ENGINEERING CHEMISTRY

Department of Science and Humanities

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Corrosion Chemistry

Class content:

- ***Factors affecting rate of corrosion***

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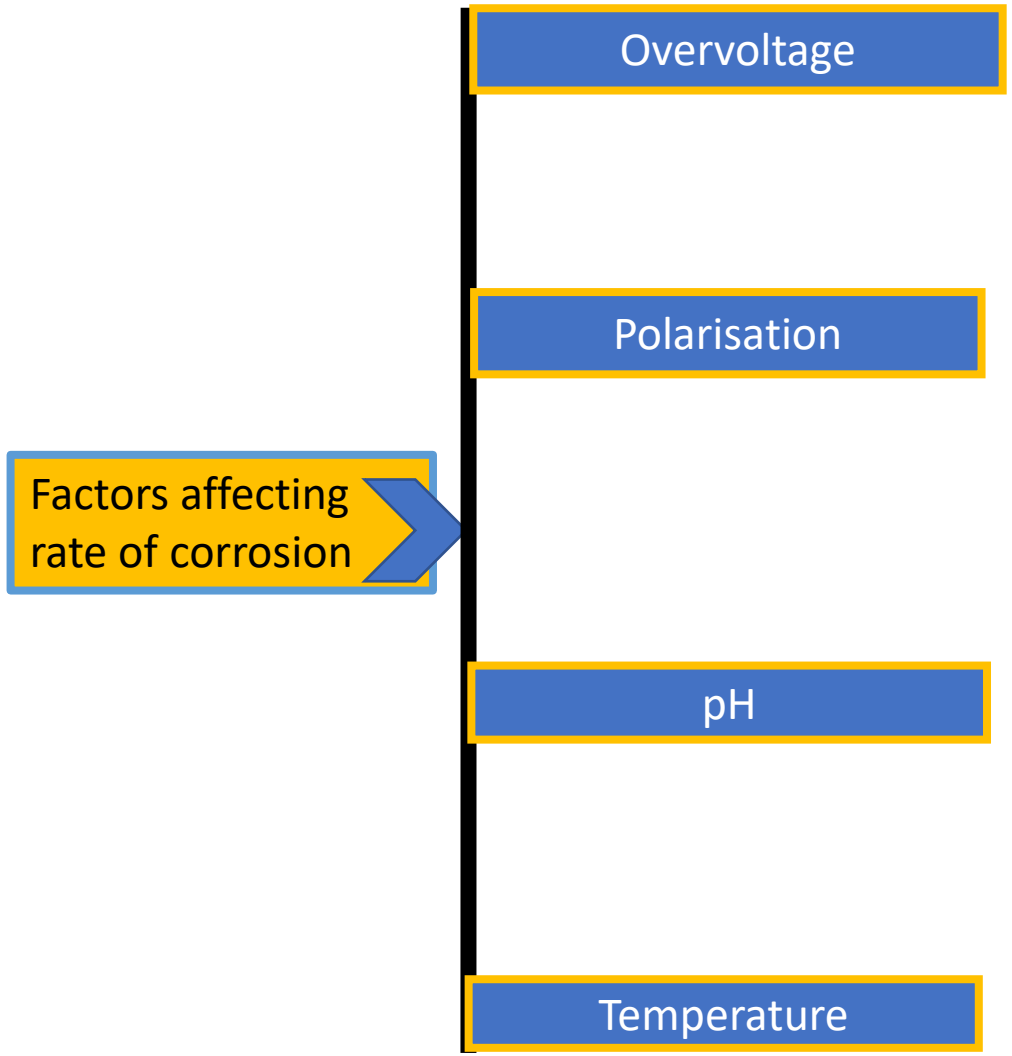

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Hydrogen overvoltage:

Overvoltage is defined as the **extra voltage over the theoretical voltage** required for an electrode reaction to take place

Applicable especially for evolution of **gases**

Depends on the **surface**; if overvoltage of a gas is high on a surface, liberation of the gas on that surface will be less

TABLE 19–3
Overvoltage for Hydrogen and Oxygen Formation at Various Electrodes at 25°C*

Electrode Composition	Overvoltage (V) (Current Density 0.001 A/cm²)		Overvoltage (V) (Current Density 0.01 A/cm²)		Overvoltage (V) (Current Density 1 A/cm²)	
	H_2	O_2	H_2	O_2	H_2	O_2
Smooth Pt	−0.024	−0.721	−0.068	−0.85	−0.676	−1.49
Platinized Pt	−0.015	−0.348	−0.030	−0.521	−0.048	−0.76
Au	−0.241	−0.673	−0.391	−0.963	−0.798	−1.63
Cu	−0.479	−0.422	−0.584	−0.580	−1.269	−0.793
Ni	−0.563	−0.353	−0.747	−0.519	−1.241	−0.853
Hg	−0.9[b]		−1.1[c]		−1.1[d]	
Zn	−0.716		−0.746		−1.229	
Sn	−0.856		−1.077		−1.231	
Pb	−0.52		−1.090		−1.262	
Bi	−0.78		−1.05		−1.23	

* National Academy of Sciences, *International Critical Tables*, Vol. 6, pp. 339–340, McGraw-Hill: New York, 1929.
[b] −0.556 V at 0.000077 A/cm²; −0.929 V at 0.00154 A/cm².
[c] −1.063 V at 0.00769 A/cm².
[d] −1.126 V at 1.153 A/cm².

Source:https://chemistry.mdma.ch/hiveboard/serious/000490034.html

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- A metal with **low hydrogen overvoltage** on its surface is more susceptible to corrosion

- Hydrogen evolution is a **cathodic reaction**

- If cathodic reaction is hydrogen evolution type, **hydrogen gas is liberated easily** and thus the cathodic reaction rate is faster

- This will **make anodic reaction also fast**, thereby promoting overall corrosion reaction

- When the hydrogen overvoltage on the metal surface is **high**, cathodic reaction is slower and the **corrosion of the metal also becomes slower**

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Temperature:

- The **rate of a chemical reaction**, in general, **increases** with rise in temperature

- For **corrosion process** (redox reaction) , the rate of corrosion increases as the temperature increases as
  - Increase in **rate of reaction**
  - Increase in **conductance of the medium**- ions migrate fast at higher temperature.
  - Decrease in the **polarization effects** at the anodic and cathodic sites
  - Increase in **solubility of corrosion product** in the medium
  - **Breakdown in the protective film** that might exist on the surface

- However, if corrosion is **due to dissolved gases** like O_2, CO_2, etc., **the rate of corrosion decreases** with increase in temperature as the **solubility of these gases** in the medium decreases

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pH:

- In general, **lower the pH** of the corrosion medium, **higher** is the corrosion rate

  - At low pH ,**concentration of H^+ ions is high**; H^+ ions help for cathodic reaction facilitating anodic oxidation of the metal

    $2H^+ + 2e^- \rightarrow H_2$

  - Corrosion product becomes **more soluble** in acidic medium

    However some **metals like Al** undergo fast corrosion in highly alkaline solution as their corrosion product is soluble in alkaline medium

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Polarization at anodic and cathodic region:

Polarisation is the **drift in electrode potential** of an electrode

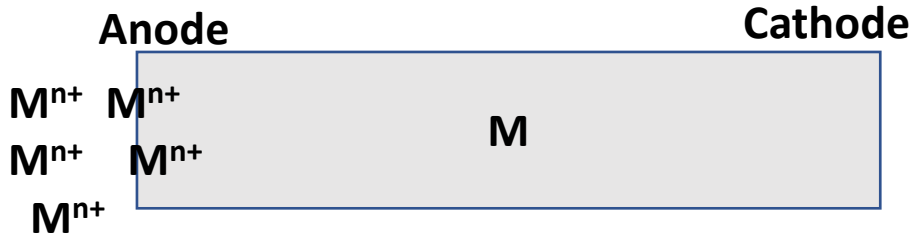
Due to **change in concentration** of species

Anodic polarisation:

At anodic area, metal is oxidized, **liberating metal ions** which move towards cathodic area

Metal ions liberated at anode **cannot move freely** towards cathodic area because of opposing factors like **lower conductivity** of the medium

Metal ions **get concentrated** at anodic area and this decreases tendency of metal to undergo oxidation ; corrosion rate falls



Anodic polarisation is **due to accumulation of ions** in the anodic region

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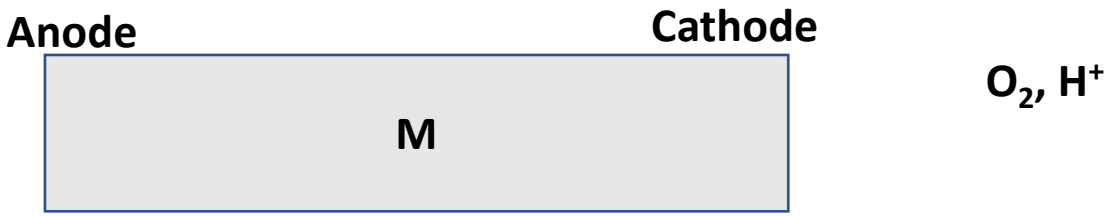
Cathodic polarisation:

•Due to **retarded movement of cathodic reactant** (O_2, H^+) towards the cathodic surface or **retarded removal of products** formed in cathodic region

•Hence, the rate of cathodic reaction decreases. A retarded cathodic reaction results in retardation of anodic reaction also which **slows down the corrosion process**

•Cathodic polarisation is **due to depletion of ions** in the cathodic region



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Polarisation effect can be reduced by :

- Use of depolarisers

  e.g., **Anodic polarisers** – complexing agents
  Cathodic polarisers – cupric ions

- Increase in temperature

- Stirring the solution

THANK YOU

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