

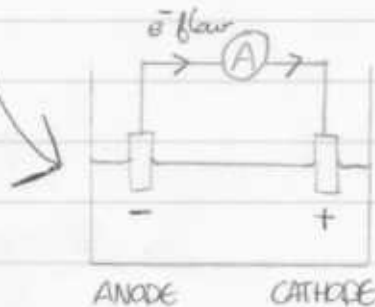
Thermodynamics of Aqueous Corrosion

Electrochemical Corrosion - electrode reactions, requires a conducting solⁿ (usually H₂O)

Chemical Corrosion - in presence of dry gases on non-conducting solⁿ.

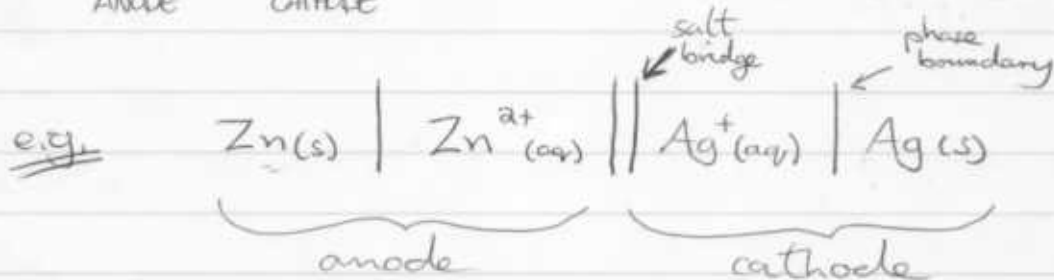
Galvanic Cell - e⁻ flow due to spontaneous chemical reaction within the cell.

Electrolytic Cell - non-spontaneous chemical reaction driven by current source.



Reduction at cathode

Oxidation at anode ← **CORRODES**



Standard Electrode Potentials E^o

- * Gives potential of half-cell under standard conditions relative to the SHE; $2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$
- * Standard conditions are of unit activity. Activity is a dimensionless concⁿ to allow for non-ideal behaviour.

Dilute soln	$a \sim \text{molar conc}^n$
Real soln	$a \approx \gamma M$ (act. coeff x molality [molal/kg])
Gases	$a = \text{partial pressure at 1 bar}$
Pure soln/solid	$a = 1$

Nernst Eqn.

$$E = E^{\circ} - \frac{RT}{nF} \ln \left[\prod a_j^{\nu_j} \right]$$

n = number of e^- involved

a = activities

ν = stoichiometric coeff.

F = Faraday's Constant (96480 C mol^{-1}) = $N_A e$

Electrode potential of a whole cell

* $E_{\text{CELL}} = E_C - E_A$ If $E_{\text{CELL}} > 0$, corrosion occurs ^{em.f.}

* $\Delta G_{\text{REACTION}} = -nF E_{\text{CELL}}$ +ve = net release of Gibbs.

So $E_{\text{CELL}} = E_C^{\circ} - E_A^{\circ} - \frac{RT}{nF} \ln \prod a_j^{\nu_j}$

* Reaction occurs if $\Delta G_{\text{REACTION}} < 0$ i.e. $E_{\text{CELL}} > 0$.

Corrosion and the Electrochemical Series

- * Corrosion needs cathode, anode, electrolyte and electrical connectivity.
- * Cathode/Anode can be on same surface, due to differences in microstructure at the surface or impurities.
- * Electrochemical Series - table of metals in order of E° value.
- * pH and O_2 are important as they determine the cathodic reaction.

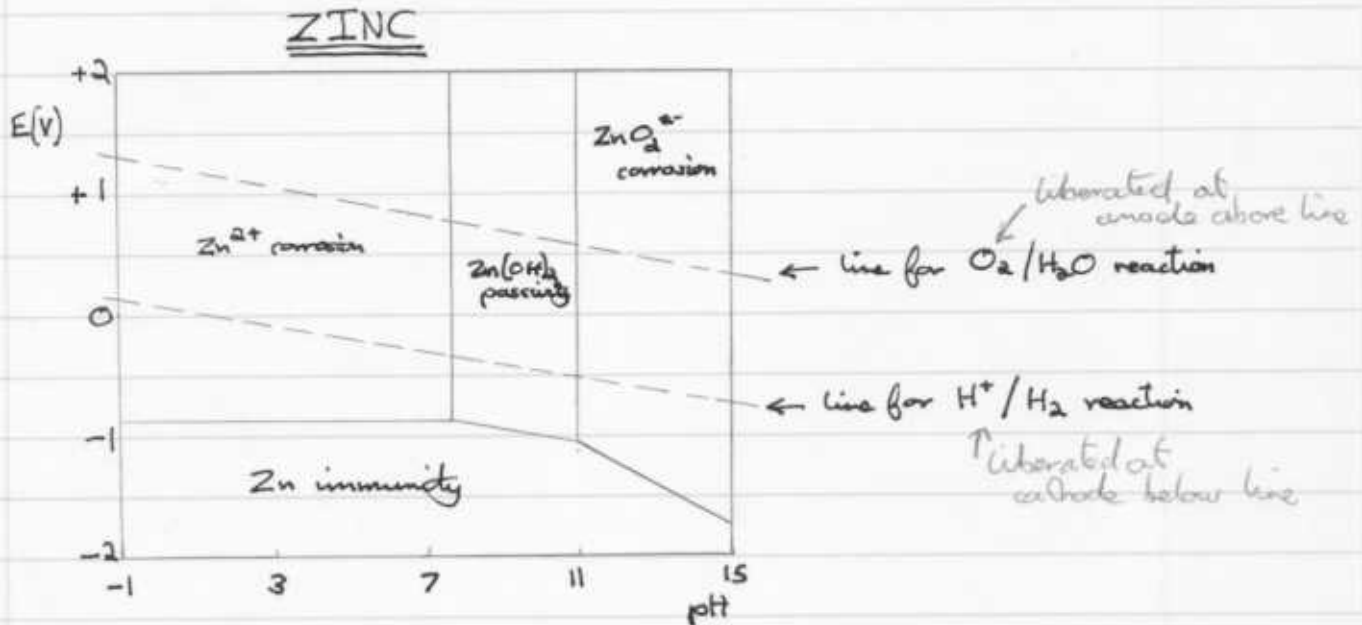
Corrosion and the Galvanic Series.

- * Often the metal may have corroded so a layer of oxide is present at the surface.
- * **PASSIVATION** is a protective oxide layer to prevent corrosion. The oxide/hydroxide layer may flake off, not giving any protection.
- * Cl ions in sea water are good at breaking down oxide layers.
- * Experimentally determined reactivities are a **GALVANIC** series and are only applicable under specified conditions.

Electrochemical	Galvanic
Quantitative	Qualitative
Pure Metals	Metals and Alloys
Standard Conditions	Any Specified Conditions

Potential-pH (Pourbaix) Diagrams;

- These show the conditions where species are thermodynamically stable.
- Corroding Condition \rightarrow conc. ions in soln $> 10^{-6}M$
- Immune Condition \rightarrow conc. ions in soln $< 10^{-6}M$
- Passive Condition \rightarrow corrosion produces a solid which MAY protect from more corrosion.



- These diagrams only apply at conditions specified. Complexes can change the diagram.
- Do not give nature of passivity \rightarrow does it actually stop corrosion?
- Do not tell us about corrosion rate.