

2.6. PRODUCTION OF HYDROCHLORIC ACID, CHLORINE AND ALKALI

Electrochemical production. Electrochemical process. Theoretical bases of electrolysis of aqueous solutions and molten medium. Production of chlorine and alkali. Types of chemical baths (diaphragm and mercury cathode). Electrolytic production of hydrochloric acid

Electrochemistry is a branch of physical chemistry that considers systems containing ions (solutions or melts of electrolytes) and processes occurring at the boundary of two phases with the participation of charged particles.

Now electrochemistry is divided into *theoretical* and *applied*. Thanks to the use of electrochemical methods, it is associated with other branches of physical chemistry, as well as analytical chemistry and other sciences.

Electrode processes are processes associated with the transfer of charges across the boundary between the electrode and the solution. The cathodic processes are associated with the reduction of molecules or ions of the reacting substance, the anodic processes are associated with the oxidation of the reacting substance and with the dissolution of the electrode metal.

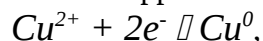
The possibility of a particular electrode process is generally determined by the change of ΔH and ΔS in the course of the corresponding chemical reaction. Knowing these changes, *the Helmholtz equation* can be used to calculate the minimum value of the voltage that must be applied to the electrodes for this electrode process to occur.

For example, based on the thermodynamic data for the reaction: $2H_2 + O_2 = 2H_2O$, it was found that the minimum voltage required for the electrochemical decomposition of H_2O into H_2 and O_2 is 1.23 V. However, at this voltage between the *Hg* cathode and the *Pt* anode to obtain only 1 cm³ of H_2 would take about 400 thousand years.

To increase the speed of electrode processes without changing the nature of the electrodes, it is necessary to impose on the electrodes a much larger potential difference. For example, for the passage of an electric current in the considered system with a density of 1 A/cm², the potential difference between the electrodes should be 3.5 V. In this case, only 35% of the electric energy is spent on the implementation of the electrode process, the remaining 65% is spent on heating the electrolyte. However, the efficiency of electrical energy can be dramatically increased if the *Hg* cathode is replaced with *Pt*. This example shows that the thermodynamic approach to the study of the electrode process is insufficient.

Much more important is the study of the kinetics of electrode processes. With the help of labeled atoms, it can be shown that the electrode processes always go in two directions.

For example, when Cu^{2+} is reduced on a copper electrode simultaneously with the reaction:



and Cu ionization occurs, although at a lower rate. In the absence of an external current, the speeds of the forward and reverse electrode process are equal to each other and equal to the density of the exchange current, which characterizes the intrinsic speed of the electrode process.

When passing an external current, the speed of the electrode process in the forward and reverse directions differ by the value of *the current density* i . Under these conditions, the potential of the electrode differs from its equilibrium value.

The shift of the potential of the electrode from its equilibrium value during the electrode process is *polarization*.

Absolute value of polarization (overvoltage)

The higher the exchange current density, the smaller the deviation of the electrochemical system from equilibrium at a given value i , and the smaller the overvoltage.

Thus, at a given value i , the value characterizes the intrinsic speed of this electrode process. Therefore, the task of electrochemical kinetics is to link the speed value with the current density and