Lecture 5. Reactions in an electric discharge. Plasma chemistry. Types of Electric Discharges. Plasma-chemical reactions.

The purpose of the lecture: to give information about plasma-chemical reactions, types of electrical discharges, and the formation of active particles in plasma.

Expected results: to give students information about the characteristics of plasma-chemical reactions, the formation of active particles in plasma.

Plasma chemistry studies chemical reactions that occur under conditions of partially-ionized gas. In physics, this object is called a low-temperature plasma (weakly ionized plasma with a temperature of heavy particles $<10^5$ K; a cold plasma with a temperature of ~ 10^3 K is also isolated). It is most often formed as a result of the passage of an electric current through a gas (gas-discharge plasma), and is characterized by the presence of high concentrations of chemically active particles: charged particles (electrons, positive and negative ions), atoms and free radicals, excited molecules, and also photons.

Properties:

1) quasineutrality (separation of charges can be neglected at distances greater than the Debye radius - i.e., the movement of a particle during its thermal motion for a time equal to the period of plasma oscillations);

2) electrostatic collective interaction of charged particles (only 2 particles interact in a sufficiently rarefied gas at n.o.);

3) a strong dependence of the plasma is the absence of thermodynamic equilibrium in it, i.e. only nonequilibrium chemical kinetics is applicable to it.

Types of Electric Discharges

The nature of the electric discharge depends on the gas pressure, electric field strength and current density.

A quiet discharge is obtained at a pressure of ~ 10^5 Pa and relatively high tensions between the electrodes; due to the conductivity of the gas due to its residual ionization.

A corona discharge arises from a quiet discharge at a much higher electric field strength; In the case of field inhomogeneity, a corona appears near the electrode with a small radius of curvature, in which shock ionization of the gas occurs, which is absent in the region outside the corona.

A spark discharge is formed from a corona discharge with increasing current strength; occurs intermittently due to a change in the radius of the discharge gap during the discharge process.

A glow discharge is formed at a pressure of $\leq 10^4$ Pa; there is a cathode glow, an astono solid space, a smoldering (negative) glow, a dark Faraday space, a positive glow and anode glow.

The gas in the region of positive emission is in the form of a plasma; voltage - hundreds and thousands of volts.

Arc discharge occurs at a higher current density than a glow discharge; due to evaporation of the electrodes, the lines of the metal of the electrodes prevail in the spectrum; gas in the form of plasma; the potential difference is small (tens of volts).

The technology of the plasma chemical process requires:

1) low-temperature plasma generator;

2) mixing raw materials with plasma (input reagents);

3) plasma-chemical transformations;

4) tempering products.

The choice of the type of plasma generator must satisfy the kinetic and thermodynamic features of the process being studied or being implemented.

Generators (plasmatrons) are:

1) arc;

2) glow discharge;
3) corona discharge;
4) high-frequency induction;
5) high-frequency capacitive;
6) microwave and others.

The most widely used plasma arc torches are electric arc direct and alternating currents of industrial frequency - the most powerful (up to 50 MW).

Plasma-chemical reactions

Features:

1) Ed. interacting particles >> 0.1 eV;
2) commensurate populations of the ground and excited states of molecules;
3) significant (or determining) interactions of molecules with electrons and ions (and the latter among themselves);
4) a significant proportion of the products are in an excited state;
5) there is no strong prevalence of elastic collisions over inelastic ones;
6) the characteristic times of physical and chemical processes are close in order of magnitude, and therefore affect one another.

The resulting chemical reaction is not just characterized by nonequilibrium kinetics - it is a fundamentally multichannel (going along different paths) process in which channels interact in different ways at different times and at different energies. In plasma, the concept of a single temperature does not make sense for any particles, and therefore, the rejection of the Arrhenius rate constant of a chemical reaction is allowed.

In general, the inability to separate chemical kinetics from physical requires a single equation to describe both. Therefore, the Pauli equation is popular for plasma chemistry:

$$\frac{dP_i}{dt} = \sum_k (a_{ik} P_k - a_{ki} P_p)$$

where P_i (t) is the probability of the i^{th} state at time t; a_{ik} and a_{ki} are the probability of transitions per unit time from the i- to k-state and vice versa. This equation takes into account both the transitions between the quantum states of particles and their chemical interaction, and the possibility of pumping the excitation of a part with external energy. It is easy to show that this stochastic equation (taking into account the internal fluctuations of the system), if you do not take into account the transitions between levels (let them end before the chemical processes go), comes down to the usual Arrhenius kinetics.

The formation of reactive particles in plasma

Excitation of a molecule or atom occurs (both vibrational and electronic) in collisions with heavy particles, photons and electrons. For electrons - it depends on the energy of electrons and the structure of the molecule. It can be direct excitation (from the ground state), or stepwise (cascade) - in portions. E_{kin} electron should be greater than $E_{excitation}$. The most effective is resonant excitation: the dependence on the electron energy of the probability of energy transfer from the electron to the molecule is called the excitation function and can have 1-2 maximums.

Ionization of atoms and molecules occurs in a collision with an electron in which E_{kin} is greater than the ionization potential; the dependence of the ionization probability of a molecule or atom (ionization function) passes through a maximum. Possible ionization in collisions with energy atoms or molecules.

Negative ions are formed upon the attachment of a slow electron to a molecule with high electron affinity, for example:

$$e^- + Cl_2 \rightarrow Cl^\bullet + Cl^-.$$

Reactions (some) in plasma. Ions have a high chemical activity. An important role is played by reloading processes.:

symmetrical $He^+ + He \rightarrow He + He^+$;

asymmetrical $He^+ + {}^\bullet H \rightarrow He + H^+$;

non-dissociative $Xe^+ + C_2H_6 \rightarrow C_2H_6^+ + Xe$;

dissociative $Ar^+ + CH_4 \rightarrow CH_3^+ + H^\bullet + Ar$.

Heavy particle transition reactions: $H^\bullet$ atom transition -

$N_2^+ + H_2 \rightarrow {}^\bullet N_2H^+ + H^\bullet$;

$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3^\bullet$;

$Ne^+ + H_2 \rightarrow NeH^+ + H^\bullet$;

proton transition - $H_2^+ + H_2O \rightarrow H_3O^+ + H^\bullet$;

heavy atom transition $J^+ + CH_3J \rightarrow J_2^+ + CH_3^\bullet$;

regrouping - $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$;

association - $CH_3J^+ + CH_3J \rightarrow (CH_3J)_2^+$.

The rate constants of ion-molecular reactions are very high (~ 10^{-9} cm^3/s).

Examples of reactions in an electric discharge. Ozone production - O_2 is passed through a quiet discharge; the ozone yield is 30-50 g/kWh, i.e. much lower than theoretical (1.5 eV/mol-a); this is due to the decay of O_3 by the action of electrons:

$$O_2\,(^3\Sigma_g^-) \rightarrow O_2^*\,(^3\Sigma_u^-) \rightarrow 2O: ;\quad O: + O_2 \rightarrow O_3.$$

Ammonia synthesis - NH_3 yield in a glow discharge of 1-10 g/kWh; the minimum electron energy for the formation of NH_3 is 17 eV; scheme

$$N_2 \rightarrow N_2^+;\quad N_2^+ + H_2 \rightarrow N_2H^+ + H;$$

$$N_2H^+ + H_2 \rightarrow N_2H_2 + H^+;\quad N_2H_2 \rightsquigarrow NH_3.$$

Synthesis of acetylene from methane. In an arc discharge, a current output of C_2H_2 of 120 g/kWh is assumed:

$$CH_4 \rightarrow CH_3 \rightarrow CH_2 \rightarrow C_2H_4 \rightarrow C_2H_2.$$

Literature

1. Richard I. M. Chemical Kinetics and Catalysis. Wiley-Interscience publication, 2001. - p. 968.
2. Бугаенко Л.Т., Кузьмин М.Г., Полак Л.С. Химия высоких энергий. М.: Химия, 1988.