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E. P. Shabalin

PROBABILISTIC MODEL OF SPONTANEOUS RELEASE OF ACCUMULATED ENERGY IN IRRADIATED ICES

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Шабалин Е. П. E12-2004-75

Вероятностная модель явления спонтанного выделения энергии в облучаемых льдах

Формируются условия для начала быстрой цепной реакции рекомбинации радикалов в твердом метане и водяном льду, подвергаемых облучению. На основе предложенной автором гипотезы о вероятностном характере данного явления выводится соотношение для среднего времени ожидания начала процесса. С помощью экспериментальных данных оцениваются пределы значений параметров этого соотношения.

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Probabilistic Model of Spontaneous Release of Accumulated Energy in Irradiated Ices

Conditions for ignition of fast chain process of recombination of radicals in solid methane and water ice under irradiation are formulated. Based on the hypothesis of probabilistic character of the phenomenon, proposed by the author, the relation for the mean expectation time of the ignition of the process is derived. By invoking experimental facts, the limits of values of parametres, which may be used in the relation, are estimated.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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INTRODUCTION

Cases of spontaneous release of energy («burp») were observed numerously in solid methane, water ice and other hydrogenous compounds irradiated in fast neutron fields with absorbed dose 2–10 MGy [1–7]. Nature of this phenomenon is that accumulation of radicals and thermal instability of a sample under due concentration of radicals culminate in autocatalytic reaction of their recombination. The phenomenon exhibits some strange regularities, the most odious of which is that irradiation time, before a spontaneous burp (SB) occurs, varies significantly even in identical irradiation conditions. Respectively, amount of released energy varies as well. For example, in URAM-2 experiments [5–7] with water ice, before appearance of spontaneous burp, irradiation time varied from 5 to 11 h for equal samples and up to 20 h for the smallest sample. Several theories of spontaneous chemical reaction including recombination of radicals are known — namely, Semenov's and Frank-Kamenetski's conditions of thermal instability of a sample as a whole [8], Jackson's relation for chain process of recombination of uniformly distributed radicals [9], critical condition for local ignition [10], critical condition for irregular distribution of radicals proposed by the author of this article [4, 10, 11], etc. But none of these theories predicts casual character of a burp on macroscale basis.

The suggested probabilistic model helps to understand the reason for the strange behavior of spontaneous burping.

1. CONCEPTION OF THE MODEL

A basis of this model was outlined in previous papers of the author [11, 12]. It was stated that a key to understand features of fast spontaneous reaction of recombination of radicals is in taking into account irregularities in space distribution of radicals and in deposited energy. Radicals are generated in the tracks of recoil protons, and therefore, they are arranged mainly in lines or in spurs. Because diffusion of radicals at low temperatures (10–30 K) is too slow to get them away from their origins, we come to the conclusion about nonuniform distribution of radicals and their concentration in clusters. Beside their original distribution due to tracks formation, clusters of radicals may occupy structure defect sites as well. Structure defects can be caused by radiation or generated in the course of freezing of a sample. Two-dimensional computer simulation of proton track distribution revealed high dispersion of concentration of radicals on a small-scale base: three-fourfold increase in local density of radicals as compared to the density averaged over a sample [11]. As rate of recombination reaction is square proportional to density of radicals, such an increase in local density of radicals may lead to initiation of autocatalytic reaction in this local area of high density of radicals. Therefore, clustered structure of distribution of radicals decreases critical density of radicals as compared to those determined by thermal instability of a sample.

This paper gives a more detailed insight into the model and some consequences of its application. It explains why SB has a stochastic character.

Into the basis of the model we have put three qualitative conditions for SB appearance, which are necessary and sufficient:

1. In a sample under irradiation, there are clusters of radicals highly enriched with radicals occupying a tiny region of definite size (let us call such clusters «burnable»). Both density of radicals and size of the clusters are big enough that any perturbation («ignition») inside the cluster actuates recombination of all the radicals inside the cluster and, besides, an amount of heat released in the burnable cluster can trigger a process of propagation of recombination reaction beyond the cluster.

2. The second condition is appearance of a source of ignition, a kind of «detonator», «match», which stimulates recombination in the burnable cluster.

3. Finally, space-averaged density of radicals over the sample, size of the sample, and cooling condition are those which can sustain propagation of recombination reaction through the sample, either in the form of a wave of recombination or in the form of soliton-like temperature spikes. In this phase of the process, recombination is, most probably, stimulated by thermoplastic deformation of the matrix [13, 14].

The last condition is widely used in literature of chemical kinetics and suffice it to say that in the cases of the current interest (solid methane at 20–30 K, water ice at 20–40 K, used as cold neutron moderators) this condition is necessary but not enough to start the SB process. Therefore, the first two conditions are significant to study.

2. ANALYSIS

2.1. General Approach. Let us denote density of radicals in a «burnable» cluster by n_0, averaged volume of a burnable cluster by V_0, volume of a sample by V, space-averaged density of radicals over the sample by $\tilde{n}$. Then, number of burnable cluster concurrently existing in the sample at the instant t may be expressed in the form

$$N(t) = p(n_0, V_0, \tilde{n}, t)(V/V_0), \tag{1}$$

where function $p(n_0, V_0, \tilde{n}, t)$ is probability that volume V_0 chosen at random appears to be a burnable cluster. Of course n_0 and V_0 are, to some extent, not strictly defined, though they are bounded in definite ranges of values. We imply that n_0 and V_0 are equal to averaged values in the ranges. If «lifetime» of a burnable cluster is denoted by τ_s, then probability of SB appearance in a unit time is

$$P = p(n_0, V_0, \tilde{n}, t)(V/V_0)/\tau_s, \tag{2}$$

and mean expectation time of burping at the instant t is

$$T_{\mathrm{SB}} = 1/P = V_0\tau_s/p(n_0, V_0, \tilde{n}, t)/V. \tag{3}$$

It is most probable to assume that burnable clusters are ignited with a hot track of proton or, which is more probable, with some superimposed tracks. Then, the «lifetime» of a burnable cluster τ_s can be expressed as

$$\tau_s \sim 1/(V_0\check{D}),$$

where $\check{D}$ is the absorbed dose rate. Now, a mean expectation time of burping at the instant t appears to be

$$T_{\mathrm{SB}} \sim 1/p(n_0, V_0, \tilde{n}, t)/(V\check{D}). \tag{3a}$$

It is important: even this quite general relation with uncertain parameters n_0, V_0 says definitely that *appearance of SB is inversely proportional to volume of a sample*, not characteristic size or geometry of a sample, as it is for thermal instability conditions. However, it is clear that characteristic size and geometry of a sample play an important part in the third condition of SB formulated above. Appearance of SB is also *inversely proportional to the rate of absorbed dose.*

2.2. Gauss Approximation. Now we'll try to specify parameters in (3a).

Let us suggest that density of radicals n in volume V_0 chosen at random is distributed by Gaussian; after normalization we have

$$p(n, V_0, \tilde{n}, t) = 1/(V_0\tilde{n}\sqrt{2\pi}\sigma)\,\exp\left(-(n/\tilde{n}-1)^2/2\sigma^2\right). \tag{4}$$

The σ-quantity is a dimensionless mean square deviation. Value of n_0 can be evaluated from Jackson's condition for uniform distribution of radicals:

$$n_{\mathrm{crit}}^2 = \frac{0.62C_m(T_{\mathrm{act}} - T_0)}{xQ}, \tag{5}$$

where x is the number of the nearest radical trap sites plus one (for the methane matrix, x is 13); $C_m = c_pM$ is the molar specific heat; Q is the heat of recombination per mole; T_0 is the irradiation temperature, and $n_{\mathrm{crit}} \equiv n_0$. Jackson did not apply the Arrhenius law to the recombination rate, but only considered that a trapped radical is freed if $T \geqslant T_{\text{act}}$, and the free radical reacts at once with its neighbor if there is at least one.

Its estimate lays between 3 and 4 mol % for solid methane. Now, the mean expectation time of burping at the instant t may be expressed through only one unknown parameter σ, not including dimensional factors T_0, $\check{D}_0$, and V_0:

$$T_{\text{SB}} = (T_0 \check{D}_0 V_0)\tilde{n}\sigma \, \exp\left((n_0/\tilde{n} - 1)^2/2\sigma^2\right)/(V\check{D}) = \\ = C\tilde{n}\sigma \, \exp\left((n_0/\tilde{n} - 1)^2/2\sigma^2\right)/(V\check{d}). \quad (6)$$

Time dependence of T_{SB} is hidden in $\tilde{n}$. Factor C seems to be independent of size and geometry of a sample under irradiation, and on time of irradiation, except temperature: $C = f(T_{\text{irr}})$. Thus, we have an opportunity to make estimation of both σ-value and C-factor by comparing experimental values of mean expectation time of burping for different $\tilde{n}$.

2.3. Estimation of Parameters C and σ in (6).

2.3.1. Mean Square Deviation of Density of Radicals. First, it is required of the σ-value that the mean expectation time of burping T_{SB} is rather weakly dependent on $\tilde{n}$, at least, in the range of $\tilde{n}$ typical for SB, that is, 0.5–0.8% for solid methane and 0.7–1.5% for water ice [4, 6, 7, 12]. Otherwise, no (or only small) dispersion of time of SB appearance would be observed in URAM-2 experiments. Really, SB in solid methane sample of URAM-2 experiments occurred once after 10 h of irradiation but no burp occurred in three longer irradiations up to 26 h. Dispersion of time to SB for water ice has similar character as has already been said in the introduction.

Now, based on this requirement, it becomes possible to select value of σ. Thus, mean expectation time of burping is proportional to the complex

$$F(\tilde{n}, \sigma, n_0) = \tilde{n}\sigma \, \exp\left((n_0/\tilde{n} - 1)^2/2\sigma\right)^2. \quad (7)$$

Calculated values of this complex, i.e., relative value of the mean expectation time of burping for a given sample, as function of $\tilde{n}$ for $n_0 = 3\%$ and for some values of σ, are in Table 1.

Spontaneous burps in water ice occurred in samples of 2.5–3 g mostly at $\tilde{n}$ between 0.7–1% after 8.4 h in the average, and one time — at 1.7–1.8% after 19 h for a small sample of 0.4 g. Having in mind that time of appearance of SB is inversely proportional to volume of a sample, it is easy to conclude that values of σ^2 from 2 to 3 satisfy almost equally experimental data for ice. As for the solid methane case, there is only one way to check which value of σ is most adequate, namely, to compare situation at URAM-2 and IPNS solid methane moderators [15]. In URAM-2 there was one SB at $\tilde{n} \sim 0.8\%$ after about 300 g-hours of total irradiation («g-hours» means a product of irradiation time by mass of a sample) whereas IPNS moderators suffered from SB each 24–28 h

Table 1. Relative value of a mean expectation time of burping; see the relation (7)

σ^2	$\tilde{n} = 0.4\,\%$	$\tilde{n} = 0.5\,\%$	0.6 %	0.75 %	1.0 %	1.25 %	1.5 %
1	—	$1.34\ 10^5$	1788	67.5	7.39	3.33	2.47
1.5	—	2547	152	18.4	4.65	2.94	2.56
2	—	296	45	10.0	3.85	2.88	2.73
2.5	—	114	23.2	7.18	3.51	2.93	2.89
3	792	55.9	15	5.8	3.37	3.00	3.07
4	157	22.7	8.87	4.62	3.3	3.19	3.40

at $\tilde{n} \sim 0.5-0.6\%$. Bearing in mind that space-averaged density of radicals for some time during initial period of each irradiation run is lower than limit for propagation of recombination wave through a sample ($\sim 0.4\%$ for methane and $\sim 0.6\%$ for ice of water), one needs to subtract this time from total time in order to receive expectation time of burping. After this operation we have about 150–200 g-hours for URAM-2 and 300–1000 g-hours for IPNS (ratio of mass of methane in URAM-2 to that of IPNS is about 1:100 and dose rate ratio is 5:1). Having relation (6) and Table 1, one may conclude that σ^2-value should be closer to 4 to have the best fit for all experimental data.

It is interesting to note that $\sigma^2 \sim 3 \div 4$ was estimated by computer simulation of recoil proton tracks in 2D-geometry for radical distribution in the region of $\sim 10^{-5}$ cm [11]. With the same computer code, results of PC simulation for probability of propagation of fast process of recombination beyond the cluster of radicals of 10^{-4} cm were returned. Values, which are inversely proportional to this evaluated probability, are placed in Table 2. Comparing the tables, it is easy to see that analytically evaluated variations of expectation time of burping with space-averaged density of radicals (Table 1, $\sigma^2 \approx 3-4$) is close to that for PC simulation in 2D-geometry, Table 2, third row.

Table 2. Probability of propagation of fast process of recombination beyond the cluster enriched with radicals, p, and its inverse value; computer simulation

Mean density of radicals →	$\tilde{n} = 0.4\%$	0.5%	0.6%	0.7%	0.8%
p	0.01	0.04	0.18	0.4	0.65
$1/p$	100	25	5.55	2.5	1.54

2.3.2. Evaluation of Factor C. Factor $C(T)$ for solid methane can be estimated also from experimental data of IPNS and URAM-2 project. Reciprocally compatible value of $C(T)$ was received to be between 300–600 $\mathrm{cm^3hW/g}$ at $T = 20{-}22$ K. Temperature dependence is very small in the range $20{-}26$ K. For water ice, factor $C(T)$ appeared to be much less: 7.5–15 at $T = 20{-}25$ K. This fact is almost evident: due to a very low heat capacity of ice (about 1/150 of heat capacity of methane at 30 K [16]) both parameters n_0 and V_0 are, most probably, less than those of methane.

Weak dependence of probability of propagation of fast process of recombination beyond the burnable cluster of radicals on temperature of irradiation was checked by PC simulation in 2D-geometry. In Table 3 the probability of propagation of fast process of recombination (in solid methane) is shown versus temperature of irradiation for the given space-averaged density of radicals $\tilde{n} = 0.7\%$.

Table 3. Probability of propagation of fast process of recombination (in solid methane) versus temperature of irradiation for the given space-averaged density of radicals 0.7 mol %; computer simulation

Temperature, K	20	22	24	25
Probability	0.23	0.40	0.63	0.72

2.4. Result. Finally, expression for the mean expectation time of burping at the instant t may be expressed as

$$T_{\mathrm{SB}} = C(T_{\mathrm{irr}})\tilde{n}(t)\sigma \, \exp\left((n_0/\tilde{n} - 1)^2/2\sigma^2\right)/(V\check{D}), \tag{8}$$

where $C(T_{\mathrm{irr}})$ is a factor depending on material of a moderator (strong dependence) and temperature of irradiation (weak dependence); $\tilde{n}(t)$ is space-averaged density of radicals (mol. part); σ is dimensionless mean square deviation of density of radical inside some small volume V_0 whose size is not presented in an explicit form in (8); n_0 is the critical density of radicals uniformly distributed in small limited volume (evaluated, for example, by Jackson's relation), and V and $\check{D}$ are volume of the sample and absorbed dose rate, respectively.

It should be borne in mind, according to the three conditions for SB stated in the beginning, that total expectation time of SB is a sum of two values: T_{SB} by (8) and time T_0 needed to accumulate radicals up to $\tilde{n}_{\mathrm{crit}}$ limit which can sustain propagation of recombination reaction through the sample as a whole.

Note: $\tilde{n}_{\mathrm{crit}}$ is defined by size and shape of a sample, by its thermal properties, by cooling condition, and by kinetics of radicals; evaluation of this value is not a subject of this probabilistic model. It is only worth to note that $\tilde{n}_{\mathrm{crit}} < n_0$.

Really, less concentration of reagents is needed to sustain reaction, which has already been in action, than to initiate the process. Let us take an extreme case: the sample of infinite size. Radicals of any low concentration will then react sooner or later: $\tilde{n}_{\rm crit} \approx 0$; but the higher concentration the sooner process of recombination begins.

T_0-value can be evaluated from the relation

$$\tilde{n}_{\rm crit} = R\tau(1 - \exp(-T_0/\tau)),$$

where τ and R are «lifetime» of radicals and radical production rate, respectively. For low dose rate (and low value of R accordingly) and/or big volume of a sample, T_0 may prevail over $T_{\rm SB}$ resulting in deterministic character of SB appearance (if this is principally possible, i.e., if $\tilde{n}_{\rm crit} < R\tau$). T_0 will also prevail over $T_{\rm SB}$ for high dose rate and big volume of a sample, situation that is typical for cold moderators of advanced spallation neutron sources.

CONCLUSION

The relation (8) for the mean expectation time of the ignition of the chain process of recombination of radicals in solid methane and water ice under irradiation is derived. By invoking experimental facts, the limits of values of parameters, which may be used in the relation, are estimated. The author understands that there is a certain arbitrariness in the procedures used in the work. Function (4) is only one of many possible types of distribution of radicals in small volume of definite size chosen at random. Actually, type of the distribution is defined by many factors, such as structural defects, microcracks, crystallite interstitials, and diffusion of radicals, which are quite unlikely to be analyzed with enough degree of certainty. This model may serve only for rough estimation of probability of spontaneous burping in solid methane and water ice until more rigorous theory is developed.

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141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6.
E-mail: publish@pds.jinr.ru
www.jinr.ru/publish/