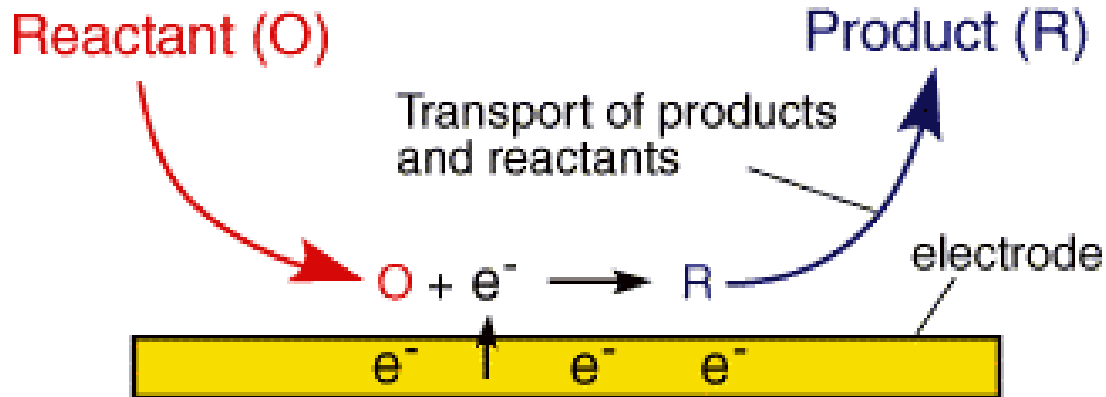


# **Lecture 13: Basics of Voltammetry**

Chemical reactions: control and  
measurement at electrode  
surfaces

# Electrode reactions



## ***A simple surface reaction***

A reactant moves towards an electrode, exchanges an electron and moves away:

As in any reaction, the system can be affected by:

- The reactivity of the reactants (in this case the electrode and the surface).
- The temperature

But in addition, is crucially affected by:

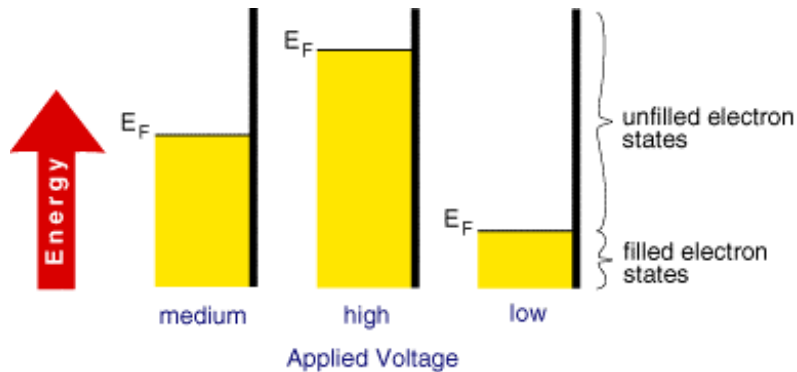
- The applied voltage at the electrode
- The structure of the interfacial region where the electron transfer takes place.
- The nature of the electrode surface

# Basic concepts

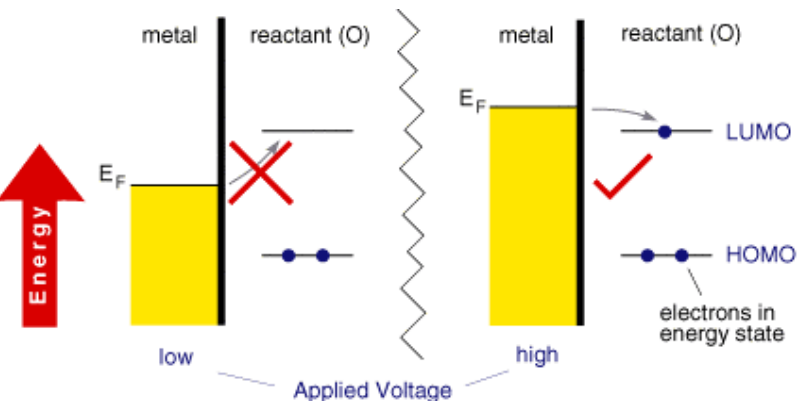
Energy applied to an electrochemical system is a functional of voltage (potential)

$$V = \text{Joule} / \text{Coulomb}$$

Or, to put it another way, voltage is the energy (J) to move charge (c). So 1 V is the energy required to change the energy of an 1 Coulomb of charge by 1 Joule.



This figure illustrates the effect of the applied voltage on the energy of the Fermi level ( $E_F$ ) in the metal.



Since in electrochemistry one can control the applied voltage of an electrode, one can also control the  $E_F$  of the metal – and hence the „reactivity“ of the electrode as the next figure illustrates:

# Factors that effect an electrochemical reaction

An (over) simplistic view of an electrochemical reaction is to use remember what happens in bulk reactions:

$$\begin{aligned} \textit{Thermodynamic possibility} &= \Delta G \\ \text{rate} &= k[\text{O}] \end{aligned}$$

In Electrochemistry one can control both the  $\Delta G$  (by application of a voltage)

$$\Delta G = -nFE$$

So we can approximate and say in an electrochemical reaction:

$$\begin{aligned} \text{rate} &\propto k[\text{A}] \\ i &= -nFAk[\text{O}]_{\text{electrode}} \end{aligned}$$

$k$  is the electron transfer rate constant,  $F$  Faraday's constant,  $A$  electrode area

Clearly:

**Mass transport control [A]**  
**Electrode properties control  $k$**

- Applied Voltage (Potential) changes the **energy** of the electrochemical system.
- The current that flows is a measure of the **reaction rate**

But be careful:

$[O]_{\text{electrode}} \neq [O]_{\text{bulk}}$  (in non-equilibrium situation )

# Thermodynamics of electrochemical reduction

- The standard reduction potential is a measure of how easily a substance can gain an electron. Values are generally listed as being relative to the SHE (standard hydrogen electrode). This is arbitrarily defined as having a potential of 0.00V for the system:
- $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  for 1 mol dm<sup>-3</sup> H<sup>+</sup> at a Pt electrode. 1 atm H<sub>2</sub>, 1M H<sup>+</sup>, 298K
- The standard reduction potential (often referred to as the standard electrode potential) is related to the free energy of the reduction process by:  
$$\Delta G^\circ = -nFE^\circ$$
- So clearly, reduction reactions with a positive E<sup>°</sup> will (if kinetically able) proceed spontaneously, those that have a negative E<sup>°</sup> will not (though of course the reverse situation, an oxidation could then proceed spontaneously).

# Thermodynamics of electrochemical redox reactions

- The slight complication is that reduction (or oxidation) reactions rarely take place in isolation. There is generally an associated oxidation reaction (liberating electrons) or reduction reaction (using up electrons) coupled to the system under study.
- So, if considering whether a reaction will (or won't take place spontaneously), one should consider the total electrode potential difference between the oxidation and reduction reactions, which we can define as  $E_{\text{cell}}$ .
- $E_{\text{cell}}$  is always defined (by convention) as the standard electrode potential of the reduction reaction – the standard electrode potential of the oxidation reaction:
- $$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$
- The terms refer to the standard **reduction** potentials of the system being reduced and the standard **reduction** potential of the system being oxidised.

# Example: Reducing Fe<sup>2+</sup> with Zn

In the manufacture of steel, Fe<sup>2+</sup> is reduced to Fe. The standard reduction potential of this process (this half reaction) is -0.44 V vs. SHE.

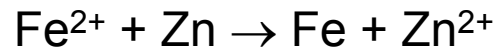
For this reaction to be thermodynamically feasible, the cell potential must be positive.

| <b>Electrode reaction</b>                          | <b>E° vs. SHE</b> |
|--|-------------------|
| 2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub> | 0.00 V            |
| Fe <sup>2+</sup> + 2e <sup>-</sup> → Fe            | -0.44 V           |
| Zn <sup>2+</sup> + 2e <sup>-</sup> → Zn            | -0.76 V           |

So, considering the systems above. Fe<sup>2+</sup> will not be reduced by H<sup>+</sup>, since the E<sub>cell</sub> for this system is -0.44 V, so the free energy of this system is +42 kJ mol<sup>-1</sup>.

Since ΔG is positive, the reaction is not feasible. However, the standard reduction potential of Zn<sup>2+</sup> is negative of the Fe<sup>2+</sup> reduction potential. Therefore E<sub>cell</sub> for this system is +0.32 V, ΔG = -31 kJ mol<sup>-1</sup>.

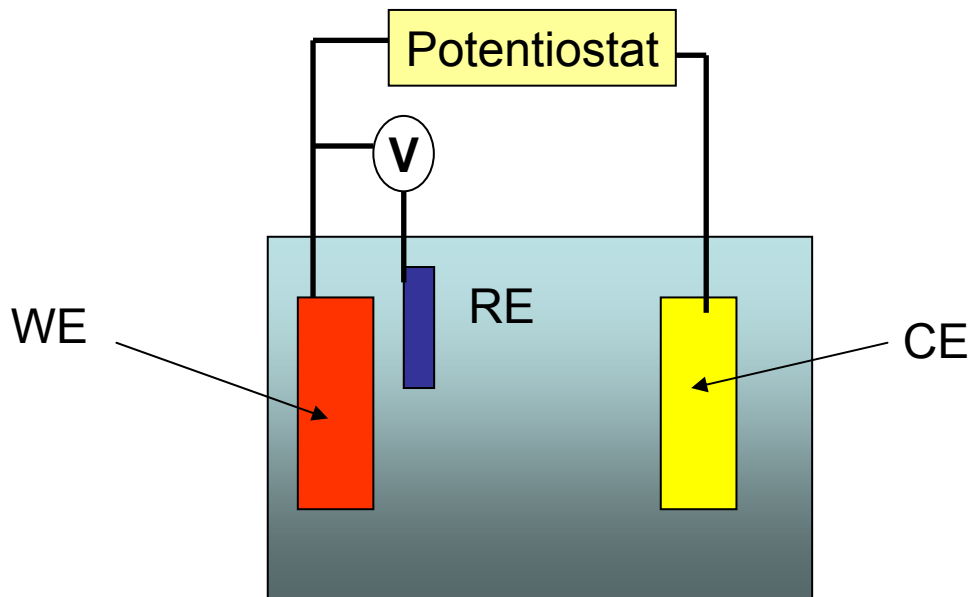
Therefore, zinc can (by thermodynamics) reduce Fe<sup>2+</sup>:



Of course in industry, using zinc is not economic, and coke (oxidised to CO) is used as the reductant.

# Practical aspects – The 3 Electrode Cell

- The electrode where oxidation / reduction takes place (where potential is controlled) is the **Working Electrode**.
- The **Counter electrode** polarises the working electrode.
- The **reference electrode** takes up a stable potential. No current flows through it. The potential of the working electrode is measured relative to it.

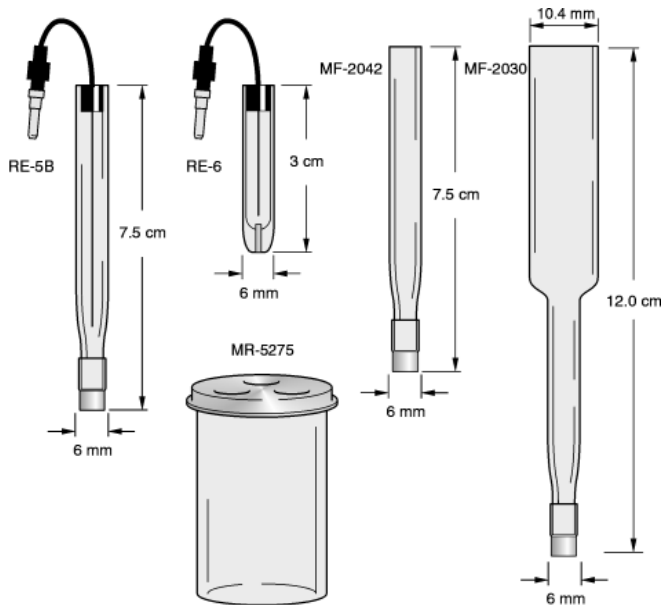


The potentiostat is a feedback amplifier which controls the potential on the working electrode

# Practical aspects: reference electrodes

- Standard electrode potentials are measured vs.  $\text{Pt}/\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$ . This electrode couple is arbitrarily defined as 0.00 Volts. However, practically using this electrode is not at all easy – it requires a steady flow of hydrogen bubbling onto high surface area platinum.
- Much easier is to use an electrode couple that has a clearly defined potential relative to the SHE.
- A commonly employed system is:
$$\text{Ag} / \text{AgCl} = \text{Ag}^+ + \text{Cl}^-$$
- The potential of this system is determined by the concentration of  $\text{Cl}^-$  ions in the solution from the Nernst equation. By measuring relative to this electrode one can simply determine the potential relative to the SHE. This is why in electrochemistry, voltages must always be given relative to a known reference electrode.

# Reference electrodes



## Various types

- Ag / AgCl
- Saturated Calomel
- Mercury / Mercury sulphate

Take up a potential defined by the Nernst equation

$$E = E^o + \frac{RT}{nF} \ln \frac{\prod a_{ox}}{\prod a_{red}}$$

Consider the Ag / AgCl system:



Since only Cl<sup>-</sup> is in solution, other concentrations are unity

$$E = E^o + \frac{RT}{F} \ln \left( \frac{1}{[\text{Cl}^-]} \right)$$