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MATHEMATICAL MODELING OF PROCESSES OF RADIOLYSIS OF WATER, HEXANE AND WATER–HEXANE MIXTURE

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There were carried out modeling of radiolysis processes in the water–hexane system for the purpose of to identify the mechanism of radiolysis and comparison of theoretical and experimental data.

INTRODUCTION

In identifying the mechanism of radiation-chemical processes modeling and determination of kinetic parameters are of particular importance. Comparison of experimental and calculated values of the parameters of the radiation-chemical processes makes it possible to judge the reliability of the proposed mechanism.

Therefore based on the known literature data about the mechanism and model calculations of the radiation-chemical processes in water and hydrocarbon systems there were simulated radiolysis processes in hexane and hexane-water system by us [1, 2].

In order to explain the obtianed experimental data and reveal possible mechanisms of the reactions upon radiolysis of water, hexane and ware-hexane mixture modeling of the processes occuring in these systems has been carried out. In this modeling the following factors were taken into account: dose rate, volume of the irradiated system, time of irradiation, concentartions of components, constants of the reactions rates, etc. Modeling of the process kinetics has been made wich computer program GEPASI 3 for the Windows operating system. Description of this program is given in [3, 4]. Constants of the reactions rates are taken from [5, 11].

The main purpose of the modeling is to study the processes occuring in the water – hexane mixture upon γ-raiolysis. However, for comparison with the literature, separate radiolysis separately of liquid water and hexane was first modeled. In the case of liquid water rate constants from [5, 9, 11] as well as our own experimental data were used:

Dose rate – 1,42 Gy/s.

Volume of ampoules – 0,5 ml.

Time of irradiation – from 1 to 20 hr.

The reactions and rate constants of the reactions taken from [5] are given below:

Table 1

Namber of reaction	Reaction	K_1-constant of direct reaction, l/mole·s	K_2-constant of direct reaction, l/mole·s
1	$2e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$	$4{,}97\cdot10^9$	
2	$e_{aq}^- + H + H_2O \rightarrow H_2 + OH^-$	$1{,}89\cdot10^{10}$	
3	$e_{aq}^- + OH \rightarrow OH^-$	$3\cdot10^{10}$	
4	$e_{aq}^- + O + H_2O \rightarrow 2\,OH^-$	$2{,}2\cdot10^{10}$	
5	$e_{aq}^- + HO_2 \rightarrow HO_2^-$	$2\cdot10^{10}$	
6	$e_{aq}^- + O_2^- + H_2O \rightarrow OH^- + HO_2^-$	$1{,}3\cdot10^{10}$	
7	$e_{aq}^- + H_2O_2 \rightarrow OH^- + OH$	$1{,}2\cdot10^{10}$	
8	$e_{aq}^- + HO_2^- \rightarrow OH^- + O^-$	$3{,}5\cdot10^9$	
9	$e_{aq}^- + O_2 \rightarrow O_2^-$	$1{,}8\cdot10^{10}$	
10	$e_{aq}^- + H^+ \rightarrow H$	$2{,}3\cdot10^{10}$	
11	$e_{aq}^- + H_2O \rightarrow OH^- + H$	19	
12	$2H \rightarrow H_2$	$7{,}8\cdot10^9$	
13	$H + OH \rightarrow H_2O$	$2{,}5\cdot10^{10}$	
14	$H + HO_2 \rightarrow H_2O_2$	$2\cdot10^{10}$	
15	$H + O_2^- \rightarrow HO_2^-$	$2\cdot10^{10}$	
16	$H_2O_2 + H \rightarrow OH + H_2O$	$8{,}42\cdot10^6$	
17	$O_2 + H \rightarrow HO_2$	$2{,}1\cdot10^{10}$	
18	$OH^- + H \rightarrow H_2O^-$	$2{,}2\cdot10^7$	
19	$2\,OH \leftrightarrow H_2O_2$	$5{,}5\cdot10^9$	$1{,}33\cdot10^{-7}$
20	$OH + O^- \rightarrow HO_2^-$	$2\cdot10^{10}$	
21	$OH + HO_2 \rightarrow O_2 + H_2O$	$6{,}3\cdot10^9$	
22	$OH + O_2^- \rightarrow O_2 + OH^-$	$8{,}2\cdot10^9$	
23	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$4{,}06\cdot10^7$	
24	$OH + HO_2^- \rightarrow OH^- + HO_2$	$7{,}5\cdot10^7$	
25	$H_2 + OH \rightarrow H + H_2O$	$3{,}8\cdot10^7$	
26	$OH^- + OH \leftrightarrow O^- + H_2O$	$1{,}2\cdot10^{10}$	$1{,}75\cdot10^6$

27	$2\ O^- + H_2O \rightarrow OH^- + HO_2^-$	$1\cdot10^9$	
28	$O_2^- + O^- + H_2O \rightarrow O_2 + 2\ OH^-$	$6\cdot10^8$	
29	$H_2O_2 + O^- \rightarrow O_2^- + H_2O$	$5\cdot10^8$	
30	$O^- + HO_2^- \rightarrow OH^- + O_2^-$	$4\cdot10^8$	
31	$H_2 + O^- \rightarrow OH^- + H$	$8\cdot10^7$	
32	$2\ HO_2 \rightarrow H_2O_2 + O_2$	$8{,}3\cdot10^5$	
33	$HO_2 + H_2O_2 \rightarrow O_2 + OH + H_2O$	0,2	
34	$O_2^- + HO_2 \rightarrow O_2 + HO_2^-$	$9{,}7\cdot10^7$	
35	$HO_2 \leftrightarrow H^+ + O_2^-$	$7{,}5\cdot10^5$	$5{,}1\cdot10^{10}$
36	$2\ O_2^- + 2H_2O \rightarrow H_2O_2 + O_2 + 2\ OH^-$	0,3	
37	$H_2O_2 + O_2^- \rightarrow O_2 + OH^- + OH$	0,13	
38	$O_2^- + HO_2^- \rightarrow O_2 + OH^- + O^-$	0,13	
39	$H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O$	$1\cdot10^{10}$	$1{,}13\cdot10^6$
40	$H^+ + HO_2^- \rightarrow H_2O_2$	$2\cdot10^{10}$	
41	$H^+ + OH^- \leftrightarrow H_2O$	$1{,}4\cdot10^{11}$	$2{,}52\cdot10^{-5}$
42	$O_2 + O^- \leftrightarrow O_3^-$	$3\cdot10^9$	300
43	$O^- + O_3^- \rightarrow 2\ O_2^-$	$7\cdot10^9$	
44	$H_2O_2 + O_3^- \rightarrow O_2 + O_2^- + H_2O$	$1{,}6\cdot10^6$	
45	$HO_2^- + O_3^- \rightarrow O_2 + OH^- + O_2^-$	$8{,}9\cdot10^5$	
46	$H_2 + O_3^- \rightarrow O_2 + OH^- + H$	$2{,}5\cdot10^5$	
47	$H^+ + O^- \rightarrow OH$	$1\cdot10^{10}$	
48	$OH^- + HO_2 \rightarrow O_2^- + H_2O$	$1\cdot10^{10}$	

In the modeling the values of the particles yielde given in [5] werw also used:

Table 2

Particle	G, particles/100 eV
H_2O^-	2,7
H	0,6
H_2	0,45
OH	2,7
H_2O_2	0,7
O_2-	0,02
H^+	3,42
OH^-	0,7
e_{aq}	2,7

Based on these data we have built several graphs and then carried out their comparison with the graphs given in literature,in particular, in [5, 6].

Sufficient coincidence is observed which may serve as an evidence of correctness of the selected scheme and the used program.In the case of hexane the rate constants of the reactions from [6–8, 10] wereused and the experimental data remained as in the case of liquid water.

The reactions and the rate constants of the reactions taken from [6, 7] and [9] are given belo.

Table 3

Namber of reaction	Reaction	K_1-constant of direct reaction, l/mole·s
1	$C_6H_{14}^+ + e \rightarrow C_6H_{14}^*$	$3\cdot10^9$
2	$C_6H_{14}^* \rightarrow C_6H_{13}^\bullet + H$	$8\cdot10^{-4}$
3	$C_6H_{14}^* \rightarrow C_6H_{12} + H_2$	$4\cdot10^{-4}$
4	$C_6H_{14} + H \rightarrow C_6H_{13}^\bullet + H_2$	$1{,}5\cdot10^8$
5	$C_6H_{13}^\bullet + C_6H_{13}^\bullet \rightarrow C_6H_{12} + C_6H_{14}$	$1\cdot10^{10}$
6	$C_6H_{14}^* \rightarrow CH_3^\bullet + C_5H_{11}^\bullet$	$2{,}7\cdot10^{-5}$
7	$C_6H_{14}^* \rightarrow C_2H_5^\bullet + C_4H_9^\bullet$	$4\cdot10^{-6}$
8	$C_6H_{14}^* \rightarrow C_3H_7^\bullet + C_3H_7^\bullet$	$6\cdot10^{-3}$
9	$C_2H_5^\bullet + C_2H_5^\bullet \rightarrow C_4H_{10}$	$1\cdot10^{10}$
10	$C_3H_7^\bullet + C_3H_7^\bullet \rightarrow C_3H_8 + C_3H_6$	$1\cdot10^{10}$
11	$C_2H_6 + H \rightarrow C_2H_5^\bullet + H_2$	$3\cdot10^4$
12	$CH_4 + H \rightarrow CH_3^\bullet + H_2$	$1\cdot10^4$
13	$C_3H_8 + H \rightarrow C_3H_7^\bullet + H_2$	$4{,}5\cdot10^4$
14	$C_4H_{10} + H \rightarrow C_4H_9^\bullet + H_2$	$6{,}21\cdot10^4$
15	$C_5H_{12} + H \rightarrow C_5H_{11}^\bullet + H_2$	$9{,}1\cdot10^4$
16	$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6$	$1\cdot10^{10}$
17	$CH_3^\bullet + H \rightarrow CH_4$	$2{,}3\cdot10^9$
18	$C_2H_5^\bullet + H \rightarrow C_2H_6$	$3\cdot10^9$
19	$C_3H_7^\bullet + H \rightarrow C_3H_8$	$8\cdot10^9$
20	$C_4H_9^\bullet + H \rightarrow C_4H_{10}$	$5{,}2\cdot10^9$
21	$C_5H_{11}^\bullet + H \rightarrow C_5H_{12}$	$5\cdot10^9$

22	$C_6H_{13}^{\bullet} + H \rightarrow C_6H_{14}$	$5{,}5 \cdot 10^9$
23	$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	$6 \cdot 10^{11}$
24	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3^{\bullet}$	$7{,}6 \cdot 10^{11}$
25	$C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+$	$1{,}2 \cdot 10^{11}$
26	$C_2H_4^+ + C_2H_4 \rightarrow C_4H_7^+ + H$	$9 \cdot 10^{10}$
27	$C_2H_6 + C_2H_6^+ \rightarrow C_4H_{10}^+ + H_2$	$2{,}4 \cdot 10^9$
28	$C_2H_6 + C_2H_6^+ \rightarrow C_4H_9^+ + H_2 + H$	$6 \cdot 10^9$

In the modelling the values of the particles yieds given in [6] were also used:

Table 4

Particle	G, particles/100 eV
CH_3	0,7
C_2H_5	0,3
C_3H_7	0,3
C_4H_9	0,27
C_6H_{13}	4,1
e	0,12
H_2	5
CH_4	0,18
C_2H_6	0,42
C_3H_8	0,41
C_3H_6	0,19
C_4H_{10}	0,35
C_5H_{12}	0,1
C_6H_{12}	0,86
C_2H_4	0,25
C_4H_8	0,14
$C_6H_{14}^+$	0,12

Based on these data we have built kinetic curves for H_2, CH_4, $\Sigma C_2=[C_2H_6]+[C_2H_4]$, $\Sigma C_3=[C_3H_8]+[C_3H_6]$, $\Sigma C_4=[C_4H_{10}]+[C_4H_8]$ and $\Sigma C_5=[C_5H_{12}]$. In these graphs, along the ordinate axis the amount of molecules of a given substance is set while along the abscissa axis time in hours is shown (Fig. 1–4).

According to these curves the rates of accumulation of radiolysis products and their radiation-chemical yields were calculated. The results also coincide with the data given in literature, for example, in [6].

Bellow, the values of particle accumulation rate W and yield G are given which were obtained upon radiolysis of hexane at the dose rate of 1,42 Gy/s.

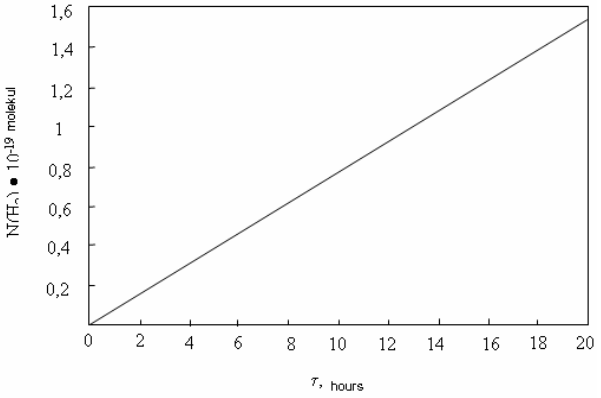

Fig.1. Kinetics of molecular hydrogen accumulation upon radiolysis of hexane at T=300 K and dose rate of 1,42 Gy/s

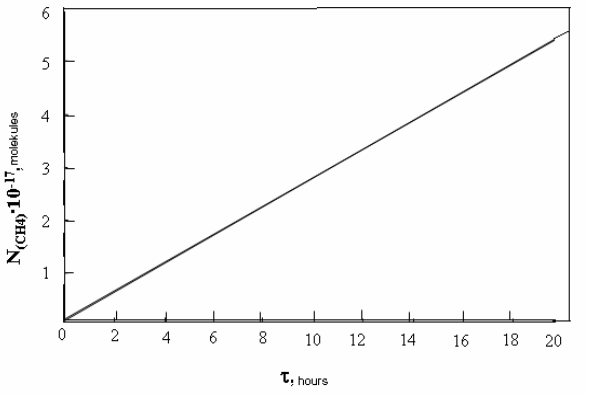

Fig. 2. Kinetics of methane accumulation upon radiolysis of hexane at T=300 K and dose rate of 1,42 Gy/s

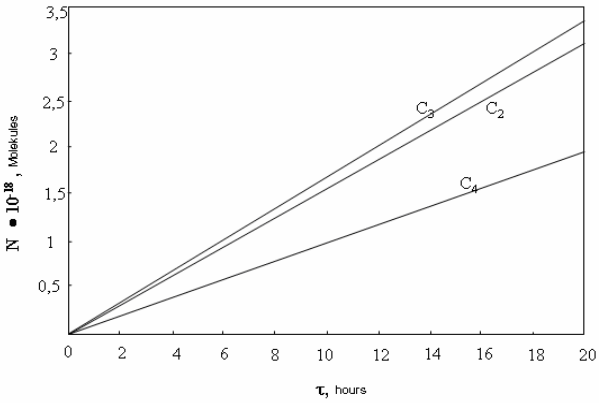

Fig. 3. Kinetics of ethane, propane and butane accumulation upon radiolysis of hexane at T=300 K and dose rate of 1,42 Gy/s

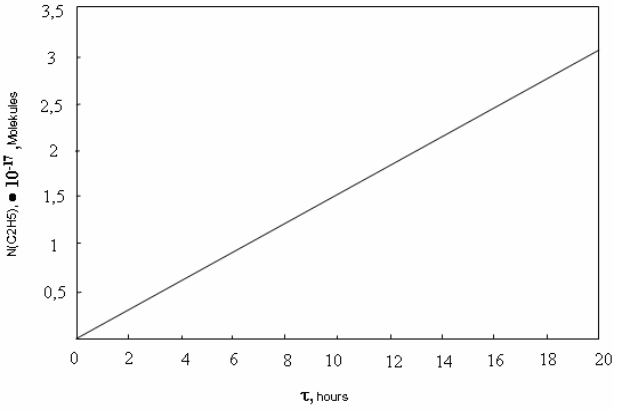

Fig. 4. Kinetics of pentane accumulation upon radiolysis of hexane at T=300 K and dose rate of 1,42 Gy/s

Modeling of radiolysis of water – hexane mixture has been carried out taking into consideration slight solubility of water in hexane and vice versa. For this reason it was assumed that radiolysis of this system is similar to the radiolysis of each of the components in seperate. However, taking into account possibility of diffusion of the radiolysis primary products from one phase into another, several new reactions with the respective rate constants [10] were added to the above-indicated reactions:

Table 5

Products of radiolysis	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
W ($\times 10^{-14}$), molecules/s	3	0,12	0,56	0,57	0,3	0,06
G, molecules/100 eV	3,4	0,14	0,6	0,6	0,34	0,07

Modeling was performed for the mixture of the following percentage content of the components: 50 % C_6H_{14} + 50 % H_2O, which in the experiment corresponded to the following volume ratio of the components: 0,2 ml C_6H_{14} + 0,2 ml H_2O. The kinetic curves were built for H_2, CH_4, $\Sigma C_2 = [C_2H_6]+[C_2H_4]$, $\Sigma C_3 = [C_3H_8]+[C_3H_6]$, $\Sigma C_4 = [C_4H_{10}]+[C_4H_8]$ and $\Sigma C_5 = [C_5H_{12}]$, where along the ordinate axis the number of molecules of a given substance and along the abscissa axis time in hours have been set. Our experimental data are shown as dotted curves in these graphs (Fig. 5–9):

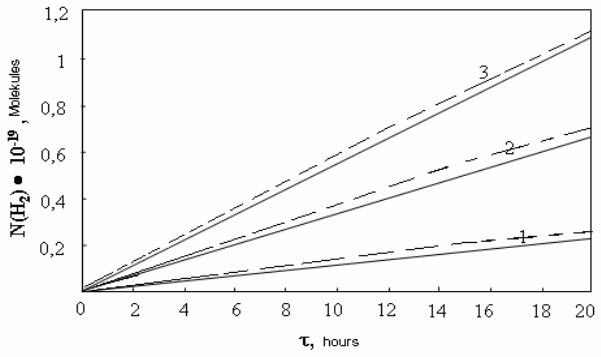

Fig. 5. Kinetics of molecular hydrogen accumulation upon radiolysis of the water-hexane mixture at dose rate of 0,9 Gy/s and of various ratios of the components:
1 – C_6H_{14}/ H_2O=0,05 ml/0,45 ml;
2 – C_6H_{14}/ H_2O=0,15 ml/0,35 ml;
3 – C_6H_{14}/ H_2O=0,25 ml/0,25 ml

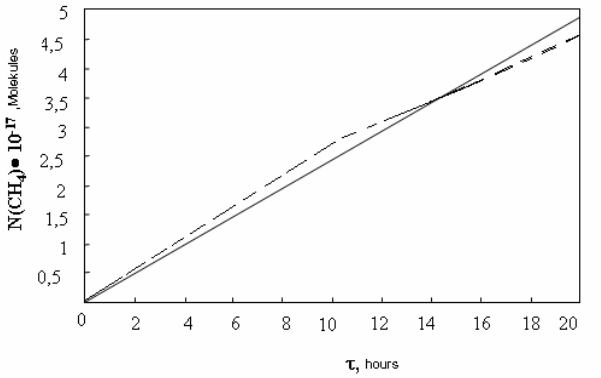

Fig. 6. Kinetics of methane accumulation upon radiolysis of water-hexane mixture at T=300 K and dose rate of 0,9 Gy/s

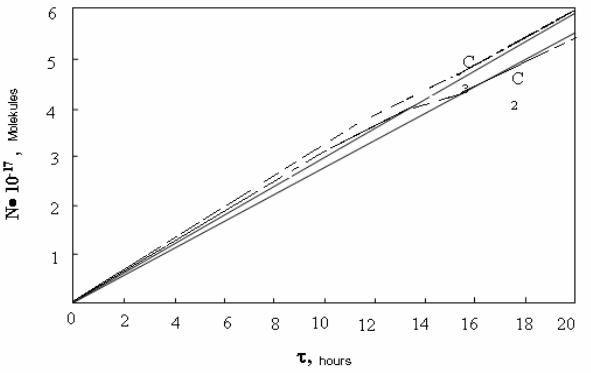

Fig. 7. Kinetics of ethane and propane accumulation upon radiolysis of water-hexane mixture at T=300 K and dose rate of 0,9 Gy/s

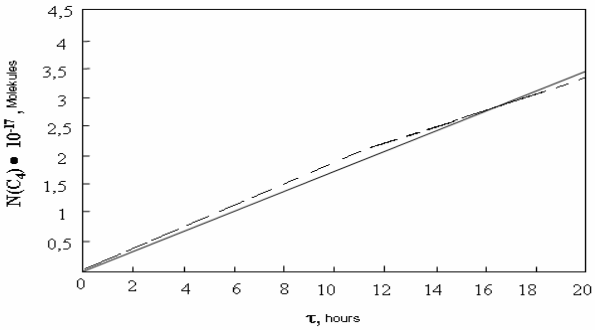

Fig. 8. Kinetics of butane accumulation upon radiolysis of water - hexane mixture at T=300 K and dose rate of 0,9 Gy/s

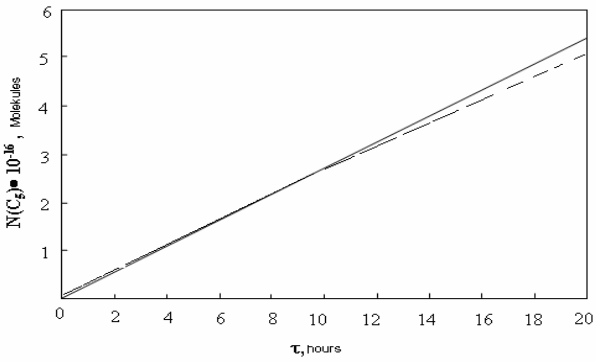

Fig. 9. Kinetics of pentane accumulation upon radiolysis of waterhexane mixture at T=300 K and dose rate of 0,9 Gy/s

Based on these values of rates of particle accumlation W and their yield G have been calculated. The obtained data were compared with the experimental data at the same volume ratio of components, which correspond to dotted lines.

The comparison shows quite a good coincidence of the results that may serve as an evidence of correctness of the assumptions made. The results of modeling of radiolysis of the mixture $C_6H_{14} + H_2O$ dose rate of 0,9 Gy/s is given bellow:

Table 6

Products of radiolysis	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
W ($\times 10^{-14}$), molecules/s	0,7	1,12	1,12	0,56	0,14
G, molecu-es/100 eV	0,13	0,2	0,2	0,1	0,025

Modeling was separately made for kinetics of hydrogen formation upon radiolysis of $C_6H_{14} + H_2O$ mixture of the above-shown percentage ratio of the components at dose rate of 1,42 Gy/s:

Products of radiolysis ..... H_2

W ($\times 10^{-14}$), molecules/s..... 2,8

G, molecules/100 eV 3,3

All of the afore-cited reaction rate constants obtained from data about the stationary radiolysis, and there were taken into an account the presence of a gas volume over the irradiated liquid. Although the radiolysis occurring in the gas phase at room temperature can almost always be neglected, but such products of radiolysis of water as hydrogen and oxygen, depending on the experimental conditions are distributed differently between the phases. In addition, in the presence of initially dissolved hydrogen some reactions may have a chain character and the beginning of the chain is atoms of hydrogen. So, without proper taking into account of this circumstance the final result of radiolysis is quantitatively unpredictable. However, if the irradiated volume is constantly shaking, the distribution of radiolysis gas between the phases become to equilibrium. All these requirements were taken into account when selecting certain constants from different sources.

Thus, the simulation data of water radiolysis coincide with the published data, which confirms the loyalty of chosen methodology. But model data of the radiolysis of hexane and hexane-water mixture coincided with the experimental data within the accuracy of the determination of the rate constant of used reactions.

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МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ ПРОЦЕССОВ РАДИОЛИЗА ВОДЫ, ГЕКСАНА И СМЕСИ ВОДА–ГЕКСАН

Т.Н. Агаев

Проведено математическое моделирование процессов радиолиза воды, гексана и смеси вода–гексан с целью выявления механизма радиолиза и сравнение теоретических данных с экспериментальными.

МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ ПРОЦЕСІВ РАДІОЛІЗУ ВОДИ, ГЕКСАНУ ТА СУМІШІ ВОДА–ГЕКСАН

Т.Н. Агаєв

Проведено математичне моделювання процесів радіолізу, води, гексану та суміші вода–гексан з метою виявлення механізму радіолізу та порівняння теоретичних даних з експериментальними.