



## ELECTROCHEMISTRY

- The study of the relations between chemical reactions and electricity
- The study of the interconversion of chemical energy and electrical energy
- The study of redox reactions
- Electrochemical processes involve the transfer of electrons from one substance to another



## ELECTROCHEMISTRY

### Electroactive Species

- Species that undergoes an oxidation or a reduction during reaction
- Species may be complexed, solvated, molecule, or ion
- Species may be in aqueous or nonaqueous solution



## ELECTROANALYTICAL CHEMISTRY

- The use of electrochemical techniques to characterize a sample
- Deals with the relationship between electricity and chemistry
- Analytical calculations are based on the measurement of electrical quantities (current, potential, charge, or resistance) and their relationship to chemical parameters



## ELECTROANALYTICAL CHEMISTRY

### Advantages

- Measurements are easy to automate as they are electrical signals
- Low concentrations of analytes are determined without difficulty
- Far less expensive equipment than spectroscopy instruments

## FUNDAMENTAL CONCENPTS

### Redox Reaction

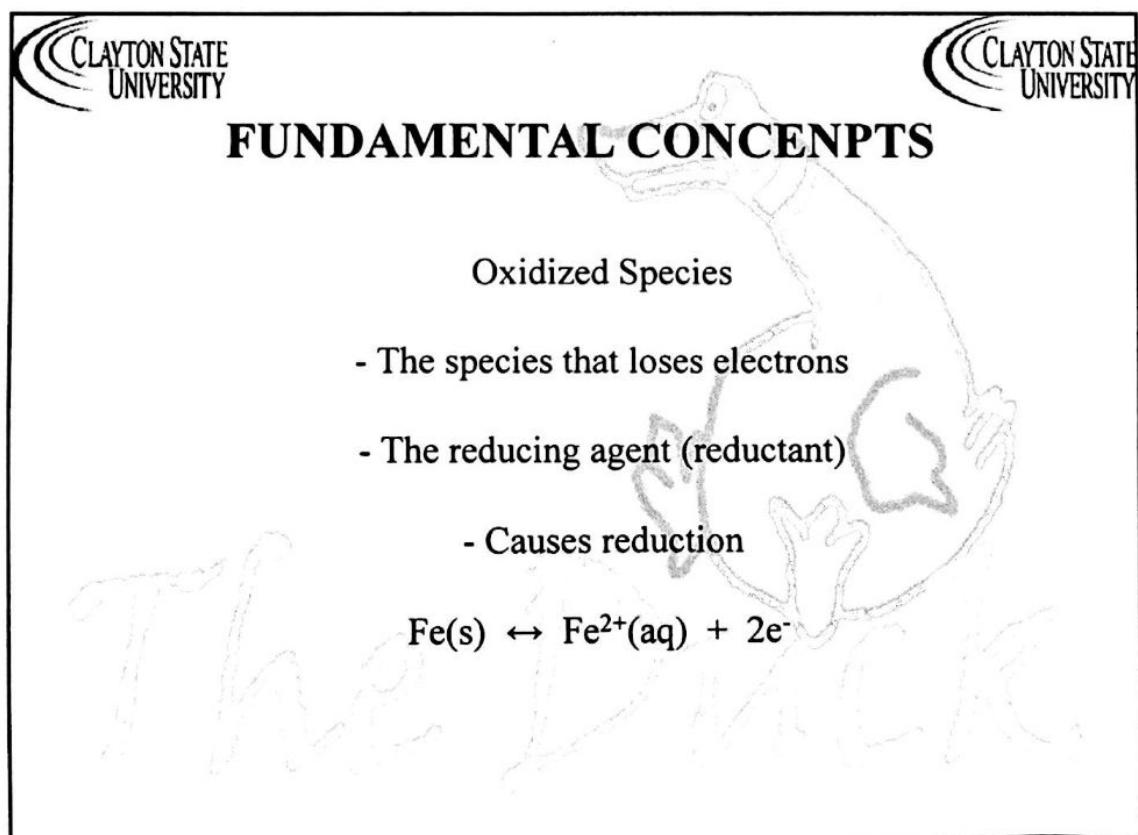
- Oxidation-reduction reaction
- Reactions in which electrons are transferred from one substance to another

#### Oxidation

- Loss of electrons

#### Reduction

- Gain of electrons



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## FUNDAMENTAL CONCENPTS

### Oxidized Species

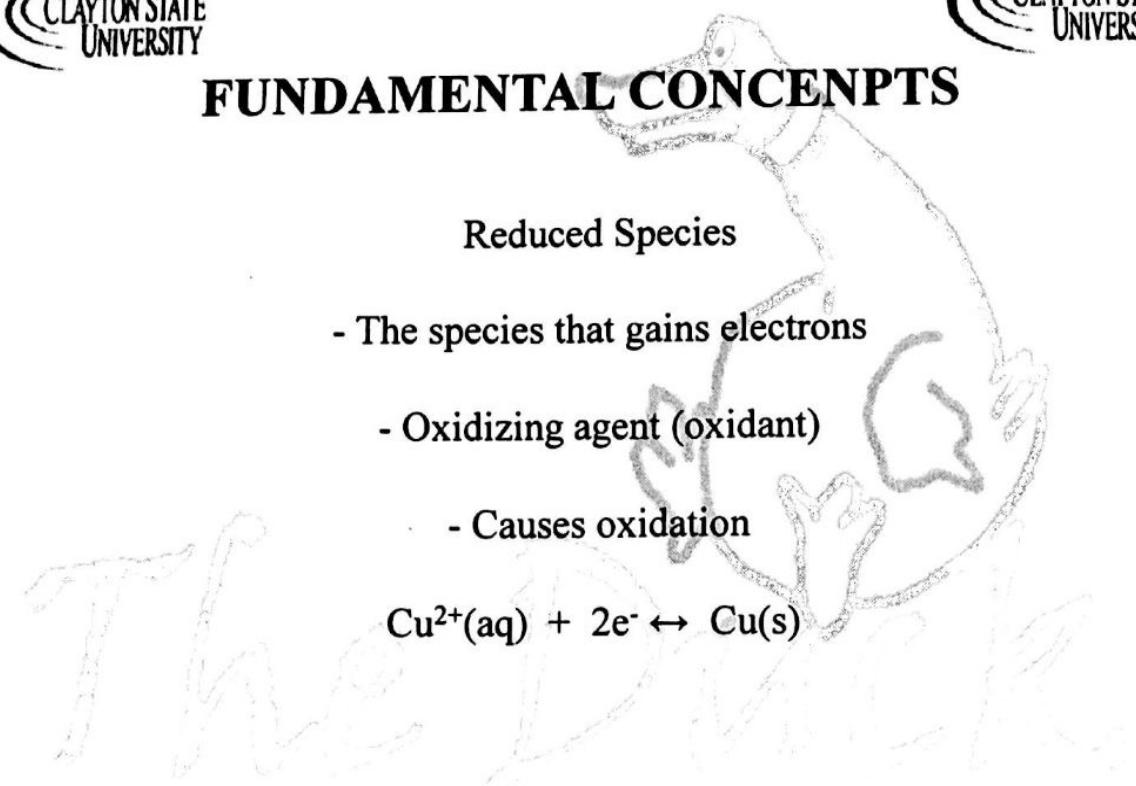
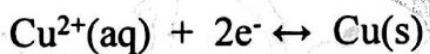
- The species that loses electrons
- The reducing agent (reductant)
- Causes reduction

$$\text{Fe(s)} \leftrightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$$

## FUNDAMENTAL CONCENPTS

### Reduced Species

- The species that gains electrons
- Oxidizing agent (oxidant)
- Causes oxidation



## FUNDAMENTAL CONCENPTS

### Half Reactions

- Just the oxidation or the reduction is given

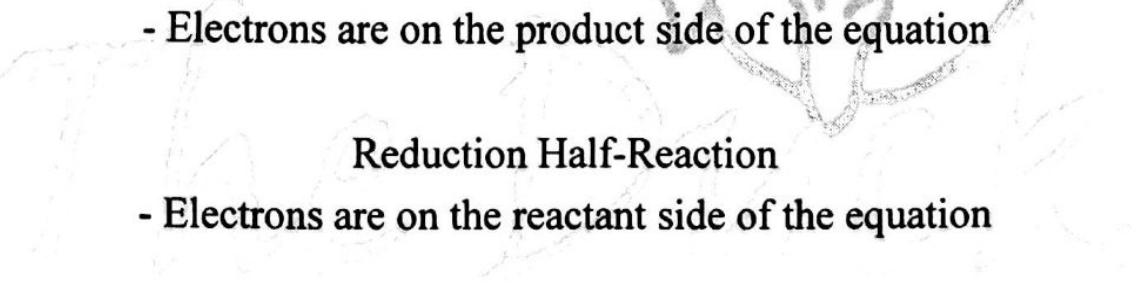
- The transferred electrons are shown

### Oxidation Half-Reaction

- Electrons are on the product side of the equation

### Reduction Half-Reaction

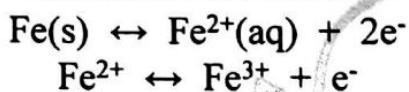
- Electrons are on the reactant side of the equation



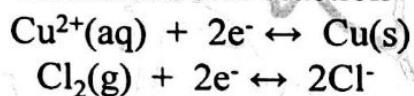
## FUNDAMENTAL CONCENPTS

### Half Reactions

Oxidation half reaction



Reduction half reaction



## FUNDAMENTAL CONCENPTS

- Many redox reactions are reversible
- Reduction reaction becomes oxidation reaction when it is reversed and vice versa
- Sum of oxidation and reduction half-reactions gives the net redox reaction or the overall reaction
- No electrons appear in the overall reaction

## FUNDAMENTAL CONCEPTS

### The Overall Reaction

- Both an oxidation and a reduction must occur in a redox reaction
- The oxidizing agent accepts electrons from the reducing agent



- Oxidizing agent  
- Reduced species  
- Electron gain

- Reducing agent  
- Oxidized species  
- Electron loss

## FUNDAMENTAL CONCEPTS

### Charge (q)

Charge (q) of an electron =  $-1.602 \times 10^{-19}$  C

Charge (q) of a proton =  $+1.602 \times 10^{-19}$  C

C = coulombs

Charge of one mole of electrons

$$= (1.602 \times 10^{-19} \text{ C})(6.022 \times 10^{23}/\text{mol}) = 96,485 \text{ C/mol}$$

= Faraday constant (F)

- The charge (q) transferred in a redox reaction is given by

$$q = n \times F$$

## FUNDAMENTAL CONCENPTS

### Current (i)

- The quantity of charge flowing past a point in an electric circuit per second

$$i = q/\text{time}$$

Units

Ampere (A) = coulomb per second (C/s)

$$1\text{A} = 1\text{C/s}$$

The flow of charge

## FUNDAMENTAL CONCENPTS

### Voltage or Potential Difference (E)

- The amount of energy required to move charged electrons between two points
- Work done by or on electrons when they move from one point to another

$$w = E \times q \quad \text{or} \quad E = w/q$$

Units: volts (V or J/C)

$$1\text{V} = 1\text{J/C}$$

The flow of energy

## FUNDAMENTAL CONCENPTS

Ohm's Law

$$i = E/R$$

R = resistance

Units

$\Omega$  (ohm) or V/A

## FUNDAMENTAL CONCENPTS

Electrode

- Conducts electrons into or out of a redox reaction system
- The electrode surface serves as a junction between an ionic conductor and an electronic conductor

Examples

platinum wire

carbon (glassy or graphite)

Gold

Silver

## FUNDAMENTAL CONCENPTS

### Electroactive Species

- Donate or accept electrons at an electrode
- Can be made to oxidize or reduce

### Electrochemical Measurements

- Occur at the electrode – solution interface

### Chemical Measurements

- Involve homogeneous bulk solutions

## ELECTROCHEMICAL CELL

- Made up of the electrodes and the contacting sample solution
- Electrical conductor is immersed in a solution of its own ions
- A potential difference (voltage) is created between the conductor and the solution
  - The system is a half-cell
  - The metal conductor is an electrode and the solution is an electrolyte

## ELECTROCHEMICAL CELL

### Electrode Potential

- A measure of the ability of the half-cell to do work  
(the driving cell for the half-cell reaction)

**Anode**

- Electrode where oxidation occurs

$$M^{\circ} \rightarrow M^{n+} + ne^-$$

- Metal loses electrons and dissolves (enters solution)

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

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

*Table 3.10*

## ELECTROCHEMICAL CELL

### Cathode

- Electrode where reduction occurs

$$M^{n+} + ne^- \rightarrow M^{\circ}$$

- Positively charged metal ion gains electrons
- Neutral atoms are deposited on the electrode
- The process is called electrodeposition

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

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

*Table 3.10*

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## ELECTROLYSIS

- Voltage is applied to drive a redox reaction that would not otherwise occur

Examples

- Production of aluminum metal from  $\text{Al}^{3+}$
- Production of  $\text{Cl}_2$  from  $\text{Cl}^-$

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## ELECTROLYTIC CELL

- Nonspontaneous reaction
- Requires electrical energy to occur
- Consumes electricity from an external source



## GALVANIC CELL

- Spontaneous reaction
- Produces electrical energy
- Can be reversed electrolytically for reversible cells

Example  
Rechargeable batteries

### Conditions for Non-reversibility

- If one or more of the species decomposes
- If a gas is produced and escapes



## GALVANIC CELL

- Also known as voltaic cell
- A spontaneous redox reaction generates electricity
- One reagent is oxidized and the other is reduced
- The two reagents must be separated (cannot be in contact)
- Electrons flow through a wire (external circuit)

**GALVANIC CELL**

**Oxidation Half-Reaction**

- Loss of electrons
- Occurs at anode (negative electrode)
- The left half-cell by convention

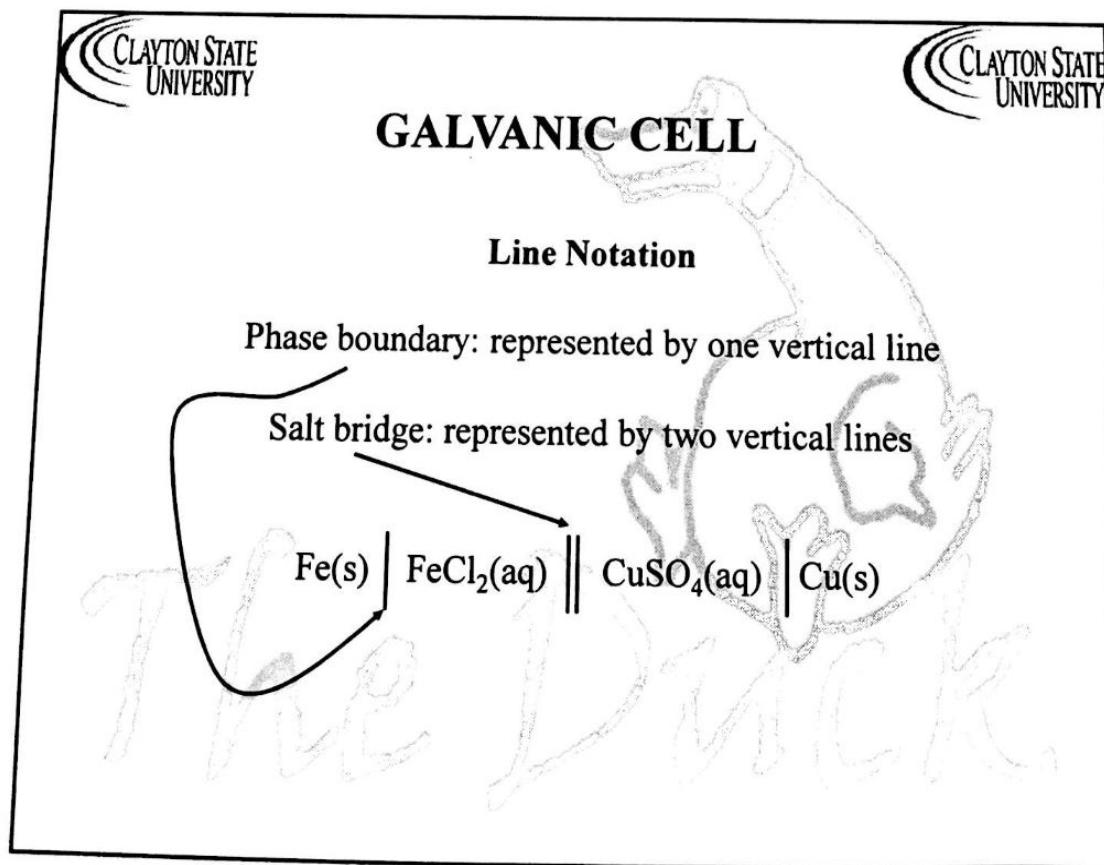
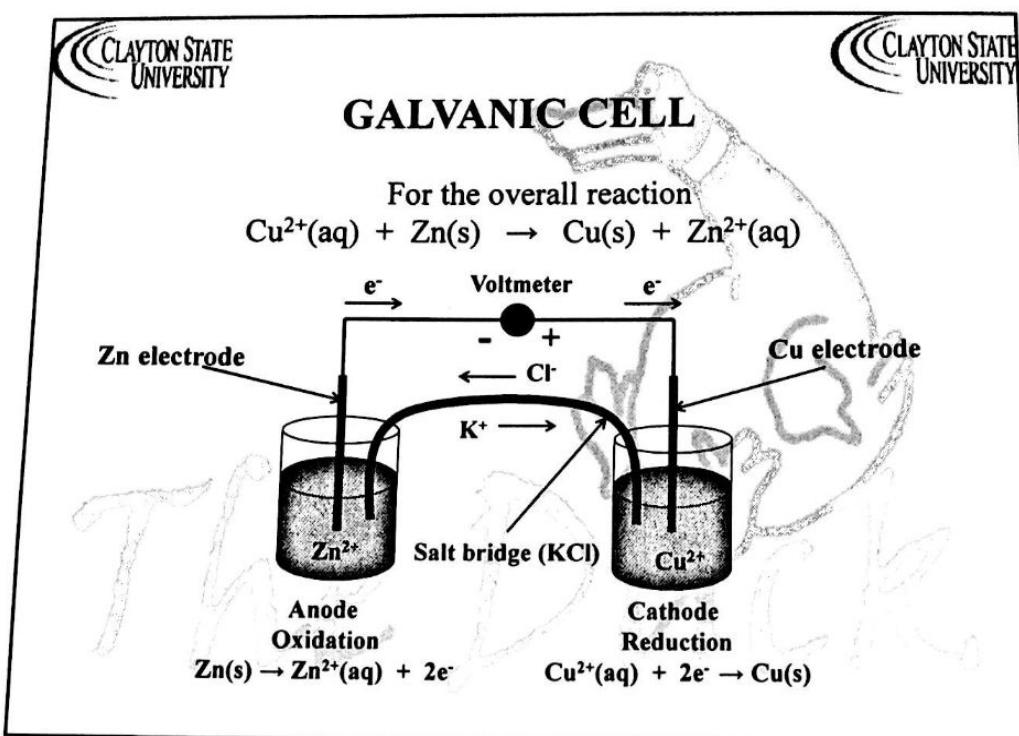
**Reduction Half-Reaction**

- Gain of electrons
- Occurs at cathode (positive electrode)
- The right half-cell by convention

**GALVANIC CELL**

**Salt Bridge**

- Connects the two half-cells (anode and cathode)
- Filled with gel containing saturated aqueous salt solution (KCl)
- Ions migrate through to maintain electroneutrality (charge balance)
- Prevents charge buildup that may cease the reaction process



## STANDARD POTENTIALS

### Standard Reduction Potential ( $E^\circ$ )

- Used to predict the voltage when different cells are connected
  - Potential of a cell as cathode compared to standard hydrogen electrode
  - Species are solids or liquids
  - Activities = 1
- We will use concentrations for simplicity
  - Concentrations = 1 M
  - Pressures = 1 bar

## STANDARD POTENTIALS

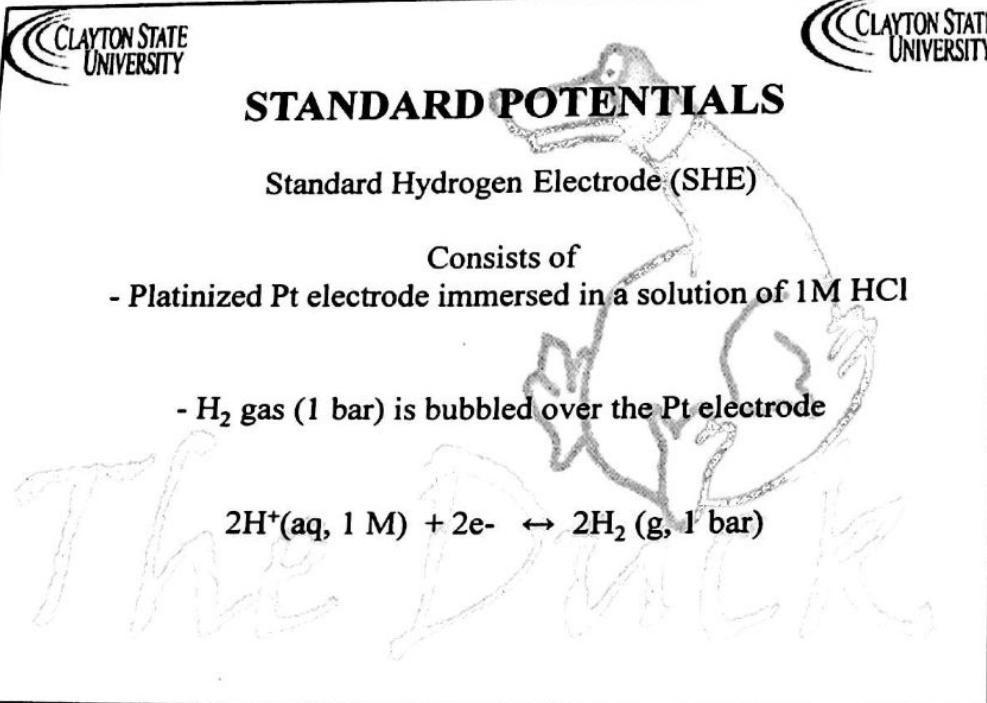
### Standard Hydrogen Electrode (SHE)

- Reference electrode half-cell
- Used to measure  $E^\circ$  for half-reactions (half-cells)
  - Connected to negative terminal (anode)

Assigned  $E^\circ = 0.000$  under standard state conditions  
( $T = 25^\circ\text{C}$ , concentration = 1M, pressure = 1 bar,  
pure solid or liquid)

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## STANDARD POTENTIALS



Standard Hydrogen Electrode (SHE)

Consists of

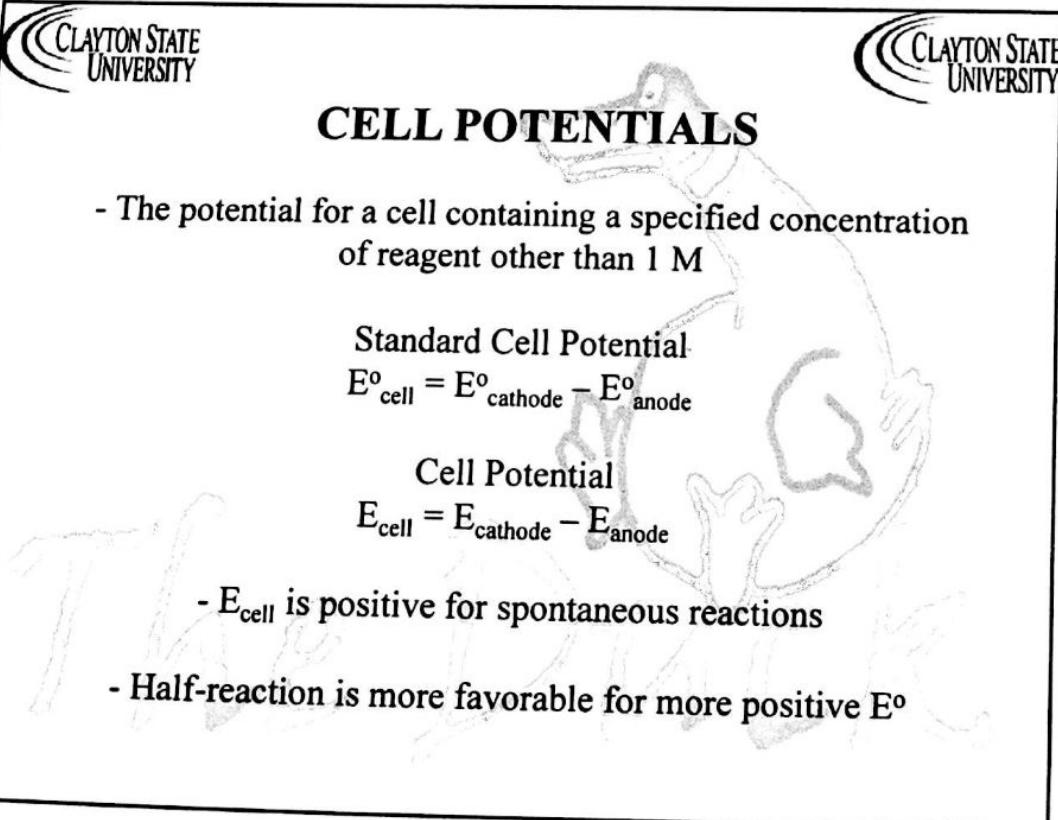
- Platinized Pt electrode immersed in a solution of 1M HCl
- H<sub>2</sub> gas (1 bar) is bubbled over the Pt electrode

$$2\text{H}^+(\text{aq}, 1 \text{ M}) + 2\text{e}^- \leftrightarrow 2\text{H}_2(\text{g}, 1 \text{ bar})$$

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## CELL POTENTIALS



- The potential for a cell containing a specified concentration of reagent other than 1 M

Standard Cell Potential

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

Cell Potential

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

- E<sub>cell</sub> is positive for spontaneous reactions
- Half-reaction is more favorable for more positive E<sup>o</sup>

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## CELL POTENTIALS

**Junction Potential**

- Is produced when there is a difference in concentration or types of ions of the two half-cells
- Is created at the junction of the salt bridge and the solution
- Is a source of error
- Minimized in KCl salt bridge due to similar mobilities of  $K^+$  and  $Cl^-$

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## CELL POTENTIALS

Oxidizing agents	Half Reaction	Reducing agents	$E^\circ$ (V)
	$F_2 + 2e^- \leftrightarrow 2F^-$		2.890
	$MnO_4^- + 5e^- \leftrightarrow Mn^{2+}$		1.507
	$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ (in HCl)		1.280
	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$		1.229
	$Ag^+ + e^- \leftrightarrow Ag(s)$		0.799
	$Cu^{2+} + 2e^- \leftrightarrow Cu(s)$		0.339
	$2H^+ + 2e^- \leftrightarrow H_2(g)$		0.000
	$Cd^{2+} + 2e^- \leftrightarrow Cd(s)$		-0.402
	$Fe^{2+} + 2e^- \leftrightarrow Fe(s)$		-0.440
	$Zn^{2+} + 2e^- \leftrightarrow Zn(s)$		-0.763
	$Al^{3+} + 3e^- \leftrightarrow Al(s)$		-1.659
	$K^+ + e^- \leftrightarrow K(s)$		-2.936
	$Li^+ + e^- \leftrightarrow Li(s)$		-3.040

Increasing oxidizing power ↑

↓ Increasing reducing power

## CELL POTENTIALS

- Elements that are more powerful reducing agents than hydrogen show negative potentials
- Elements that are less powerful reducing agents than hydrogen show positive potentials
- Metals with more negative  $E^\circ$  are more active
- More active metals displace less active metals from solution

Fe will displace  $Cu^{2+}$  out of solution  
Zn dissolves in HCl but Cu does not

## NERNST EQUATION

Gives relationship between the potential of an electrochemical cell and the concentration of reactants and products



$$E = E^\circ + \frac{2.3RT}{nF} \log\left(\frac{[O]}{[R]}\right)$$

E = electrode potential

$E^\circ$  = standard potential for the redox reaction

R = gas constant = 8.314 J/K-mol

T = absolute temperature in Kelvin

F = Faraday's constant = 96,485 C/mol

n = number of electrons transferred



## NERNST EQUATION

For the half reaction



The half-cell potential (at 25 °C), E, is given by

$$E = E^{\circ} - \frac{2.3RT}{nF} \log\left(\frac{[B]^b}{[A]^a}\right)$$

$$E = E^{\circ} - \frac{RT}{nF} \ln\left(\frac{[B]^b}{[A]^a}\right)$$

$$E = E^{\circ} - \frac{0.05916}{n} \log\left(\frac{[B]^b}{[A]^a}\right)$$



## NERNST EQUATION

For the overall reaction



The potential at 25 °C is given by

$$E = E^{\circ} - \frac{2.3RT}{nF} \log\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

$$E = E^{\circ} - \frac{RT}{nF} \ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

$$E = E^{\circ} - \frac{0.05916}{n} \log\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

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## NERNST EQUATION

-  $E = E^\circ$  when  $[O] = [R] = 1M$

- Concentration for gases are expressed as pressures  
in bars or atm

- Concentrations for pure solids, liquids, and solvents  
are omitted (activity = 1)

- Reduction is more favorable on the negative side of  $E^\circ$

- When a half reaction is multiplied by a factor  
 $E^\circ$  remains the same

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## REFERENCE ELECTRODES

- An ideal reference electrode

- Has a fixed potential over time and temperature

- Long term stability

- Ability to return to the initial potential after exposure to  
small currents (reversible)

- Obey the Nernst equation

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## REFERENCE ELECTRODES

### Standard Hydrogen Electrode (SHE)

$$E = 0.000 \text{ V}$$

### Saturated Calomel Electrode (SCE)

- Composed of metallic mercury in contact with saturated solution of mercurous chloride (calomel,  $\text{Hg}_2\text{Cl}_2$ )
- Pt wire is in contact with the metallic mercury
- Calomel is in contact with saturated KCl solution

$$E = +0.244 \text{ V at } 25^\circ\text{C}$$



## REFERENCE ELECTRODES

### Silver/Silver Chloride Reference Electrode (Ag/AgCl)

- Consists of silver metal coated with silver chloride paste
- Immersed in saturated KCl and AgCl solution

$$E = +0.199 \text{ V at } 25^\circ\text{C}$$



## ELECTROANALYTICAL METHODS

Two main types

- Potentiometric and Potentiostatic

- The type of technique reflects the type of electrical signal used for quantitation

- Techniques require at least two electrodes and an electrolyte (containing solution)

### Electrodes

Working (indicator) electrode, reference electrode, counter electrode



## ELECTROANALYTICAL METHODS

### Potentiometric Technique

- Based on a static (zero-current) situations

- Based on measurement of the potential established across a membrane

- Used for direct monitoring of ionic species ( $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{H}^+$ )

## ELECTROANALYTICAL METHODS

### Potentiostatic Technique

- Controlled-potential technique
- Based on dynamic (non-zero-current) situations
- Deals with the study of charge transfer processes at the electrode-solution interface
- Chemical species are forced to gain or lose electrons

## ELECTROANALYTICAL METHODS

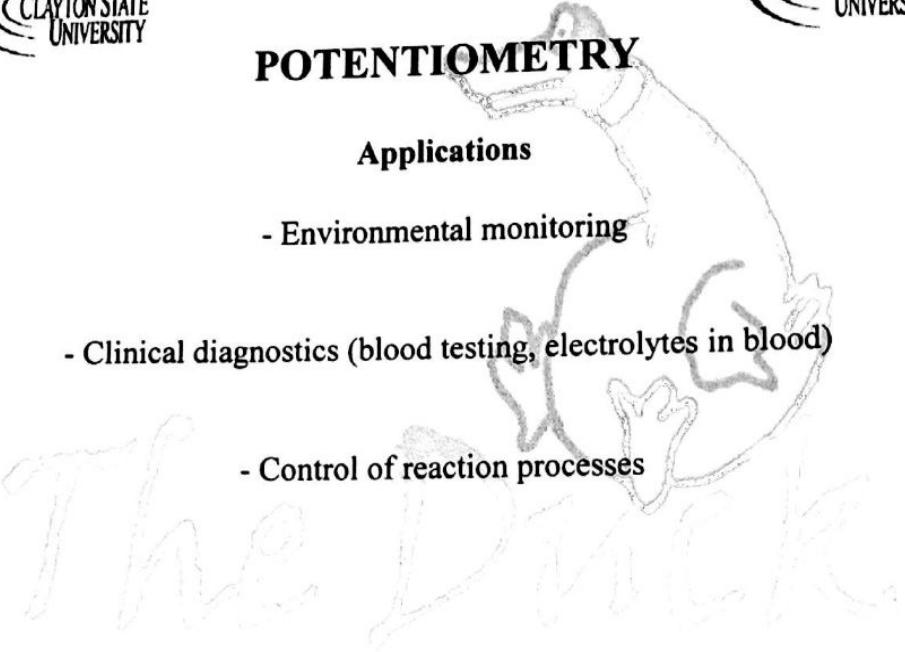
- Potentiometry
  - Coulometry
  - Voltammetry
  - Polarography
- Methods are classified according to the variable being measured
  - One variable (current, voltage, charge) is measured and the others are controlled

## POTENTIOMETRY

- Based on static (zero-current) measurements
- Involves measurement of potential (voltage) of an electrochemical cell
- Used to obtain information on the composition of an analyte
- Potential between two electrodes is measured (indicator electrode and reference electrode)
- Indicator (sensing) electrode responds to the concentration of the analyte species

## POTENTIOMETRY

- The analyte concentration is related to the potential difference between the indicator electrode and the reference electrode (by applying the Nernst equation)
- Indicator electrode is connected to a reference electrode (SCE, Ag/AgCl) to form a complete cell
  - Implies  $E_{\text{total}} = E_{\text{indicator}} - E_{\text{reference}}$
- Reference electrode is connected to the negative terminal of the readout device (potentiometer)



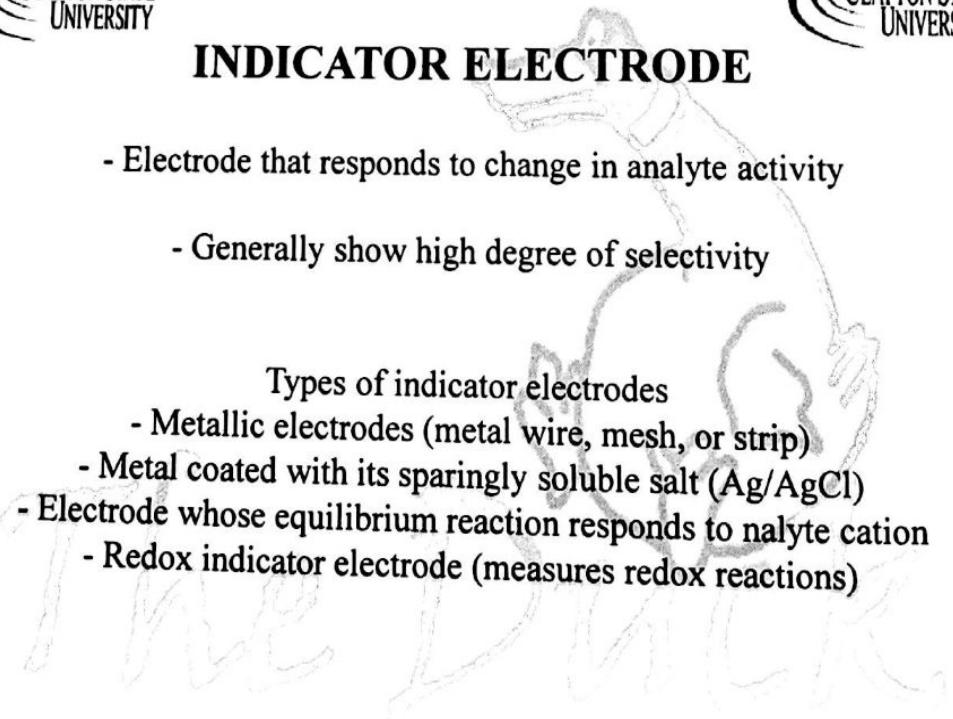
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## POTENTIOMETRY

### Applications

- Environmental monitoring
- Clinical diagnostics (blood testing, electrolytes in blood)
- Control of reaction processes



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## INDICATOR ELECTRODE

- Electrode that responds to change in analyte activity
- Generally show high degree of selectivity

#### Types of indicator electrodes

- Metallic electrodes (metal wire, mesh, or strip)
- Metal coated with its sparingly soluble salt (Ag/AgCl)
- Electrode whose equilibrium reaction responds to nalyte cation
- Redox indicator electrode (measures redox reactions)

## ION-SELECTIVE ELECTRODES (ISE)

- Are indicator electrodes
- Respond directly to the analyte
- Used for direct potentiometric measurements
- Selectively binds and measures the activity of one ion  
(no redox chemistry)

### Examples

pH electrode

Calcium ( $\text{Ca}^{2+}$ ) electrode

Chloride ( $\text{Cl}^-$ ) electrode

## ION-SELECTIVE ELECTRODES (ISE)

### Advanteages

- Exhibit wide response
- Exhibit wide linear range
- Low cost
- Color or turbidity of analyte does not affect results
- Come in different shapes and sizes

## ION-SELECTIVE ELECTRODES (ISE)

- Made from a permselective ion-conducting membrane (ion-exchange material that allows ions of one electrical sign to pass through)
- Reference electrode is inbuilt
- Internal solution (solution inside electrode) contains ion of interest with constant activity
- Ion of interest is also mixed with membrane
- Membrane is nonporous and water insoluble

## ION-SELECTIVE ELECTRODES (ISE)

- Responds preferentially to one species in solution

Internal (filling)  
solution

Ion-selective membrane

Internal reference  
electrode

## ION-SELECTIVE ELECTRODES (ISE)

- If  $C^+$  is the preferential ion
- $[C^+]$  inside the electrode  $\neq [C^+]$  outside the electrode
- Results in a potential difference across the membrane

$$E = \frac{RT}{z_i F} \ln \left( \frac{[C^+]_{\text{outer}}}{[C^+]_{\text{inner}}} \right)$$

$$\text{At } 25^\circ\text{C}, E = \frac{0.05916}{z_i} \log \left( \frac{[C^+]_{\text{outer}}}{[C^+]_{\text{inner}}} \right)$$

Generally (at 25 °C)

- 10-fold change in activity implies  $59/z_i$  mV change in E
- $z_i$  is the charge on the selective ion (negative for anions)
  - $z_i = +1$  for  $K^+$ ,  $z_i = +2$  for  $Ca^{2+}$ ,  $z_i = -2$  for  $CO_3^{2-}$

## ION-SELECTIVE ELECTRODES (ISE)

- Let  $c_i$  = molarity of  $C^+$
- Activity ( $a_i$ ) rather than molarity is measured by ISEs
- Activity is the effective (active) concentration of analyte (effective concentration decreases due to ionic interactions)

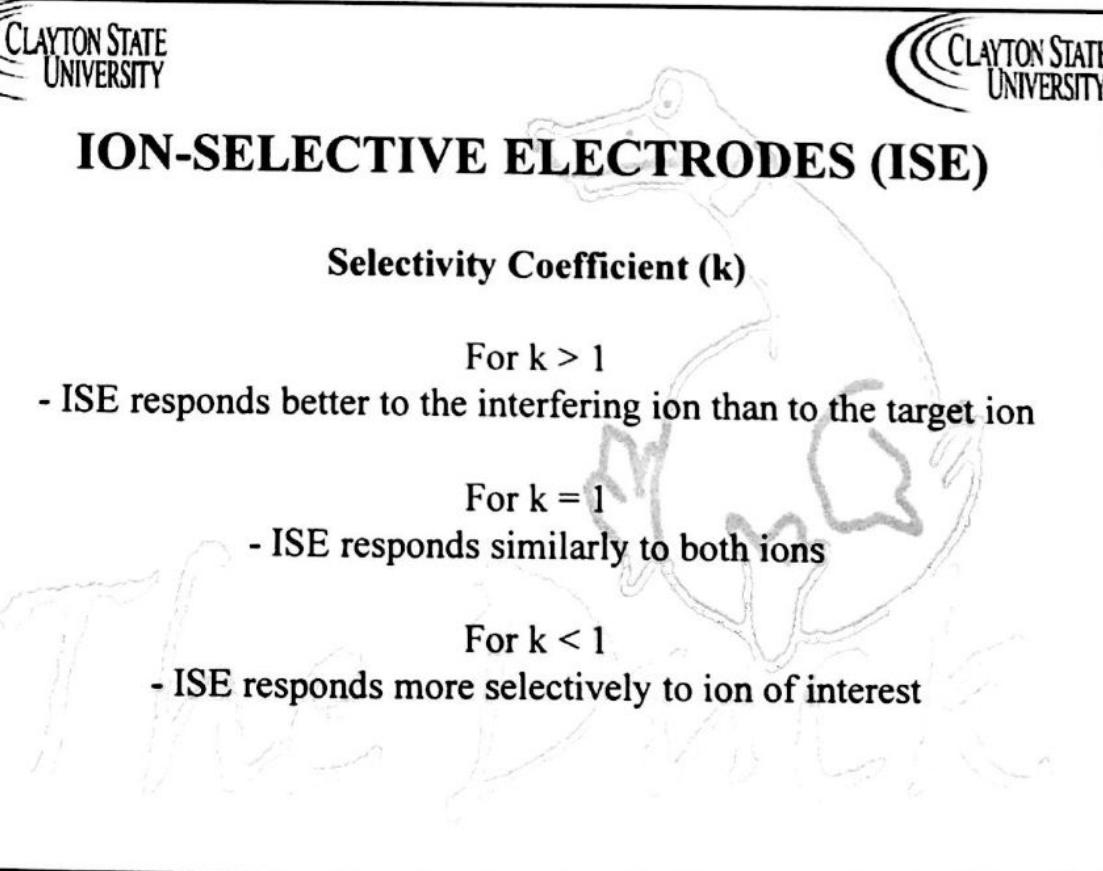
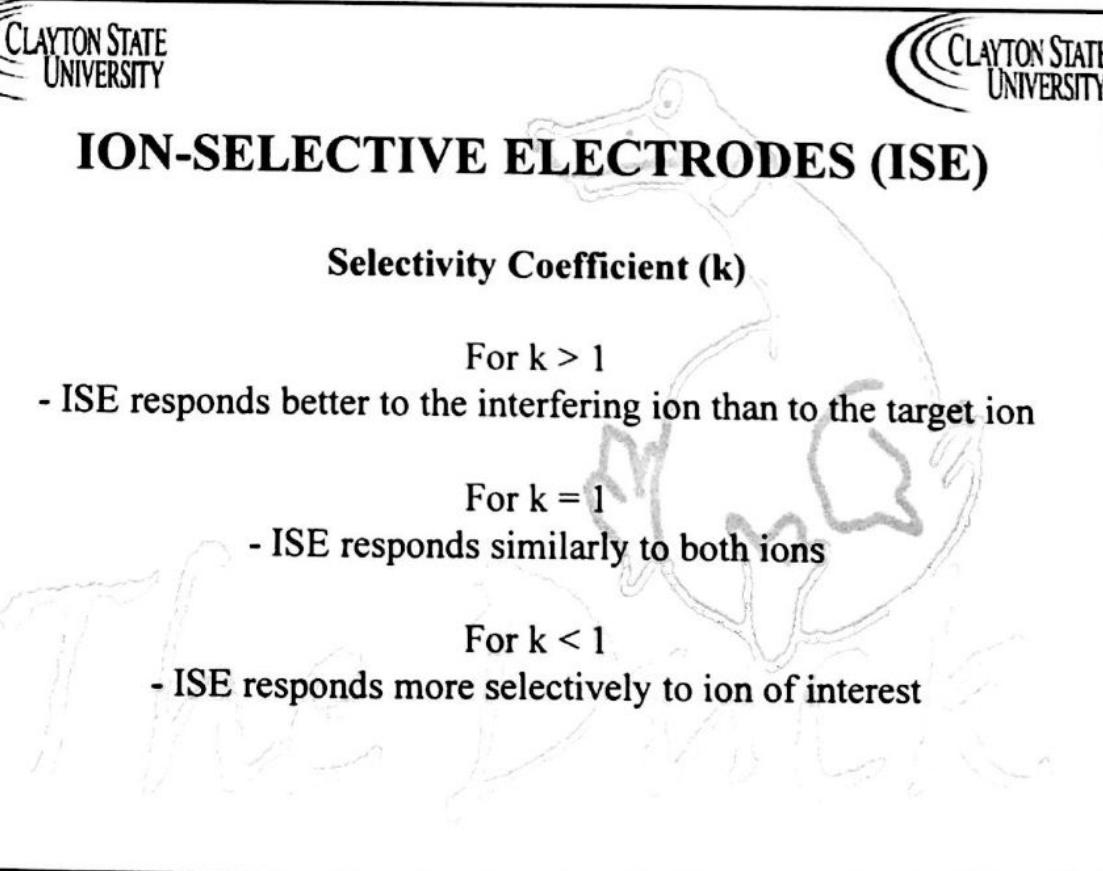
$$a_i = \gamma_i c_i$$

where  $\gamma_i$  = activity coefficient (between 0 and 1)

## ION-SELECTIVE ELECTRODES (ISE)

### Selectivity Coefficient (k)

- A measure of the ability of ISE to discriminate against an interfering ion
- It is assumed that ISEs respond only to ion of interest
- In practice, no electrode responds to only one specific ion
- The lower the value of k the more selective is the electrode
- $k = 0$  for an ideal electrode (implies no interference)



## ION-SELECTIVE ELECTRODES (ISE)

### Selectivity Coefficient (k)

For  $k > 1$

- ISE responds better to the interfering ion than to the target ion

For  $k = 1$

- ISE responds similarly to both ions

For  $k < 1$

- ISE responds more selectively to ion of interest

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## ION-SELECTIVE ELECTRODES (ISE)

### Empirical Calibration Plot

Potential (mV)

$p[C^+]$

Slope =  $59/z_i$  mV

$z_i$  = charge of ion

Called Nernstian slope

- Used to determine the unknown concentration of analytes
- Departure from linearity is observed at low concentrations

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## ION-SELECTIVE ELECTRODES (ISE)

### Three groups of ISEs

- Glass electrodes
- Liquid electrodes
- Solid electrodes

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## GLASS ELECTRODES

- Responsive to univalent cations

- Employs thin ion-selective glass membrane

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## pH GLASS ELECTRODE

- The most widely used

- For pH measurements (selective ion is H<sup>+</sup>)

- Response is fast, stable, and has broad range

- pH changes by 1 when [H<sup>+</sup>] changes by a factor of 10

- Potential difference is 0.05196 V when  
[H<sup>+</sup>] changes by a factor of 10

For a change in pH from 3.00 to 6.00 (3.00 units)  
Potential difference =  $3.00 \times 0.05196 \text{ V} = 0.177$

## pH GLASS ELECTRODE

- Thin glass membrane (bulb) consists of  $\text{SiO}_4$
  - Most common composition is  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{CaO}$
- Glass membrane contains
- dilute HCl solution saturated in AgCl
  - inbuilt reference electrode (Ag wire coated with AgCl)

## pH GLASS ELECTRODE

Glass Electrode Response at 25 °C  
(potential across membrane with respect to  $\text{H}^+$ )

$$E = K + \beta(0.05916) \Delta\text{pH}$$

$$E = K - 0.05916 \log(a_{\text{H}^+})$$

$\Delta\text{pH}$  = pH difference between inside and outside of glass bulb

$\beta \approx 1$  (typically ~ 0.98)  
(measured by calibrating electrode in solutions of known pH)

K = asymmetry potential (system constant, varies with electrodes)

## pH GLASS ELECTRODE

### Sources of Error

- Standards used for calibration
  - Junction potential
  - Equilibration time
- Alkaline (sodium error)
  - Temperature
  - Strong acids
- Response to H<sup>+</sup> (hydration effect)



## POTENTIOMETRY INSTRUMENTATION

- Employs a potential measuring device (handheld device)  
(high-impedance circuit)
- Example is the pH meter (or pIon meter)
- Designed to work with various electrodes
- Have built-in temperature measurement and compensation
  - Three-point or more auto calibration
  - Two-electrode system  
(auxiliary reference electrode and working electrode)

## APPLICATIONS OF POTENTIOMETRY

- Determination of titration curves, equivalence point, end-point, half-equivalence point, inflection point.
- Determination of molar concentration of solutes.
- Determination of molecular weight.
- Determination of dissociation constants.
- Determination of ionization constants.

## APPLICATIONS OF POTENTIOMETRY

- Determination of pH.
- Determination of ionic strength.
- Determination of equilibrium constants.
- Determination of solubility product constants.
- Determination of acid dissociation constants.
- Determination of ionization constants.
- Determination of equilibrium constants.

# CONTROLED POTENTIAL TECHNIQUES

## Instrumentation

- Potentiostat
- Electrochemical cell with a three-electrode system.
  - Working Electrode (WE)
  - Reference Electrode (RE)
  - Counter/auxiliary Electrode (CE)
- Power
- Other components may be required depending on the type of experiment.

# CONTROLED POTENTIAL TECHNIQUES

## Potentiostat

- Instrument that controls the potential at a working electrode

## Electrochemical Cell

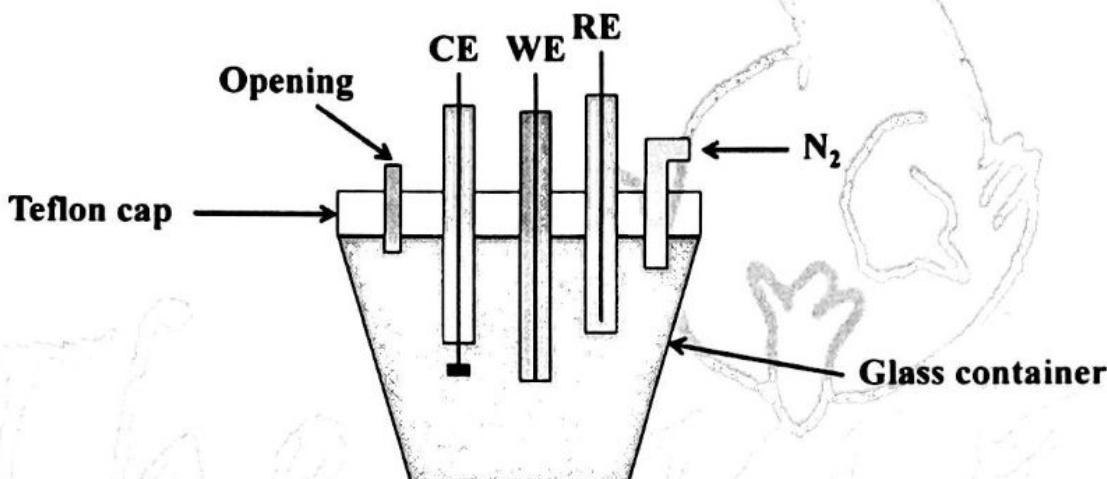
- Covered glass container of 3 - 50 ml volume
- Contains the three electrodes immersed in the sample solution
- Electrodes are inserted through holes in the cell cover
  - N<sub>2</sub> gas used as deoxygenated gas

## CONTROLLED POTENTIAL TECHNIQUES

- RE is placed as close as possible to WE to minimize potential drop caused by the cell resistance ( $iR$ )
- Flow cannot occur through RE hence the need for CE to complete the current path
- Current flows through solution between WE and CE
- Voltage is measured between WE and RE

# CONTROLLED POTENTIAL TECHNIQUES

## Electrochemical Cell



## COULOMETRY

- Method in which charge is measured
- Species being measured is converted quantitatively to a new species

### The Methods Based on Electrolysis

- Electrogravimetry
- Constant-potential coulometry
- Constant-current coulometry (coulometric titrimetry)

### Electrolysis

- A process causing a thermodynamically nonspontaneous oxidation or reduction reaction to occur by application of potential or current

# COULOMETRY

## Electrogravimetry

- Product of electrolysis is plated on a pre-weighed electrode
- Electrode is weighed again after process and the amount plated is determined by difference
- Metal dissolves from the anode and deposits on the cathode (electroplating, electrowinning, or electrorefining)

Examples of metals commonly determined

Cd, Bi, Co, Cu, Sb, Zn, Ni, In, Ag

# COULOMETRY

## Controlled Potential Coulometry

- Three electrode system
- Permits applied potential pulse or ramp at the working electrode
- Metal elements are deposited as potential is increased which increases charge passing through cell
- The instrument is the coulometer which measures  $q$



# COULOMETRY

## Controlled Potential Coulometry

### Applications

- Used to eliminate interferences from other reactions that take place at different potentials
- Used to determine the number of electrons involved in a reaction
  - Used for coulometric titrations

# COULOMETRY

## Instrumentation

Apparatus comprises of

- Potentiostat with DC output voltage
- Inert cathode and anode
- Stirring rod set-up
- Solution may be heated
- Working electrode can be either anode or cathode
- Controlled potential conditions

# VOLTAMMETRY

- Voltage between two electrodes is varied as current is measured
  - Solid working electrodes are used
- Oxidation-reduction takes place at or near the surface of the working electrode
- Graph of current versus potential is obtained
- Peak current is proportional to concentration of analyte

## VOLTAMMOGRAM

- Current versus potential plot
- Current on vertical axis and excitation potential on horizontal axis
- Electrode reactions involve several steps and can be complicated
- The rate is determined by the slowest step and depends on the potential range

## POLAROGRAPHY

- Voltammetry in which the working electrode is dropping mercury
- Makes use of potential ramp
- Conventional DC
- Wide cathodic potential range and a renewable surface
- Hence widely used for the determination of many reducible species

## POLAROGRAPHY

- Diffusion current is obtained by subtracting response due to supporting electrolyte (background current)
- Analyte species entering region close to the electrode surface undergo instantaneous electron transfer reaction
  - Maximum rate of diffusion is achieved
- Current-potential plot provides polarographic wave (polarogram)

The diagram shows a beaker containing a liquid electrolyte. A dropping mercury electrode (DME) is suspended from a vertical glass tube by a thin wire. A platinum wire or foil (CE) is partially submerged in the liquid. A reference electrode (RE) is also present in the beaker. The beaker is labeled "Dropping mercury electrode (DME)" and "Pt wire or foil". The reference electrode is labeled "SCE".

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## DC POLAROGRAPHY

- Three electrode system

WE = dropping mercury electrode (DME)

CE = Pt wire or foil

RE = SCE

The diagram shows a beaker containing a liquid electrolyte with a dropping mercury electrode (DME) at the bottom. The beaker is labeled "Dropping mercury electrode (DME)".

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## DC POLAROGRAPHY

The Ilkovic Equation

$$i_L = 708nD^{1/2}m^{2/3}t^{1/6}C$$

$D = \text{cm}^2/\text{s}$        $C = \text{mol}/\text{cm}^3$        $m = \text{g}/\text{s}$        $t = \text{s}$

$i_L$  is current at the end of drop life (the limiting current)

$i_L$  is a measure of the species concentration



## DC POLAROGRAPHY

### Half Wave Potential ( $E_{1/2}$ )

- Potential at which the current is one-half its limiting value

-  $E_{1/2}$  is independent of concentration of species

$$E_{1/2} = E^\circ + \frac{RT}{nF} \log\left(\frac{D_R}{D_O}\right)^{1/2}$$

$D_R$  = diffusion coefficient of reduced species

$D_O$  = diffusion coefficient of oxidized species

- Experimental  $E_{1/2}$  is compared to literature values to identify unknown analyte



## DC POLAROGRAPHY

### Half Wave Potential ( $E_{1/2}$ )

At 25 °C

$$E = E_{1/2} + \frac{0.05916}{n} \log\left(\frac{i_L - i}{i}\right)$$

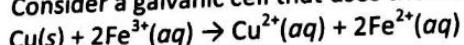
- A graph of  $E$  versus  $\log[(i_L - i)/i]$  is linear if reaction is reversible (Nernstian behavior)

- Slope =  $0.05916/n$  and intercept =  $E_{1/2}$

$E = E_{1/2}$  when  $[Ox] = [Red]$

**Example Problem**  
**Nernst Equation**

Consider a galvanic cell that uses the reaction:



What is the potential of a cell at 25 °C that has the following ion concentrations?

$$[\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M} \quad [\text{Cu}^{2+}] = 0.25 \text{ M} \quad [\text{Fe}^{2+}] = 0.20 \text{ M}$$

What is Q, reaction quotient?

$$Q = \frac{[\text{Cu}^{2+}] \times [\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} = \frac{(0.25) \times (0.20)^2}{(0.00010)^2} = 1.00 \times 10^6$$

Notice that solid copper is omitted.

Cell is not under standard conditions, so the Nernst Equation must be used:

$$E = E^\circ_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (\text{What should it be under standard conditions})$$

$$E^\circ_{\text{cell}} = 0.77 \text{ V} - 0.34 \text{ V} = 0.43 \text{ V}$$

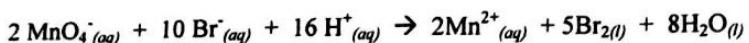
Total of 2 electrons transferred, n = 2

$$E = 0.43 \text{ V} - \frac{0.0592 \text{ V}}{2} \log(1.00 \times 10^6) = 0.43 \text{ V} - 0.0296 \text{ V} \times 6 = 0.25 \text{ V}$$

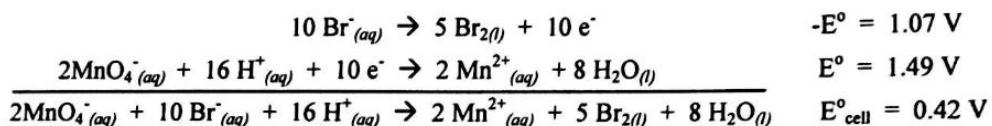
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**Problem Set 32: Nernst equation - SOLUTIONS**

- 1) Calculate the cell potential for a cell operating with the following reaction at 25°C, in which  $[MnO_4^-] = 0.010 \text{ M}$ ,  $[Br^-] = 0.010 \text{ M}$ ,  $[Mn^{2+}] = 0.15 \text{ M}$  and  $[H^+] = 1.0 \text{ M}$ .



The half cell reactions, the corresponding to half-cell potentials, and their sums are displayed below:



Note that  $n = 10$  in this reaction. Using the above concentrations, the reaction quotient becomes:

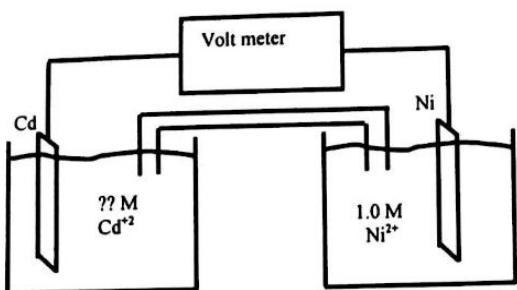
$$Q = \frac{[Mn^{2+}]^2}{[MnO_4^-]^2 [Br^-]^{10} [H^+]^{16}} = \frac{(0.15)^2}{(0.010)^2 (0.010)^{10} (1.0)^{16}} = 2.25 \times 10^{22}$$

$E^\circ_{\text{cell}} = 0.42 \text{ V}$ , substituting this into the Nernst equation yields:

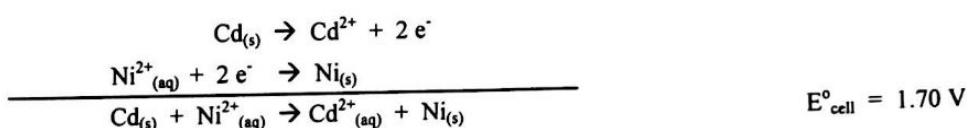
$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q = 0.42 - \frac{0.0592}{10} \log(2.25 \times 10^{22}) \\ &= 0.42 - (0.1323) = 0.2876 = 0.29 \text{ V} \end{aligned}$$

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- 2) The potential for a voltaic cell shown below is 0.240V at 25°C and the standard cell potential is  $E_{\text{cell}}^{\circ} = 0.170 \text{ V}$ . What is the concentration of the cadmium ion solution?



The half cell reactions, the corresponding to half-cell potentials, and their sums are displayed below:



Note that  $n = 2$  in this reaction. Using the final reaction, the reaction quotient becomes:

$$Q = \frac{[\text{Cd}^{2+}]}{[\text{Ni}^{2+}]} = \frac{[\text{Cd}^{2+}]}{1.0} = [\text{Cd}^{2+}]$$

Here, the value for  $Q$  is equal to the concentration of  $[\text{Cd}^{2+}]$ , we can solve the Nernst equation for  $Q$  to determine this concentration. Using the values,  $E_{\text{cell}}^{\circ} = 0.170$  and  $E_{\text{cell}} = 0.240$ , the Nernst equation becomes:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.092}{n} \log Q$$

$$0.240 \text{ V} = 0.170 - \frac{0.092}{2} \log Q$$

Rearrange and solve for  $\log Q$

$$\log Q = \frac{2}{0.092} \times (0.240 - 0.170) = -2.3648$$

$$Q = [\text{Cd}^{2+}] = \text{antilog}(-2.3648) = 4.31 \times 10^{-3}$$

$$[\text{Cd}^{2+}] = 0.004$$

## 7.7 Exemplar questions

- How to construct full cell reaction equations is dealt with on the Redox Part 2 page section 6.2.
  - See also Electrolysis calculations and Redox volumetric titration calculations
  - Detailed notes on corrosion of iron and prevention is on the Transition Metal page on iron
- 

### Appendix 1. The Nernst Equation

- The Nernst equation allows the calculation–prediction of what a half-cell potential will be for a different ion concentration (or temperature) from that of the standard conditions i.e. 1.0 mol dm<sup>-3</sup> and 298K.
- The Nernst equation is not needed (as far as I know?) for UK GCE–A2 and IB courses, but it may be needed in coursework projects! You do NOT have to present the thermodynamic derivation of the equation!
  - For a reduction half-cell equilibrium i.e. **oxidised state + electrons  $\rightleftharpoons$  reduced state**, the Nernst equation for the variation of the half-cell potential is
  - **$E = E^\theta + (RT/nF) \ln \{[ox]/[red]\}$** 
    - $E$  = half-cell potential in V which varies with the molar concentrations [mol dm<sup>-3</sup>] of the oxidised and reduced species.
    - $E^\theta$  is the standard half-cell potential e.g. at 298K when the molarities are 1.0 mol dm<sup>-3</sup>.
    - in the case of two aqueous ions like Fe<sup>2+</sup>/Fe<sup>3+</sup>, [red] = [ox] i.e. equal concentrations, so that  $E$  varies with the ratio of the two ion concentrations.
    - $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  (the ideal gas constant).
    - $T$  the absolute temperature in K (Kelvin = °C + 273).
    - $n$  = moles of electrons transferred per mole of reactants.
    - $F = 96500 \text{ C mol}^{-1}$  (the Faraday constant).
    - $\ln$  = natural/Napierian logarithm.
    - **[ox/red]** = molar concentration of the oxidised or reduced species. University students might well be using activity values as well as molarity values, in which case the activity of the metal is considered to be unity, i.e.  $a_{M(s)} = 1.000$  (see next paragraph).
    - **Note the equivalent equations** ( $\lg = \log$  to base 10,  $\log$  or  $\log_{10}$ )
      - $E = E^\theta - (RT/nF) \ln \{[red]/[ox]\}$
      - $E = E^\theta - (2.303RT/nF) \lg \{[red]/[ox]\}$
      - $E = E^\theta + (2.303RT/nF) \lg \{[ox]/[red]\}$
- For a metal–metal half-cell equilibrium:  **$M^{n+}_{(aq)} + ne^- \rightleftharpoons M_{(s)}$** 
  - the Nernst equation is  **$E_{M^{n+}/M} = E^\theta_{M^{n+}/M} + (RT/nF) \ln \{[M^{n+}_{(aq)}]/[M_{(s)}]\}$**

**BUT** the concentration of the metal cannot change so its molarity or 'thermodynamic activity' is considered to be unity, in which case the Nernst equation for the simple metal–metal ion equilibrium is

- (i)  $E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\circ} + (\text{RT}/\text{nF}) \ln [\text{M}^{n+}]_{\text{(aq)}}$
- (using natural logarithm ln, watch on calculator!)
- or (ii)  $E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\circ} + (2.303\text{RT}/\text{nF}) \log_{10} [\text{M}^{n+}]_{\text{(aq)}}$
- (log to base 10, lg, log or  $\log_{10}$ )
- at 298K for ln expression:  $\text{RT}/\text{nF} = (8.314 \times 298)/(n \times 96500) = 0.0257/\text{n}$
- for lg or  $\log_{10}$ :  $\text{RT}/\text{nF} = (2.303 \times 8.314 \times 298)/(n \times 96500) = 0.0591/\text{n}$

Note: (i), (ii)

- **Five examples of calculations using the Nernst equation** are outlined below.

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1. What is the half-cell potential for copper when dipped into a 2.0 mol dm<sup>-3</sup> solution of copper(II) sulphate?

- $\text{Cu}^{2+}_{\text{(aq)}} + 2\text{e}^- \rightleftharpoons \text{Cu}_{\text{(s)}}$  ( $E^{\circ} = +0.342\text{V}$ )
- $E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + (\text{RT}/\text{nF}) \ln [\text{Cu}^{2+}]_{\text{(aq)}}$
- $E = +0.342 + \{(8.314 \times 298)/(2 \times 96500)\} \ln [2.0]$
- $E = +0.342 + 0.01284 \ln(2)$
- $E_{\text{Cu}^{2+}/\text{Cu}} = +0.342 + 0.009 = 0.351\text{ V}$  (3sf, 0.35V 2sf)
- Le Chatelier comment: The increase in Cu<sup>2+</sup> concentration increases the oxidising potential of the half-cell i.e. a more positive half-cell potential acting from left to right in the equilibrium.

2. What is the half-cell potential of zinc dipped into a 0.1 molar zinc sulphate solution?

- $\text{Zn}^{2+}_{\text{(aq)}} + 2\text{e}^- \rightleftharpoons \text{Zn}_{\text{(s)}}$  ( $E^{\circ} = -0.763\text{V}$ )
- $E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + (2.303\text{RT}/\text{nF}) \lg [\text{Zn}^{2+}]_{\text{(aq)}}$
- $E = -0.763 + \{(2.303 \times 8.314 \times 298)/(2 \times 96500)\} \lg [0.1]$
- $E_{\text{Zn}^{2+}/\text{Zn}} = -0.763 + (-0.029) = -0.792\text{ V}$  (3sf, -0.79 V 2sf)
- Le Chatelier comment: The decrease in Zn<sup>2+</sup> concentration increases the reducing potential of the half-cell i.e. a more negative potential half-cell potential acting from right to left in the equilibrium.

3. What is the theoretical half-cell potential of aluminium dipped into a 0.001 molar aluminium sulphate solution?

- $\text{Al}^{3+}_{\text{(aq)}} + 3\text{e}^- \rightleftharpoons \text{Al}_{\text{(s)}}$  ( $E^{\circ} = -1.662\text{V}$ )
- $E_{\text{Al}^{3+}/\text{Al}} = E_{\text{Al}^{3+}/\text{Al}}^{\circ} + (\text{RT}/\text{nF}) \ln [\text{Al}^{3+}]_{\text{(aq)}}$
- $E = -1.662 + \{(8.314 \times 298)/(3 \times 96500)\} \ln [0.001]$
- $E_{\text{Al}^{3+}/\text{Al}} = -1.662 + (-0.059) = -1.721\text{ V}$  (4sf, -1.72V 3sf)
- Le Chatelier comment: The decrease in Al<sup>3+</sup> concentration increases the reducing potential of the half-cell i.e. a more negative potential half-cell potential acting from right to left in the equilibrium.

4. What is the half-cell potential for a solution of iron(II) and iron(III) ions, containing 0.20 mol dm<sup>-3</sup> of Fe<sup>2+</sup> and 0.10 mol dm<sup>-3</sup> of Fe<sup>3+</sup>?

- $\text{Fe}^{3+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}_{(\text{aq})} (E^\theta = +0.771\text{V})$
- $E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E^\theta_{\text{Fe}^{3+}/\text{Fe}^{2+}} + (\text{RT}/n\text{F}) \ln [\text{ox}]/[\text{red}]$
- $E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E^\theta_{\text{Fe}^{3+}/\text{Fe}^{2+}} + (2.303\text{RT}/n\text{F}) \lg [\text{Fe}^{3+}_{(\text{aq})}]/[\text{Fe}^{2+}_{(\text{aq})}]$
- $E = +0.771 + (0.0591/1) \log_{10} (0.1/0.2)$
- $E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.771 + (-0.018) = +0.753 \text{ V}$  (3sf, **0.75V** 2sf)
- Le Chatelier comment: The lower  $\text{Fe}^{3+}$  concentration compared to  $\text{Fe}^{2+}$ , decreases the oxidising potential of the half-cell i.e. a less positive potential half-cell potential acting from left to right in the equilibrium.

5. **Very accurate measurement half-cell electrode potentials can be used to determine the concentration of an ion** (e.g. pH with glass electrode). When a copper strip (+ve pole) is dipped into a copper(II) ion solution, and combined with a saturated KCl-calomel electrode (–ve pole,  $E = 0.244\text{V}$  at 298K), the cell voltage measured 0.088 V at 298K. From the information deduce the concentration of copper(II) ions in the solution.

- (i) You first need to calculate the copper half-cell potential.
- $E_{\text{cell}} = E_{+\text{pole}} - E_{-\text{pole}}$
- $E_{\text{cell}} = E_{\text{Cu}/\text{Cu}^{2+}} - E_{\text{calomel}}$
- $E_{\text{cell}} = 0.088 = E_{\text{Cu}/\text{Cu}^{2+}} - (+0.244) = E_{\text{Cu}/\text{Cu}^{2+}} - 0.244$
- therefore  $E_{\text{Cu}/\text{Cu}^{2+}} = E_{\text{cell}} + 0.244 = 0.088 + 0.244 = +0.332 \text{ V}$
- (ii) You then need to rearrange the Nernst equation to calculate the concentration.
- $E^\theta_{\text{Cu}^{2+}/\text{Cu}} = +0.342\text{V}$ , and from example 1.
- $E_{\text{Cu}^{2+}/\text{Cu}} = E^\theta_{\text{Cu}^{2+}/\text{Cu}} + (\text{RT}/2\text{F}) \ln [\text{Cu}^{2+}_{(\text{aq})}]$
- rearranging (with care!) gives
- $(\text{RT}/2\text{F}) \ln [\text{Cu}^{2+}_{(\text{aq})}] = E_{\text{Cu}^{2+}/\text{Cu}} - E^\theta_{\text{Cu}^{2+}/\text{Cu}}$
- $\ln [\text{Cu}^{2+}_{(\text{aq})}] = (E_{\text{Cu}^{2+}/\text{Cu}} - E^\theta_{\text{Cu}^{2+}/\text{Cu}})/(\text{RT}/2\text{F})$
- $[\text{Cu}^{2+}_{(\text{aq})}] = e^{\{(E_{\text{Cu}^{2+}/\text{Cu}} - E^\theta_{\text{Cu}^{2+}/\text{Cu}})/(\text{RT}/2\text{F})\}}$
- $[\text{Cu}^{2+}_{(\text{aq})}] = e^{\{(0.332 - 0.342)/0.01284\}}$
- $[\text{Cu}^{2+}_{(\text{aq})}] = e^{\{(-0.01)/0.01284\}} = e^{-0.7788} = \underline{\underline{0.459 \text{ mol dm}^{-3}}}$
- NOTE that even a small and expected error in the cell Emf can lead to a large concentration calculation error e.g. if the  $E_{\text{Cu}^{2+}/\text{Cu}}$  of 0.332 is assumed to be absolutely correct, but was actually measured as 0.328 ( $\approx 1.2\%$  measurement error) the calculation would give  $e^{\{(-0.014)/0.01284\}} = e^{-1.0903} = \underline{\underline{0.336 \text{ mol dm}^{-3}}}$  which is only 73% of the 'real' concentration, i.e. a 27% calculation error! Check it out for yourself and note I've used 3sf Emf's in the calculation, so you need a very accurate voltmeter or potentiometer system to have any hope of accurate analytical data.

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## **Appendix 2. Free Energy, cell Emf and equilibrium constant $K_{\text{equilibrium}}$**

- The concentration equilibrium constant  $K_c$ 
  - for a reaction  $aA + bB \rightleftharpoons dD + eE \dots$
  - $K_c = [A]^a [B]^b \dots / [D]^d [E]^e \dots$
- The standard Gibbs free energy change  $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta_{\text{sys}}$
- and  $\Delta G^\theta = -RT \ln(K_c) = -RT \ln([A]^a [B]^b \dots / [D]^d [E]^e \dots)$
- The free energy change for a reversible electrode reaction is  $\Delta G^\theta = -nE^\theta F$
- $n$  is the number of electrons transferred in the theoretical cell reaction and  $F$  is the Faraday constant.
- therefore for a redox equilibria  $\Delta G^\theta = -nE^\theta F = -RT \ln(K_c)$
- so  $nE^\theta F = RT \ln(K_c)$  from which the equilibrium constant  $K_c$  can be calculated.
- **REMEMBER ...**
- **$\Delta G^\theta$  must be negative, and  $E^\theta$  positive, for the theoretical overall redox reaction, for it to be feasible.**

# Nernst Equation Example Problems

Note: all half reactions are written as reductions in this document. Standard cell potentials from Bard and Faulkner, Electrochemical Methods; New York: Wiley, 1980.

Constants

$$T := 298 \cdot K$$

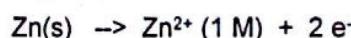
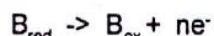
$$R := 8.31441 \cdot \text{joule} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

$$F := 96484.6 \cdot \text{coul} \cdot \text{mole}^{-1}$$

For the electrochemical system:  $Zn | Zn^{2+} (1 M) || Cu^{2+} (1 M) | Cu$

Anode (oxidation occurs at the anode, on the left in the cell notation):

Oxidation Reaction



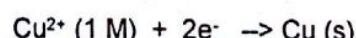
Reduction potential for  $B_{\text{ox}}$

$$E_{Zn} := -0.763 \cdot \text{volt}$$

$$E_{\text{anode}} := E_{Zn}$$

Cathode (reduction occurs at the cathode, on the right in cell notation):

Reduction Reaction

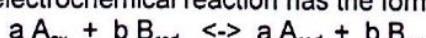


Reduction potential for  $A_{\text{ox}}$

$$E_{Cu} := 0.3402 \cdot \text{volt}$$

$$E_{\text{cathode}} := E_{Cu}$$

Reaction: The overall electrochemical reaction has the form:



$E^{\circ}_{\text{cell}}$  (Calculate the standard cell potential for this system):

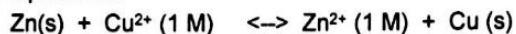
$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 1.1032 \text{ volt}$$

Next, change the concentrations so that the system is not at standard conditions:

$$M := \text{mole-liter}^{-1} \quad C_{Zn} := 1.0 \cdot M \quad C_{Cu} := 0.1 \cdot M$$

Since the electrochemical system is an equilibrium system, changing the concentration of one of the species will shift the equilibrium. The cell potential is a measure of this equilibrium. Recall the balanced overall equation is:



Since the  $\text{Cu}^{2+}$  concentration is less than under standard conditions, the equilibrium will shift to the left. This means that the cell potential will be less positive (keep in mind that the cell potential is greater than 0 for a spontaneous reaction).

Use the Nernst equation to account for this shift in equilibrium. This calculation may be done several ways. I'll show two here:

Calculate the potential for each half reaction under these conditions:

The Anode:  $n := 2$

$$E_{\text{anode}} := E_{Zn} + \frac{R \cdot T}{n \cdot F} \cdot \ln(C_{Zn} \cdot M^{-1})$$

$$E_{\text{anode}} = -0.763 \text{ volt}$$

Notice that the Anode potential is unchanged ( $E_{Zn} = -0.763 \text{ volt}$ ), since the concentration of  $\text{Zn}^{2+}$  is the same as under standard conditions. Notice that the concentration of the solid is not included. Also, the value within the  $\ln$  must be unitless. More detailed treatments use the activity coefficient ( $\alpha$ ).

The Cathode:  $n := 2$

$$E_{\text{cathode}} := E_{Cu} + \frac{R \cdot T}{n \cdot F} \cdot \ln(C_{Cu} \cdot M^{-1})$$

$$E_{\text{cathode}} = 0.31064 \text{ volt} \quad E_{Cu} = 0.3402 \text{ volt}$$

Notice that the Cathode potential has changed ( $E_{Cu} = 0.3402 \text{ volt}$ ), since the concentration of  $\text{Cu}^{2+}$  is different from the standard conditions.

The Cell:

$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 1.07364 \text{ volt}$$

We may also solve the entire equation in one step using a different form of Nernst equation.

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Zn}}}{C_{\text{Cu}}} \right)$$

$$E_{\text{cell}} = 1.07364 \text{ volt}$$

This equation is occasionally rearranged different ways, take a careful look at the following:

Flip values inside the log and change sign to add:

$$E_{\text{cell}} := E_{\text{std\_cell}} + \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Cu}}}{C_{\text{Zn}}} \right) \quad E_{\text{cell}} = 1.07364 \text{ volt}$$

At 25 C, combine R, T, and F; switch from ln to log:

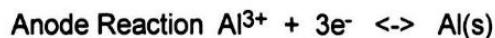
$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{0.05916 \cdot \text{volt}}{n} \cdot \log \left( \frac{C_{\text{Zn}}}{C_{\text{Cu}}} \right) \quad E_{\text{cell}} = 1.07362 \text{ volt}$$

Find the cell potential for the following:



$$E_{\text{Al}} := -1.706 \cdot \text{volt}$$

$$E_{\text{Fe}} := -0.409 \cdot \text{volt}$$



$$E_{\text{anode}} := E_{\text{Al}}$$



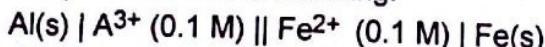
$$E_{\text{cathode}} := E_{\text{Fe}}$$

$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

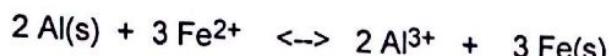
$$E_{\text{std\_cell}} = 1.297 \text{ volt}$$

Comments: Notice that the cathode reaction is more favorable as a reduction (higher reduction potential) and the anode reduction is more favorable as an oxidation (lower reduction potential). The reaction is spontaneous in the direction that is written so  $E$  is positive. Since all species are at their standard states (either solutions with 1M concentration or solids) the potential for this cell is the same as the standard state.

Find the cell potential for the following:



Since the cell is not in its standard state we need to pay attention to the concentrations. This requires using the balanced redox equation and the Nernst equation. The  $n$  used for the Nernst equation is from the number of electrons in the balanced redox reaction:



This redox reaction involves six electrons

The following constants are required:

$$T := 298 \cdot \text{K}$$

$$n := 6$$

$$F := 96484.6 \cdot \frac{\text{coul}}{\text{mole}}$$

$$R := 8.31441 \cdot \text{joule} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

$$C_{\text{Al}} := 0.1$$

Note, actually the activities are needed for the Nernst equation. We will assume that the activity coefficients are 1. In which case the activity is the same as the concentration but is unitless.

$$C_{\text{Fe}} := 0.1$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left[ \frac{(C_{\text{Al}})^2}{(C_{\text{Fe}})^3} \right]$$

$$E_{\text{cell}} = 1.28715 \text{ volt}$$

Notice that the cell potential does change in this example even though the concentrations of both species are the same. This only occurs for systems where different species have different coefficients. This result should make sense based on LeChatlier's principle since this equilibrium is more dependent upon the concentration of  $\text{Fe}^{2+}$ , as a result reducing its concentration has a greater effect and the equilibrium shifts backwards. So the cell potential decreases. The reaction is less spontaneous.

Next find the cell potential for the following:



We can solve this with the same setup used above:

$$C_{\text{Al}} := 0.1$$

$$C_{\text{Fe}} := 0.01$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left[ \frac{(C_{\text{Al}})^2}{(C_{\text{Fe}})^3} \right]$$

$$E_{\text{cell}} = 1.25758 \text{ volt}$$

Notice that reducing the  $\text{Fe}^{2+}$  concentration should shift the reaction backwards. It becomes less spontaneous. So the cell potential is reduced.

Alternatively this problem may be solved for each half reaction and then the half reactions combined. This is the procedure used in your textbook. For comparisons I will show the above problem worked this way.

$$E_{\text{anode}} := E_{\text{Al}} - \frac{R \cdot T}{3 \cdot F} \cdot \ln \left( \frac{1}{0.1} \right)$$

$$E_{\text{cathode}} := E_{\text{Fe}} - \frac{R \cdot T}{2 \cdot F} \cdot \ln \left( \frac{1}{0.01} \right)$$

$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 1.25758 \text{ volt}$$

Note that both of these methods work because of some unique properties of logs. These properties are shown in the rearrangements below:

$$\ln\left(\frac{a}{b}\right) \quad \text{expands to} \quad \ln(a) - \ln(b)$$

$$\ln(a^x) \quad \text{expands to} \quad x \cdot \ln(a)$$

$$\ln\left(\frac{1}{a^x}\right) \quad \text{expands to} \quad -x \cdot \ln(a)$$

As a result the following expressions are equivalent. Take a moment to convince yourself of this:

$$\frac{R \cdot T}{6 \cdot F} \cdot \ln\left[\frac{(C_{Al})^2}{(C_{Fe})^3}\right] \quad \text{expands to} \quad \frac{1}{3} \cdot R \cdot \frac{T}{F} \cdot \ln(C_{Al}) - \frac{1}{2} \cdot R \cdot \frac{T}{F} \cdot \ln(C_{Fe})$$

Or you can take the expressions used for the second solution and combine them since:

$$E_{cell} = E_{cathode} - E_{anode}$$

Where

$$E_{anode} = E_{Al} - \frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{C_{Al}}\right)$$

$$E_{cathode} = E_{Fe} - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{C_{Fe}}\right)$$

Substitutes in as

$$E_{cell} = \left(E_{Fe} - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{Fe}\right)\right) - \left(E_{Al} - \frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{Al}\right)\right)$$

This rearranges in the following steps

$$E_{cell} = (E_{Fe} - E_{Al}) + \left(\frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{Al}\right) - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{Fe}\right)\right)$$

$$\text{Since } E_{\text{std\_cell}} = E_{\text{Fe}} - E_{\text{Al}}$$

$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{3 \cdot F} \cdot \ln \left( \frac{1}{\text{Al}} \right) - \frac{R \cdot T}{2 \cdot F} \cdot \ln \left( \frac{1}{\text{Fe}} \right) \right)$$

The common denominator is 6 for the number of moles. To change this need to change the power inside the log. See above identities to check how this step works.

$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{6 \cdot F} \cdot \ln \left( \frac{1}{\text{Al}^2} \right) - \frac{R \cdot T}{6 \cdot F} \cdot \ln \left( \frac{1}{\text{Fe}^3} \right) \right)$$

rearranges to

$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left[ \frac{R \cdot T}{6 \cdot F} \left( \ln \left( \frac{1}{\text{Al}^2} \right) - \ln \left( \frac{1}{\text{Fe}^3} \right) \right) \right]$$

rearranges to

$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{6 \cdot F} \cdot \ln \left( \frac{\text{Fe}^3}{\text{Al}^2} \right) \right)$$

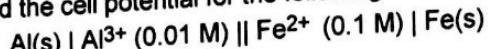
Check the numbers for these expressions:

$$\left( E_{\text{Fe}} - \frac{R \cdot T}{2 \cdot F} \cdot \ln \left( \frac{1}{C_{\text{Fe}}} \right) \right) - \left( E_{\text{Al}} - \frac{R \cdot T}{3 \cdot F} \cdot \ln \left( \frac{1}{C_{\text{Al}}} \right) \right) = 1.25758 \text{ volt}$$

$$(E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{6 \cdot F} \cdot \ln \left( \frac{C_{\text{Fe}}^3}{C_{\text{Al}}^2} \right) \right) = 1.25758 \text{ volt}$$

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Next find the cell potential for the following:



We can solve this with the same setup used above:

$$C_{\text{Al}} := 0.01$$

$$C_{\text{Fe}} := 0.1$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left[ \frac{(C_{\text{Al}})^2}{(C_{\text{Fe}})^3} \right]$$

$$E_{\text{cell}} = 1.30685 \text{ volt}$$

Notice that reducing the  $\text{Al}^{3+}$  concentration should shift the reaction forwards. It becomes more spontaneous. So the cell potential is increased.

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