CHEMISTRY

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Last class…

❑ Thermodynamics and redox reactions

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In this class…

❑ Thermodynamics and redox reactions, continuation

❑ Problem solving
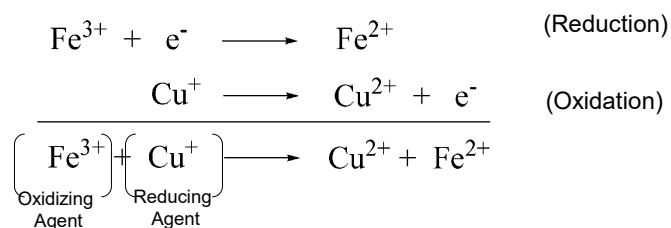
❑ Applications in water electrolysis and corrosion

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Redox reactions

❑ Oxidation–reduction (redox) reaction – a type of chemical reaction that involves a transfer of electrons between two species.

❑ An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron

Reduction-<u>oxidation</u> reaction

❑ A substance is _reduced_ when it _gains_ electrons from another substance

❑ A substance is _oxidized_ when it _loses_ electrons to another substance

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad \text{(Reduction)}$$

$$Cu^+ \longrightarrow Cu^{2+} + e^- \qquad \text{(Oxidation)}$$

$$Fe^{3+} + Cu^+ \longrightarrow Cu^{2+} + Fe^{2+}$$

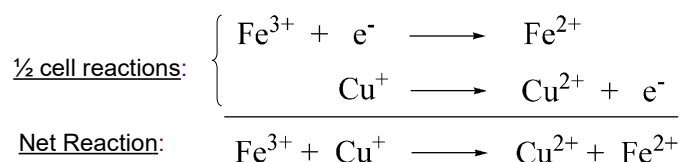Oxidizing Agent   Reducing Agent

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Redox reactions

The first two reactions are known as **"1/2 cell reactions"**
  ➢   Include electrons in their equation
The net reaction is known as the total cell reaction
  ➢   No free electrons in its equation

½ cell reactions:
$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$
$$Cu^+ \longrightarrow Cu^{2+} + e^-$$

Net Reaction:
$$Fe^{3+} + Cu^+ \longrightarrow Cu^{2+} + Fe^{2+}$$

❑   In order for a redox reaction to occur, both reduction of one compound and oxidation of another must take place *simultaneously.* *Total number of electrons is constant*

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Fundamentals of Electrochemistry

Electric Charge (q)
  ➢   Measured in coulombs (C)
  ➢   Charge of a single electron is 1.602×10^{-19}C
  ➢   Faraday constant (F) – 9.649×10^4C is the charge of a mole of electrons (96485 C mol^{-1})

Relation between charge and moles:

$$q = n \bullet F$$

Coulombs   moles $\frac{Coulombs}{mol\ e^-}$

Electric current
    Quantity of charge flowing each second through a circuit
    Ampere: unit of current (C/sec)

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Fundamentals of Electrochemistry

Electric Potential (*E*)
  - Measured in volts (V)
  - Work (energy) needed when moving an electric charge from one point to another
    - Measure of force pushing on electrons

$$\Delta G = -work = -E \bullet q$$

Joules   Volts   Coulombs

Relation between free energy, work and voltage:

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Fundamentals of Electrochemistry

Electric Potential (*E*)
  - Combining definition of electrical charge and potential

$$\Delta G = -work = -E \bullet q \qquad q = n \bullet F$$

Relation between free energy difference and electric potential difference:
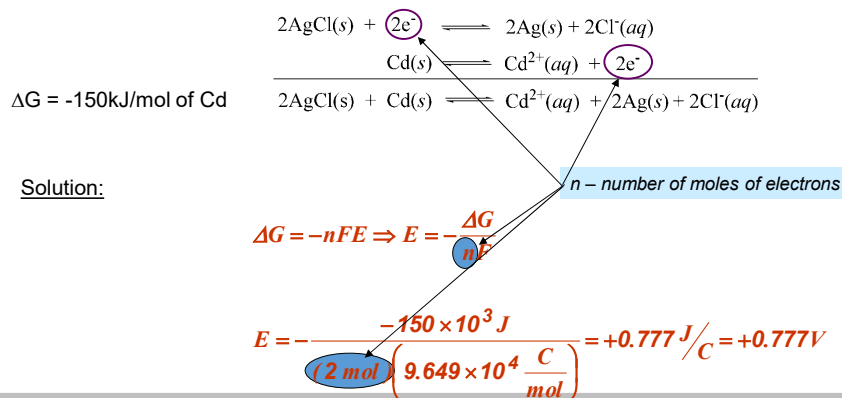
$$\Delta G = -nFE$$

Describes the <u>voltage</u> that can be generated by a chemical reaction

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Fundamentals of Electrochemistry

> **Example**: Calculate the voltage for the following chemical reaction

$$2AgCl(s) + 2e^- \rightleftharpoons 2Ag(s) + 2Cl^-(aq)$$
$$Cd(s) \rightleftharpoons Cd^{2+}(aq) + 2e^-$$

ΔG = -150kJ/mol of Cd

$$2AgCl(s) + Cd(s) \rightleftharpoons Cd^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$$

Solution:

n – number of moles of electrons

$$\Delta G = -nFE \Rightarrow E = -\frac{\Delta G}{nF}$$

$$E = -\frac{-150 \times 10^3 \, J}{(2 \, mol)\left(9.649 \times 10^4 \, \frac{C}{mol}\right)} = +0.777 \, J/C = +0.777V$$

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Fundamentals of Electrochemistry

Cell Potential vs. ΔG

> Reaction is spontaneous if it does not require external energy

Reaction Type	E	ΔG	Cell Type
Spontaneous	+	−	Galvanic
Nonspontaneous	−	+	Electrolytic
Equilibrium	0	0	Dead battery

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Galvanic and Electrolytic Cells
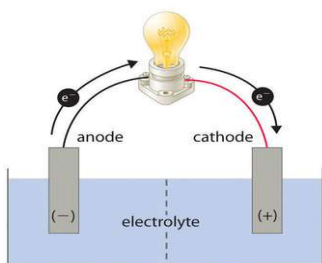
Spontaneous redox reaction
Separate compartment
Different chemical environment

Nonspontaneous redox
Single compartment
Same chemical environment

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Cell notation, Daniel cell
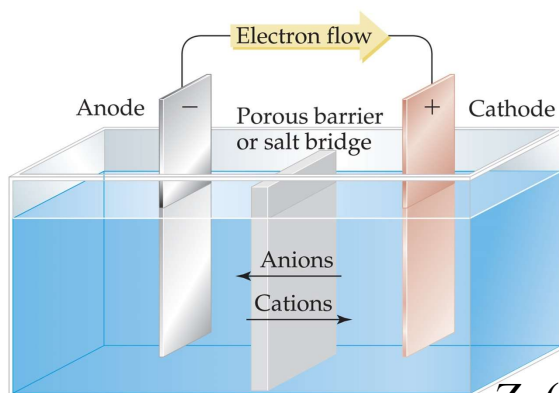
$$Zn(s) = Zn^{2+}(aq) + 2e$$
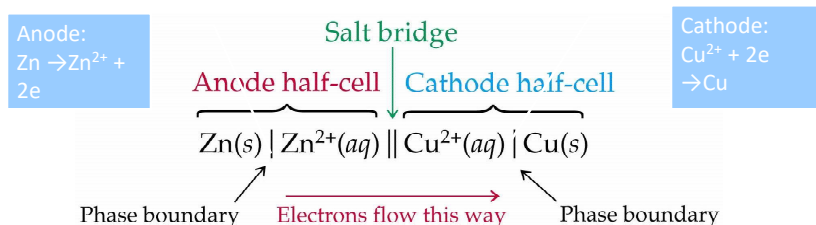
$$Cu^{2+}(aq) + 2e = Cu(s)$$
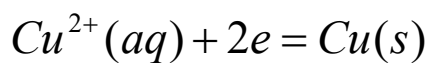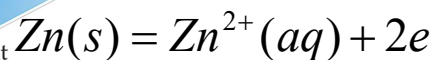
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Cell notation

- ❑ Anode on left, cathode on right
- ❑ Electrons flow from left to right
- ❑ Oxidation on left, reduction on right
- ❑ Single vertical = electrode/electrolyte boundary
- ❑ Double vertical = salt bridge

Anode:
Zn →Zn^{2+} + 2e

Salt bridge

Anode half-cell | Cathode half-cell

Cathode:
Cu^{2+} + 2e →Cu

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

Phase boundary   Electrons flow this way   Phase boundary

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Cell Potential

❑ The cell potential, E$_{cell}$, is the measure of the **potential difference between two half cells** in an electrochemical cell.

❑ The cell potential (E$_{cell}$) is measured in voltage (V), which allows us to give a certain value to the cell potential.

$$E^o_{Cell} = E^o_{Red,Cathode} - E^o_{Red,Anode}$$

$$E^oCell = E^o_{reduction} - E^o_{oxidation}$$

varies with concentration, temperature, metals/ions used.

Standard cell potential : The cell potential under standard state conditions, [ions] = 1 M, T = 25°C, 1 atm gas pressure.

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Standard Electrode Potential, E^0

❑ We can only measure E_{cell} so **how do we get E°$_{red}$ and E°$_{ox}$?**

❑ Although we can only measure differences in potential, a number called the standard reduction potential (E$_{o\ red}$ or simply E$_o$) can be assigned to every half-reaction by assigning **a value of zero to a reference half-reaction.**

❑ The reference half-reaction is: **2H$^+_{(aq)}$ + 2e$^-$ → H$_2$ (g) E$_o$ = 0 V**

❑ **Reductions that occur more easily than this one are given a positive E°$_{red}$.**

❑ **Reductions that occur less easily have a negative E°$_{red}$.**

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Whitten/Davis/Peck, General Chemistry, 6/e
Table 21.2

TABLE 21-2 *Standard Aqueous Reduction Potentials in Aqueous Solution at 25°C*

Element	Reduction Half-Reaction	Standard Reduction Potential E^0, volts	
Li	Li$^+$ + e$^-$ ⟶ Li	−3.045	
K	K$^+$ + e$^-$ ⟶ K	−2.925	
Ca	Ca^{2+} + 2e$^-$ ⟶ Ca	−2.87	
Na	Na$^+$ + e$^-$ ⟶ Na	−2.714	
Mg	Mg^{2+} + 2e$^-$ ⟶ Mg	−2.37	
Al	Al^{3+} + 3e$^-$ ⟶ Al	−1.66	
Zn	Zn^{2+} + 2e$^-$ ⟶ Zn	−0.763	
Cr	Cr^{3+} + 3e$^-$ ⟶ Cr	−0.74	
Fe	Fe^{2+} + 2e$^-$ ⟶ Fe	−0.44	
Cd	Cd^{2+} + 2e$^-$ ⟶ Cd	−0.403	
Ni	Ni^{2+} + 2e$^-$ ⟶ Ni	−0.25	
Sn	Sn^{2+} + 2e$^-$ ⟶ Sn	−0.14	
Pb	Pb^2 + 2e$^-$ ⟶ Pb	−0.126	
H$_2$	2H$^+$ + 2e$^-$ ⟶ H$_2$	0.000	(reference electrode)
Cu	Cu^{2+} + 2e$^-$ ⟶ Cu	+0.337	
I$_2$	I$_2$ + 2e$^-$ ⟶ 2I$^-$	+0.535	
Hg	Hg^{2+} + 2e$^-$ ⟶ Hg	+0.789	
Ag	Ag$^+$ + e$^-$ ⟶ Ag	+0.799	
Br$_2$	Br$_2$ + 2e$^-$ ⟶ 2Br$^-$	+1.08	
Cl$_2$	Cl$_2$ + 2e$^-$ ⟶ 2Cl$^-$	+1.360	
Au	Au^{3+} + 3e$^-$ ⟶ Au	+1.50	
F$_2$	F$_2$ + 2e$^-$ ⟶ 2F$^-$	+2.87	

Increasing strength as oxidizing agent; increasing ease of reduction

Increasing strength as reducing agent; increasing ease of oxidation

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Slide 17

Calculate $\Delta G°$ for the following reaction at 25°C

$$Pb(s) + Ni^{2+}(aq) \rightleftharpoons Pb^{2+}(aq) + Ni(s)$$

$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s),$ $E° = -0.13$ V
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s),$ $E° = -0.25$ V
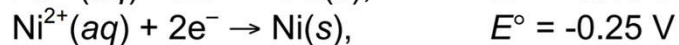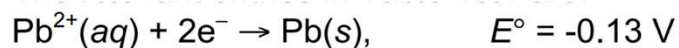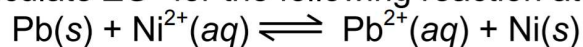
The given reaction runs nickel as a reduction and lead as an oxidation reaction, thus $E°_{cell} = -0.25$ V $+ 0.13$ V $= -0.12$ V. Since $E°_{cell} < 0$ this reaction is not spontaneous and $\Delta G° > 0$.

$$\Delta G° = -n\mathcal{F}E°_{cell} = -(2)(96500)(-0.12) = 23.16 \text{ kJ/mol}$$

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Slide 18

Nernst equation

❑ The Nernst equation enables the determination of cell potential under non-standard conditions.

❑ It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

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Nernst equation

The Nernst Equation is derived from the Gibbs free energy under standard conditions.

$$E^o = E^o_{reduction} - E^o_{oxidation} \qquad (1)$$

ΔG is also related to E under general conditions (standard or not) via

$$\Delta G = -nFE \qquad (2)$$

with
n is the number of electrons transferred in the reaction (from balanced reaction),
F is the Faraday constant (96,500 C/mol), and
E is potential difference.

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Nernst equation

Under standard conditions, Equation 2 is then

$$\Delta G^o = -nFE^o \qquad (3)$$

Hence, when E^o is positive, the reaction is spontaneous and when E^o is negative, the reaction is non-spontaneous. From thermodynamics, the **Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard conditions** via

$$\Delta G = \Delta G^o + RT\ln Q \qquad (4)$$

Substituting $\Delta G = -nFE$ and $\Delta G^o = -nFE^o$ into Equation 4 , we have:

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Nernst equation

$$-nFE = -nFE^o + RT\ln Q \qquad (5)$$

Divide both sides of the Equation above by −nF, we have

$$E = E^o - \frac{RT}{nF}\ln Q \qquad (6)$$

Equation 6 can be rewritten in the form of log10:

$$E = E^o - \frac{2.303RT}{nF}\log_{10} Q \qquad (7)$$

At standard temperature T = 298 K, the 2.303RT/F term equals 0.0592 V and Equation 7 can be rewritten:

$$E = E^o - \frac{0.0592\,V}{n}\log_{10} Q \qquad (8)$$

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Nernst equation

❑ The Equation above indicates that the electrical potential of a cell depends upon the reaction quotient Q of the reaction. As the redox reaction proceeds, reactants are consumed, and thus concentration of reactants decreases. Conversely, the products concentration increases due to the increased in products formation.

❑ As this happens, cell potential gradually decreases until the reaction is at equilibrium, at which $\Delta G=0$. At equilibrium, the reaction quotient $Q=K_{eq}$. Also, at equilibrium, $\Delta G=0$ and $\Delta G=-nFE$, so $E=0$.

❑ Therefore, substituting $Q=K_{eq}$ and $E=0$ into the Nernst Equation, we have:

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Nernst equation

$$0 = E^o - \frac{RT}{nF} \ln K_{eq}$$

At room temperature, Equation 9 simplifies into (notice natural log was converted to log base 10):

$$0 = E^o - \frac{0.0592\,V}{n} \log_{10} K_{eq}$$

This can be rearranged into:

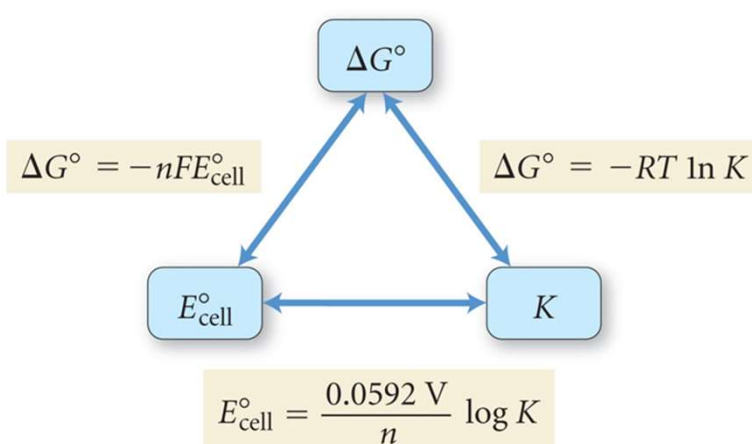$$\log K_{eq} = \frac{nE^o}{0.0592\,V}$$

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Nernst equation

❑ The Equation above indicates that the equilibrium constant K_{eq} is proportional to the standard potential of the reaction. Specifically, when:

❑ K>1,E°>0 , reaction favors products formation.
❑ K<1,E°<0 , reaction favors reactants formation.

❑ This result fits LeChâtlier's Principle, which states that when a system at equilibrium experiences a change, the system will minimize that change by shifting the equilibrium in the opposite direction.

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$$\Delta G^\circ$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -RT \ln K$$

$$E^\circ_{\text{cell}}$$

$$K$$

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

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type of reaction	thermodynamics	electrochemistry	equilibria
spontaneous reaction	ΔG is negative	E is positive	K is > 1
non-spontaneous reaction	ΔG is positive	E is negative	K is < 1

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Key equations

- $E_{\text{cell}}^{\circ} = \dfrac{RT}{nF} \ln K$
- $E_{\text{cell}}^{\circ} = \dfrac{0.0257 \text{ V}}{n} \ln K = \dfrac{0.0592 \text{ V}}{n} \log K \qquad (\text{at } 298.15 \, K)$
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \dfrac{RT}{nF} \ln Q \qquad (\text{Nernst equation})$
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \dfrac{0.0257 \text{ V}}{n} \ln Q = E_{\text{cell}}^{\circ} - \dfrac{0.0592 \text{ V}}{n} \log Q \qquad (\text{at } 298.15 \, K)$
- $\Delta G = -nFE_{\text{cell}}$
- $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$
- $w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$

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Problem - 1

How much work does it take to move over 2.36 x 10^{-3} moles of electrons across a 1.05 V potential?

Work (J) = (1.05V) q

= (1.05V)(2.36 x 10^{-3}moles e-))(9.65 x 10^{4}C/mol)

Work = 239 J

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Problem – 2

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PROBLEM: A voltaic cell houses the reaction between aqueous bromine and zinc metal:

$$Br_2(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + 2Br^-(aq) \qquad E^0_{cell} = 1.83V$$
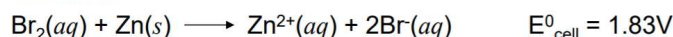
Calculate $E^0_{bromine}$ given E^0_{zinc} = -0.76V

PLAN: The reaction is spontaneous as written since the E^0_{cell} is (+). Zinc is being oxidized and is the anode. Therefore the $E^0_{bromine}$ can be found using $E^0_{cell} = E^0_{cathode} - E^0_{anode}$.

SOLUTION: anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ E = +0.76

E^0_{Zn} as $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ is -0.76V

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$ = 1.83 = $E^0_{bromine}$ - (-0.76)
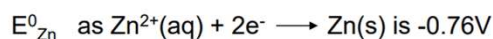
E_0bromine = 1.83 - 0.76 = 1.07V

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Problem - 3

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Calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction.

$$2Ag^+_{(aq)} + Fe(s) \rightleftharpoons 2Ag_{(s)} + Fe^{2+}_{(aq)}$$

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \qquad E^\circ_{Fe^{2+}/Fe} = -0.447 \text{ V}$$

$$2 \times (Ag^+(aq) + e^- \longrightarrow Ag(s)) \quad E^\circ_{Ag^+/Ag} = 0.7996 \text{ V}$$
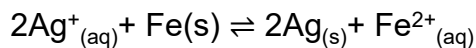
$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = \qquad E^\circ_{Ag^+/Ag} - E^\circ_{Fe^{2+}/Fe} = +1.247 \text{ V}$$

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$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \times 96{,}485 \, \tfrac{\text{C}}{\text{mol}} \times 1.247 \, \tfrac{\text{J}}{\text{C}} = -240.6 \, \tfrac{\text{kJ}}{\text{mol}}$$

$$E^\circ_{\text{cell}} = \tfrac{0.0592 \text{ V}}{n} \log K$$

$$K = 10^{n \times E^\circ_{\text{cell}}/0.0592 \text{ V}}$$

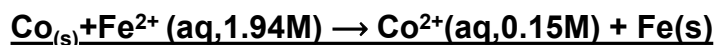$$K = 10^{2 \times 1.247 \text{ V}/0.0592 \text{ V}}$$
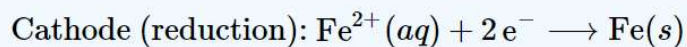
$$K = 10^{42.128}$$

$$K = 1.3 \times 10^{42}$$

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Problem - 4

Consider the following reaction at room temperature:

Co$_{(s)}$+Fe^{2+} (aq,1.94M) $\longrightarrow$ Co^{2+}(aq,0.15M) + Fe(s)
E°$_{\text{Co2+/Co}}$= −0.28V, E°$_{\text{Fe2+/Fe}}$= −0.447V

Is the process spontaneous? What happens at standard condition?

Anode (oxidation): $\text{Co}(s) \longrightarrow \text{Co}^{2+}(aq) + 2\,e^-$

Cathode (reduction): $\text{Fe}^{2+}(aq) + 2\,e^- \longrightarrow \text{Fe}(s)$
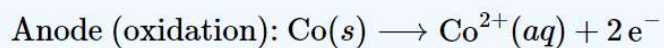
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.447 \text{ V} - (-0.28 \text{ V}) = -0.17 \text{ V}$$

The process is non-spontaneous.

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$$Q = \frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} = \frac{0.15\ M}{1.94\ M} = 0.077$$

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

$$= -0.17\ \text{V} - \frac{0.0592\ \text{V}}{2} \log 0.077$$
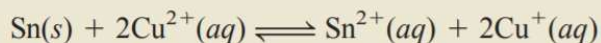
$$= -0.17\ \text{V} + 0.033\ \text{V} = -0.14\ \text{V}$$
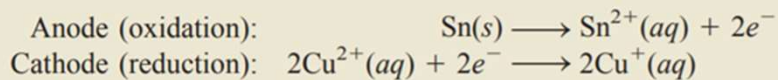
The process is (still) non-spontaneous.

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Problem – 5

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Calculate the equilibrium constant for the following reaction at 25°C:

$$\text{Sn}(s) + 2\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\text{Cu}^{+}(aq)$$

Given, $E^0_{\text{Cu2+/Cu+}} = 0.15\ \text{V}$; $E^0_{\text{Sn2+/Sn}} = -0.14\ \text{V}$

Solution The half-cell reactions are

Anode (oxidation): $\text{Sn}(s) \longrightarrow \text{Sn}^{2+}(aq) + 2e^{-}$
Cathode (reduction): $2\text{Cu}^{2+}(aq) + 2e^{-} \longrightarrow 2\text{Cu}^{+}(aq)$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$
$$= E^{\circ}_{\text{Cu}^{2+}/\text{Cu}^{+}} - E^{\circ}_{\text{Sn}^{2+}/\text{Sn}}$$
$$= 0.15\ \text{V} - (-0.14\ \text{V})$$
$$= 0.29\ \text{V}$$

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$$E^{\circ}_{cell} = \frac{0.0592 \text{ V}}{n} \log K \qquad E^{\circ}_{cell} = \frac{0.0257 \text{ V}}{n} \ln K$$

$$\ln K = \frac{nE^{\circ}}{0.0257 \text{ V}}$$

In the overall reaction we find $n = 2$. Therefore,

$$\ln K = \frac{(2)(0.29 \text{ V})}{0.0257 \text{ V}} = 22.6$$
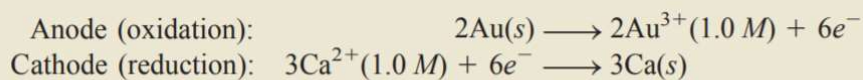$$K = e^{22.6} = 7 \times 10^9$$

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Problem - 6

Calculate the standard free-energy change for the following reaction at 25°C:

$$2Au(s) + 3Ca^{2+}(1.0 \text{ } M) \longrightarrow 2Au^{3+}(1.0 \text{ } M) + 3Ca(s)$$

Predict at equilibrium, reaction favours reactants or products ?

Given, $E^0_{Ca2+/Ca}$ = - 2.87V ; $E^0_{Au3+/Au}$ = 1.5 V

Solution The half-cell reactions are

Anode (oxidation): $\qquad\qquad\qquad 2Au(s) \longrightarrow 2Au^{3+}(1.0 \text{ } M) + 6e^-$
Cathode (reduction): $\quad 3Ca^{2+}(1.0 \text{ } M) + 6e^- \longrightarrow 3Ca(s)$

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$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$
$$= E^{\circ}_{Ca^{2+}/Ca} - E^{\circ}_{Au^{3+}/Au}$$
$$= -2.87\ V - 1.50\ V$$
$$= -4.37\ V$$

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

The overall reaction shows that $n = 6$, so

$$\Delta G^{\circ} = -(6)(96{,}500\ J/V \cdot mol)(-4.37\ V)$$
$$= 2.53 \times 10^{6}\ J/mol$$
$$= 2.53 \times 10^{3}\ kJ/mol$$

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❑ **The large positive value of ΔG_{0} tells us that the reaction favors the reactants at equilibrium.**

❑ **The result is consistent with the fact that E_{0} for the galvanic cell is negative.**
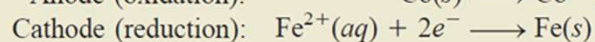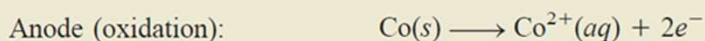
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Problem – 7

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Predict whether the following reaction would proceed spontaneously as written at 298 K:

$$Co(s) + Fe^{2+}(aq) \longrightarrow Co^{2+}(aq) + Fe(s)$$

given that $[Co^{2+}] = 0.15\ M$ and $[Fe^{2+}] = 0.68\ M.$

Solution The half-cell reactions are

Anode (oxidation): $\quad\quad\quad Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Cathode (reduction): $\quad Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$

$$
\begin{aligned}
E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\
&= E^\circ_{Fe^{2+}/Fe} - E^\circ_{Co^{2+}/Co} \\
&= -0.44\ V - (-0.28\ V) \\
&= -0.16\ V
\end{aligned}
$$

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Check your understanding !

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$$
\begin{aligned}
E &= E^\circ - \frac{0.0257\ V}{n} \ln Q \\
&= E^\circ - \frac{0.0257\ V}{n} \ln \frac{[Co^{2+}]}{[Fe^{2+}]} \\
&= -0.16\ V - \frac{0.0257\ V}{2} \ln \frac{0.15}{0.68} \\
&= -0.16\ V + 0.019\ V \\
&= -0.14\ V
\end{aligned}
$$

Because E is negative, the reaction is not spontaneous in the direction written.

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Fundamentals of Electrochemistry

Nernst equation

potential of half-cell reaction   reaction product

$$\Delta E = \Delta E^\circ - \frac{0.059\ V}{n_e} \log_{10}(Q)$$

standard potential of half-cell reaction   number of electrons involved

(at 25°C)

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Fundamentals of Electrochemistry

$$\Delta G^\circ$$

$$\Delta G^\circ = -nFE^\circ_{cell}$$ $$\Delta G^\circ = -RT \ln K$$

$$E^\circ_{cell}$$ $$K$$

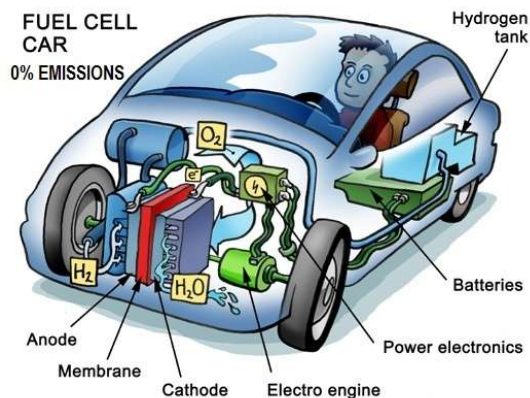$$E^\circ_{cell} = \frac{0.0592\ V}{n} \log K$$

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Water electrolysis, Hydrogen as fuel

There is no free lunch. Splitting water requires **40–50 kiloWatt hours of energy per kilogram of H_2 produced**. That electricity must come from somewhere and has a cost.

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Proton reduction, reference reaction

$$2H^+ + 2e^- \rightarrow H_{2\,(g)}$$

proton reduction

$$\Delta E_{red} = \Delta E^\circ_{red} - \frac{0.059\ V}{n_e} \log_{10} (Q_{red})$$

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Proton reduction

$$n_e = 2 \qquad Q = \frac{P_{H_2}}{a_{H^+}^2 \, a_{e^-}^2}$$

$$E_{H^+} = E^{\circ}_{H^+} - \frac{0.059\,V}{n_e} \log_{10}(Q_{H^+})$$

$$E_{H^+} = E^{\circ}_{H^+} - \frac{0.059\,V}{2} \log_{10}\left(\frac{1}{a_{H^+}^2 \cdot 1}\right)$$

with partial pressure of hydrogen and activity of the electron taken as 1

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Proton reduction

$$pH = \log_{10}\left(\frac{1}{a_{H^+}}\right)$$

$$E_{H^+} = E^{\circ}_{H^+} - 0.059\,V \log_{10}\left(\frac{1}{a_{H^+}}\right)$$

$$E_{H^+} = E^{\circ}_{H^+} - 0.059\,V\ pH.$$

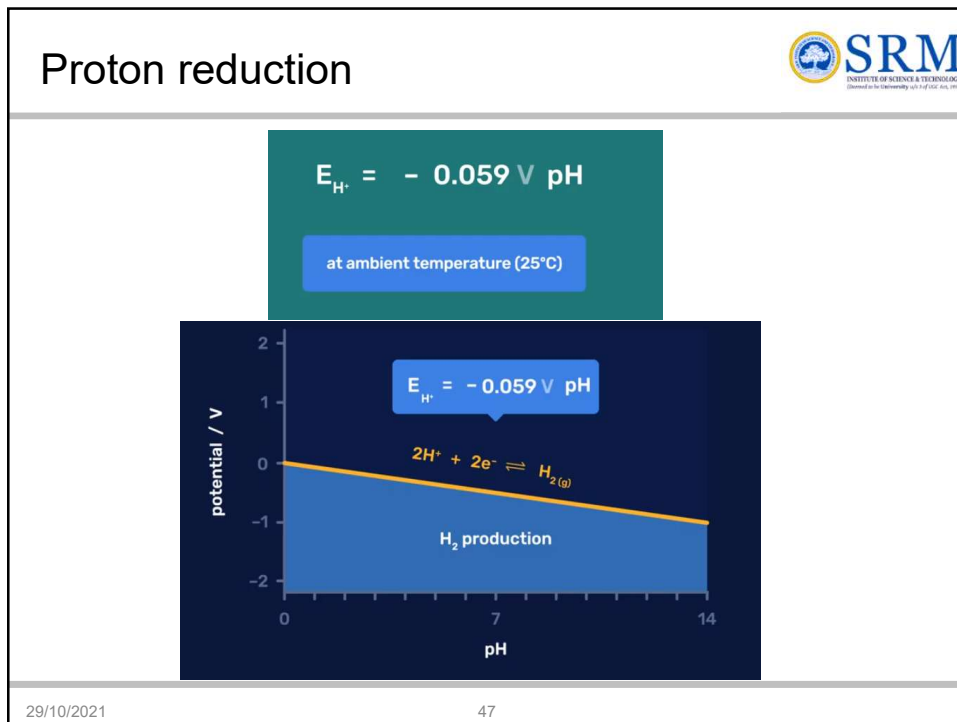$$E^{\circ}_{H^+} = 0\,V \qquad a_{H^+} = 1$$

$$E_{H^+} = E^{\circ}_{H^+} - 0.059\,V\ pH \qquad pH = 0$$

reference for all other half-cell potentials

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Proton reduction

$$E_{H^+} = -0.059 \text{ V pH}$$

at ambient temperature (25°C)

$$E_{H^+} = -0.059 \text{ V pH}$$

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

H₂ production

potential / V

pH

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Other half cell reaction, reduction of oxygen

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightleftharpoons 4OH^-$$

$$E_{O_2} = 1.23 \text{ V} - 0.059 \text{ V pH}$$

at ambient temperature (25°C)

potential / V

pH
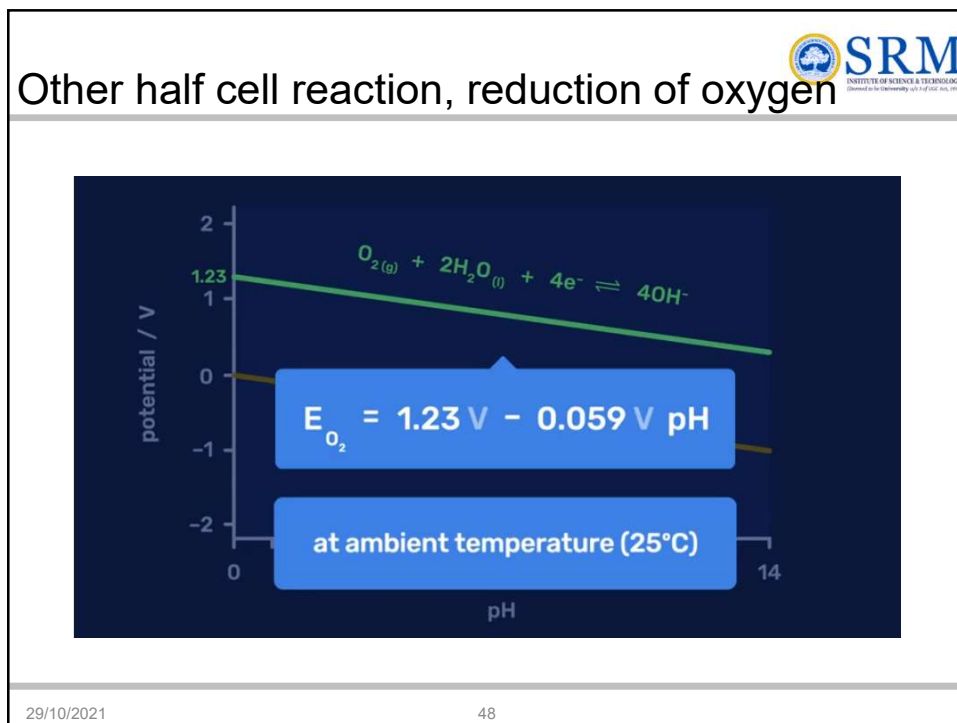
48
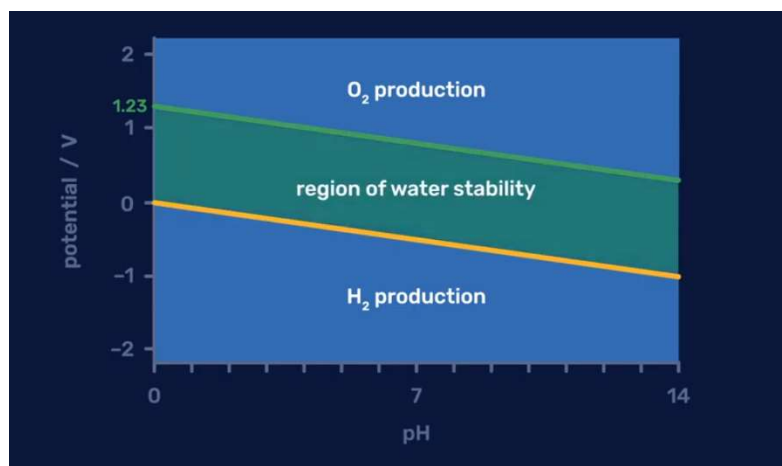
Electrolysis of water

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Electrolysis of water, equations

$$4H^+ + 4e^- \rightleftharpoons 2H_{2(g)}$$

reduction of protons

+

$$4OH^- \rightleftharpoons O_{2(g)} + 2H_2O_{(l)} + 4e^-$$

oxidation of hydroxyls

↓

$$4OH^- + 4H^+ \rightleftharpoons 2H_2O_{(l)} + 2H_{2(g)} + O_{2(g)}$$

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Electrolysis of water

$$E_{O_2} = 1.23\ V - 0.059\ V\ pH$$

$$E_{H^+} = -\ 0.059\ V\ pH$$

$$E_{electrolysis} = -\ 0.059\ V\ pH - (\ 1.23\ V - 0.059\ V\ pH\ )$$
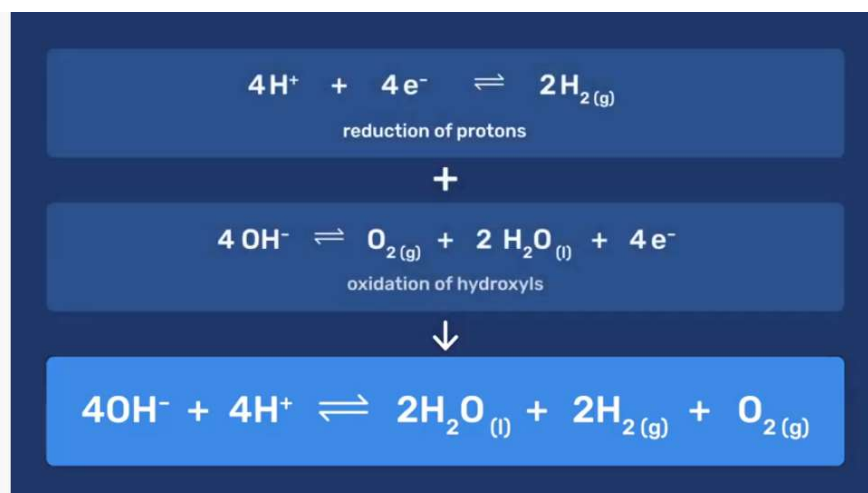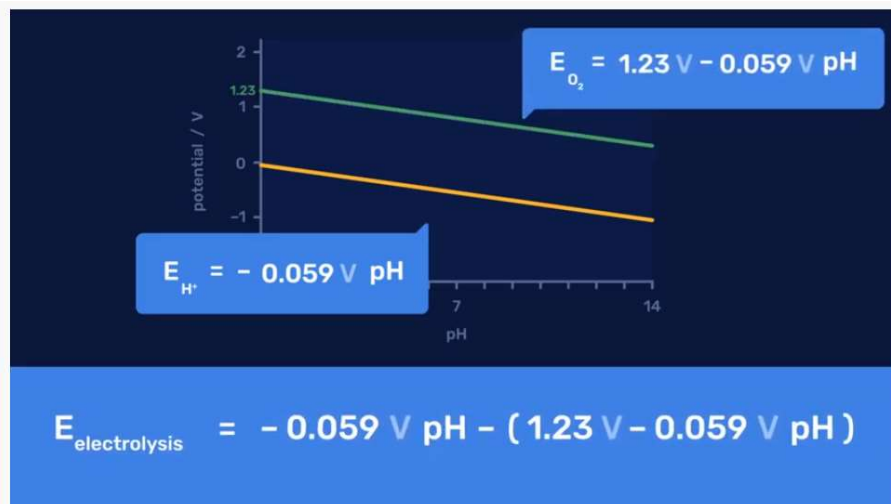
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Electrolysis of water, thermodynamics

≥ 1.23 V must be applied for the reaction to take place

$$E_{electrolysis} = -\ 1.23\ V$$
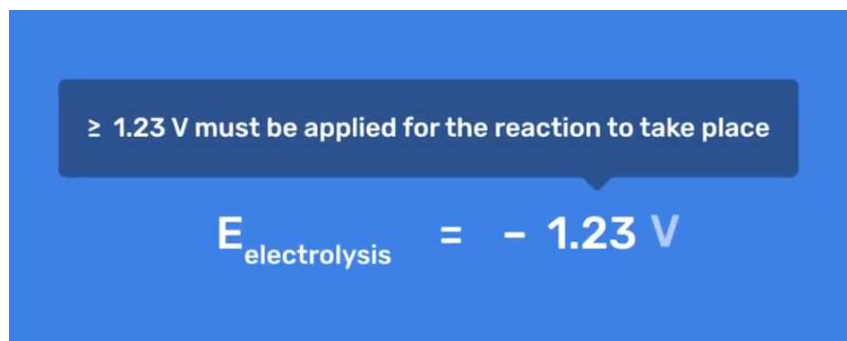
❑ **E is negative, so $\triangle$G will be positive : non-spontaneous !!**

❑ **For two water molecules electrolysed and hence two hydrogen molecules formed, n = 4, and ΔG° = 474.48 kJ /2 mol(water) = 237.24 kJ/mol(water).**

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Corrosion

❑ If we expose iron to **air and/or water** rust forms in a **short/long time duration**, showing the familiar color of reddish brown iron oxide (can be any metal – more details later).

❑ Depending on the environment the rust may develop in minutes.

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Corrosion

❑ **Deterioration** of a material because of reaction with the environment

❑ Corrosion involves the **interaction (reaction) between a metal or alloy and its environment**

❑ Corrosion is affected by the **properties** of both the metal or alloy and the environment. The environmental variables include:

   pH (acidity), temperature & concentration (solution constituents)

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Classification of corrosion
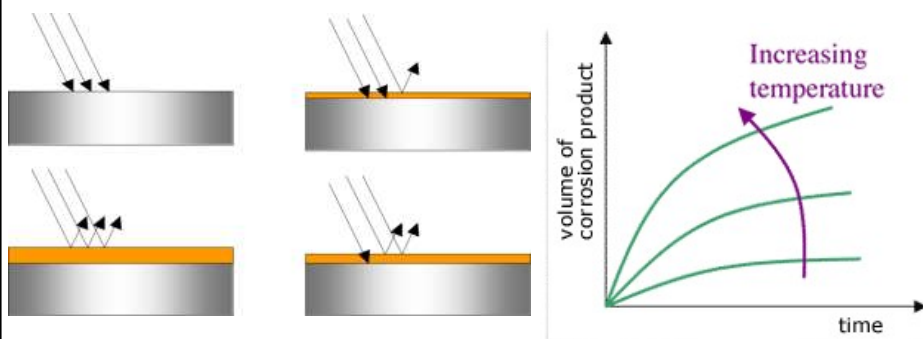
❑ Dry corrosion

❑ Wet corrosion

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Dry corrosion

❑ Dry corrosion occurs when the metals are exposed to gaseous environment

❑ **Dry corrosion** occurs <u>when there is no water or moisture to aid the **corrosion**, and the metal oxidises with the atmosphere alone</u>

❑ The extent of corrosion & protective values depends on the following factors

1. **Chemical affinity** between the environment & the metal
2. **Adhesion** between the film & the metal surface
3. **Nature of film** formed
4. **Protective value** of film

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Dry corrosion

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Dry corrosion

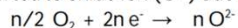## CORROSION BY OXYGEN or OXIDATION CORROSION:

Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized. The reactions of oxidation corrosion are as follows:

Mechanism:
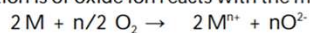1) Oxidation takes place at the surface of the metal forming metal ions M2+

$$M \quad \rightarrow \quad M^{2+} + 2e^-$$

2) Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.

$$n/2\ O_2 + 2n\ e^- \rightarrow \quad n\ O^{2-}$$

3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

$$2\ M + n/2\ O_2 \rightarrow \quad 2\ M^{n+} + n O^{2-}$$

The Nature of the Oxide formed plays an important part in oxidation corrosion process.

$$\text{Metal} + \text{Oxygen} \quad \rightarrow \quad \text{Metal oxide (corrosion product)}$$
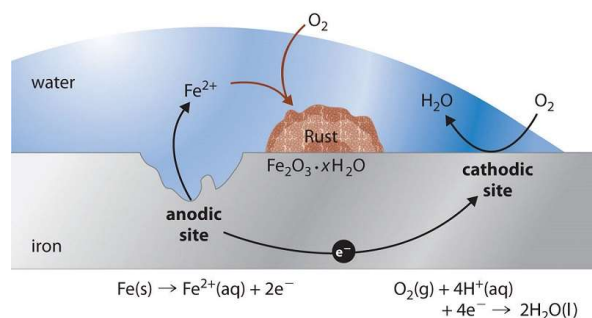
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Wet corrosion

- ❏ Wet corrosion occur when a metal or an alloy comes in contact with **water or an aqueous solution of salt, acid or alkali** by an electrochemical type of reaction.
- ❏ When a metal is immersed in an aqueous electrolyte, it dissolve / dissociate into metal ion + electron.
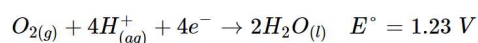- ❏ Forms an electrochemical cell : anode, cathode, electrolyte etc
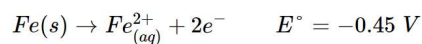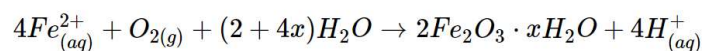

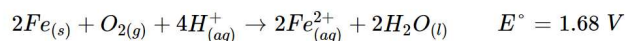18CYB101J-Chemistry   59

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Wet corrosion

- at cathode:

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \quad E^\circ = 1.23\ V$$

- at anode:

$$Fe(s) \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad E^\circ = -0.45\ V$$

- overall:

$$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad E^\circ = 1.68\ V$$

$$4Fe^{2+}_{(aq)} + O_{2(g)} + (2 + 4x)H_2O \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+_{(aq)}$$

- ❏ The sign and magnitude of E° for the corrosion process indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions

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Why iron corrodes faster in water but not gold ?

Standard Electrode Potentials

Metal Reaction	$E_o(V)$
$Au \rightarrow Au^{3+} + 3e^-$	+1.498
$Ag \rightarrow Ag^+ + e^-$	+0.799
$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$	+0.401
$Cu \rightarrow Cu^{2+} + 2e^-$	+0.337
$2H^+ + 2e^- \rightarrow H_2$	0
$Pb \rightarrow Pb^{2+} 2e^-$	-0.126
$Sn \rightarrow Sn^{2+} + 2e^-$	-0.136
$Ni \rightarrow Ni^{2+} + 2e^-$	-0.250
$Fe \rightarrow Fe^{2+} + 2e^-$	-0.440
$Zn \rightarrow Zn^{2+} + 2e^-$	-0.744
$Al \rightarrow Al^{3+} + 3e^-$	-1.662
$Mg \rightarrow Mg^{2+} + 2e^-$	-2.363

❑ If iron is corroding then it has to be the anode. We therefore look at the equation: $Fe \longrightarrow Fe^{2+} + 2e^-$

❑ The water reaction will occur at the cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4(OH)^-$

❑ So we take the cathode potential and subtract the anode potential:

❑ E_oV cathode (water) minus E_oV anode (iron) = +0.401 - (-0.440) = +0.841V, therefore iron corrodes in water.

E_oV cathode (water) minus E_oV anode (gold) = +0.401- (+1.498) = **-1.097V**, therefore gold will not corrode in water.

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Dry vs Wet corrosion

DRY CORROSION	WET CORROSION
• Corrosion occurs in the absence of moisture.	• Corrosion occurs in presence of conducting medium.
• It involves direct attack of chemicals on the metal surface.	• It involves formation of electrochemical cells.
• The process is slow.	• It is a rapid process.
• Corrosion products are produced at the site of corrosion.	• Corrosion occurs at anode but rust is deposited at cathode.
• The process of corrosion is uniform.	• It depends on the size of the anodic part of metal.

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Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.

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