# Electroanalysis

measure the variation of an electrical parameter (potential, current, charge, conductivity) and relate this to a chemical parameter (the analyte concentration)

Selectivity: by choice of operating parameters (potential, current etc…) and/or the electrode material

**applications**

- environmental analyses
- quality control
- biomedical analyses etc

# Fundamentals

## **Redox reactions**

$$Ox_1 \quad + \quad \mathrm{Re}\,d_2 \;\Leftrightarrow\; \mathrm{Re}\,d_1 \quad + \quad Ox_2$$

oxidant reductant

examples:

$$M^{a+} + ne^- \rightarrow M^{(a-n)+} \qquad M^{a+} \rightarrow M^{(a+n)+} + ne^-$$

# Electrochemical Cells

**galvanic**:

spontaneous chemical reactions to produce electrical energy ($\Delta G = -nFE$, negative)

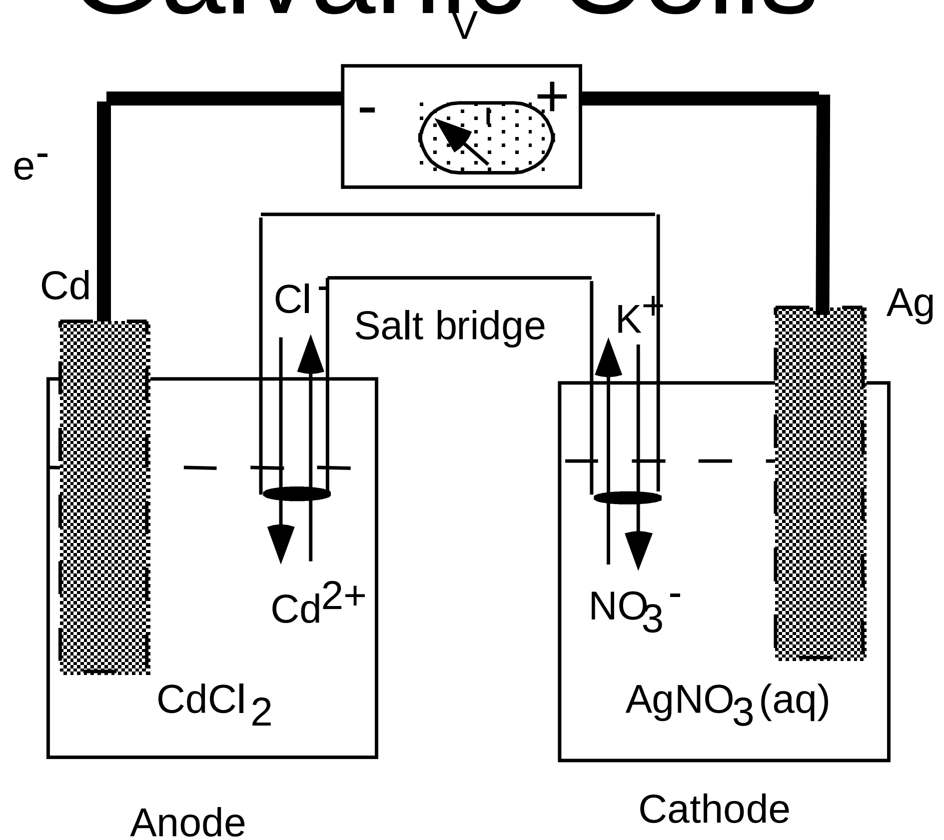
- applications: batteries, potentiometry (pH, ISE)

**electrolytic**:

utilisation of energy (ex: applied V) to force a chemical rxn to take place ($\Delta G$ +)

- applications: coulometry, voltametry

# Galvanic Cells




Cd(s) --> $Cd^{2+}$(aq) +2$e^-$ 2$Ag^+$(aq) + 2$e^-$ -->2Ag(s)

**line notation (shorthand)**

| interface between two phases. || salt bridge

Cd(s) | $CdCl_2$(aq, M) || $AgNO_3$(aq, M) | Ag(s)

# Half-Reactions

$$cathode: \ 2Ag^{+}(aq) + 2e^{-} \Leftrightarrow 2Ag(s)$$

$$anode: \quad Cd \ (s) \Leftrightarrow Cd^{2+}(aq) + 2e^{-}$$

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$$\text{net}: \ 2Ag^{+}(aq) + Cd(s) \Leftrightarrow 2Ag(s) + Cd^{2+}(aq)$$

$$E_{cell} = E_{cathode\ (+)} - E_{anode(-)}$$

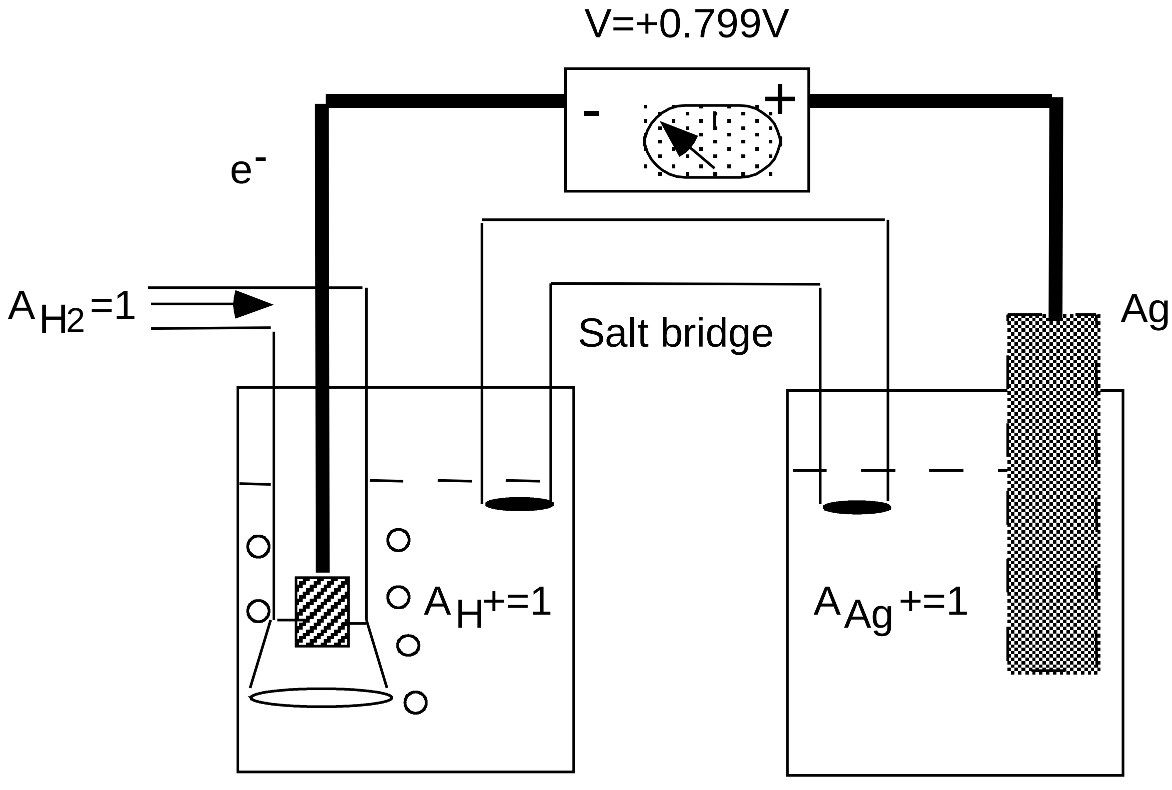
# Standard Potentials

To predict the reactivity of oxidants or reductants we need to measure the potential of each half-reaction.

impossible!!....for every oxidation we have a reduction reaction

- a **standard half-cell** of potential = 0.0 V against which all other half-**cell reduction potentials** are measured (with the std half-cell attached to the **negative terminal** of the potentiometer). Each component in these standard cells having **unit activity**

# Standard Hydrogen Electrode




Pt(s) | $H_2$(g, A=1) | $H^+$(aq, A=1) || $Ag^+$(ag, A=1)

|______________________________|

**NHE**

$H^+$(aq, A=1) + $e^-$ ⇔ 1/2$H_2$(g, A=1)   $E^0$=0 V

# Electrochemical Series

Reduction half-reactions

| oxidant ⇔ reductant | $E^0$ (V) |
| --- | --- |
| **stronger oxidant** | |
| $F_2(g) + 2e^- \Leftrightarrow 2F^-$ | 2.890 |
| $Ce^{4+} + e^- \Leftrightarrow Ce^{3+}$ | 1.720 |
| $Ag^+ + e^- \Leftrightarrow Ag(s)$ | 0.799 |
| $Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$ | 0.771 |
| $O_2 + 2H^+ + 2e^- \Leftrightarrow H_2O_2$ | 0.695 |
| $Cu^{2+} + 2e^- \Leftrightarrow Cu(s)$ | 0.339 |
| $2H^+ + 2e^- \Leftrightarrow H_2(g)$ | 0.000 |
| $Cd^{2+} + 2e^- \Leftrightarrow Cd(s)$ | -0.402 |
| $Zn^{2+} + 2e^- \Leftrightarrow Zn(s)$ | -0.762 |
| $K^+ + e^- \Leftrightarrow K(s)$ | -2.936 |
| $Li^+ + e^- \Leftrightarrow Li(s)$ | -3.040 |
| **stronger reducer** | |

# Nernst Equation

<u>for a half-rxn</u>

a Ox + ne- ⇔ b Red

$$E = E^0 - \frac{RT}{nF}\ln\left(\frac{a_{\mathrm{Re}d^b}}{a_{Ox^a}}\right)$$

R= gas constant

T= temperature in Kelvin

n= number of electrons in half-reaction

F= Faraday constant (96485 A·s/mol)

a = activity (= 1 for a pure solid, liquid or solvent and expressed in mol/L for solutes and in bar for gases)

# Nernst Equation

Converting **ln** to **log10** (x 2,303) and at 25$^0$C (298.15K)

$$E = E^0 - \frac{0.0592}{n}\log(\frac{a_{\mathrm{Re}d^b}}{a_{Ox^a}})$$

# Potentiometry

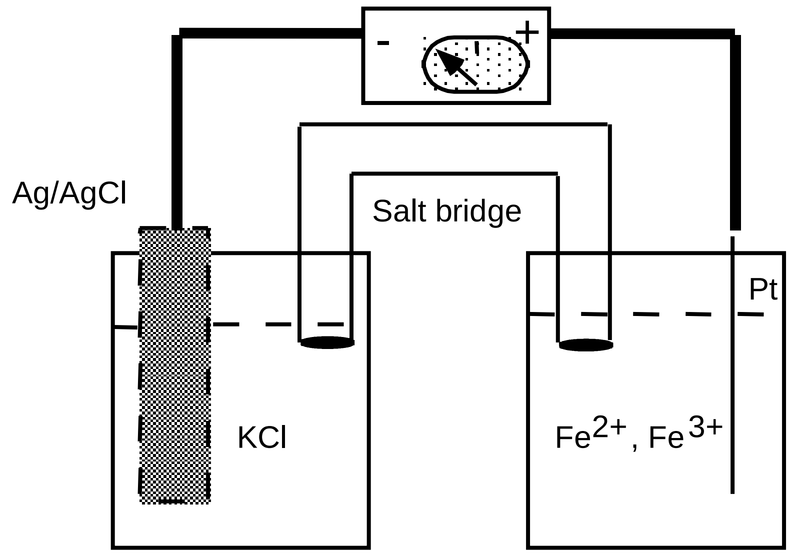
the measure of the cell potential to yield chemical information (conc., activity, charge)

Measure difference in potential between two electrodes:

reference electrode (E constant)

indicator electrode (signal α analyte)

# Reference electrodes



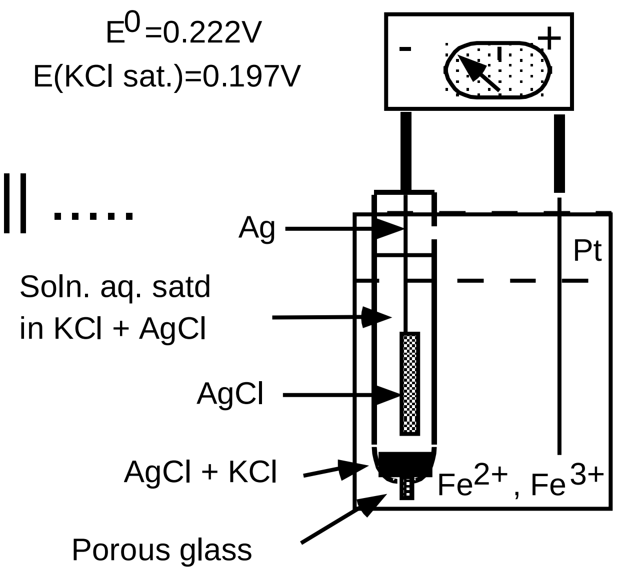

$AgCl(s) + e^- \Leftrightarrow Ag(s) + Cl^-$

$E^0 = 0.222V$

E(KCl sat.)=0.197V

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

$E^0 = 0.771V$



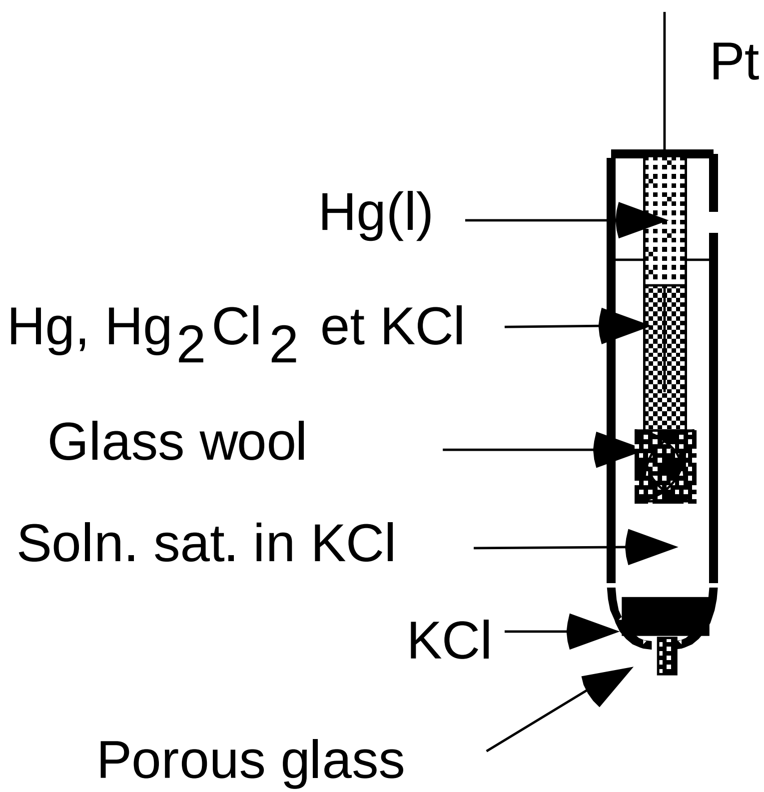

Ag/AgCl:

Ag(s) | AgCl (s) | $Cl^-$(aq) || .....

# Reference Electrodes

SCE:

Pt(s) | Hg(l) | $Hg_2Cl_2$ (l) | KCl(aq., sat.) ||.....




$$Hg_2Cl_2 + 2e^- \Leftrightarrow 2Hg(l) + 2Cl^-$$

$E^0$ =0.268V

E(KCl sat.)=0.241V

# Indicator Electrodes

- Inert:
  Pt, Au, Carbon.    Don't participate in the reaction.

  example:    SCE || $Fe^{3+}$, $Fe^{2+}$(aq) | Pt(s)

- Certain metallic electrodes: detect their ions
  (Hg, Cu, Zn, Cd, Ag)
  example    SCE || $Ag^{+}$(aq) | Ag(s)
  $Ag^{+}$ + e- ⇔ Ag(s)    $E^{0}_{+}$= 0.799V
  $Hg_2Cl_2$ + 2e ⇔ 2Hg(l) + $2Cl^{-}$    $E_{-}$= 0.241V

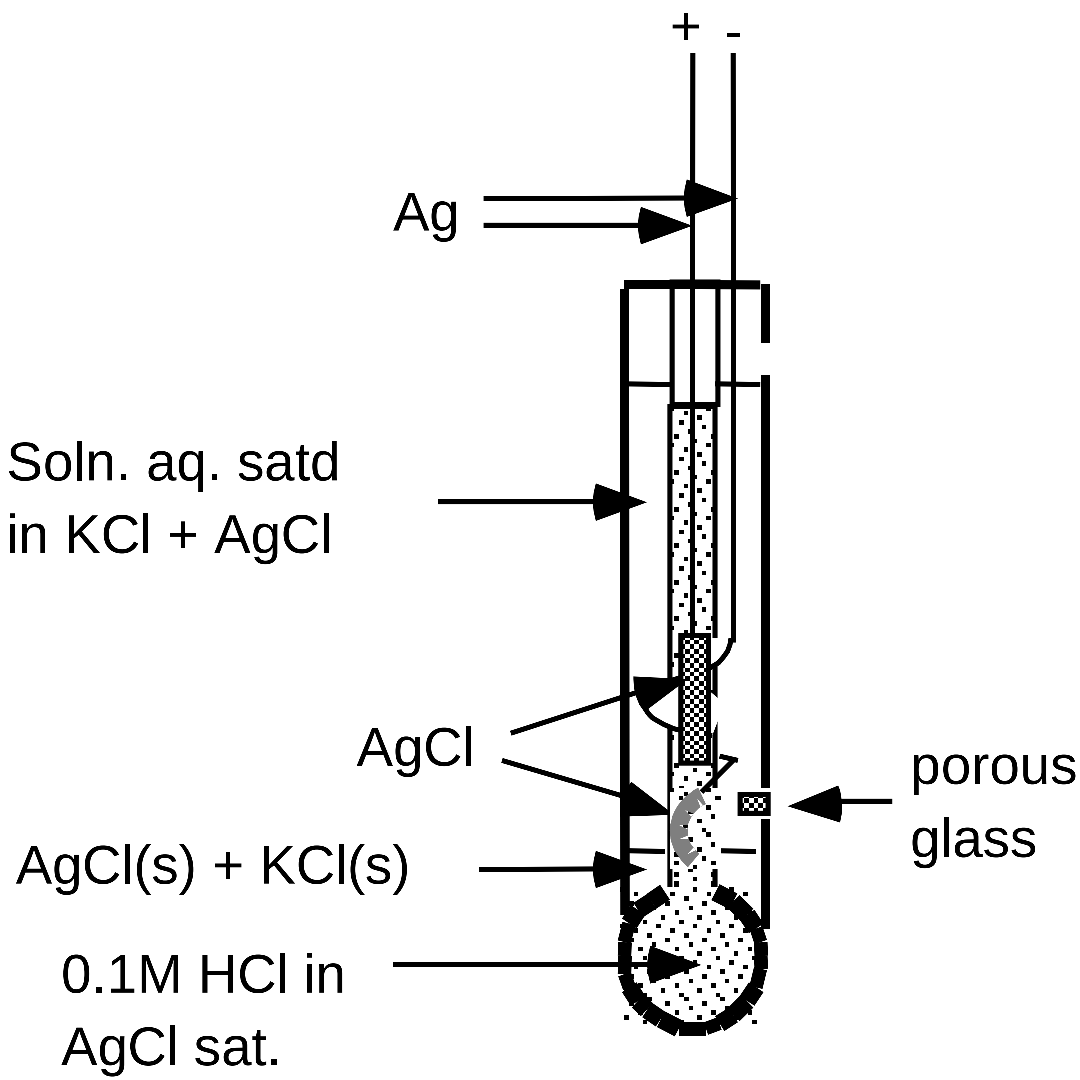
  E = 0.799 + 0.05916 log [Ag+] - 0.241 V

# Ion Selective Electrodes

$$\Delta G = -RT \ln \frac{a_1}{a_2} = -nFE$$

$$\Rightarrow E = \frac{RT}{nF} \ln \frac{a_1}{a_2} = \frac{0.0592}{n} \log \frac{a_1}{a_2} (@\, 25\mathrm{C})$$

# Combination glass pH Electrode



# Other ISEs

- by changing the composition of the glass, ISE selective for different ions can be fabricated
- By replacing the glass with a perm-selective barrier incorporating a selective binding agent (ion-exchanger, host, doped crystal) ISEs for different ions can be fabricated