19/XII-64

ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E-1851
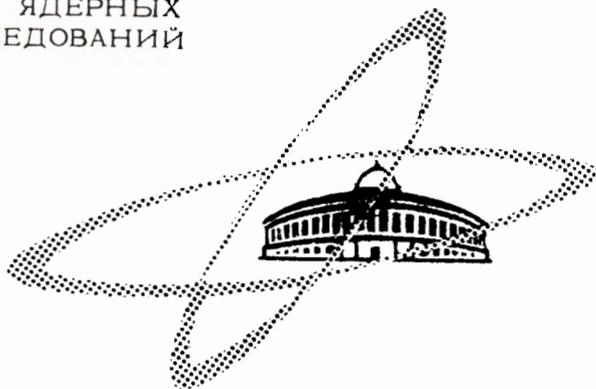
J.Dema and N.G.Zaitseva

THE CHEMICAL STATES OF RADIOIODINE FORMED BY 660 MeV PROTON IRRADIATION OF CAESIUM CHLORIDE CRYSTALS

1964

E-1851

J.Dema[x] and N.G.Zaitseva

THE CHEMICAL STATES OF RADIOIODINE
FORMED BY 660 MeV PROTON IRRADIATION
OF CAESIUM CHLORIDE CRYSTALS

[x] Institute of Atomic Physics, Bucharest, Rumania
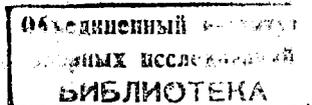
The chemical effects of nuclear transformations have been reported in a series of papers, alkali halides have been mostly used as target materials[1-8]. The detailed investigation of these phenomena is desirable in connection with some relatively insufficiently studied domains of hot-atom chemistry, solid-state chemistry, and radiation chemistry. On the other hand, the foundation of a controlled hot-atom chemistry made it possible to prepare radioisotopes in high specific activity and synthesis of labelled-species.

In spite of a large number of studied systems the attention was focused on the neutral-particle irradiation in the reactions of the type (n, γ), (n,p), (n,α), (γ , n), etc. A considerably smaller number of papers on irradiation by charged particles has been published in literature. The charged particle beam irradiation is a convenient source for obtaining a large diversity of isotopes and give us the possibility of studying the nuclear reactions as (p , xn), (d, xp), (α , xn) , etc. Thus, the basis of the radiochemical methods for the separation of the radioactive elements from the target material is the knowledge of the fact in what chemical states the fragments are after irradiation. It can be also mentioned that a great number of works was performed by low and medium energy bombardments (to 20 MeV) and only recently some experiments dealing with the chemical conse-quences of the high energy bombardments[4,9-11] have been initiated.

Radioiodine atoms are a very interesting object for such investigations, since they have some stable valency states ($Z = -1$; 0; +5; +7) the isotopic exchange of which does not occur at certain experimental conditions. Besides, radioiodine has a series of relatively long lifetime isotopes[12], which is convenient for research.

The chemical behaviour of radioiodine recoils arising from the nuclear trans-formations has been studied[11, 13-15]. In[11] it has been shown the chemical states of radioiodine were formed by bombarding caesium and iodine by high energy protons. These results show that the radioiodine yield in one or another form appear to depend on the chemical composition of target material, on the degassing before bombardment and on the proton beam intensity. Thus, the irradiation by beams of $\phi = 10^{16}$ protons/(m^2. sec), reflected the concomitant influence of two factors: dose and temperature, i.e. irradiation was performed in the internal beam of the synchrocyclotron. In this case the beam heated the target to a temperature of 350-400°C. These observations led to a detailed study of the behaviour of radioiodine with respect to each factor.

It is known that the thermal annealing treatments, as a method for investigat-ing radiation displacements which are induced in the irradiated crystals, are used in a large series of papers[1,16,17] and a first useful consequence is that it may

3

give the possibility to compute the appropriate activation energy of investigated processes. Therefore, one may obtain some information from the energy requirements necessary for the crystal to transit to its initial state as the thermal annealing results in the crystaline-damage changes which can, in the end, entirely disappear.

The purpose of this work is to investigate the influence of the irradiation dose and subsequently thermal-annealing phenomena on the relative yield of the radioiodine in the oxidated and relative reduced states obtained by 660 MeV-proton irradiation of crystaline caesium chloride and nitrate, respectively. The kinetical treatments of the irradiated crystals have permitted to calculate the rate of transition of the radioiodine from higher to lower valency states, activation energy of this process and subsequently the order of the reaction. The obtained results are explained from the standpoint of theories which deal with radiation induced defects in alkali halides.

Experimental Procedure

CsCl and $CsNO_3$ analytical grade materials were used as targets which had undergone a pre-irradiation treatment, i.e. samples were outgassed at about $250^{\circ}C$ and about 10^{-2} mm Hg in small quartz ampules which were irradiated at room temperature in an external 660 MeV proton beam of the synchrocyclotron of the Joint Institute for Nuclear Research.

The non-degassed samples were irradiated in the same manner. The range of proton beam intensity was above 10^{12} to 10^{15} p/(m^2 sec) and was determined with the aid of Al-foils by the yield of ^{24}Na in the nuclear reaction $^{27}Al(p,3pn)^{24}Na$. The samples were irradiated for periods of 10 to 12 hours. The yield of radioiodine in higher oxidation states obtained by irradiation at a certain beam intensity for different periods of time (Table 1) is practically unchanged for periods of time from 8 to 16 hours and come to increase only after longer periods (20 hours).

Table 1

The radioiodine yield in higher oxidation state ($J^{>3+}$) obtained by irradiation of CsCl at a determined dose and at various intervals of time.

Time of irradiation, hours	2	4.5	8	12	16	20
$P_{ox.}$,%	$14.7^{\pm}3.8$	$17.8^{\pm}3.3$	$24.2^{\pm}6.0$	$27.2^{\pm}3.8$	$28.9^{\pm}4.3$	$42.9^{\pm}2.1$

Proton beam intensity = $(2.20^{\pm}0.59).10^{13}$ p/(m^2.sec)

Thermal annealing experiments were conducted at temperatures of 41, 55, 77 and $100^{\circ}C$ in electrical oven with an automatic control of temperature, the temperature variation at a given temperature being about $^{\pm}1^{\circ}C$. The heating of the samples was accomplished in vacuum in quartz ampules. A chromatographic technique was used for the separation of radioiodine valency state products consisting in the chromatographic column with anionit IRA-400 in NO_3^--form and with subsequent radiochemical purification[11,18]. In the end, the radioiodine samples were counted as PdJ_2 using a conventional standard technique. The radioiodine yield in oxidation states (the fraction with $Z > +3$) or in reduced forms (the fraction with $Z \leq +1$) was calculated in percent from total radioiodine specific activity.

Results

The results given in Fig.1 show the radioiodine yield in the oxidation state (P_{ox}, %) at various proton beam intensities obtained by irradiation of the outgassed CsCl with 660 MeV protons. Each point in Fig. 1 and in other Figures represents the arithmetical average of three-six independent determinations, respectively. It may be seen from Fig. 1 that with the increase of irradiation dose from about 10^{12} to about 10^{15} p/(m^2. sec), the yield of radioiodine in higher oxidation state increases and at a relatively higher beam intensity amounts to a saturation value of about 98%.

The results including the thermal annealing experiments are given in Figs. 2,3 and 4, some results are omitted for clarity. The interesting feature of all these experimental curves consists in some paternity, i.e. a reduction process of radioiodine recoils occurs during the heating of irradiated CsCl and $CsNO_3$ crystals, with a rapid initial rise followed by a slowly rising "plateau" characteristic for the given temperature. The dotted line in Fig. 2 shows the yield of radioiodine in irradiated outgassed CsCl preserved at room temperature for about a week. It may be seen that within experimental accuracy no reduction or oxidation process was observed.

Fig. 5 and 6 illustrate the kinetical curves of isothermal annealing experiments of outgassed CsCl irradiated at different beam intensities and in Fig. 7 is plotted the rate of the radioiodine-reduction process $\Delta P_{ox} = P_o - P_\infty$ (%) against the beam intensity (ϕ), where P_o means the initial distribution in higher oxidation state for each sample, and P_∞ – the pseudo-equilibrium values obtained from annealing curves at 77 and $100^{\circ}C$, respectively.

It may be seen that the rate of transition of radioiodine from a higher valency state to a lower one, i.e. reduction process increases for outgassed CsCl with the increasing of radiation dose.

4

5

The results obtained by thermal annealing of outgassed CsCl are plotted in Fig. 2 in a similar manner as in identical works, i.e. a plot of log $(P_t - P_\infty)_{ox}$ against time of heating was given for the temperature of 41, 55, 77 and $100^\circ C$, respectively, where P_t means the percent distribution of the radioiodine in higher valency state at various times of heating. For the fast process (to 6 hours of annealing) linear plots were obtained and from the slopes of individual straight lines the half-times ($T\frac{1}{2}$) and the reaction rate-constants ($K = \frac{0.693}{T\frac{1}{2}}$) were computed (Table II). From the plot of log K versus $1/T$, by the Arrhenius equation, an apparent activation energy may be calculated which is, within experimental accuracy, in the range of 0.15 to 0.35 eV.

Table II

The half-times and the reaction rate-constants for the radioiodine reduction process of thermal annealed outgassed CsCl

Temperature $^\circ C$	P_0 (ox) %	P_∞ (ox) %	$\Delta P = P_0 - P_\infty$	$T\frac{1}{2}$ ksec	K sec^{-1}
41	37.5	26.5	11.0	9.60	$7.22 \cdot 10^{-5}$
55	37.5	11.9	25.6	7.20	$9.62 \cdot 10^{-5}$
77	37.5	4.5	33.0	5.10	$1.35 \cdot 10^{-4}$
100	37.5	1.5	36.0	1.14	$5.70 \cdot 10^{-4}$

$$\phi = 4.2 \cdot 10^{13} p/(m^2 \cdot sec)$$

In order to determine the nature of the fast annealing process, the fraction of the radioiodine-recoils annealed $\Delta P = P_0 - P_t$, was plotted against the logarithm of time of heating (Fig.8). After Fletcher and Brown[1,16,19] by adjusting the time-scale by appropriate factors (ν) an equivalent annealing curve for $77^\circ C$ was composed (Fig.9). By plotting the multiplicating factors, used for obtaining the composite annealing curve of Fig.8, against $1/T$ an activation energy of 0.68 eV was obtained. This value is in disagreement with those obtained by Arrhenius"s method. Thus the opportunity to make other calculations of activation energy appeared which are employed in similar works. An attempt was made to calculate the distribution of activation energy for the annealing process by the method of Vand- Primak [1,20,21]. The distribution of activation energy thus calculated for the radioiodine reduction process by thermal annealing of irradiated outgassed CsCl is given in Fig. 10. It may be seen that the majority of activation energies of the annealing processes are distributed between 0.70 and 0.90 eV, i.e. there is not a large range. By the method of Parkins-Dienes[22] we obtained the values between 0.61 and 1.16 eV. These are in the vicinity of the value obtained by Fletcher-Brown's analysis.

Discussion

In accordance with earlier papers[23,24] the very high energy bombardments of alkali halides produce a high degree of electronic excitation (ionization effects) and lead to an extensive damage in crystal lattices (displacement effects). At very high energy the radiation effects produced by the secondary nucleons with energy of about 10-50 MeV originating in inelastic collisions are more important than those produced directly by elastic collisions of incident primaries. The chemical states in which an atom produced by a nuclear transformation in a solid is stabilized in crystaline lattice may depend on the loss of electrons during the initial nuclear event, loss or capture of electrons during the recoil through the lattice. These states may also be dependent on the chemical reactions undergone by the recoils with lattice ions or in terminal "hot zone".

The results illustrated in Fig. 1 and Table 1 showing the change in the radioiodine yield in higher oxidation states, by irradiation of outgassed CsCl, with the increase in the proton beam intensity, may be explained by Varley's multiple ionization mechanism[23]. This mechanism provides, by irradiation of alkali halides with high energy protons, the formation of the lattice defects as F-type centres represented by the electrons trapped at the chlorine vacancies and V-type centres which may be represented by the chlorine atoms trapped in some lattice defect sites.

The increase of radioiodine yield in higher oxidation state with the increasing irradiation-dose (proton beam intensity or time of irradiation) shown in Fig. 1 and Table I, can be explained if one assumes that there exists an interaction between the radioiodine recoils and the lattice defects as V-type centres, i.e. chlorine atoms. Thus, the radioiodine recoils could gain a progressively higher oxidation state. It was pointed out, that the concentration of V-centres and free chlorine in alkali halides increases with the increase in the irradiation dose[25,26] that is the corresponding increase in the radioiodine oxidation forms with the increasing proton beam intensity which are observed in our experiments. The mutual interaction between the radioiodine recoils and V-centres takes place probably as in crystaline lattice as well as by dissolution processes of the irradiated crystals. This assumption on interaction between the radioiodine fragments

and lattice defects is made according to the results shown in Fig.1, which may be fitted with reasonable accuracy by an expression giving the relation between the total number of damage in a solid and the total number of the incident particles[27,28]. Assuming that the yield of radioiodine atoms in the higher oxidation state (P_{ox}) is proportional to the number of defects of a particular type, one could obtain the following expression for the plot P against ϕ :

$$P = P_{max}(1 - e^{- \phi/10^{n}}) , \qquad (1)$$

where P_{max} is the maximum percentage of radioiodine in higher oxidation state, and n is the index. This equation within the experimental accuracy describes the experimental results illustrated in Fig.1. The dotted curve corresponds to $P_{max} = 98.0\%$ and n = 14.

The thermal annealing results of the irradiated caesium salts shown in Fig. 2-6 predict for a similar process of radioiodine reduction (an initial fast process, and subsequently the lower reduction study with corresponding pseudo-plateu) which do not depend on the presence of lattice oxigen or traces of hygroscopical water and on the dose of irradiation. These factors affect only the rate of the radioiodine transition from the higher oxidation states to lower ones.

Thus by thermal annealing of non-outgassed CsCl and deaerated $CsNO_3$, the radioiodine-reduction process becomes lower (Fig. 4) than by annealing the outgassed samples (Fig.2, temperature 77° C). In the non-degassed CsCl a relative complete reduction is obtained for the period of about 140 hours, in $CsNO_3$ probably for a relatively longer time. The similar results have been reported in other works[27,30] where a marked difference in the thermal annealing experiments with the aerated and non-degassed alkali halides also was not observed. This allows us to assume that a lattice-defect mechanisms are acting by heating the irradiated samples[1,31]. The difference in the radioiodine reduction-rates observed in the samples having different pre-irradiation history (Fig.2,4) or in samples irradiated under different doses (Fig.5) can be explained by a mechanism of the above type in which the lattice defect concentration responsible for the radioiodine transition to lower valency states, changes with the experimental conditions. On the other hand, a satisfactorily linear relationship has been observed between the change in radioiodine yield on annealing to the onset of the slow process of the experimental curves of Fig.2, plotted against $1/T$[1,31].

It can be supposed that the radioiodine-reduction process observed by heating the irradiated CsCl is governed by trapped electrons of F-centres[26,32] which by "thermal bleaching" could be captured by positive holes or by radioiodine-fragments. It is known that by heating the coloured alkaline halides crystals the colour centers are gradually bleached. In our experiments after proton irradiations the CsCl samples reached an intensive-blue colour and $CsNO_3$ samples- a dark-brown colour, by thermal annealing a gradual bleaching of crystals was observed, the bleaching was complete for all samples heated at 200° C for 2 hours. In Süe and Caillat "s experiments there was observed a similar effect by heating the neutron irradiated crystals of LiCl, NaCl, KCl[6].

For the putgassed CsCl samples the decrease of the radioiodine yield in higher oxidation states by thermal annealing occurs at different rates characteristic for each temperature (Fig.2,3) and the higher the heating temperature, the faster the reduction process. Thus, at 200° C the reduction process reached a saturation value in about 20 minutes (Fig.3).

The difference in reduction yields in irradiated CsCl at different temperatures (Fig.2) can be due probably to various stabilities of colour centres[33].

On the basis of the results illustrated in Fig. 9 it may be supposed that the fast annealing process involves kinetics of the first order. The composite annealing curve can be approximated by an unimolecular expression:

$$P = P_{max}(1 - e^{-kt}) \qquad (2)$$

where t is the annealing time $P_{max}=36.0$ and $k =1/9.10^{3}$. Other arguments are straight lines obtained for the fast annealing process by plotting log. $(P_0 - P_t)$ against $1/T$ for a fixed period of isothermal-annealing and the plot of $\ln t$ against $1/T$ for a given degree of annealing. By plotting $dP/dt =kP^{\gamma}$ one obtains also the straight lines for the fast process that means a formally unimolecular process, i.e. $\gamma = 1$.

The calculations for the activation energy of reduction process in CsCl and Vand-Primak"s distributions of activation energy give the values within 0.60-1.16 eV, near the binding energies of the electron in F- type centres in alkali halides (0.84-1.0 eV)[34]. This can support our assumption that the F-type centres serve as a reducing agent for radioiodine recoils.

SUMMARY

1. It is shown that the irradiation dose and subsequent thermal annealing affect the chemical forms of radioiodine obtained by 660 MeV-proton irradiation of caesium chloride and caesium nitrate crystals.

2. On the basis of kinetical investigations of the fast thermal annealing process the rate of radioiodine transition from a higher oxidation state to a lower one was calculated, as well as the corresponding activation energy of the reduction process and the order of reaction.

3. It is suggested that in the fate of radioiodine-recoils the mechanisms involving the interactions between radioiodine fragments and lattice defects of the irradiated crystals are of great importance.

References

1. G.Harbottle, N.Sutin, Advances in Inorganic Chemistry and Radiochemistry, 1, 267, Acad. Press. Inc. New York (1959)

2. A.G.Maddock, R.M.Pearson. Proc. Chem.Soc., Aug. 275, (1962).

3. T.A.Carlson, W.S.Koski, J. Chem. Phys. 23, 9, 1596 (1955).

4. R.H.Herber, Proc. Symp. Chemical Effects of Nuclear Transformations, 2, 201. IAEA, Vienna (1961).

5. A.H.W.Aten, Phys. Rev., 71, 9, 641 (1947).

6. P.Süe, R.Caillat, C.R.Acad. Sci., 230, 1666, 1864 (1950).

7. J.S.Butterworth, I.G.Campbell, Trans. Faraday Soc., 59, 11, 2618 (1963).

8. A.Adams, I.G.Campbell, Trans. Faraday Soc., 59, 9, 2001 (1963).

9. S.R.Veljkovic, G.Harbottle, J.Inorg. Nuclear Chem., 24, Dec. 1517 (1962).

10. A.N.Murin, S.N.Banasevich, R.V.Bogdanov, Proc. Symp. Chemical Effects of Nuclear Transformations, 2, 191, IAEA, Vienna (1961).

11. Н.Г.Зайцева, Ло Вэн-чжун, Радиохимия 2,5, 614 (1960).

12. D.Strominger, M.Hollander, G.T.Seaborg, Rev. Mod. Phys., 30, 2, 806 (1958).

13. A.H.W.Aten, G.K.Koch, G.A.Wesselink, A.M.de Roos, J.Am.Chem.Soc., 79, 1,63 (1957).

14. R.E.Cleary, W.H.Hamill, R.R.Williams, J.Am.Chem.Soc., 74, 18, 4675 (1952).

15. G.N.Walton, B.Bowles, I.F.Croall., Proc. Int. Conf. PUAE, 1955,7, 155, UN New York (1956).

16. F.P.Clarke, Disc. Faraday Soc., 23, 2, 141 (1957).

17. Т. Костя, И.Дема, К. Мэнтеску, Rev. Phys. (Roumanie), 8, 1, 59 (1963).

18. M.L.Good. M.B.Purdy, T.Hoering, J.Inorg. Nuclear Chem., 6, 1, 73 (1958).

19. R.C.Fletcher, W.L.Brown, Phys. Rev., 92, 3, 585 (1953).

20. V.Vand, Proc. Phys. Soc., 55, 3, 222 (1943).

21. W.Primak, Phys. Rev., 100, 6, 1677 (1955).

22. W.E.Parkins, G.J.Dienes, F.W.Brown, J.Appl. Phys., 22,8,1012 (1951).

23. Д.Варли, Центры окраски, 305, ИЛ, Москва (1958).

24. R.Smoluchowsky, Proc. Int. Conf. PUAE, 1955, 7, 676, UN New York (1956).

25. J.Z.Damm, Proc. Symp. Radiation Damage in Solids and Reactor Materials, 3, 163 , IAEA, Vienna, (1963).

26. W.G.Burns, T.F.Williams, Nature, 175, 4467, 1043 (1955).

27. F.Seitz, J.S.Koehler, Proc. Int. Conf., PUAE, 1955, 7, 615, UN New York (1956).

28. J.W.Marx, H.S.Cooper, J.W.Henderson, Phys. Rev., 88, 1, 106 (1952).

29. U.Croatto, A.G.Maddock, Nature, 164, 4171, 613 (1949).

30. J.Cifka, J.Inorg. Nuclear. Chem., 26, 5, 683 (1964).

31. A.G.Maddock, M.M. de Maine, Can, J. Chem., 34, 275 (1956).

32. P.Avakian, A.Smakula, Phys. Rev., 120, 6, 2007 (1960).

33. W.D.Lynch, Phys. Rev., 127, 5, 1537 (1962).

34. R.Casler, P.Pringsheim, P.Yuster, J.Chem. Phys., 18, 6, 887 (1950).
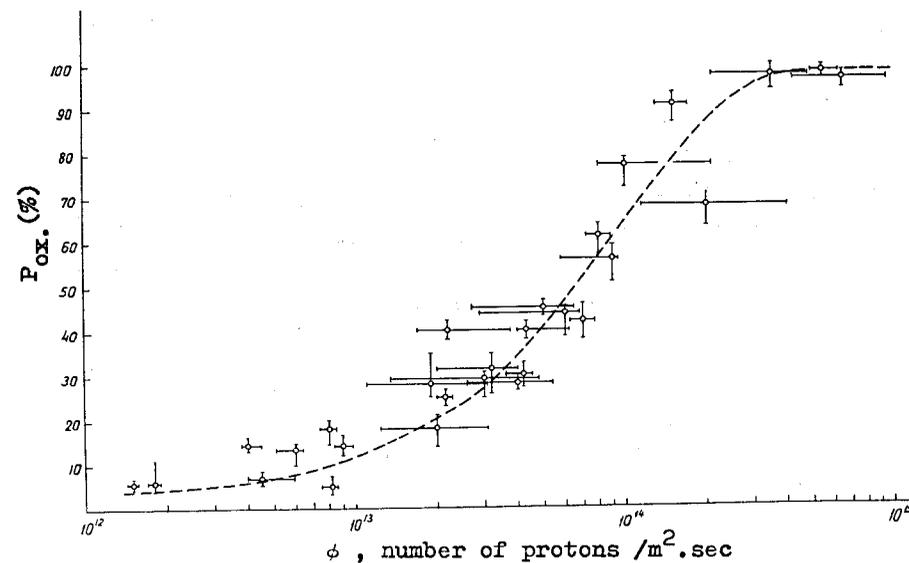
Fig. 1. Effect of proton beam intensity on the radioiodine yield in higher valency state in the outgassed irradiated CsCl.

ϕ , number of protons /m^2.sec

$P_{ox.}$ (%)
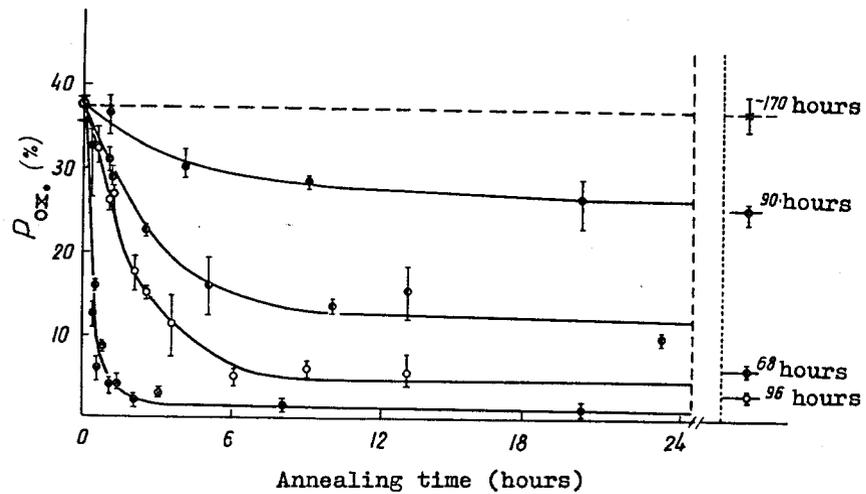
Fig. 2. Effect of thermal annealing of outgassed CsCl targets on the yield of radioiodine present in higher valency forms:

x – the room temperature (≈ 23° C)

● 41°C;   ◐ 55° C;   ○ 77° C, ◉ 100° C.
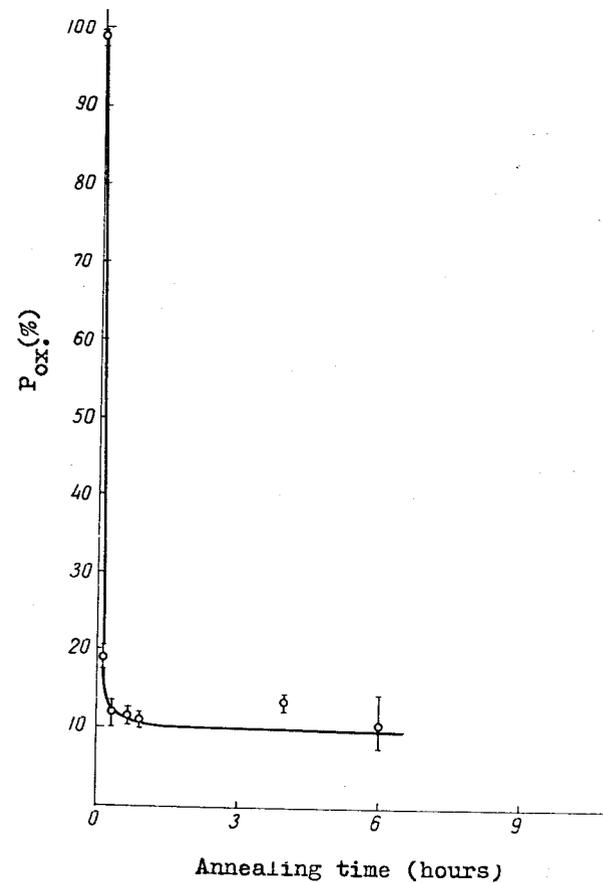
Fig. 3. Effect of thermal annealing of outgassed CsCl crystals on the yield of radioiodine in higher valency state at 200° C.
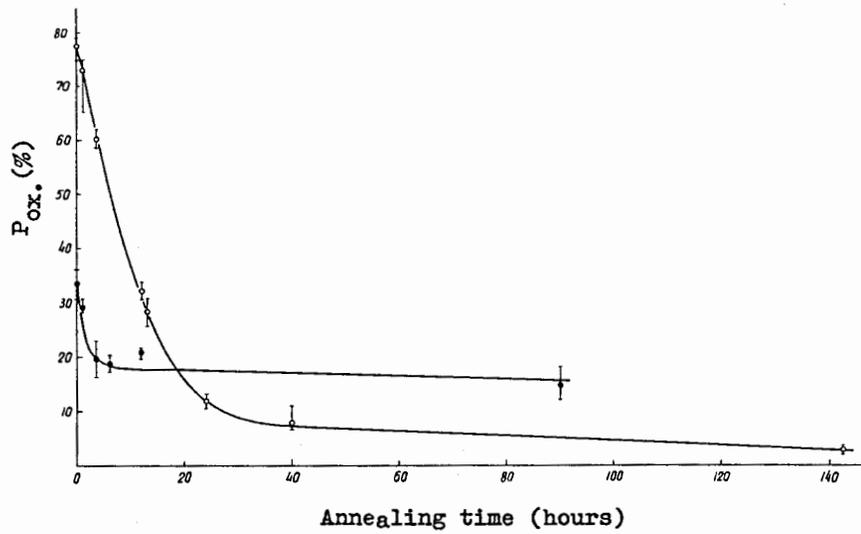
Fig.4. Effect of thermal annealing of outgassed CsCl crystals on the yield of radioiodine in higher valency state at 77° C.

o – non-degassed CsCl; $\phi = 6.0.10^{14}$ p/(m^2.sec)

● – outgassed $CsNO_3$; $\phi = 4.7.10^{14}$ p/(m^2.sec)
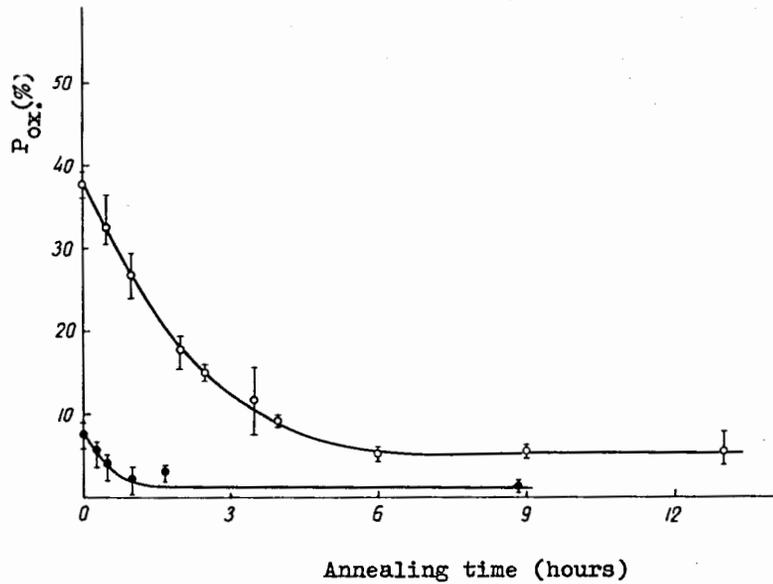
Fig. 5. Effect of the thermal annealing of outgassed CsCl crystals, irradiated at various doses, on the radioiodine yield in higher valency state at 77° C:

o $\phi = 4.2.10^{13}$ p/(m^2.sec)

● $\phi = 7.0.10^{12}$ p/(m^2.sec)

14
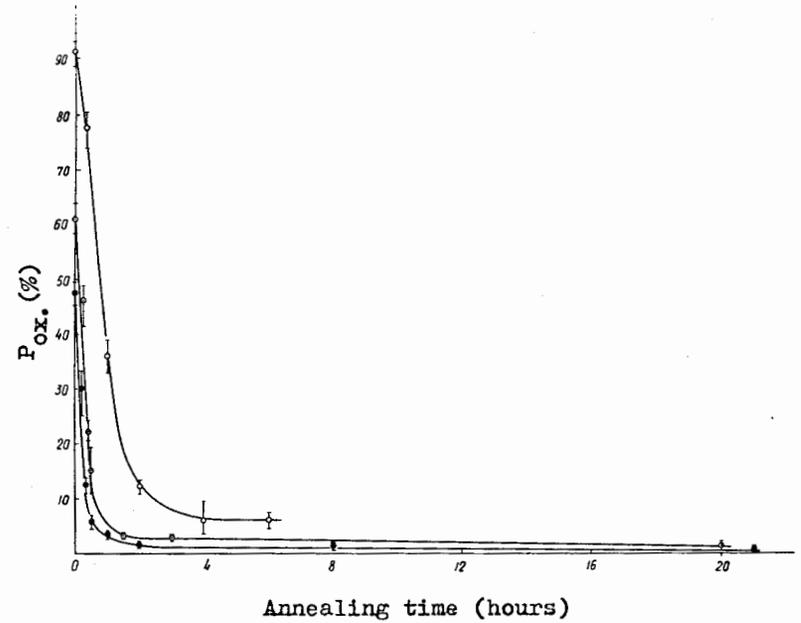
Fig. 6. Effect of the thermal annealing of outgassed CsCl crystals, irradiated at various doses, on the radioiodine yield in higher valency state at 100° C.

o $\phi = 1.1.10^{14}$ p/(m^2.sec)

◉ $\phi = 7.8.10^{13}$ p/(m^2.sec)

● $\phi = 4.8.10^{13}$ p/(m^2.sec)

15
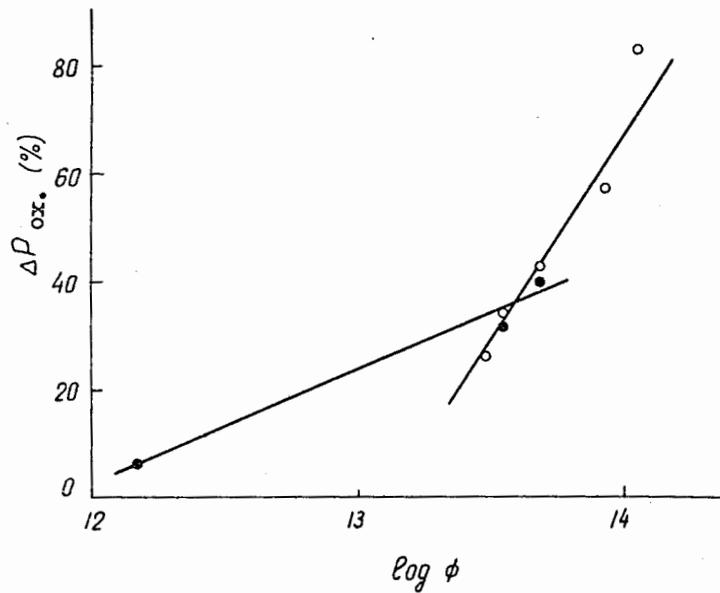
Fig.7. The rate of radioiodine reduction (ΔP) in outgassed CsCl as a function of dose of radiation:

● 77° C,   ○ 100° C.
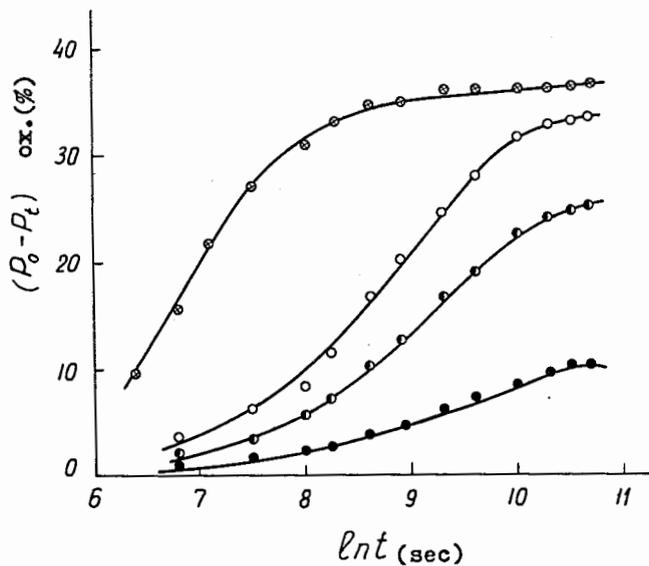
Fig.8.   Isothermal annealing curves for outgassed CsCl:

○ 41° C;   ● 55° C,   ○ 77° C;   ● 100° C.
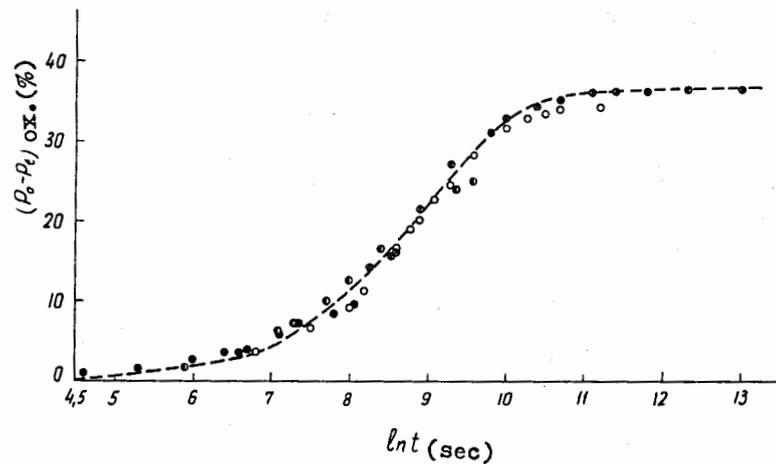
Fig.9. The composite annealing curve obtained by adjusting the time scales by appropriate factors (ν) for superposition of the curve of Fig.8 with respect to the curve at 77° C. The theoretical curve is shown by the dotted curve. The values of ν : -2.2(41°C); -0.9(55° C); +1.8(100° C). ● 41° C; ● 55° C; ○ 77° C; ● 100°C .
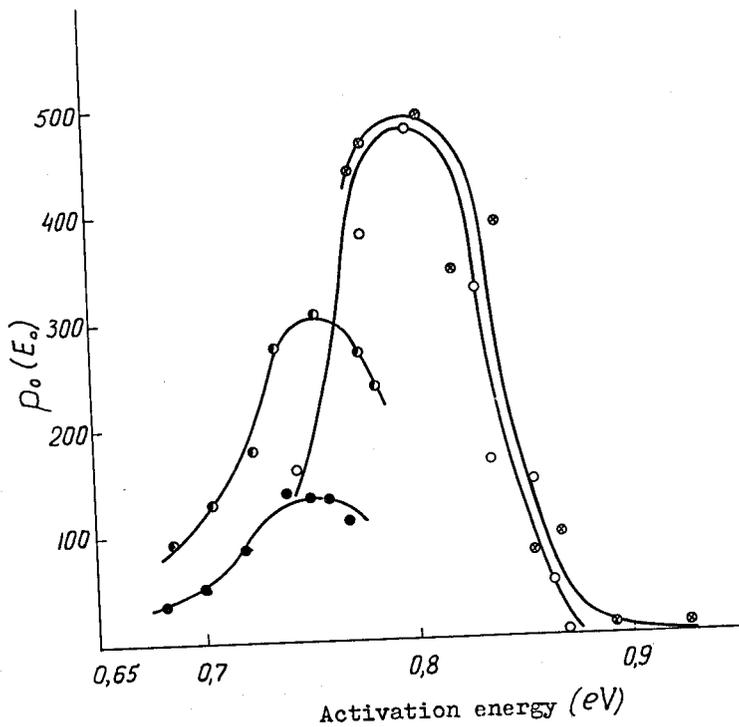
Fig. 10. Vand–Primak distribution of activation energy of radioiodine reduction process by thermal annealing of outgassed CsCl ($B = 10^8$ sec^{-1}):
● 41° C; ◑ 55° C; ○ 77° C; ⊗ 100° C.