MOLECULAR ION MECHANISM OF HI FORMATION
IN THE FIRST LOOP

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A model for the formation of hydrogen iodide gas directly in the channels of the first loop of a reactor during a serious accident initiated, by a source of radiation, in a mixture of vapors of fission products and water during radiative decay is described. The main parameters of the model are determined. It is shown that substantial conversion of cesium iodide vapor into hydrogen iodide is possible.

Modeling the formation of different iodine constants in the first loop of a reactor in the event of a hypothetical unanticipated accident is a necessary condition for evaluating the consequences of radionuclides escaping into the room of the containment shell and radiation contamination of the environment [1]. For such accidents, aside from the formation of a large number of aerosols of fission products, a characteristic effect is the occurrence of different chemical reactions that can have a large effect on the formation of volatile forms of radionuclides and thereby determine their transport outside the plant’s containment shell. The most dangerous such compounds are hydrogen iodide HI, molecular iodine I₂ and CH₃I.

In an accident with loss-of-seal of the core, radioactive inert gases released from the damaged fuel elements are transported together with superheated water vapor and form the main radioactive source in the gas volume of the coolant. Radioactive iodine is released predominately in the form of cesium iodide vapor, which on cooling forms a radioactive aerosol together with other fission products. However, volatile compounds of radioactive iodine can also form, for example, on interaction with organic substances on the surfaces of the walls of the rooms in the containment shell [2].

The present article examines the formation of uncondensed hydrogen iodide gas as a result of ion-molecular reactions initiated in the first loop of the reactor by radioactive decay of fission products in a mixture with water vapor.

Model Parameters. In an accident with loss-of-seal in the first loop the coolant pressure decreases sharply and the fuel elements are strongly heated because not enough heat is removed. As a result, the coolant in the core becomes superheated and transforms from the liquid state into vapor. In this case, the action of the radiation source as fission products leave the fuel occurs in superheated water vapor. As a result, positive ions, mainly H₃O⁺, and negative ions, for example, OH⁻, are formed in the vapor [3]. The qualitative scheme of the accompanying processes can be represented as follows: escape of radionuclides in the first loop, formation of H₃O⁺ and OH⁻, recombination of ions and ion-molecular conversion H₃O⁺ + CsI = = Cs⁺ + HI + H₂O.

Escape of Fission Products and Ion Formation. For simplicity, the intensity of the source, which the α- and β-radiation from radioactive inert gases is, is assumed to be uniform. Positive and negative ions are formed as a result of coolant radiolysis in the vapor phase and accompanying ion-molecular reactions and reactions with electron participation. Their subsequent evolution depends on the mechanisms of destruction, the main process being ion-ion recombination. In addition, the ions can react with the fission products, thereby initiating a change in their composition. Analysis showed that for VVER the intensity of the ion source can reach \( Q_i = 10^{14} - 10^{18} \) m⁻³/sec [3, 4].

**Ion Recombination.** A characteristic feature of the thermodynamic conditions in a serious accident is the state of the coolant – water vapor at relatively high temperature and pressure 0.1–0.5 MPa. This must be taken into account in evaluating the effect of ion-ion recombination.

Binary recombination of ions at normal temperature $H_2O^+ + OH^- = 2H_2O$ (rate $\beta_2$) is significant only at pressures below atmospheric. At moderate pressure, the contribution of three-particle recombination $H_2O^+ + OH^- + M = 2H_2O + M$ (rate $\beta_3$), where the excess kinetic energy of the interaction ions is transferred to the gas of particles (Thompson–Nathanson theory), must be taken into account. At this stage of the escape of fission products from the core at temperature 700–2000 K and pressure 0.1–0.5 MPa, the recombination rate will be determined by the expression $\beta(T) = \beta_2(T) + \beta_3(T)[M]$, where $[M]$ is the concentration of gas molecules [5].

The recombination rate as a function of temperature can be determined using the relations given in [6] and empirical fits for ion pairs with similar properties. According to the theory, the rate constant $\beta_3 \propto T^{-1/2}$ and depends on the mass of the ions and the electron affinity energy of a negative molecular ion. The rate constant $\beta_3 \propto T^{-1/3}$ and depends on the mass of the ions as well as the polarizability and the mass of the particles. For example, at pressure 0.3 MPa and temperature 1000 K $\beta_2 = 5.4 \times 10^{-8}$ cm$^3$/sec, $\beta_3 = 7.1 \times 10^{-27}$ cm$^3$/sec, $[M] = 2.2 \times 10^{19}$ cm$^{-3}$, $\beta(1000) = 2.1 \times 10^{-7}$ cm$^3$/sec. For comparison, at another temperature $\beta(700) = 6.9 \times 10^{-7}$ cm$^3$/sec, $\beta(1500) = 7.4 \times 10^{-8}$ cm$^3$/sec, $\beta(2000) = 4.7 \times 10^{-8}$ cm$^3$/sec.

**HI Formation.** The reaction leading to the formation of the HI molecule is an exothermal ion-molecular reaction of the ion $H_2O^+$ with the polar molecule CsI [7] $H_2O^+ + CsI + M = Cs^+ + HI + H_2O + M$; the reaction enthalpy $\Delta H = -190$ kJ/mole. Here, the following thermodynamic relations were used to determine the standard formation enthalpy $\Delta H_f^0$ of the ions [8]:

$$\Delta H_f^0(H_2O^+) = -PA(H_2O) + \Delta H_f^0(H_2O) + \Delta H_f^0(H^+);$$

$$\Delta H_f^0(Cs^+) = IE_d(Cs) + \Delta H_f^0(Cs) - \Delta H_f^0(electron),$$

where $PA(H_2O) = 691$ kJ/mole is the proton affinity energy of the water molecule; $\Delta H_f^0(H^+) = 1530$ kJ/mole; $IE_d(Cs) = 3.894$ eV is the adiabatic ionization energy of the cesium atom.

The reaction rate can be determined using the capture model of [9] for the ion-dipole mechanism of the interaction between the $H_2O^+$ ion and the CsI molecule with constant dipole moment $\mu = 11.7D$ (1D $= 3.34 \times 10^{-30}$ C·m) and electric polarizability $\alpha = 9.29A^3$ (1A $= 10^{-10}$ m) [10]. According to this theory, the rate constant of the binary reaction is $7.7 \times 10^{-9}$ cm$^3$/sec at 1000 K, $5.6 \times 10^{-9}$ at 2000 K, and $9.1 \times 10^{-9}$ cm$^3$/sec at 700 K, respectively. Its value will be more accurate as the rate of a three-particle collision with the formation and stabilization of an intermediate complex [6]. In this approximation, the formation rate of the excited complex $[H_2O^+CsI]^*$ and its stabilization (dissociation) in a collision with buffer gas molecules $M$ corresponds to the capture rate constant for the corresponding ion–dipole pair, where $\mu(H_2O) = 1.85D$. The characteristic lifetime of the complex is determined by the capture radius of the CsI molecule captured by $H_3O^+$ and their average relative velocity. As a result, for example, for a gas at temperature 1000 K and pressure 0.3 MPa the rate $k_3 = 2.6 \times 10^{-29}$ cm$^3$/sec and $k_{2M} = k_3[M] = 5.6 \times 10^{-10}$ cm$^3$/sec. The ionization energy of the cesium atom and cesium iodide molecule are appreciably less than the ionization energy of the hydrogen atom $–IE_d(Cs) = 3.9$ eV, $IE_d(CsI) = 7.3$ eV, and $IE_d(H) = 13.6$ eV. Therefore, the rate of the exothermal reaction of nonresonance charge exchange on $H_2O^+$ should correspond in order of magnitude to the capture rate of the CsI dipole molecule in the field of the $H_2O^+$ ion [11].

The dissociation probability of an excited complex in a collision with molecules is determined by the sum of the binding energy of the ion with a dipole, equal to 1.5 eV and distributed over internal degrees of freedom of the complex, and the average thermal energy of the gas molecules in the range 0.1–0.3 eV at 600–1000 K. Obviously, this energy is sufficient to break the Cs$^+$–I bond (dissociation energy 0.23 eV).

The rate $k_D$ of the dissociation reaction $Cs^+ + M = Cs^+ + I + M$ can be determined by taking account of the fact that $M = H_2O$ is a dipole molecule. Dissociation is possible only for collisions, where the kinetic energy exceeds the binding energy $D$. This signifies that the relative velocities satisfy the condition $v > v_0$, where $v_0 = (2D/\mu)^{1/2}$, and $\mu$ is the reduced mass of the colliding particles. For a Maxwellian velocity distribution, the probability of such a collision $f_D = (8D/\pi kT)^{1/2} \exp(-D/kT)$, where $k$ is Boltzmann’s constant. The rate constant of the reaction is determined as $k_D = k_2f_D$, where $k_2$ is the capture rate