# Electrochemical methods of analysis

# Definition

**Electroanalytical methods** – are analytical techniques that use measurement of potential, charge or current to determine an analyte's concentration or to characterize an analyte's chemical reactivity

# Equalize equation of this chemical reaction

$$KMnO_4 + K_2SO_3 + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + H_2O$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$SO_3^{2-} + H_2O - 2e^- \rightarrow SO_4^{2-} + 2H^+$$

$$2MnO_4^- + 5SO_3^{2-} + 16H^+ + 5H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 10H^+ + 8H_2O$$

$$2KMnO_4 + 5K_2SO_3 + 3H_2SO_4 \rightarrow 2MnSO_4 + 6K_2SO_4 + 3H_2O$$

# Electric charge

The charge of a single electron is $1.602 \times 10^{-19}$ C (coulombs)

1 Mole of electrons has a charge of $9.649 \times 10^{4}$ C (Faraday constant, F)

$$q = n \cdot F$$

Coulombs — mol $e^-$ — $\frac{\text{Coulombs}}{\text{mol } e^-}$

# Calculation of charge

$$Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}$$

If 5.585 g of $Fe^{3+}$ were reduced in this reaction, how many coulombs must have been transferred from $V^{2+}$ to $Fe^{3+}$?

Lets find the number of moles of $Fe^{3+}$:

$$n = \frac{5.585\ g}{55.845\ \frac{g}{mol}} = 0.1000\ mol$$

Now we can calculate the number of coulombs using F constant:

$$q = 0.1000\ mol\ \times 9.649\ \frac{C}{mol} = 9.649\ \times 10^3\ C$$

# Homework task

How many moles of $Sn^{4+}$ are reduced to $Sn^{2+}$ by 1.00 C of electric charge?

# Electric current

Electric current – flow of electric charge (electrons, protons or ions)

**Current** is the **quantity of charge** flowing each second through a circuit

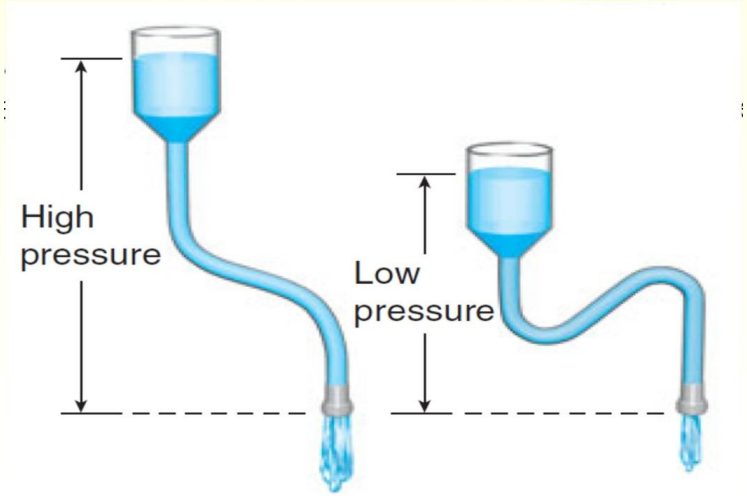
Current of 1 ampere (A) represents a charge of 1 coulomb (C) per second (s) flowing past a point in a circuit (1A = 1C/s)

HW: Understand the example on Page 281 (Harris book)

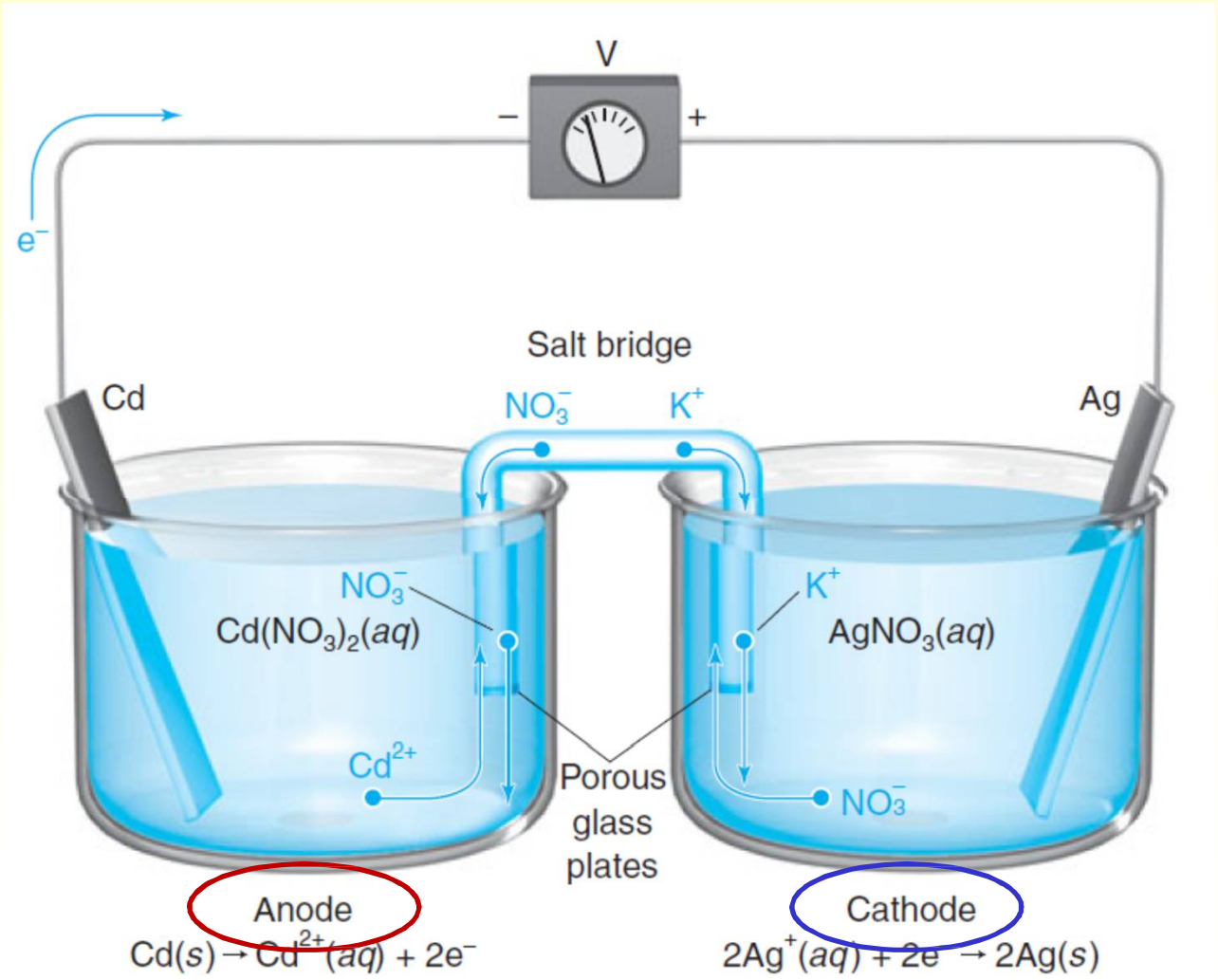
# Potential difference

The work needed (or that can be done) when moving an electric charge from one point to the other

The greater the potential difference between two points, the stronger will be the “push” on a charged particle traveling between those points



# Galvanic cell



# Standard potential

Potential measured at standard conditions (Activity = 1; Pressure = 100 kPa, Temperature = 298K) versus hydrogen electrode

| Oxidizing agent | Reducing agent | $E°$(V) |
|---|---|---|
| $F_2(g) + 2e^- \rightleftharpoons 2F^-$ | | 2.890 |
| $O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$ | | 2.075 |
| $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ | | 1.507 |
| $Ag^+ + e^- \rightleftharpoons Ag(s)$ | | 0.799 |
| $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ | | 0.339 |
| $2H^+ + 2e^- \rightleftharpoons H_2(g)$ | | 0.000 |
| $Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$ | | −0.402 |
| $K^+ + e^- \rightleftharpoons K(s)$ | | −2.936 |
| $Li^+ + e^- \rightleftharpoons Li(s)$ | | −3.040 |

Oxidizing power increases ↑

Reducing power increases ↓

# Nernst equation

$$aA + ne^- \leftrightarrow bB$$

$$E = E^0 - \frac{RT}{nF}\ln\frac{A_B^b}{A_A^a} = E^0 - \frac{0.05916\,V}{n}\ln\frac{A_B^b}{A_A^a}$$

$E^0$ – standard reducing potential ($A_A = A_B = 1$);

R – gas constant (8.314 J/(mol · K));

T – temperature, K;

n – number of electrons in half-reaction;

F – Faraday constant (9.649 x $10^4$ C/mol)

$A_i$ – activity of species i

# Homework

On Page 290 (Harris book) understand Nernst equation for a complete reaction and corresponding Example

# Electrodes

Indicator (working) - electrode sensitive to analyte's concentration

Reference – electrode that maintains a fixed (reference) potential and completes the circuit

# Electroanalytical methods

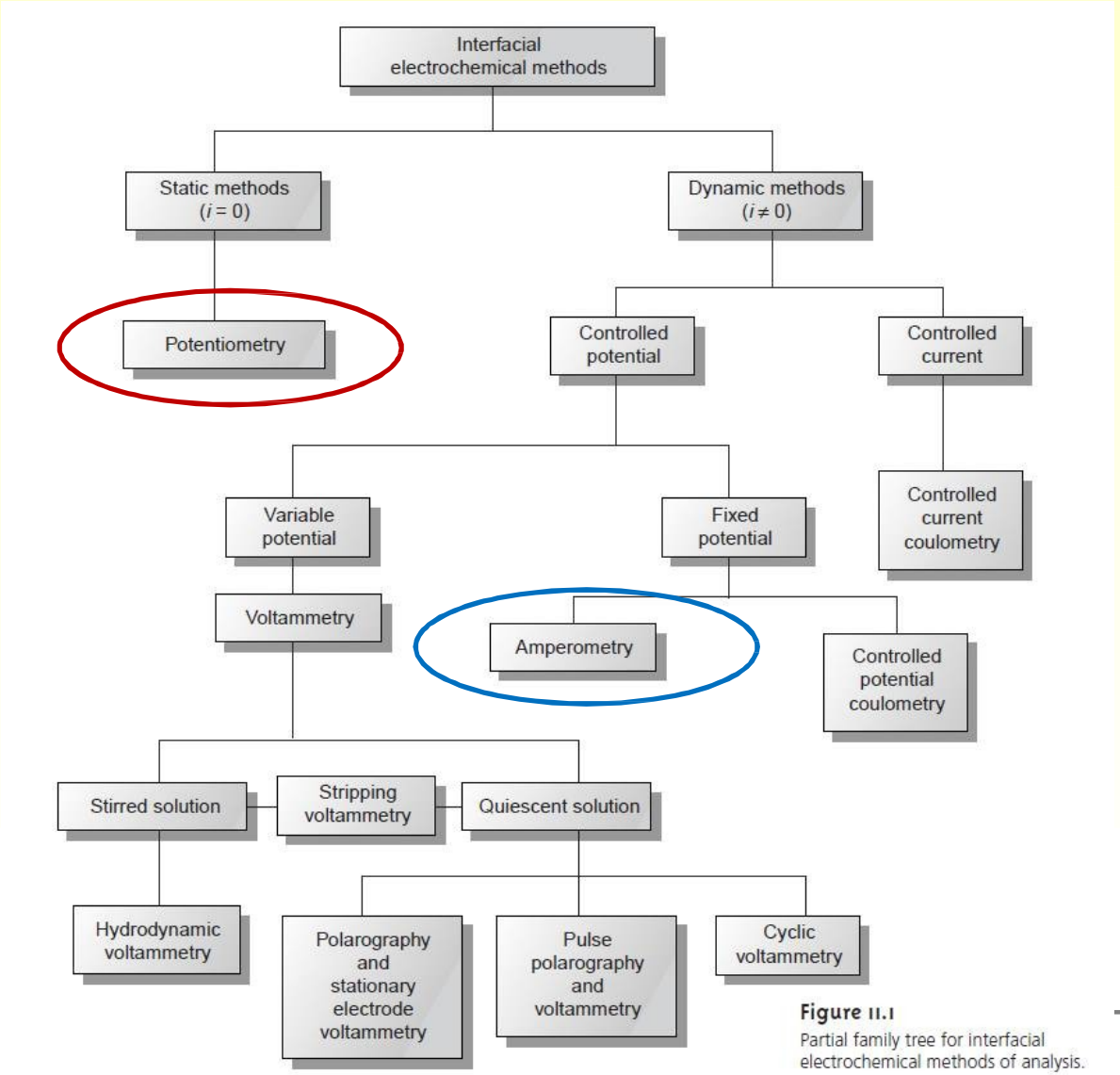



**Figure 11.1**
Partial family tree for interfacial electrochemical methods of analysis.

# Potentiometry

Based on measurement of potential when current is "zero" (0)

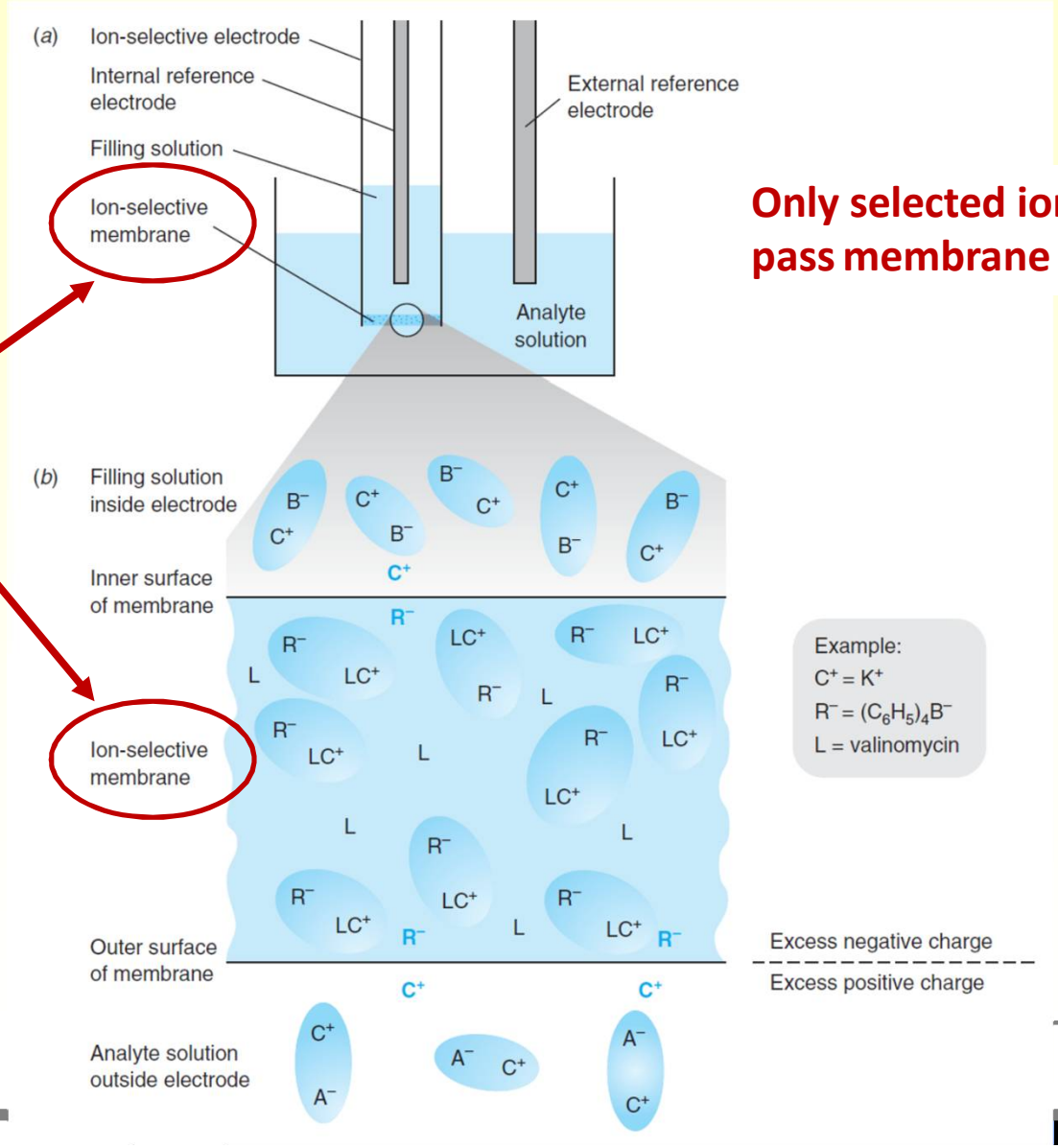
# Application of potentiometry

Ion selective electrodes

Potentiometric sensors

Potentiometric titration

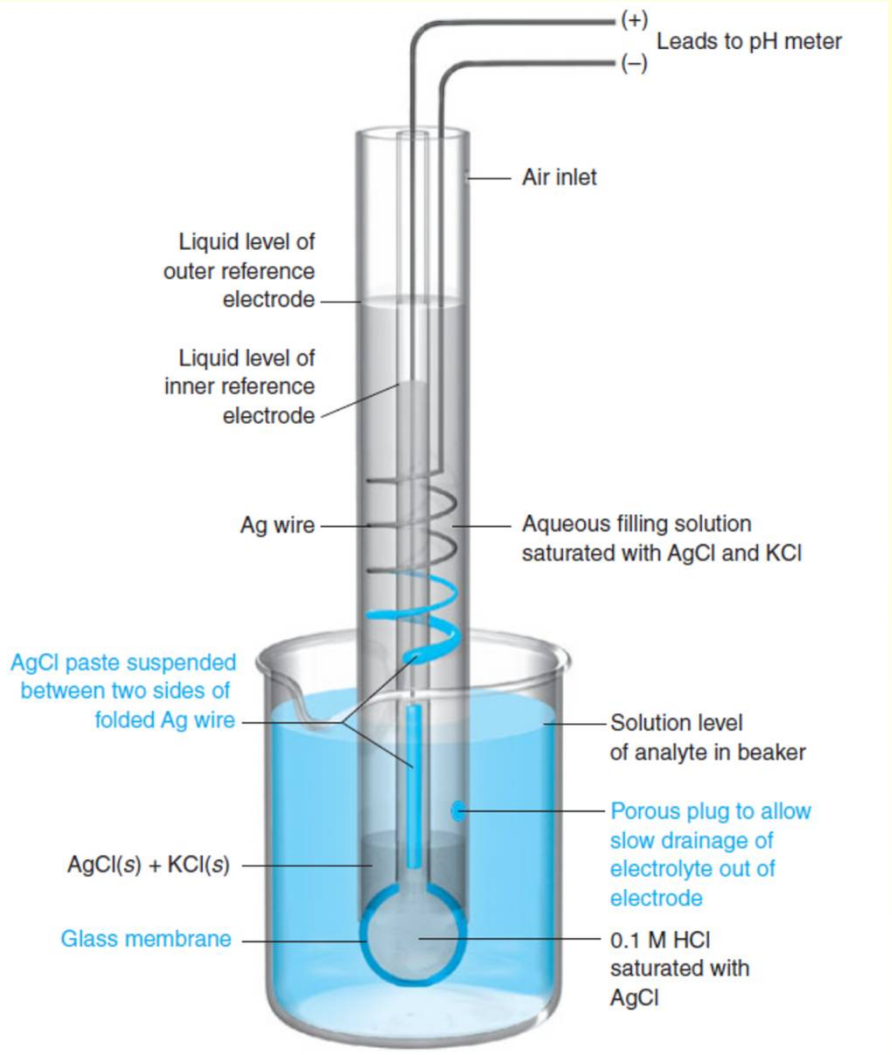
# Ion selective electrodes




**Only selected ion can pass membrane**

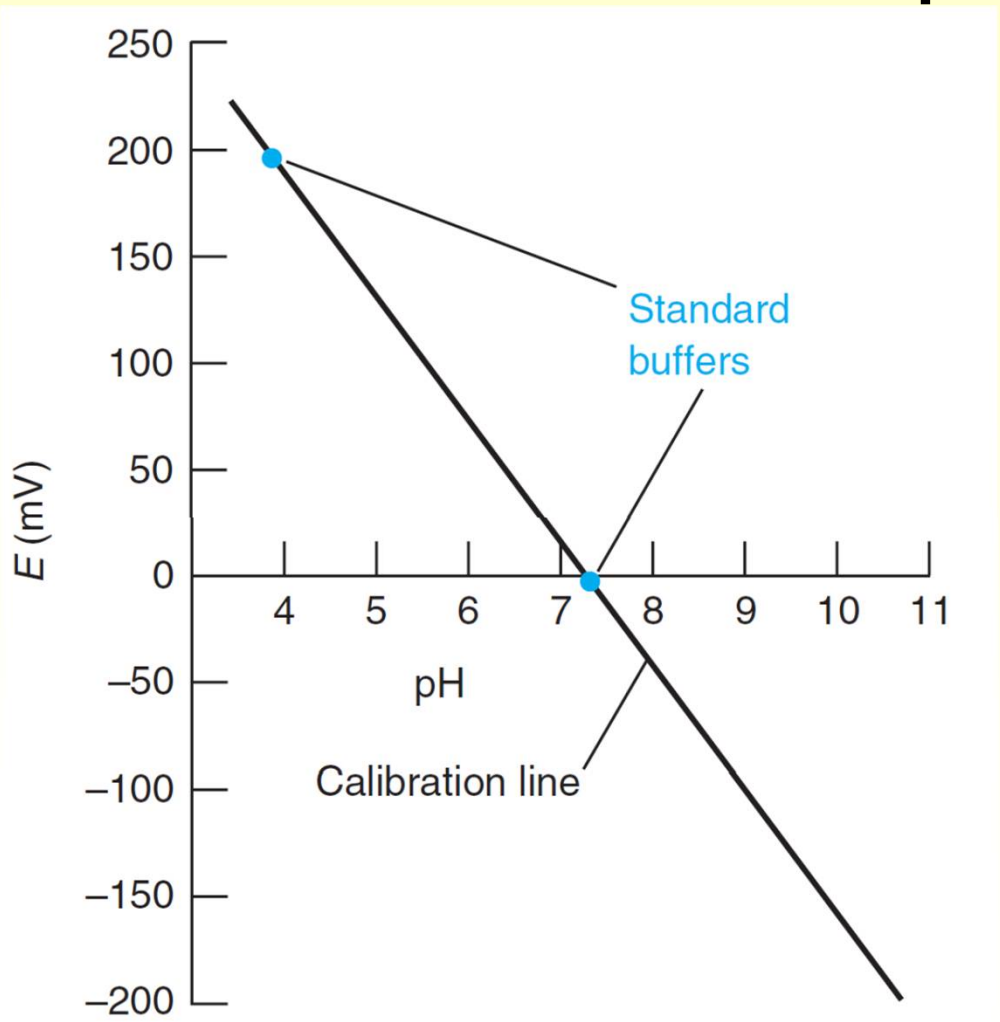
**Membrane**

# pH measurement



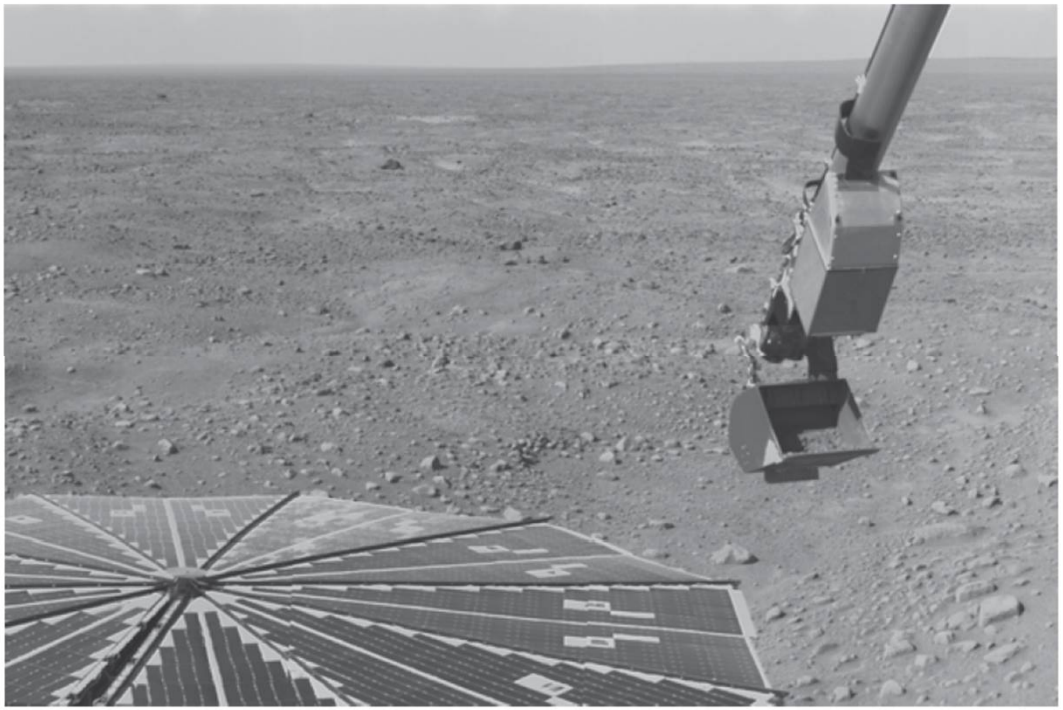

Glass combination electrode with a silver-silver chloride reference electrode

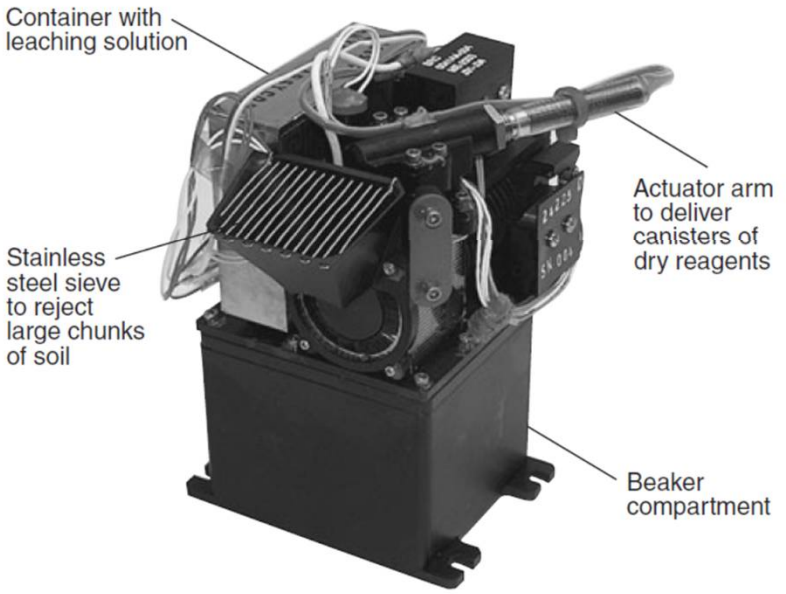
# Calibration of pH electrode




1) Analyze 2-3 calibration buffer solutions in the desired pH range
2) Store the calibration in pH meter
3) Repeat as necessary

# Wet Chemistry laboratory working on Mars





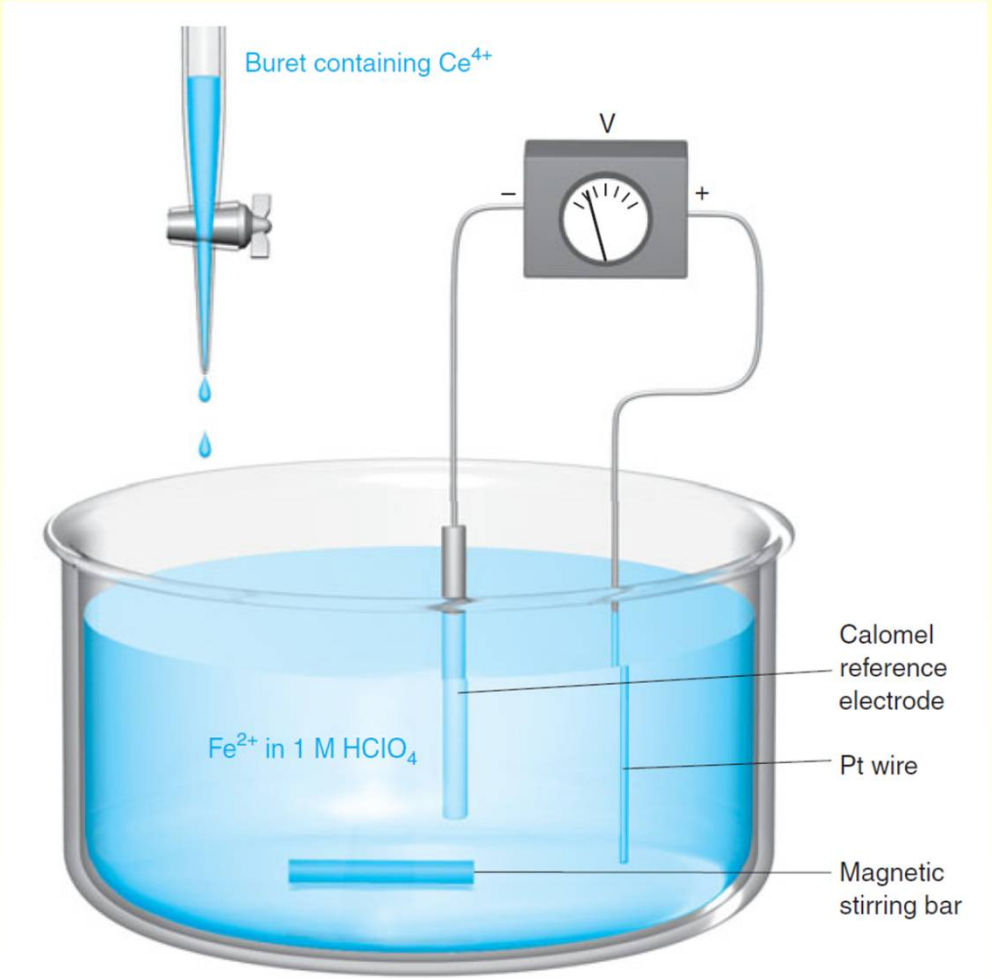
# Problem with Nitrate ion-selective electrode

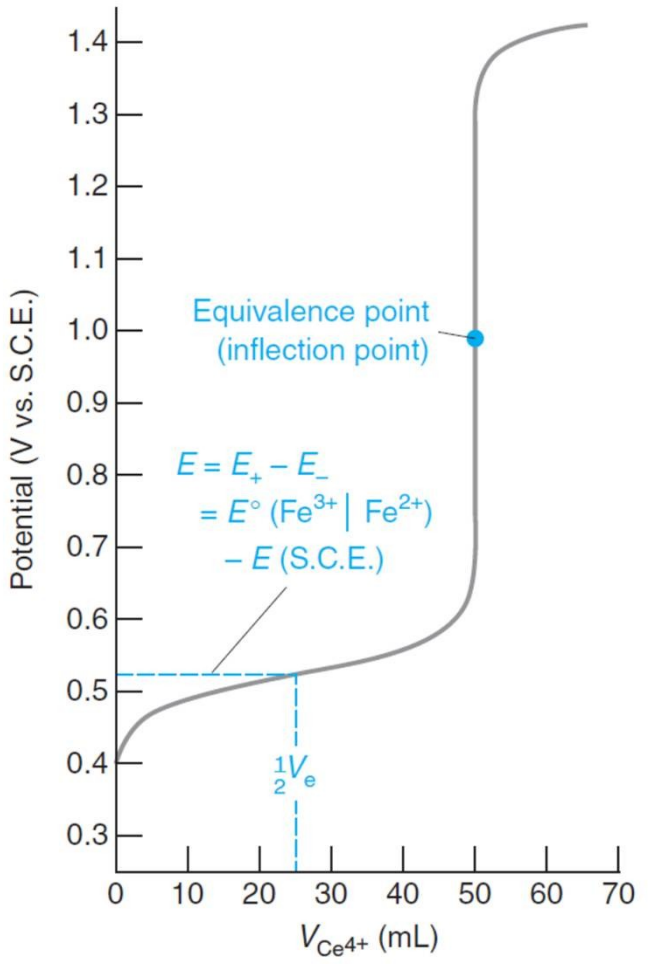
**BOX 14-3 How Was Perchlorate Discovered on Mars?[29]**

Nobody expected perchlorate ($ClO_4^-$) to be abundant on Mars, so the *Phoenix Mars Lander* Wet Chemistry Laboratory was not designed to look for $ClO_4^-$. However, the nitrate ion-selective electrode sent to Mars was 1 000 times *more sensitive* to $ClO_4^-$ than to $NO_3^-$. That is, $K^{Pot}_{NO_3^-,ClO_4^-} = 10^3$. Liquid used to leach ions from the soil had a constant $NO_3^-$ background near 1 mM. Nitrate would only be detected if it were present at concentrations above 1 mM.

When salts were leached from soil in the Wet Chemistry Laboratory, the $NO_3^-$ electrode potential changed by 200 mV, corresponding to an apparent $NO_3^-$ concentration above 1 M, which would have required more $NO_3^-$ than the mass of soil that was analyzed. However, 4–6 mg of $ClO_4^-$ in 1 g of soil would have produced the observed response. Heating the soil released a product at 400°–600°C with a molecular mass of 32 (likely $O_2$), consistent with thermal decomposition of $ClO_4^-$. Perchlorate occurs at similar levels on Earth in arid regions including the Atacama Desert. On Earth, $ClO_4^-$ is thought to arise from photochemical reactions of ozone ($O_3$) with chlorine species in the atmosphere.

# Potentiometric titration



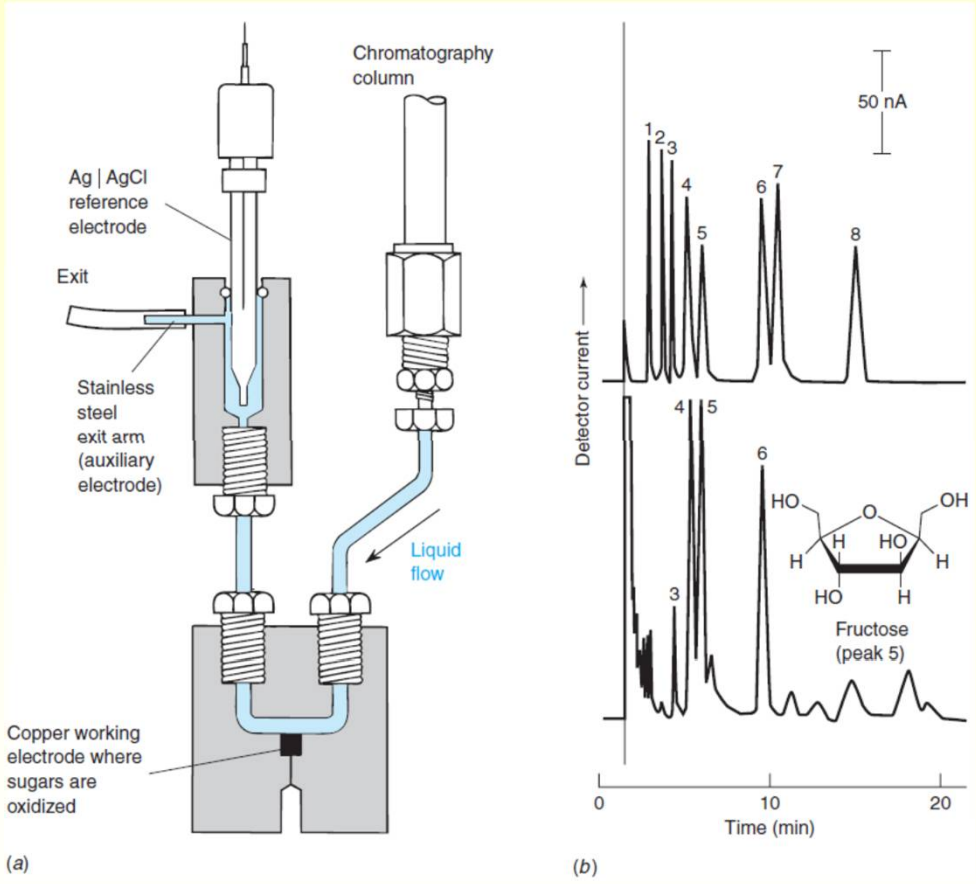
# Amperometry

A method based on measurement of oxidation/reduction **current** at **constant electrochemical potential**

Amperometry is most often used in the construction of **chemical sensors** that are used for the quantitative analysis of single analytes.

One important example, for instance, is the Clark $O_2$ electrode, which responds to the concentration of dissolved $O_2$ in solutions such as blood and water.

# Amperometric detection inLC




(1) fucose, (2) methylglucose, (3) arabinose, (4) glucose, (5) fructose, (6) lactose, (7) sucrose, and (8)cellobiose

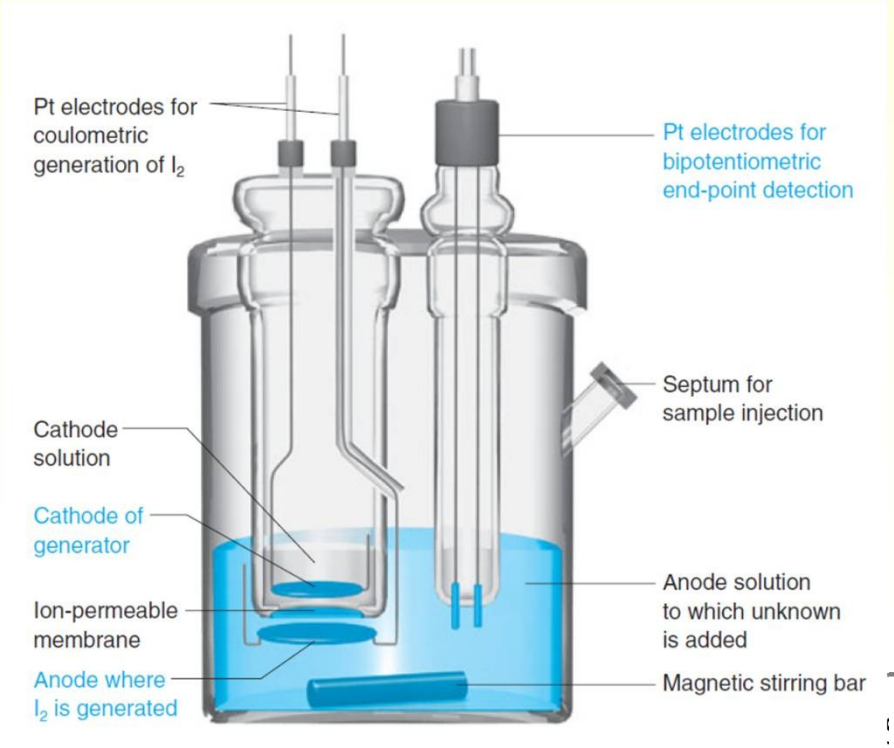
# Carl Fischer titration

Measures traces of **water** in transformer oil, solvents, foods, polymers, and other substances, is performed half a million times each day

$$H_2O + I_2 + ROSO_2^- + 2B \rightarrow ROSO_3^- + 2BH^+I^-$$

R – alkyl radical ($CH_3$); B – base (imidazole, diethanolamine)

**Method sensitivity – 1 ppm**




# Five important concepts

The electrode's **potential** determines the analyte's **form** at the electrode's surface

The concentration of analyte at the electrode's **surface** may not be the same as its concentration in **bulk solution**

In addition to oxidation-reduction reaction, the analyte may participate in **other reactions**

**Current** is a measure of the **rate** of the analyte's oxidation or reduction

We can not simultaneously control **current** and **potential**

** Faulkner, 1983*