



19CH201 - ENGINEERING CHEMISTRY

UNIT-1 - ELECTROCHEMISTRY

ELECTRODE POTENTIAL

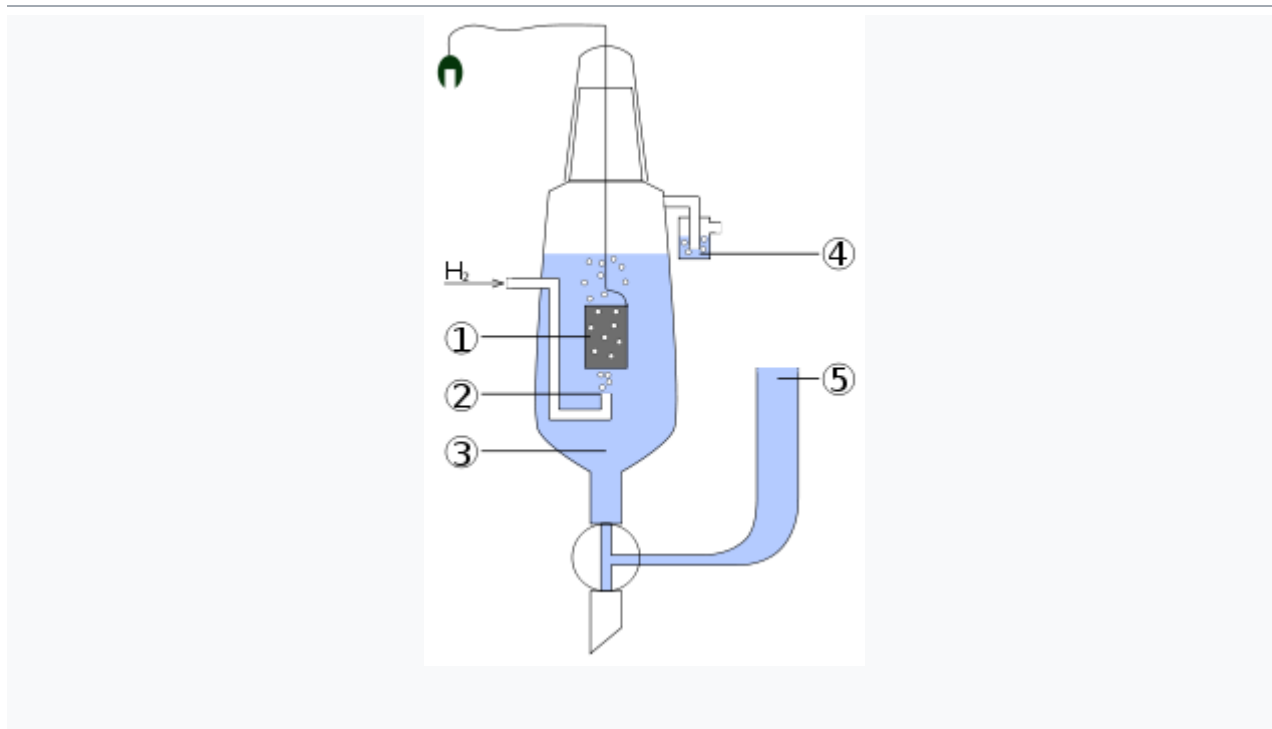
In electrochemistry, electrode potential is the electromotive force of a galvanic cell built from a standard reference electrode and another electrode to be characterized.^[1] By convention, the reference electrode is the standard hydrogen electrode (SHE). It is defined to have a potential of zero volts. It may also be defined as the potential difference between the charged metallic rods and salt solution.

The electrode potential has its origin in the potential difference developed at the interface between the electrode and the electrolyte. It is common, for instance, to speak of the electrode potential of the M^+/M redox couple.

STANDARD HYDROGEN ELECTRODE

The standard hydrogen electrode (abbreviated SHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. Its absolute electrode potential is estimated to be 4.44 ± 0.02 V at 25 °C, but to form a basis for comparison with all other electroreactions, hydrogen's standard electrode potential (E°) is declared to be zero volts at any temperature. Potentials of any other electrodes are compared with that of the standard hydrogen electrode at the same temperature.

Construction

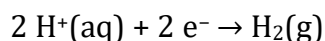




The scheme of the standard hydrogen electrode:

1. platinized platinum electrode
2. hydrogen gas
3. solution of the acid with activity of $H^+ = 1 \text{ mol dm}^{-3}$
4. hydroseal for preventing oxygen interference
5. reservoir through which the second half-element of the galvanic cell should be attached. The connection can be direct, through a narrow tube to reduce mixing, or through a salt bridge, depending on the other electrode and solution. This creates an ionically conductive path to the working electrode of interest.

Hydrogen electrode is based on the redox half cell:



This redox reaction occurs at a platinized platinum electrode. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced form and oxidised form is maintained at unity. That implies that the pressure of hydrogen gas is 1 bar (100 kPa) and the activity coefficient of hydrogen ions in the solution is unity. The activity of hydrogen ions is their effective concentration, which is equal to the formal concentration times the activity coefficient. These unit-less activity coefficients are close to 1.00 for very dilute water solutions, but usually lower for more concentrated solutions.