Lecture 4. Radiation chemistry. Radiation chemical yield.

The purpose of the lecture: to familiarize students with radiation chemistry, radiation sources, parameters of ionizing radiation, radiation-chemical processes.

Expected results: students gaining knowledge about radiation-chemical processes, the laws of their course, and a description of their parameters.

Corpuscular radiation (electrons, neutrons, protons, α-particles, positive and negative ions, recoil atoms);

Energy from 10^3 to 10^7 eV; Electromagnetic radiation (x-rays and γ-rays);

Energy is above 50 eV. Chemical reactions that occur under the influence of such radiation are called radiolysis.

The source of energy can be the radiation of radioactive atoms, which are waste during the operation of a nuclear reactor.

Artificial radioactive isotopes obtained by neutron irradiation.

Convenient: Co^{60}, $T_{1/2} = 5.3$ years, the energy of γ-rays 1.12 and 1.32 MeV; Cs^{137}, $T_{1/2} = 33$ years, γ-ray energy 0.661 MeV; Sr^{90}, $T_{1/2} = 28$ years, β-rays with $E_{av} = 0.205$ MeV.

As sources, they use beams of fast electrons (accelerators of various types with E = 0.8-15 MeV); beams of protons, deuterons, α particles, etc. (cyclotrons, Van de Graaff generators, synchrocyclotrons, etc. with E usually from 2 to 660 MeV), neutron beams (nuclear reactor). Neutrons are also obtained from Ra and Po-Be sources or from special accelerators. Powerful X-ray tubes or the braking of fast electrons emerging from the accelerator are used to obtain γ-rays.

Changes in the irradiated object depend mainly on the absorbed energy. The energy of any type of radiation absorbed by a unit mass of the irradiated substance is called the absorbed dose or dose.

In the SI system, 1 gray = 1 J/kg; off-system: 1 rad = 0.01 gray. If we judge the effect not by energy, but by ionization produced by irradiation, then the exposure dose of radiation is used: 1 C/kg - when X-rays and γ-rays produce ions in 1 kg of dry atmospheric air, carrying a charge of 1 C of electricity of each sign.

A non-systemic unit of 1 P = $2.58 \cdot 10^{-4}$ C/kg (this is $2.08 \cdot 10^9$ one-bit ion pairs formed in 1 cm^3 of air under normal conditions) corresponds to 0.87 rad. The radiation dose rate is equal to dose/time = 1 gray/s (off-system - rad/s or P/s). The radiation intensity is equal to the radiation energy passing through 1 cm^2 in 1 s. The rate of radiation decay is characterized by a half-life.

The activity of the drug (the number of reactive substances) is the number of atoms of the reactive isotope decaying in 1 s.

In the SI system: 1 becquerel = 1 decay/s.

Out of system: 1 curie = $3.7 \cdot 10^{10}$ dec/s (determined for equilibrium decay for 1 g Ra). 1 C = $3.7 \cdot 10^{10}$ Bq.

If the lifetime $t = T_{1/2}/\ln 2$ then the mass Q (g) of the radioactive substance having an activity of 1 C is equal to

$$Q = 3.7 \cdot 10^{10} t / N_A = 3.7 \cdot 10^{10} \cdot T_{1/2} \cdot 6.02 \cdot 10^{23} / A \cdot 0.693 = 8.86 \cdot 10^{-12} AT_{1/2},$$

where A - weight 1 g-at.

Radiation chemical yield G

To quantify chemical processes under the influence of irradiation, G is used, i.e. the number of molecules formed or consumed when the system absorbs 100 eV radiation energy.

If G = 0.1÷10, then these are slow endothermic reactions (radiolysis of hydrocarbons at low temperatures, water, reaction $N_2 + H_2$, etc.); if G <20, relatively quick (often exothermic) reactions (the formation of O_3 in liquid oxygen, radiolysis of CO_2, NO_2, etc.); if G> 20, these are only chain reactions (alkylation of alkanes and arenes by olefins, cracking of alkanes at 400 °C, chlorination of alkanes, polymerization).

Distinguish true radiation-chemical yield q = (dn/dE)·100 (at t→0) from average G=(n/E)·100, where n - the number of reacted molecules over time t, and E is the absorbed radiation energy in eV.

From here

$$G = \frac{1}{t} \int\limits_{0}^{t} g\, dt$$

Because dn = υVdt, where υ - chemical reaction rate, V - radiation volume, a dT = δσAndt, where δ - geometric factor, σ - characteristics of the properties of the environment, A = const - source activity, N - number of molecules in an absorbing medium; then

g = [υV/(δσAN)]·100.

Because the δσAN = dE/dt = P - dose rate then

g = (υV/P)*100.

Thus, the true radiation yield g ~ the rate of a chemical reaction.

We have

$$G = \frac{100}{\delta\sigma At} \int\limits_{0}^{t} \frac{\upsilon V}{N}\, dt$$

If V = const, and υ = const (true for small degrees of conversion or for reactions of the zero order), then

G = [υV/(δσAtN)]·100.

In the derivation, an approximation of the homogeneous distribution of active particles in the irradiation zone was made.

Electrons knocked out of particles as a result of primary ionization, in collision with others, can again cause ionization and excitation, since they have sufficient energy. If it is still high, then secondary electrons cause the formation of their own tracks branching from the primary (secondary rays are called δ-rays). If the energy of the secondary electrons is less than 100 eV, then their ranges in the liquid and solid phases are small. The rate of loss of energy locally absorbed when a particle moves in the environment — a characteristic of the inhibitory ability of a medium - is expressed in units of linear energy loss (LEL) - keV/μm;

LEL grows with decreasing energy, so the average LEL is used - equal to the initial energy of the particle divided by the average range in the substance.

For radiation-chemical reactions, secondary processes are not only chemical, since the arising substances are subject to the further action of radiation. This means that part of the energy is not spent on necessary purposes, and therefore (calculated on monochromatic light) the radiation-chemical yield for photochemical reactions is several times higher than for the same processes under the influence of penetrating radiation (obtaining O_3 from oxygen under UV irradiation with λ = 190 nm comes with G = 30 mol·L/100 eV, and for γ-irradiation in a gas, G is 10 times lower and in the liquid phase 2 times lower).

The absorption of radiation depends on the charge of the atomic nucleus, leads to the ionization of matter, and ionization increases towards the end of the particle path and depends on its nature and mass. As long as the energy of particles and photons is greater than E ionization, all of it is spent mainly on ionization. α-particles interact mainly with the electrons that are captured by them, but due to the enormous velocity of the particles, the attached electrons are split off, and this process is repeated many times.

If E ~ 10 keV (λ> 0.15 nm), then a photon with an atom gives a photoelectric effect.

E_{kin} knocked out electron = E_{photon} - $E_{ionization}$

The photon in this case is completely absorbed, i.e. by this mechanism, $E_{photons}$ do not change, but only the total number of photons in the beam changes.

With increasing E, the <u>Compton effect</u> begins to play an important role: the photon collides with the electron of the atom and elastically scatters, transferring part of the energy to the recoil

electron, which itself causes the ionization of the substance. Therefore, photons lose energy and dissipate, still continuing to cause ionization of the substance.

Finally, if the $E_{photon} > 1.02$ MeV ($\lambda < 10^{-12}$ m), the probability of the formation of electron-positron pairs into which the photon energy is converted increases and it disappears.

The radiation-chemical effect for each system depends on a large number of factors - the concentration of system components, temperature, mass transfer, etc., which change during irradiation, therefore, in general, the output will be a function of the dose $G = f(D)$. Distinguish between the initial G_0 and the current G - output.

The initial radiation-chemical effect is understood as the yield extrapolated to a zero dose. Under the current one is the output at a given dose, which is determined either by graphical differentiation of the dose curve, or by differentiation of the analytical expression describing the dose dependence.

Under the action of ionizing radiation on a substance, the initial yield of intermediate radiolysis products (electrons, ions, and excited states) is of the order of 10. Intermediate highly reactive particles either interact with each other, or disintegrate, or react with the starting material or its impurities, so that three possible main situations.

1. Intermediates mainly interact with each other, regenerating the starting material. Then the observed yield of conversion of the starting material will be small compared with the yield of intermediate products. Such substances, materials, and systems are commonly called radiation-resistant.

2. Intermediate products, interacting with each other or disintegrating, give stable radiolysis products other than the starting material. In this case, the yield of conversion of the irradiated substance will be of the order of the yield of intermediate products. The same will happen if the intermediates react with the impurities present in the substance.

3. Intermediates are capable of conducting a chain reaction of the conversion of the starting material or a dissolved compound. Under these conditions, the yields of the final products will significantly exceed the yields of the intermediate products.

Very significant information has now been accumulated on the yields of radiation-chemical transformations in various substances, materials, and chemical systems. The observed conversion yields can range from 10^{-6} to 10^8 particles per 100 eV.

Irradiation can be carried out both under stationary conditions (a constant stream of radiation), and in variables (intermittent irradiation, when a pause follows the irradiation period, or pulsed irradiation, in which a high dose is given once).

The radiation-chemical yield G during stationary irradiation is directly related to the rate of the total chemical process v caused by the action of radiation on the system.

By definition, $G = dn/dD$ (where n is the number of molecules).

Dose D can be represented as $D = D^\bullet dt$, (where $D^\bullet$ is the dose rate; t is time).

Then $G = dn/D^\bullet dt$ and $dn = GD^\bullet dt$.

The rate of the total chemical process is $v = dn/dt$ and $dn = vdt$. Hence we have

$$v = GD^\bullet \frac{1}{100N} \text{ ,}$$

where 100N is the dimension coefficient.

Literature

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