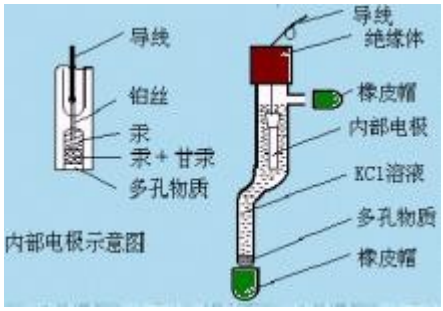
§4.2.1Electrodes and the classification

Ⅰ.Reference Electrodes

1.Standard hydrogen electrode(SHE)

Standard hydrogen electrode is the primary standard electrode, its potential is regulated as zero(any temperature).The electrode potentials of all the electrodes are obtained versus SHE. But there is much trouble in its application, generally not be used in practice. 2.Calomel electrode one of the most popular reference electrodes.



Electrode reaction: Hg2C12 + 2e- = 2Hg + 2 C1- Half cell symbol: Hg, Hg2C12 (固) KC1 Electrode potential (25℃)

$$E_{Hg_2Cl_2/Hg} = E^{\theta}_{Hg_2Cl_2/Hg} + \frac{0.059}{2}\ln\frac{a_{Hg_2Cl_2}}{a^2_{Hg}\cdot a^2_{Cl^-}}$$

$$E_{Hg_2Cl_2/Hg} = E^{\theta}_{Hg_2Cl_2/Hg} - 0.059\lg a_{Cl^-}$$

The activity of C1- in the electrode internal solution is fixed, so the potential of calomel electrode is constant

Table 4-2 The potential of calomel electrode (25℃)

KC1 concentration Electrode potential (V) 0.1mol/LCalomel Electrode 0.1 mol / L +0.3365 Normal Calomel Electrode(NCE) 1.0 mol / L +0.2828 Saturated Calomel Electrode(SCE) saturated solution +0.2438 temperature calibration: for SCE, the potential at t ℃ is:

Et = 0.2438 - 7.6×10-4(t - 25) (V)

3.Ag-AgC1 Electrode

Plating a layer of AgC1 precipitate on the silver filum, immerse it in KC1 solution with a given concentration, then Ag-AgC1 Electrode is formed. Electrode reaction: AgC1 + e- == Ag + C1- Half cell symbol: Ag, AgC1 (固) KC1 Electrode potential (25℃) : EAgC1/Ag = EøAgC1/Ag - 0.0591gaC1- Table 4-3 The potential of Ag-AgC1 Electrode (25℃) 0.1mol/LAg-AgC1 Electrode Normal Ag-AgC1 Electrode

Saturated Ag-AgC1 Electrode

KC1 concentration

0.1 mol / L

1.0 mol / L

Saturated solution

Electrode Potential (V)

+0.2880

+0.2223 +0.2000 temperature calibration, Normal Ag-AgCl Electrode, the pontential at t ℃ is:

Et = 0.2223 - 6×10-4(t - 25) (V)

Ⅱ Indicator Electrode

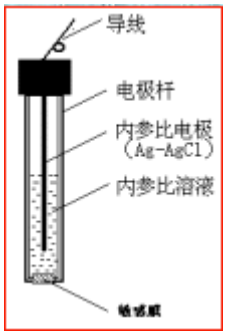
1.The first class of electrodemetal-metal ion electrode, one phase boundary eg:Ag-AgNO3 ?Electrode(silver electrode), Zn-ZnSO4 Electrode(Zinc electrode)etc.
Electrode potential: E(Mn+ / M) = Eø(Mn+ /M)- 0.0591ga(Mn+)
the potentials of the electrode are only decided by the activity of metal ion.

2.The sencond class of electrodes——Metal-Insoluble Metal Salt Electrodes Ag-AgCl ,Cl-, often used as reference electrode, two phase boundaries

3.The third class of electrodes——Mercury electrode Metal mercury (or amalgam) is immersed in the solution containing a little Hg2+-EDTA complex and determinated metal ion. According the two equillibria of Hg2+and Mn+between EDTA, the following equation can be derived:
E(Hg22+/Hg)= Eø(Hg22+/Hg) - 0.0591ga(Mn+)

4. Inert Metal Electrode An inert metal, such as platinum or gold serves as a site for redox reaction for redox couples in solution. Such as: Fe3++e=Fe2+

5. Membrane Electrodes—the most important electrodes



Characteristics: Only selectively response to certain ion in solution (Ion-Selective Electrodes) Key in the structure of ME: selective membrane--sensing element sensing element: single crystal、polycrystal、liquid membrane,etc The structure of cell consisted of a membrane electrode and a reference:

Reference | measured solution | internal solution | internal reference

sensing membrane

The potential of the cell is: $$E = E' \pm \frac{RT}{nF} \ln a_i$$

The key point of this page: to grasp the principle, structure and characteristics of calomel electrode and Ag-AgCl electrode and the factors that decide the potential of reference electrode.

Problem for this page: what basic characteristics should a reference electrode own

Problem for next page: Why does the ion selective electrodes have high selectivity