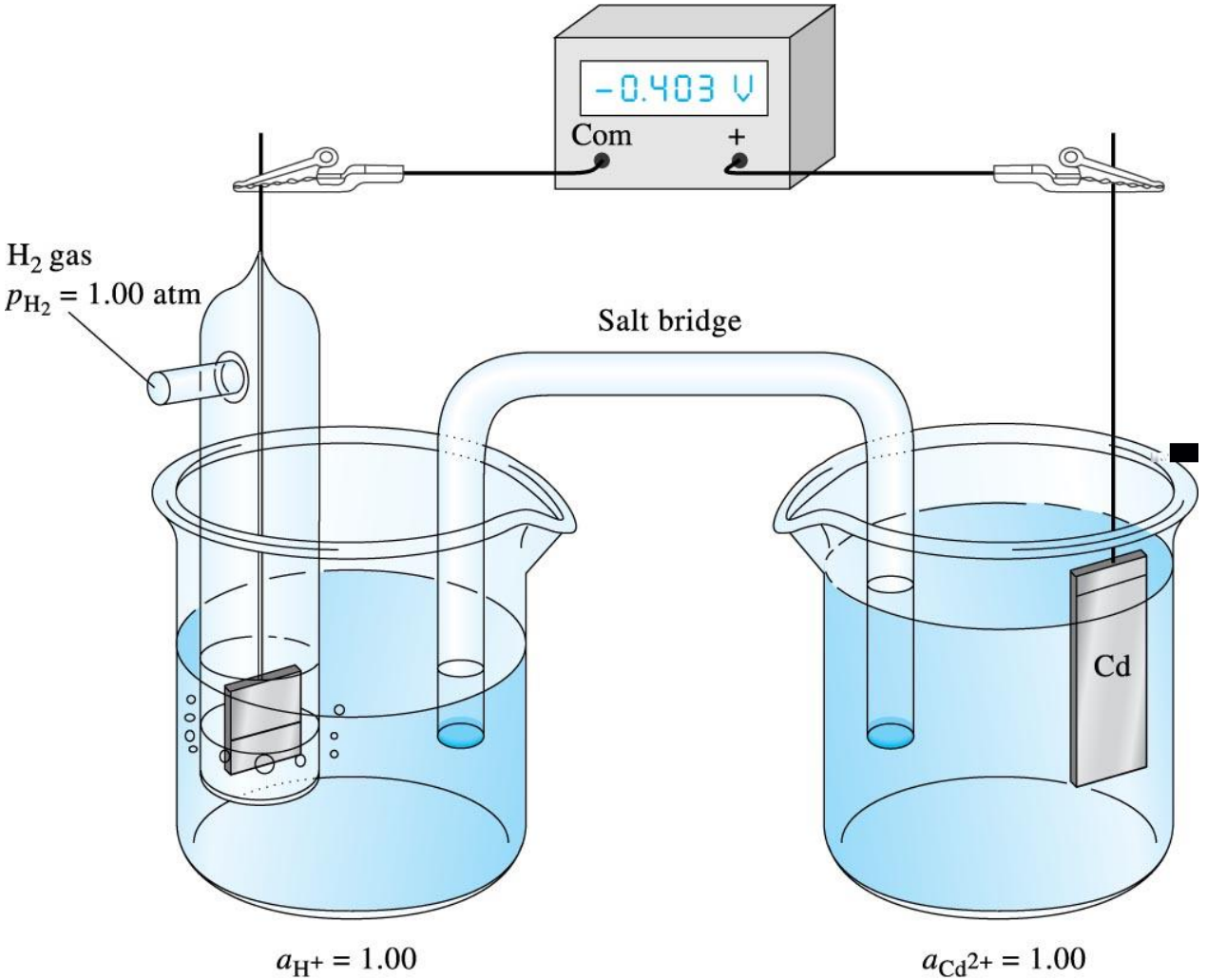
The standard electrode potential, E^0, of a half-reaction is defined as its electrode potential when the activities of all reactants and products are unity.



Pt, H_2 (p = 1.00 atm) | H^+ (aH^+ = 1.00) || Ag^+ (aAg^+ = 1.00) | Ag

SHE

STANDARD ELECTRODE POTENTIAL (E^0)



STANDARD ELECTRODE POTENTIAL (E^0)

TABLE 18-1

Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+ 0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+ 0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+ 0.337
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+ 0.334
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+ 0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+ 0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+ 0.017
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	**0.000**
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	− 0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	− 0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	− 0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	− 0.763

*See Appendix 5 for a more extensive list.

SIGN CONVENTION FOR ELECTRODE POTENTIALS

According to the IUPAC convention (1953):

Electrode potential: is reserved exclusively to describe half-reactions written as reductions.

There is no objection to the use of the term oxidation potential to indicate a process written in the opposite sense, but it is not proper to refer to such a potential as an electrode potential.

Signal of the electrode potential (+ or -) indicates whether the reduction is spontaneous or not in relation to SHE.

THE NERNST EQUATION

$aA + bB + ... + ne^- \rightleftharpoons cC + dD + ...$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^{d.....}}{[A]^a[B]^{b.....}} = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^{d.....}}{[A]^a[B]^{b.....}}$$

where

E^0 = the standard electrode potential, which is a characteristic constant for each half-reaction

R = the gas constant 8.314 J K^{-1} mol^{-1}

T = temperature in kelvins

n = number of moles of electrons that appear in the half-reaction for the electrode process as it has been written

F = the faraday = 96,485 C (coulombs)

ln = the natural logarithm = 2.303 log

NERNST EXPRESSIONS

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

(2) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

(3) $2H^+ + 2e^- \rightleftharpoons H_2(g)$

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

(5) $AgC\ell(s) + e^- \rightleftharpoons Ag(s) + C\ell^-$

STANDARD ELECTRODE POTENTIAL (E^0)

The constant E^0 is the electrode potential whenever the activity quotient has a value of one.

Limitations to the use of standard electrode potentials:

1)concentration vs. activity

2)to take into account other equilibria (dissociation, association, complex formation and solvolysis)

Formal potentials ($E^{0'}$): are empirically derived potentials that compensate for the types of activity and competing equilibria effects. The formal potential of a system is the potential of the half-cell with the renspect to the standard hydrogen electrode measure 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.

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$

Formal potential: +1.70 V in 1 mol L^{-1} $HC\ell O_4$; +1.61 V in 1 mol L^{-1} HNO_3

THE THERMODYNAMIC POTENTIAL OF ELECTROCHEMICAL CELLS

We can use standard electrode potentials and the Nernst equation to calculate the potential obtainable from a galvanic cell or the potential required to operate an electrolytic cell.

The thermodynamic potential of an electrochemical cell E_{cell} is the difference between the electrode potential of the cathode ($E_{cathode}$) and the electrode potential of the anode (E_{anode}).

$$E_{cell} = E_{cathode} – E_{anode} = E_{right} - E_{left}$$

PROBLEM

Calculate the thermodynamic potential of the following cell

$$Cu \mid Cu^{2+}\,(0.0200\ mol\ L^{-1}) \parallel Ag^{+}\,(0.0200\ mol\ L^{-1}) \mid Ag$$

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

$$Cu^{2+} + 2e^{-} \rightleftharpoons Cu(s) \qquad E^{0} = 0.337\ V$$

PROBLEM

Calculate the potential for the following cell employing (a) concentrations and (b) activities:

$$Zn \mid ZnSO_4\ (0.05\ mol\ L^{-1}),\ PbSO_4\ (sat'd) \mid Pb$$

$E^0\ PbSO_4/Pb = -0.350\ V$

$E^0\ Zn^{2+}/Zn = -0.763\ V$

$\alpha SO_4^{2-} = 0.4\ nm$

$\alpha Zn^{2+} = 0.6\ nm$

$$\mu = \frac{1}{2}\Sigma c z^2 \qquad -\log\gamma_X = \frac{0.509 z_X{}^2\sqrt{\mu}}{1+3.3\alpha_X\sqrt{\mu}}$$

REDOX EQUILIBRIUM CONSTANTS

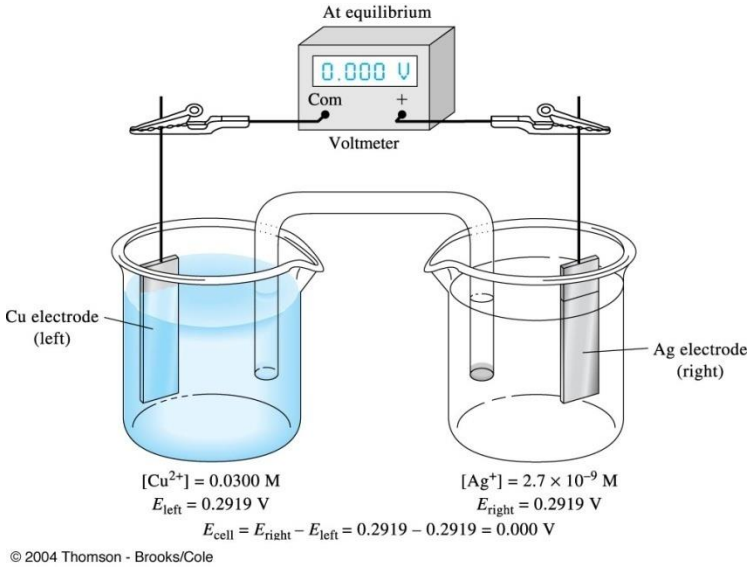
$Cu_{(s)} + 2Ag^{+} \rightleftharpoons Cu^{2+} + 2Ag_{(s)}$

$$K_{eq} = \frac{[Cu^{2+}]}{[Ag^{+}]^2}$$

$Cu \mid Cu^{2+}$ (x mol L^{-1}) || Ag^{+} (y mol L^{-1}) $\mid Ag$

$$E_{cell} = E_{right} - E_{left} = E_{Ag^{+}/Ag} - E_{Cu^{2+}/Cu}$$

At the equilibrium



$$E_{cell} = 0 = E_{right} - E_{left}$$

At the equilibrium, the electrode potentials for all half-reactions in an oxidation/reduction system are equal.

Example:

Calculate the equilibrium constant for the reaction

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_2(s) + 4H^+$$

$2MnO_4^- + 8H^+ + 6e^- \rightleftharpoons MnO_2(s) + 4H_2O$ $\quad E^0 = +1.695$ V

$3MnO_2(s) + 12H^+ + 6e^- \rightleftharpoons 3Mn^{2+} + 6H_2O$ $\quad E^0 = +1.23$ V

REDOX TITRATION CURVES

Because most redox indicators respond to changes in electrode potential, the vertical axis in oxidation/reduction titration curves is generally an electrode potential instead of the logarithmic p-functions that were used for precipitation, complex-formation, and neutralization titration curves.

Consider the titration of 50.00 mL of 0.0500 mol L^{-1} Fe(II) with 0.1000 mol L^{-1} Ce(IV) in a medium that is 1.0 mol L^{-1} in H_2SO_4 at all times.

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $E^{0'} = 1.44$ V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^{0'} = 0.68$ V

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

This reaction is rapid and reversible, so the system is at equilibrium at all times throughout the titration. Consequently, the electrode potentials for the two half-reactions are always the same: $E_{system} = E_{Fe3+} = E_{Ce4+}$

REDOX TITRATION CURVES

Initial potential:

-No cerium species

-Small but unknown amount of Fe(III) present due to air oxidation of Fe(II)

Before equivalence-point. (V = 5.00mL)

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

Ce^{3+} and Fe^{3+} are formed

Ce^{4+} - vanishingly small

$$[Fe^{3+}] = \frac{V_{Ce^{4+}\,added} x [Ce^{4+}]}{V_T} - [Ce^{4+}]_{not\,reacted}$$

$$[Fe^{2+}] = \frac{(V_{Fe^{3+}} x [Fe^{3+}]) - (V_{Ce^{4+}\,added} x [Ce^{4+}])}{V_T} + [Ce^{4+}]_{not\,reacted}$$

$$E_{system} = +0.68 - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.64V$$

At equivalence-point (V = 25.00 mL)

The concentrations of Ce(IV) and Fe(II) are minute and cannot be obtained from stoichiometry of the reaction. The potential of the system is given by both:

$$E_{eq} = E^{0}_{Ce^{4+}/Ce^{3+}} - \frac{0.0592}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

+

$$E_{eq} = E^{0}_{Fe^{3+}/Fe^{2+}} - \frac{0.0592}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

and

$$[Ce^{3+}] = [Fe^{3+}] \text{ and } [Ce^{4+}] = [Fe^{2+}]$$

$$E_{eq} = \frac{E^{0}_{Ce^{4+}/Ce^{3+}} + E^{0}_{Fe^{3+}/Fe^{2+}}}{2} = 1.06V$$

After equivalence point (V = 25.10 mL)

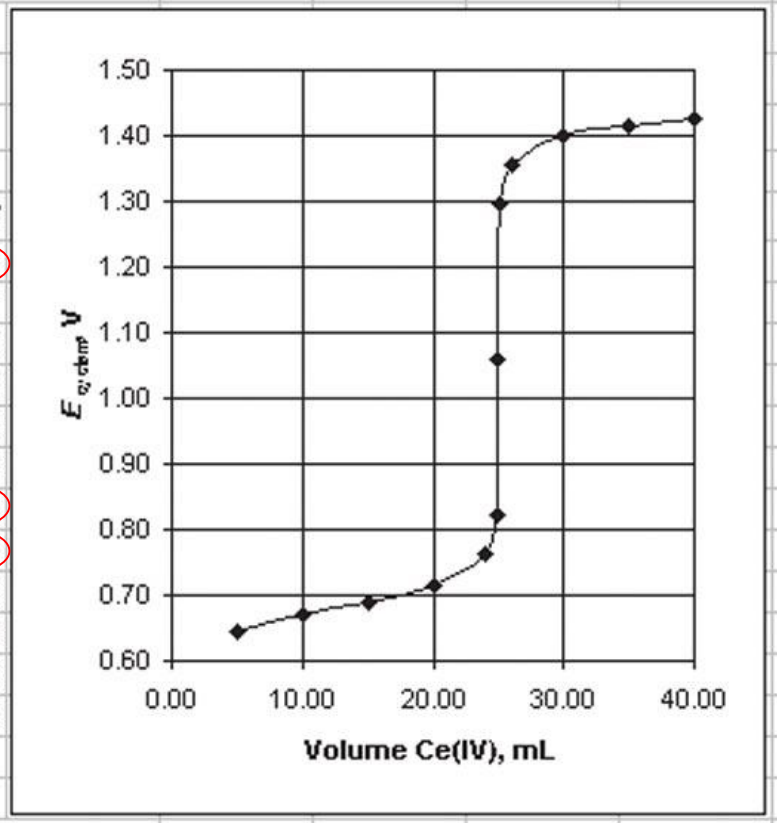
The molar concentrations of Ce(III), Ce(IV), and Fe(III) are readily computed at this point but for Fe(II) is not.

$$[Ce^{3+}] = \frac{n_{Ce^{3+}}}{V_T} - [Fe^{2+}]_{not\ reacted}$$

$$[Ce^{4+}] = \frac{(V_{Ce^{4+}\ added}\ x[Ce^{4+}]) - (V_{Fe^{2+}}\ x[Fe^{2+}])}{V_T} + [Fe^{2+}]_{not\ reacted}$$

$$E_{system} = +1.44 - \frac{0.0592}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]} = 1.30V$$

	A	B	C	D	E	F	G	H	I	J	K
1	**Spreadsheet for titration of 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+}**										
2	Initial Conc. Fe^{2+}, M	0.0500	$E^{0'}_{Fe,\ V}$	0.68							
3	Vol. Fe^{2+}, mL	50.00	$E^{0'}_{Ce,\ V}$	1.44							
4	Conc. Ce^{4+}, M	0.1000									
5											
6	**Volume Ce^{4+}, mL**	**$[Fe^{3+}]$**	**$[Fe^{2+}]$**	**$[Ce^{3+}]$**	**$[Ce^{4+}]$**	**E_{system}, V**					
7	5.00	0.009091	0.036364			0.64					
8	10.00	0.016667	0.025000			0.67					
9	15.00	0.023077	0.015385			0.69					
10	20.00	0.028571	0.007143			0.72					
11	24.00	0.032432	0.001351			0.76					
12	24.90	0.033244	0.000134			0.82					
13	25.00					1.06					
14	25.10			0.033289	0.000133	1.30					
15	26.00			0.032895	0.001316	1.36					
16	30.00			0.031250	0.006250	1.40					
17	35.00			0.029412	0.011765	1.42					
18	40.00			0.027778	0.016667	1.43					
19											
20	**Spreadsheet Documentation**										
21	Cell B7=A7*$B$4/($B$3+A7)			Cell D14=$B$2*$B$3/($B$3+A14)							
22	Cell C7=($B$2*$B$3-$B$4*A7)/($B$3+A7)			Cell E14=(A14*$B$4-$B$2*$B$3)/($B$3+A14)							
23	Cell F7=$D$2-0.0592*LOG10(C7/B7)			Cell F14=$D$3-0.0592*LOG10(D14/E14)							
24	Cell F13=($D$2+$D$3)/2										



PROBLEM

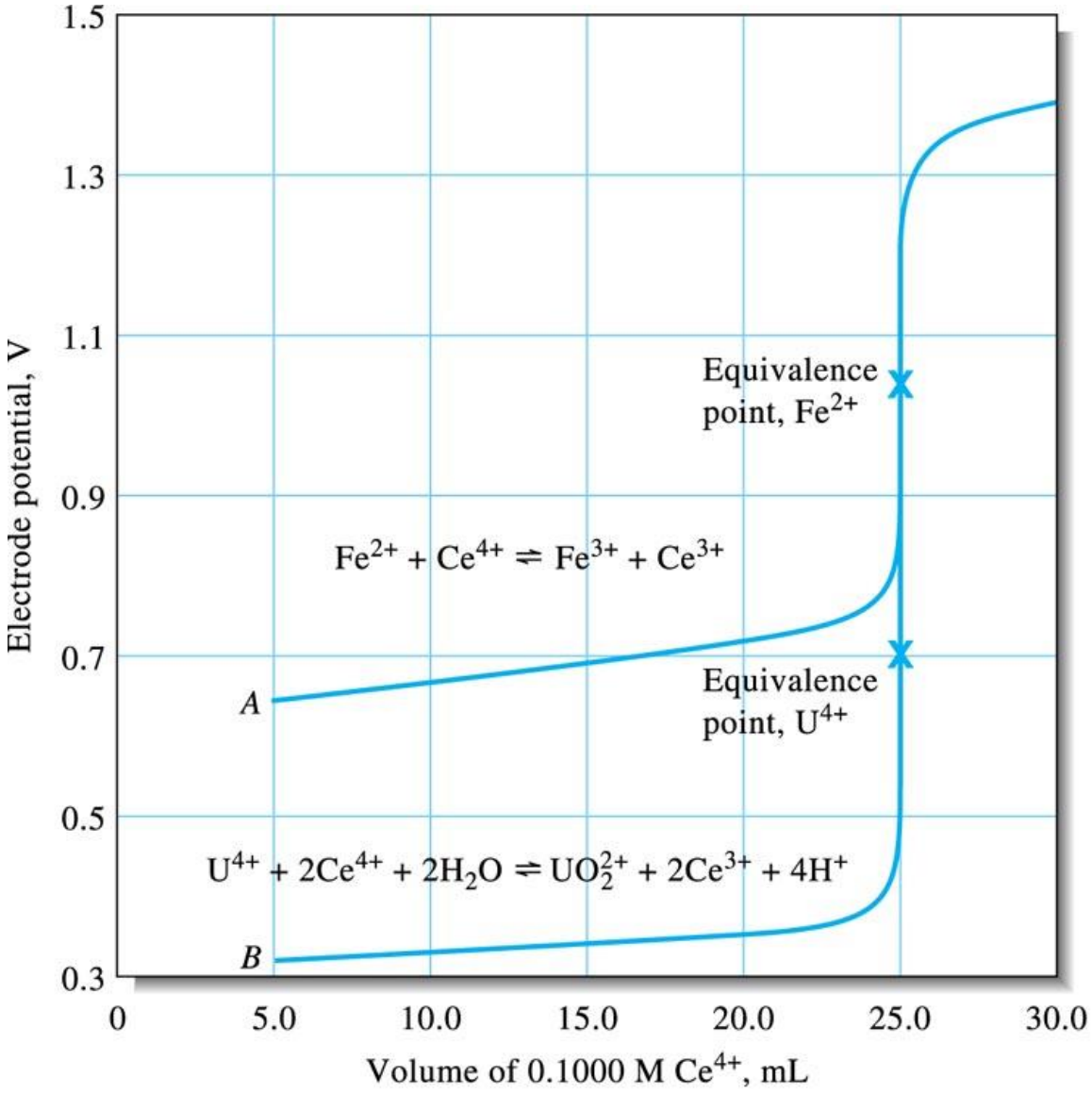
Derive a curve for the titration of 50.00 mL of 0.02500 mol L^{-1} U^{4+} with 0.1000 mol L^{-1} Ce^{4+}. The solution is 1.0 mol L^{-1} in H_2SO_4 throughout the titration (for the take of simplicity, assume that $[H^+]$ for this solution is also about 1.0 mol L^{-1}). The analytical reaction is:

$$U^{4+} + 2Ce^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Ce^{3+} + 4H^+$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44\ V$$

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^0 = 0.334\ V$$

Volumes: 5.00 / equivalence point / 25.10 mL



α values

$$E = E^0 - \frac{2.303RT}{nF}\log\frac{[R]}{[O]}$$

$$\frac{[R]}{[O]} = 10^{\frac{nF(E-E^0)}{2.303RT}}$$

25ºC

$$f = \frac{F}{2.303RT} = \frac{1}{0.0592}$$

$$\frac{[R]}{[O]} = 10^{-nf(E-E^0)}$$

$$\alpha_R = \frac{[R]}{[R]+[O]} = \frac{[R]/[O]}{[R]/[O]+1} = \frac{10^{-nf(E-E^0)}}{10^{-nf(E-E^0)}+1}$$

$$\alpha_R = \frac{10^{-nfE}\,x10^{nfE^0}}{(10^{-nfE}\,x10^{nfE^0})+1} = \frac{10^{-nfE}}{10^{-nfE}+10^{-nfE^0}}$$

$$\alpha_O = 1-\alpha_R = 1-\frac{10^{-nfE}}{10^{-nfE}+10^{-nfE^0}} = \frac{10^{-nfE^0}}{10^{-nfE}+10^{-nfE^0}}$$

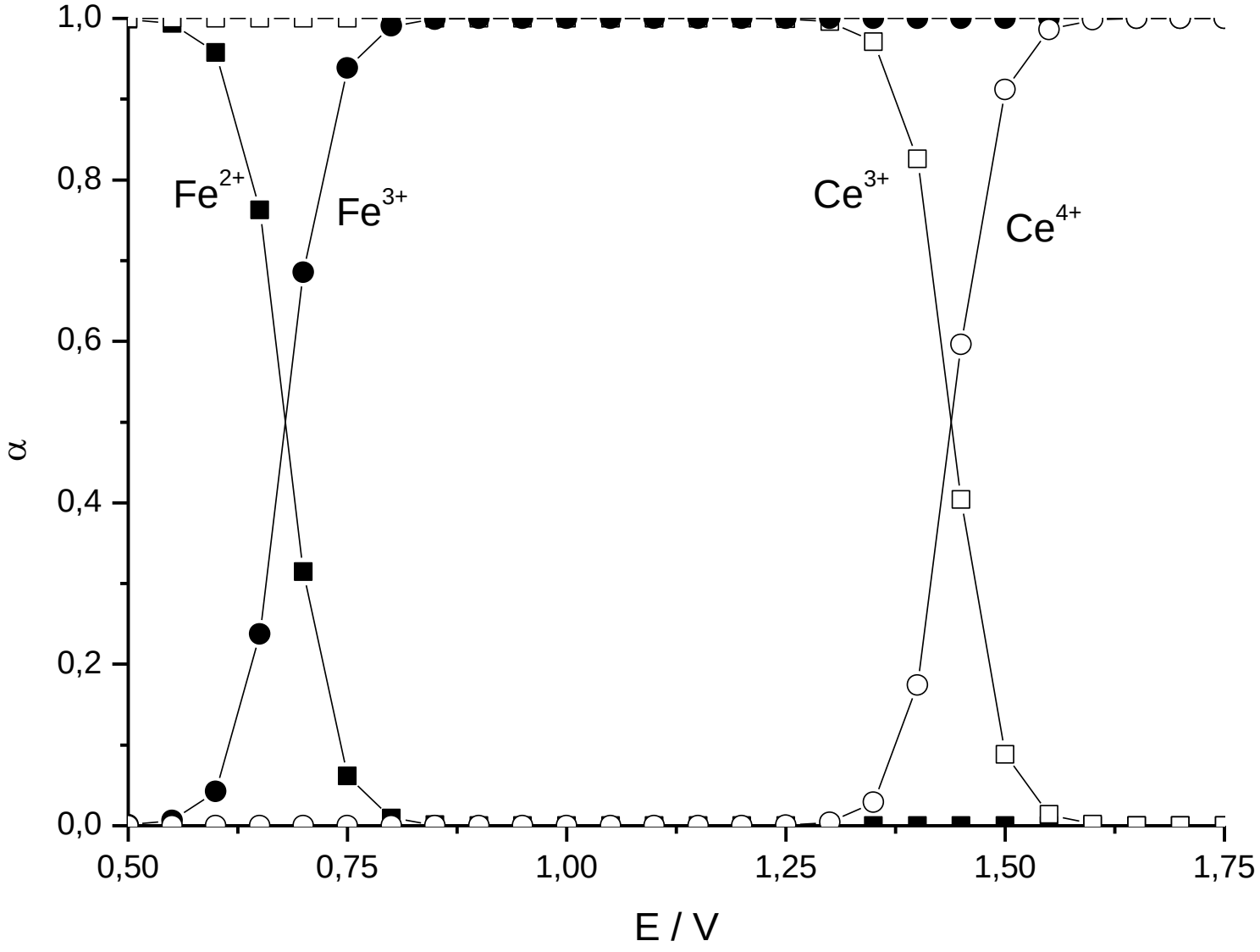
EXAMPLE

$E^{0'}$ Fe^{3+}/Fe^{2+} in 1 mol L^{-1} H_2SO_4 = 0.68 V

$E^{0'}$ Ce^{4+}/Ce^{3+} in 1 mol L^{-1} H_2SO_4 = 1.44 V

$$\alpha_{Fe^{2+}} = \frac{10^{-fE}}{10^{-fE} + 10^{-fE^{0'}_{Fe}}} \qquad \alpha_{Fe^{3+}} = \frac{10^{-fE^{0'}_{Fe}}}{10^{-fE} + 10^{-fE^{0'}_{Fe}}}$$

$$\alpha_{Ce^{3+}} = \frac{10^{-fE}}{10^{-fE} + 10^{-fE^{0'}_{Ce}}} \qquad \alpha_{Ce^{4+}} = \frac{10^{-fE^{0'}_{Fe}}}{10^{-fE} + 10^{-fE^{0'}_{Ce}}}$$


1,0
0,8
0,6
0,4
0,2
0,0
α
0,50
0,75
1,00
1,25
1,50
1,75
E / V
Fe2+
Fe3+
Ce3+
Ce4+

THE EFFECT OF SYSTEM VARIABLES

Reactant concentration:

E_{system} for an oxidation/reduction titration is ordinarily independent of dilution. This independence is in distinct contrast to that observed in the other types of titration curves.

Completeness of the reaction:

The change in E_{system} in the equivalence-point region of an oxidation/reduction titration becomes larger as the reaction becomes more complete.

OXIDATION/REDUCTION INDICATORS

•General redox indicators and specific indicators.

•General oxidation/reduction indicators: are substances that change color upon being oxidized or reduced. In contrast to specific indicators, the color changes of true redox indicators are largely independent of the chemical nature of the analyte and titrant and depend instead upon the changes in the electrode potential of the system that occur as the titration progresses.

$$In_{ox} + ne^- \rightleftharpoons In_{red}$$

$$E = E^0_{In_{ox}/In_{red}} - \frac{0.0592}{n} \log \frac{[In_{red}]}{[In_{ox}]}$$

$$\frac{[In_{red}]}{[In_{ox}]} \leq \frac{1}{10} \quad \text{Color change} \quad \frac{[In_{red}]}{[In_{ox}]} \geq 10$$

$$E = E^0_{In} \pm \frac{0.0592}{n}$$

TABLE 19-3*

Selected Oxidation/Reduction Indicators*

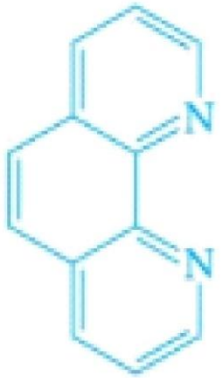
Indicator	Color		Transition Potential, V	Conditions
	Oxidized	Reduced		
5-Nitro-1,10-phenanthroline iron(II) complex	Pale blue	Red-violet	+1.25	1 M H_2SO_4
2,3′-Diphenylamine dicarboxylic acid	Blue-violet	Colorless	+1.12	7–10 M H_2SO_4
1,10-Phenanthroline iron(II) complex	Pale blue	Red	+1.11	1 M H_2SO_4
5-Methyl I,10-phenanthroline iron(II) complex	Pale blue	Red	+1.02	1 M H_2SO_4
Erioglaucin A	Blue-red	Yellow-green	+0.98	0.5 M H_2SO_4
Diphenylamine sulfonic acid	Red-violet	Colorless	+0.85	Dilute acid
Diphenylamine	Violet	Colorless	+0.76	Dilute acid
p-Ethoxychrysoidine	Yellow	Red	+0.76	Dilute acid
Methylene blue	Blue	Colorless	+0.53	1 M acid
Indigo tetrasulfonate	Blue	Colorless	+0.36	1 M acid
Phenosafranine	Red	Colorless	+0.28	1 M acid

*Data in part from I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, 2nd ed., Vol. 1, p. 140. New York: Interscience, 1942.

ORTHOPHENANTHROLINE

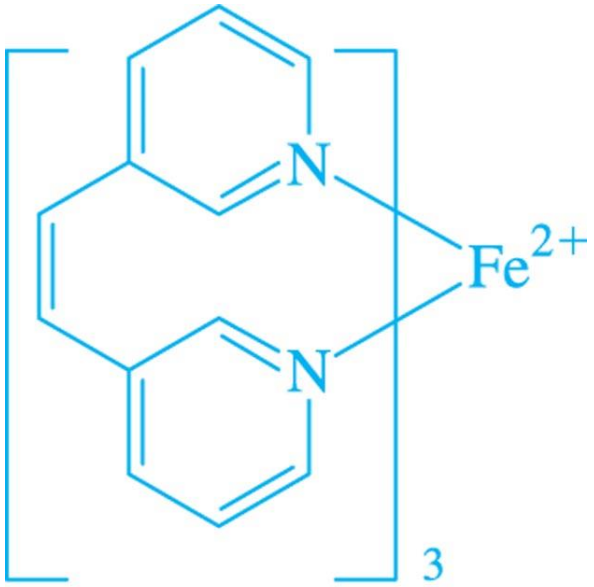
Form stable complexes with Fe(II) and certain other ions.

The compound 1,10-phenanthroline is an excellent complexing agent for Fe(II).



$(phen)_3Fe^{3+} + e^- \rightleftharpoons (phen)_3Fe^{2+}$

pale blue red



ferroin $(phen)_3Fe^{2+}$

Of all the oxidation/reduction indicators, ferroin approaches most closely the ideal substance. It reacts rapidly and reversibly, its color change is pronounced, at its solution are stable and readily prepared.

STARCH

•Starch, which forms a blue complex with triiodide ion, is a widely used specific indicator in oxidation/reduction reaction involving iodine as an oxidant or iodide ion as a reductant.

•In the presence of excess oxidizing agent, the concentration ratio of iodine to iodide is high, giving a blue color to the solution.

•With excess reducing agent, on the other hand, iodide ion predominates, and the blue color is absent.

SPECIFIC INDICATORS

•Perhaps the best-known specific indicator is starch, which forms a dark blue complex with triiodide ion.

•This complex signals the end point in titrations in which iodine is either procuced or consumed.

•Another specific indicator is KSCN. The end point involves the disappearance of the red color of the iron(III)/thiocyanate complex as a result of the marked decrease in the iron(III) concentration at the equivalence point.

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Indicator	Color		Transition Potential, V	Conditions
	Oxidized	Reduced		
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Erioglaucin A	Blue-red	Yellow-green	+0.98	0.5 M H_2SO_4
Diphenylamine sulfonic acid	Red-violet	Colorless	+0.85	Dilute acid
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p-Ethoxychrysoidine	Yellow	Red	+0.76	Dilute acid
Methylene blue	Blue	Colorless	+0.53	1 M acid
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*Data in part from I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, 2nd ed., Vol. 1, p. 140. New York: Interscience, 1942.

PROBLEM

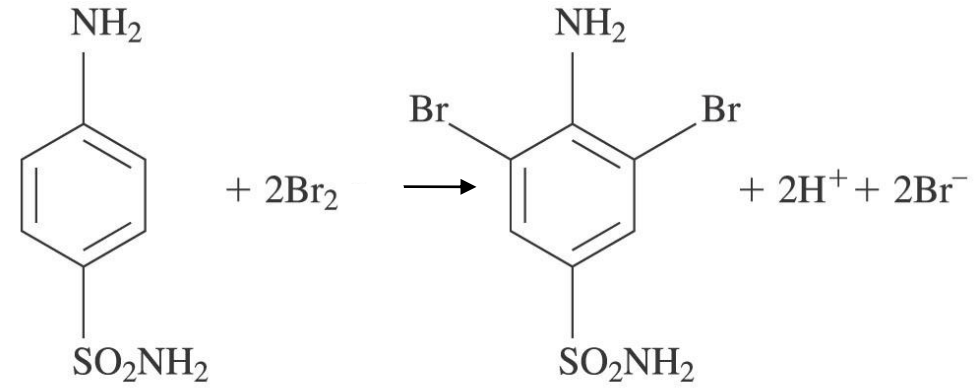
A 0.2981-g sample of an antibiotic powder containing sulfanilamide was dissolved in HCℓ and the solution diluted to 100.0 mL. A 20.00-mL aliquot was transferred to a flask, and followed by 25.00 mL of 0.01767 mol L^{-1} $KBrO_3$. An excess of KBr was added to form Br_2, and the flask was stoppered. After 10 min, during which time the Br_2 brominated the sulfanilamide, an excess of KI was added. The liberated iodine was titrated with 12.92 mL of 0.1215 mol L^{-1} soldium thiosulfate. The reactions are:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2S_4O_6^{2-} + 2I^-$$

Calculate the percent sulfanilamide in the powder.



sulfanilamide

172.21 g mol^{-1}

PROBLEM

Aqueous solutions containing approximately 3%(w/w) H_2O_2 are sold in drug stores as a disinfectant. Propose a method for determining the peroxide content of such a preparation using the standard solution. Assume that you wish to use 30 and 45 mL of the reagent for a titration.

KARL FISCHER

Water determination

Karl Fischer reagent is composed of iodine, sulfur dioxide, pyridine, and methanol. This mixture reacts with water according to the equation

$$C_5H_5N{\cdot}I_2 + C_5H_5N{\cdot}SO_2 + C_5H_5N + H_2O \rightarrow 2C_5H_5N{\cdot}HI + C_5H_5N{\cdot}SO_3$$

$$C_5H_5N^+{\cdot}SO_3^- + CH_3OH \rightarrow C_5H_5N(H)SO_4CH_3$$

$$I_2 + SO_2 + 2H_2O \rightleftharpoons 2HI + H_2SO_4$$

Undesirable:

$$C_5H_5N^+{\cdot}SO_3^- + H_2O \rightarrow C_5H_5NH^+SO_4H^-$$

Not as specific for H_2O → adding a large excess of methanol

KARL FISCHER

Karl Fischer reagent decomposes on standing.

End-point detection: is signaled by the appearance of the first excess of the pyridine/iodine complex when all water has been consumed. The color of the reagent is intense enough for a visual end point; the change is from the yellow of the reaction products to the brown of the excess reagent.