CHM 101

Redox reactions and **Electrochemistry**

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Redox Reactions (Oxidation – reduction reaction)

- Keep us alive (photosynthesis; muscle operation)
- ❖Recover metals from ores
- ❖Convert petroleum into petrochemicals & pharmaceuticals
- Generate electricity
- ❖Power CD's, portable computers, cell phones

BUT CAN ALSO DESTROY CORROSION

Redox Reactions

Definition in terms of oxygen:

Oxidation = addition of O₂ to a substance (element or compound) e.g. rusting of iron nails due to exposure to oxygen;

4Fe(s) +
$$3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Reduction = Removal of O₂ from a compound e.g. production of iron from iron-ore i.e. reduction of iron ore or iron oxide

$$2Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

Redox Reactions

Definition in terms of hydrogen:

Oxidation = removal of hydrogen from a compound

$$\text{CH}_3\text{CH}_2\text{OH(I)} \rightarrow \text{CH}_3\text{CHO(I)} + \text{H}_2$$

Reduction = addition of H₂ to an element or a compound

$$Cl_2(g) + H_2(g) \rightarrow 2HCl(g)$$

Redox Reactions

- · Definition in terms of oxidation number
- · Consider the reaction:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

• (1)
$$Zn^0 \rightarrow Zn^{2+} + 2e^-$$
 (2) $Cu^{2+} + 2e^- \rightarrow Cu^0$

(2)
$$Cu^{2+} + 2e^{-} \rightarrow Cu^{0}$$

• (1) and (2) are called 'half-reactions'

Redox Reactions

The overall equation can be obtained by adding the two 'half-reactions' together, so that the electrons cancel out on each side:

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

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

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

The overall equation is

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
 (3)

Redox Reactions

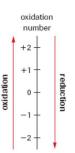
- Oxidation: in half-reaction (1), oxidation number of Zinc increases from 0 to +2, i.e.
 - (a) increase in oxidation number OR
 - (b) Zn atom loses 2 electrons to become zinc ion.
- * This process is termed $\stackrel{\mbox{\scriptsize oxidation}}{\mbox{\scriptsize oxidized}}$ and we say that Zn is oxidized to Zn^2+
- Reduction: in half-reaction (2), oxidation number of copper decreases from +2 to 0 i.e.
 - (a) decrease in oxidation number OR
 - (b) the copper atom gains two electrons from the zinc atom.
- *This process is termed reduction and we say that Cu ion is reduced

Therefore, **oxidation** occurs when electrons are lost, **reduction** occurs when electrons are gained.

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Redox Reactions in terms of O.N.

- · Oxidation is an increase in the oxidation number.
- Reduction is a decrease in the oxidation number.
- An oxidizing agent is a substance which brings
 about the oxidation of another substance. In the
 process, it is itself reduced; Cu salt
- A reducing agent is a specie which brings about the reduction of another substance. In the process, it is itself oxidized; Zn.



Example

 Do example from print out to know half reactions (oxidation/reduction), overall reaction, spectator ions

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Key points: Redox reactions

- Oxidation (electron loss) and reduction (electron gain) must always occur together.
- Electrons given up in the oxidation half-reaction are taken up in the reduction half-reaction (electrons in both half reactions are equal. Therefore, the overall reaction is independent of electrons.
- The overall reaction must be balanced in terms of matter and charge, [law of conservation of mass].

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Oxidation Numbers (O.N.)

- Definition: The oxidation number or oxidation state of an atom is a positive or negative number which is decided using agreed rules.
- We assign a *formal* "+" charge to the H and call it H⁺, and a *formal* "-" charge to Cl and call it Cl⁻.
- *Note that these are not real charges, and UNLIKE those of ions in aqueous solution, can not be measured experimentally
- Now H⁺ has O.N. of +1, and Cl⁻ has an O.N of -1.

H+ CI-

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Rules for Assigning an Oxidation Number (O.N.)

General rule

- 1. For an atom in its elemental form (uncombined) (Na, O2, Cl2, etc.): O.N. = 0
- 2. For a monoatomic ion (e.g. Cu²⁺ / O₂-): O.N. = ion charge (+2,Cu or -1,O
- 3. The sum of O.N. values for all atoms in a compound equals zero. (e.g. $\text{Ca}(\text{OH})_2$) Total O.N here = 0
- The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge on the formular unit in magnitude and sign. (e.g. NO₃⁻ = -1)

Rules for specific atoms or periodic table groups

- 1. For Group IA(1):
- O.N. = +1 in all compounds (e.g. alkali metals; Na+)
- 2. For Group IIA(2):
- O.N. = +2 in all compounds (e.g. Mg²⁺⁾
- For hydrogen:
- O.N. = +1 in combination with non-metals
- 4. For oxygen:
- O.N. = -1 in peroxides and superoxides)
 O.N. = -2 in all other compounds(except with F:
- OF₂, O₂F₂, O.N. = -1/2)
- 5. For Group VIIA(17): O.N. = -1 in combination with metals, nonmetals
 - (except O), and other halogens (\mathbf{IF}_5) lower in the group 12

Rules for Assigning an Oxidation Number (O.N.)

Rules

6. For Group VIA(16): O.N. = -2

7. For Group VA(15): O.N. = -3 when in their binary compounds with metals

NOTE! Rules 1 to 7 are in descending order i.e. 1 supercedes 2 etc.

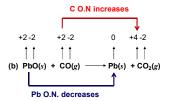
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Exercises

 Do exercises from print out to determine oxidation numbers applying the 7 rules given

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Sample Problem Recognizing Oxidizing and Reducing Agents (Do more from print out)



The O.N. of C increases; it is oxidized; it is the reducing agent.

The O.N. of Pb decreases; it is reduced; it is the oxidizing agent.

WHAT CAN BE SAID ABOUT OXYGEN ATOMS??

Summary: Redox Terminology

$$\mathsf{Zn}(s) + 2\mathsf{H}^+(aq) \longrightarrow \mathsf{Zn}^{2+}(aq) + \mathsf{H}_2(g)$$

OXIDATION

One reactant loses electrons. Zn loses electrons.

oxidized.

Oxidation number increases. The oxidation number of Zn increases from

0 to +2.

REDUCTION

Other reactant gains electrons. Hydrogen ion gains electrons.

Oxidizing agent is reduced. Hydrogen ion is the oxidizing agent and

becomes reduced.

Oxidation number decreases. The oxidation number of H decreases

from +1 to 0.

Balancing Redox Equations

To balance oxidation-reduction reactions in acidic or basic solutions we need to write the chemical equation so that on both sides of equation:

- number of atoms of each element is equal (mass conserved)
 AND
- sum of +ve and -ve charges is equal (charge conserved)

To do this, we'll need to assign oxidation numbers (O.N.) to all atoms.

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Balancing Redox Equations

- 1. Assign oxidation numbers (O.N.) and identify species with O.N. changes
- 2. Write incomplete half-reactions (oxidation and reduction)
- 3. Balance each half-reaction separately:
 - a. Balance atoms undergoing redox (put on hold O & H).
 - b. Balance remaining atoms.
 - i. Add H₂O to balance oxygens.
 - ii. Add H^{+} to balance hydrogens.
- Balance charges by adding electrons to the appropriate side of the equation.
- Multiply each half-reaction so that the same number of electrons are involved in the reduction and the oxidation.
- Add the half-reactions, bring same species together and cancel equal amounts of any species occurring on each side of the equation.
- 7. In basic solutions, add OH- (both side) to neutralize H+.

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Balancing Redox Equations (Acid Solution)

Consider the following redox reaction:

$$^{+7}$$
 MnO $_4^-$ (aq) + Fe $^{2+}$ (aq) \rightarrow Mn $^{2+}$ (aq) + Fe $^{3+}$ (aq)

$$MnO_4$$
-(aq) $\rightarrow Mn^{2+}$ (aq) (red.)

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$
 (ox.)

Note:

To carry out **step 3**, balance (i) missing oxygen atoms with equal amount of H₂O (ii) missing hydrogen atoms with equal amount of H⁺

Balance matter in each half-equation

Balancing Redox Equations (Acid Solution)

Step 3b (i): Add water to balance the oxygens:

$$MnO_4^-$$
 (aq) $\rightarrow Mn^{2+}$ (aq) + $4H_2O(I)$

Now H atoms have been introduced, so they need to be balanced with H⁺ ions on LHS of equation [i.e. **step 3b** (ii)]:

$$\label{eq:MnO4-quantum} \text{MnO}_4\text{-}(\text{aq}) + \quad \textbf{8H}^+(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O(I)} \quad (\text{red.})$$

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$
 (ox.)

Balance charge in each half-equation

Balancing Redox Equations (Acid Solution)

$$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + 4H_2O(I)$$
 (red.)

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}$$
 (ox.)

$$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + 4H_2O(I)$$
 (red.)

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(I) + 5Fe^{3+}(aq)$$

Check: Is this equation balanced i.t.o matter and charge

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In basic solutions

- Add OH⁻ (both side) to neutralize H⁺
- · We do examples from print out together

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Application: Redox Chemistry

There are many industrial and laboratory applications of redox stoichiometry. For example:

- •a mining engineer must know the concentration of iron in a sample of iron ore in order to decide whether or not a mine would be profitable.
- •Chemical technicians in industry, monitoring the quality of their companies' products, must determine the concentration of substances such as sodium hypochlorite (NaClO) in bleach, or hydrogen peroxide (H₂O₂) in disinfectants.

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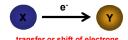
Application: Redox Chemistry

(recall your CHM 191)

- In a titration, one reagent (the titrant) is slowly added to another (the sample) until an abrupt change in a solution property (the endpoint) occurs.
- In acid-base titrations, the titrant is generally a strong acid or base.
- In redox titrations, the titrant is always a strong oxidizing or reducing agent.

Introduction: Electrochemistry

 Electrochemistry is the study of the transfer of electrons from one chemical species to another



- · In everyday life:
 - Car battery, Cell phone battery
 - Refining of metals; manufacturing of chemicals
- Why Cutlery or ornaments made of silver tarnish and become black? 4Ag(s) + O₂(g) → 2Ag₂O(s)
- · Electroplating, galvanizing of metals, etc.

Introduction: Electrochemistry

- Electrochemistry can also be put as the study of how chemical reactions can be used to produce electricity¹ and how electricity can be used to produce chemical reactions²
- i.e. there are two inherently different methods by which an electric current interacts with matter:

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- (1) An electric current can cause a chemical reaction: **Electrolytic Cell**
- (2) A chemical reaction can produce an electric current: **Voltaic/Galvanic cell**

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Metal in the solution of its ions



- When a strip of metal, M is put in a solution of its ions Mn+ then.
- M= electrode-

This is the material, either a metallic rod/bar/strip that allows passage of electrons. There are two types of electrodes (Anode and cathode)

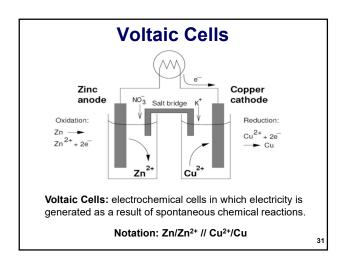
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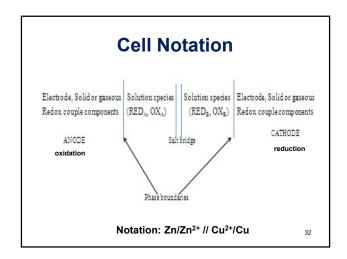
- Anode = It sends electrons into the outer circuit. It has a negative charge and it is shown as (-) in cell diagrams
- Cathode = Electrode at which electrons are received from the outer circuit. It has a positive charge and it is shown as (+) in cell diagrams
- · Current- Flow of electrons through a conductor
- Half-cell- Half of an electrochemical cell, it is actually the combination of the metal, M and the solution containing Mⁿ⁺ (i.e. electrode and solution). One half is for oxidation while the other half is for reduction.
- · The solution is called the electrolyte.

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Interaction between Electrode and

- A metal ion Mⁿ⁺may collide with the electrode and undergo no change
- A metal ion Mⁿ⁺may collide with the electrode and gain 'n' electrons and be converted to metal M. The ion is therefore said to be reduced. Mⁿ⁺(aq)+ ne⁻ → M(s)
- A metal atom may lose 'n' electrons and enter into solution. The metal atom is said to be oxidized.
 M(s) → Mⁿ⁺(aq) + ne⁻
- Overall reaction: M(s) ↔ Mⁿ⁺(aq) + ne⁻





At the anode

- The electrode is made of Zn metal
- The electrolyte is a Zn²⁺ solution (e.g. ZnSO₄)
- Zn metal loses e-s & is oxidized to Zn²⁺(aq)
- Electrode is eroded during the process and loses
 Mass
- •Electrons lost by Zn metal passes to the cathode

At the cathode

- The electrode is made of Cu metal
- The electrolyte is a Cu²⁺ solution
- Cu²⁺ is reduced to Cu metal
- Copper is deposited on the electrode and it gains mass (since electrons are gained by Cu²⁺ to form Cu

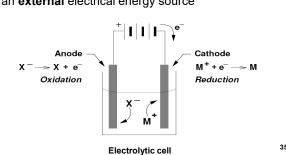
 Salt bridge consists of a tube containing a solution of KNO₃(aq) and plugged at the ends.

- As Zn is oxidized to Zn²⁺, excess cations at the anode is neutralized by NO₃⁻ from the salt bridge.
- As Cu²⁺ is reduced to Cu metal, a negative charge arises at the cathode is neutralized by K⁺ from the salt bridge.

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Electrolytic Cells

 An electrolytic cell is an electrical arrangement for driving a non-spontaneous redox reaction using an external electrical energy source



Comparison of Electrochemical cells

- · There are 2 main types
- · Voltaic (Galvanic) cells:
- ✓ Here, reaction occurs spontaneously
- ✓ The chemical changes during this reaction produce electricity
- ✓ They have a positive voltage
- √ Two electrolytes are employed
- ✓ Assume solutions of equal concentration of 1 M

Comparison of Electrochemical cells

- · Electrolytic cells
- √ Here reactions are non-spontaneous
- ✓ When electricity is applied to this type of cell, a chemical change is produced.

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Standard Electrode Potentials

- The relative oxidizing or reducing strengths of redox couples are expressed in terms of their standard electrode potentials (E⁶)
- To measure the E⁰ of any redox couples, we arbitrarily choose a reference redox couple in an electrochemical cell.
- The reference redox couple used is H⁺(aq)/H₂(g), (standard hydrogen electrode (SHE)) which (under agreed standard conditions) is given a E⁰ value of zero.

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The standard hydrogen electrode (SHE)

- H₂(g) is passed at 1 atm pressure over an inert Platinum metal surface in a solution of H⁺ whose activity is 1 at 25
 °C
- As the H₂(g) is passed, electrons are released to the H⁺ in solution and there is a cycle of reaction (clockwise flow of electrons).
- The SHE is given an E^o value (by convention) of 0.00V.All E^o values are referenced relative to this zero.

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Standard Redox Table Oxidizing agent Reducing agent E_r^r

Oxidizing agent	Reducing agent	E_{red}^0/V
$Li^+(aq) + e^- \rightarrow$	Li(s)	-3.05
$K^+(aq) + e^- \to$	K(s)	-2.93
$Na^+(aq) + e^- o$	Na(s)	-2.71
$Mg^{2+}(aq) + 2e^- o$	Mg(s)	-2.37
$Al^{3+}(aq) + 3e^- \to$	Al(s)	-1.66
$Zn^{2+}(aq) + 2e^- o$	Zn(s)	-0.76
$2\mathbf{H}^{+}(aq) + 2\mathbf{e}^{-} \rightarrow$	$\mathbf{H_2}(g)$	0.00
$Cu^{2+}(aq) + 2e^- \to$	Cu(s)	+0.34
$I_2(s) + 2e^- ightarrow$	$2I^-(aq)$	+0.53
$Br_2(l) + 2e^- o$	$2Br^-(aq)$	+1.07
$Cl_2(g) + 2e^- \to$	$2CI^-(aq)$	+1.36
$F_2(g) + 2e^- o$	$2F^-(aq)$	+2.87
▼		

This table can be found in any Chemistry 1 textbook

Key Points about E^θ

- The standard states for aqueous ions and gases are 1 M concentration and 1 atm pressure, respectively. The tabulated potentials hold only for standard conditions.
- The half-equations are all written as reductions, and the E⁰ apply to the reduction reaction. When the equations are reversed (oxidation), the sign of the E⁰ must change.
- It can be applied in many quantitative determination:
 - Determination of strength of an oxidant or reductant
 - To calculate the standard cell voltage of a cell
 - Spontaneity of redox reactions

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Standard Cell Voltage

- The standard voltage for a cell-reaction (E⁰_{tot}) is the potential difference measured across the cell when all species in solution are at 1 M concentration and all gases are at pressure of 1 atm.
- Procedure to calc. the standard cell voltage of a cell
 - Split the cell reaction into half-reactions
 - Look up E⁰ in a standard table and identify the redn. and oxidation reaction and write against each half reaction
 - $-E_{\text{red}}^{\theta}$ = half cell potential of the reduction reaction
 - $-E^{\theta}_{0x}$ = half-cell potential of the oxidation reaction

Standard Cell Voltage

- Change the reduction equation of the half-cell reaction with lower value of E^θ to an oxidation equation. The sign of the E^θ value will also change
- Balance the number of electrons in the two half equations (NOTE, this does not affect the E⁰ since it is an intensive property)
- Add up the two half equations and do the same to the E⁰
- E^{θ}_{tot} = E^{θ}_{red} + E^{θ}_{ox} , where E^{θ}_{tot} (or E^{θ}_{cell}) is the standard cell voltage

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Standard Cell Voltage: Example

Q. Given the cell reaction, calculate the standard cell potential of the cell:

$$H_2(g)+ 2Ag^+(aq) \rightarrow 2H^+(aq)+ 2Ag(s)$$

A. Half reactions:

From the table

Ag⁺(aq)+ e⁻
$$\rightarrow$$
 Ag(s) +0.80 V
2H⁺(aq)+2e⁻ \rightarrow H₂(g) 0.00 V

Reverse the hydrogen half-reaction: (Note sign changes where applicable)

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- 0.00 \text{ V}$$

Now: $\emph{E}^{\theta}_{tot} = \emph{E}^{\theta}_{red} + \emph{E}^{\theta}_{ox} = (0.80 + 0.00) \text{ V} = +0.80 \text{ V}$

NOTE

- The values of E⁰ are independent of the number of electrons transferred, therefore,
- DO NOT MULTIPLY BY STOICHIOMETRIC COEFFICIENTS!

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Spontaneity of Redox Reactions

Remember: Gibbs Free Energy Change in a cell; $\Delta G = \Delta H - T\Delta S$

ΔG = Gibbs' energy change
ΔH = enthalpy change
T = temperature and
ΔS = entropy change

Note: Maximum useful workdone by a system at constant pressure = ΔG

Workdone by a system is negative For electrochem., Wmax = Welec.

$$\therefore \Delta G^{\theta} = -w_{\text{max}} = -nFE^{\theta}_{\text{tot}}$$

 w_{max} = maximum amount of work reactant can produce

n = number of moles of electrons

F = Faraday's constant (96485 C.mol⁻¹)

Spontaneity of Redox Reactions

$$\Delta G^{\theta} = -w_{\text{max}} = -nFE_{\text{tot}}^{\theta}$$

Deductions:

- A positive E^θ_{tot} means a negative ΔG^θ and a spontaneous forward reaction
- A negative E^{θ}_{tot} means a positive ΔG^{θ} and a non-spontaneous forward reaction
- A zero E⁰_{tot} means the cell is in equilibrium and there is no net reaction in either direction

Example

Work out ΔG^0 for the following reaction:

$$\operatorname{Zn}(s) + \operatorname{Cl}_2(g, 1 \operatorname{atm}) \to \operatorname{ZnCl}_2(aq, 1 M)$$
 2.121 V
$$\operatorname{Zn^{2+}(aq)+ 2e^-} \to \operatorname{Zn(s)} \quad \text{-0.763 V}$$

$$Cl_2(g)+2e^- \rightarrow 2Cl^-(aq) 1.360 V$$

Remember:

$$\Delta G^0 = -nFE_{tot}^0$$

The oxidation state of the Zn changes from 0 to ± 2 , so two electrons were transferred.

$$\begin{array}{rcl} \Delta G^0 & = & -2 \times 96485 \, \mathrm{C} \, \mathrm{mol}^{-1} \times 2.121 \, \mathrm{J} \, \mathrm{C}^{-1} \\ & = & -409.3 \, \mathrm{kJ} \, \mathrm{mol}^{-1} \, \, \mathrm{Note} : 4 \, \mathrm{M} = 4 \, \mathrm{J} \, \mathrm{C} \end{array}$$

Note: 1 V = 1 J C⁻¹
More examples from your print out

Standard cell potential and Equilibrium constant Keq

Recall from Thermodynamics: $\Delta G^0 = -RT \ln K_{eq}$

Also, that
$$\Delta G^0 = -nFE_{\mathrm{tot}}^0$$

Re-arrange to get:
$$E_{\mathrm{cell}}^0 = \frac{RT}{nF} \ln K_{\mathrm{eq}}$$

$$E^0 = \frac{2.303RT}{nF} \log K$$

 $E^0 = \frac{2.303 RT}{nF} \log K$ At standard conditions, T= 25°C/298K, R=8.314 Jmol ^1K ^1, F=96485 C/mol of e-

$$E_{cell}^0 = \frac{0.0592}{n} \log K$$

Example

Q. Given that: $Cu(s) + 2Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$ the cell potential is 0.431 V, calculate K_{eq} at 298 K.

A. Balanced half equations to know no. of electrons

$$\begin{aligned} & 2\mathsf{Fe}^{3+}(aq) + 2\mathsf{e}^{-} \to 2\mathsf{Fe}^{2+}(aq) \\ & \mathsf{Cu}^{2+}(\mathsf{aq}) + 2\mathsf{e}^{-} \to \mathsf{Cu}(\mathsf{s}) \\ & E^0_{\mathsf{cell}} = \frac{RT}{nF} \ln K_{\mathsf{eq}} \\ & \therefore \ln K_{\mathsf{eq}} = E^0_{\mathsf{cell}} \times \frac{nF}{RT} \\ & = 0.431 \,\mathsf{J} \,\mathsf{C}^{-1} \times \frac{2 \times 96485 \,\mathsf{C} \,\mathsf{mol}^{-1}}{8.31 \,\mathsf{J} \,\mathsf{K}^{-1} \,\mathsf{mol}^{-1} \times 298 \,\mathsf{K}} \\ & = 33.6 \, (\mathsf{dimensionless}) \\ & K_{\mathsf{eq}} = e^{33.6} = 4 \times 10^{14} \, (\mathsf{dimensionless}) \end{aligned}$$

The Nernst Equation

The Nernst equation shows relationship between E⁰ and concentration of reactants. Consider a reaction:

$$a A + b B \rightarrow c C + d D$$

$$K = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

From Thermodynamics, $\Delta G = \Delta G^0 + RTInK$

$$\Delta G = \Delta G^0 + 2.303 RT logK$$

$$\Delta G$$
= -nFEcell; ΔG 0= -nFE0cell

-nFEcell = -nFE0cell + RT lnK

Divide through by (-nF)

$$E_{cell} = E_{cell}^0 - \frac{RT \ln K}{nF} or E_{cell}^0 - \frac{2.303RT \log K}{nF}$$

The Nernst Equation

· Inserting K:

$$E_{\mathit{cell}} = E_{\mathit{cell}}^0 - \frac{RT}{nF} \ln \frac{[C]^{\mathit{c}}[D]^{\mathit{d}}}{[A]^{\mathit{s}}[B]^{\mathit{b}}} \mathit{or} E_{\mathit{cell}}^0 - \frac{RT}{nF} \ln \frac{\mathit{oxidized}}{\mathit{reduced}} \mathit{or} E_{\mathit{cell}}^0 - \frac{RT}{nF} \ln M^{\mathit{n}+1}$$

•
$$E_{\text{tot}} = E^{\theta}_{\text{tot}} - \frac{0.0592}{n} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

E_{tot} = potential under non-standard conditions E_{tot}^{θ} = potential under standard conditions

n = the number of moles of electrons, and

[] = concentrations

Example (check print out for more)

Q. Calculate the value of E for the oxidation of iron(II) to iron(III) in a solution of 0.100 M Fe²⁺ and 0.500 M Fe³⁺ according to the following equations:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

A.

$$\begin{split} E_{\text{tot}} &= E^{\theta}_{\text{tot}} - \frac{0.0592}{n} \log \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \\ E_{\text{tot}} &= E^{\theta}_{\text{tot}} - \frac{0.0592}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \\ &= -0.771 - 0.0592 \log \frac{(0.500)}{(0.100)} \\ &= -0.771 - 0.0414 \\ &= -0.812 \text{ V} \end{split}$$

Example of Electrolysis: Ionic Compound

In the reaction:

$$\underbrace{2\text{NaCI(I)}}_{\text{Molten ionic cmpd}} \rightarrow \underbrace{2\text{Na(I)}}_{\text{Molten metal}} + \text{CI}_2(g)$$

Two half-reactions:

$$\begin{array}{ccc} 2\mathsf{Na}^+ + 2\mathsf{e}^- \to & 2\mathsf{Na}(l) & \text{red.: cathode} \\ & 2\mathsf{CI}^- \to & \mathsf{CI}_2(g) + 2\mathsf{e}^- & \text{ox.: anode} \\ \hline \\ 2\mathsf{Na}^+ + 2\mathsf{CI}^- \to & 2\mathsf{Na}(l) + \mathsf{CI}_2(g) & \text{net rxn} \end{array}$$

Electrolysis in Aqueous Solution

At the cathode, possible reactions are:

- $M^{n+}(aq) + ne^- \rightarrow M(s)$ for M = Transition metal
- 2H⁺(aq) + 2e⁻ → H₂(g) in solution of strong acid (HCl)
- 2H₂O + 2e⁻ → H₂(g) + 2OH⁻(aq) (If cation in solution is group 1 or 2 metal or aluminium)

Generally:

The ease of reduction is

$$Ag^+ > Cu^{2+} > H^+ > H_2O > Na^+$$

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Electrolysis in Aqueous Solution

At the anode, possible reactions are:

- $X^{n-}(aq) \rightarrow X + ne^{-}$ if X = Halogen
- 2OH⁻(aq) → 1/2O₂(g) + H₂O(I) + 2e⁻ (in solution of strong base, e.g. = NaOH)
- H₂O → 1/2O₂(g) + 2H⁺(aq) + 2e⁻ for anions which are difficult to oxidize, e.g. F⁻, NO₃⁻, SO₄²⁻

Generally:

The ease of oxidation at the anode is:

$$I^- > Br^- > Cl^- > H_2O > SO_4^{2+}$$

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Application of Electrolysis

- Extraction of metals like: sodium, magnesium, aluminium, etc.
- Industrial-scale manufacturing of chemicals (e.g., chlorine)
- Electroplating, galvanization of metals etc.