

§4.1.3 The fundamental methods of electrochemical analysis

Electrochemical cells and electrochemical device



Electrochemical cells are either galvanic cells or electrolytic cells.

Galvanic cells: the redox reaction at the two electrodes tend to proceed spontaneously, can provide electrical energy for external circuit.

Electrolytic cell: requires an external source of electrical energy for the redox reaction at the electrodes to proceed.

The two batteries are showed as follows:

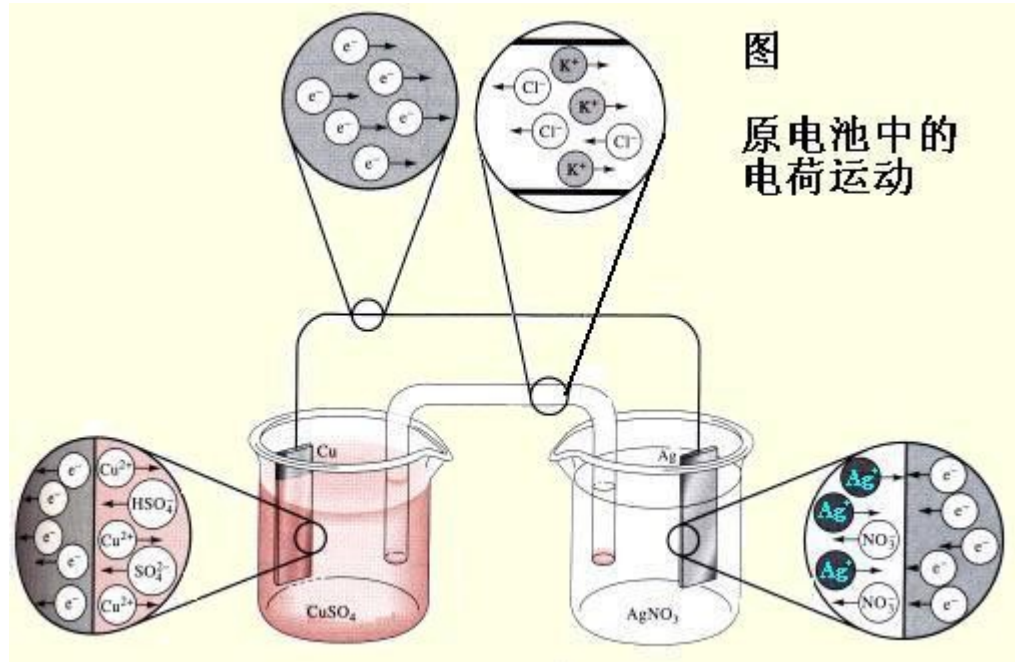
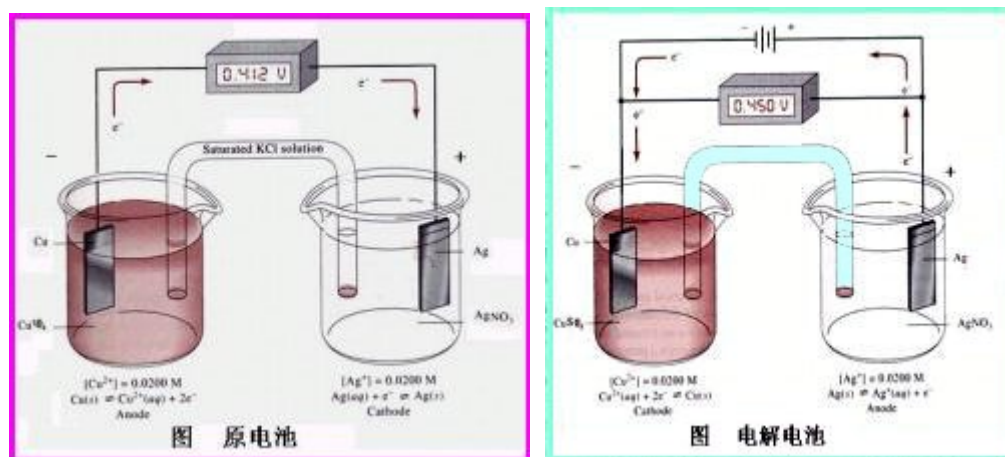


Fig. 4-03 The

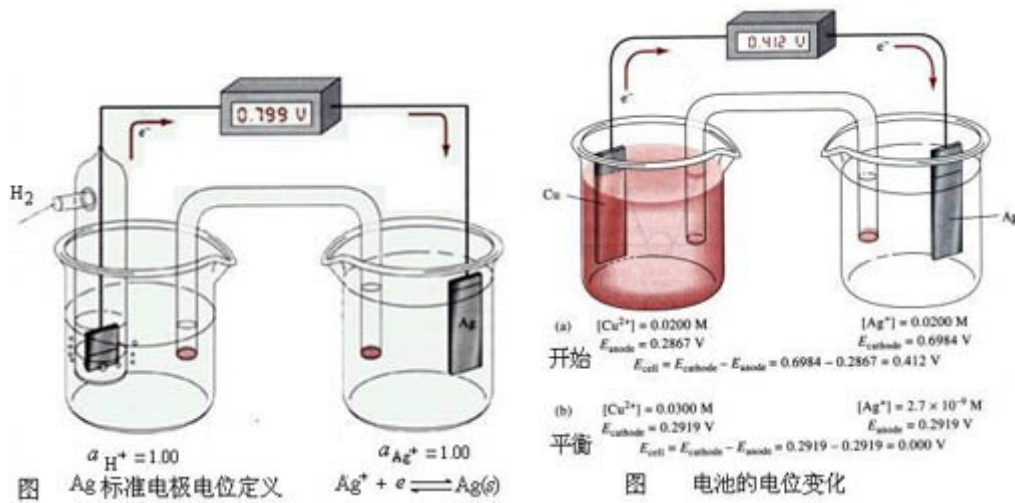
Charge Migration of The Daniell Gravity Cell

II. The fundamental principle of measuring potential and electrochemical parameters

1. According to the occurrence of electrode reaction or not, electrochemical methods can be classified to two kinds:

- no electrode reaction. Such as conductometry, electrophoresis, employing inert metal platinum as electrode.
- There is the occurrence of redox reaction at the electrodes. Such as coulometric analysis and voltammetry.

2. The measurement of electrode potential



It is

regulated that the potential of hydrogen electrode is zero. A galvanic cell is composed of hydrogen electrode and test electrode, is showed as follows: If there is current passing through the external circuit during the measuring process, the potential difference between the two electrodes will decreased gradually until arrive at the equilibrium, the potential is equal to zero, as showed in above figure.

3. The principle of potentiometry

In order to measure electrode potential, that is, electromotive force of measuring device, an equivalent backward voltage need to be provided so that the current of the circuit equal zero. (that is, there is no current passing through the electrodes during the measuring process)

$$\Delta E = E^+ - E^{++} - EL$$

$E_{\text{external}} = E_{\text{measuring}}$: the external potential changes with the potential difference between the two electrodes.

Reference electrodes: Potential of a reference is fixed and is not affected by the test solution.

Indicator electrode: Potential of an indicator electrode changes with the concentration of the selected ion.

Potentiometric methods using special indicator electrodes are unique in that they permit the measurement of the activity(related to concentration) of the selected ion.

The key point in this page: ?The main characteristics of electrochemical methods

Problems in this page: The most important difference between electrochemical method and other analytical methods?