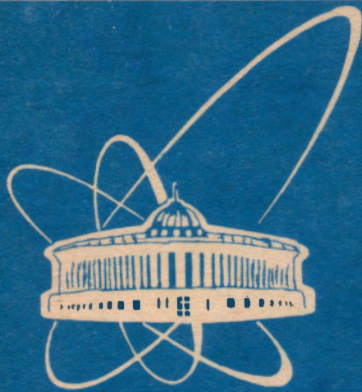


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ОБЪЕДИНЕННОГО
ИНСТИТУТА
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

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ON THE PHENOMENON OF THE FAST RELEASE
OF ENERGY IN IRRADIATED SOLID METHANE:
DISCUSSION OF MODELS CONSIDERING
THE LOCAL SPACE DISTRIBUTION OF ENERGY

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1. INTRODUCTION

It is well known that under irradiation (e.g., γ , β , recoil protons from elastic scattering of fast neutrons on hydrogen) the molecules of methane suffer radiation damage. The most substantial processes are considered to be the following [1,2]:



These are the primary reactions occurring as a result of excitation of the CH_4 molecule after kicking it by a proton or fast electron. Atomic hydrogen reacts at once with a methane molecule nearby:

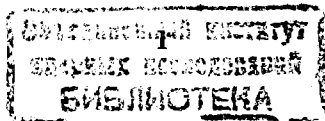


$\dot{\text{C}}\text{H}_3$ radicals can take part in the following reactions:



Most of the $\dot{\text{C}}\text{H}_3$, $\dot{\text{C}}\text{H}_2$, $\text{C}_2\dot{\text{H}}_5$ radicals recombine during the hot phase of the proton track, but some portion survives. These radicals, trapped in the CH_4 -matrix at a very low temperature, can "live" for a rather long period. From the URAM experiments [3], one may see that the lifetime of radicals amounts to 30 hours at $T=20\text{K}$ and 5.7 hours at $T=26\text{K}$. They recombine quickly when $T>30\text{K}$.

As radical recombination reactions (RRR) are exothermic (for the $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 \rightarrow \text{C}_2\text{H}_6$ reaction, the energy released is $Q_R = 336 \text{ KJ/mol C}_2\text{H}_6$, for the $\dot{\text{C}}\text{H}_3 + \text{C}_2\dot{\text{H}}_5 \rightarrow \text{C}_3\text{H}_8$ reaction $Q_R = 328 \text{ KJ/mol}$ [6]), the presence of free radicals in irradiated solid methane is the cause of energy storing, similar to Wigner energy in irradiated graphite. It was observed by Dr. J. Carpenter and others [3-6], that the stored



energy can be released violently in a spontaneous way or due to a slight change in the cooling conditions. Dr. Carpenter called the occurrence "a burp", because an ejection of radiolytic H₂ usually accompanies it. In chemical kinetics, such a phenomenon is called a "thermal explosion".

The critical conditions, consisting of the relationship between radical concentration n_R, temperature T, size of the methane slug, and cooling rate, have to be fulfilled for a fast RRR to occur. Some critical condition expressions are known [7-10]. All of them were derived from analyzing the stability of the set of differential equations for radical concentration and temperature:

$$\begin{cases} \frac{dn_R(t)}{dt} = R(t) - 2K(T)n_R^2(t) & (2) \\ \rho C \frac{dT}{dt} = \lambda \nabla^2 T(r, t) + q(t) + Q_R K(T)n_R^2(t) & (2.1) \end{cases}$$

where ρ , C , λ are the mass density, specific heat capacity and thermal conductivity of methane, respectively, $q(t)$ is the nuclear heat deposition, and R is the production rate of radicals; the recombination reaction coefficient $K(T)$ is assumed to have an Arrhenius form,

$$K(T) = K_0 e^{-T_a/T},$$

where T_a is the so called "activation energy" in terms of degrees Kelvin.

Dr. Carpenter's equation, derived for a slug of methane of any shape, cooled from the outside and heated from the inside, but neglecting the Laplacian in (2) is:

$$\frac{Q_R \cdot T_a \cdot K(T)n_R^2}{\alpha T^2} = 1 \quad (3)$$

where Q_R is an energy of recombination, $\alpha = q/(T-T_0)$, and T_0 is the coolant temperature.

Another critical condition to fulfill for the existence of RRR is defined by D.A. Frank-Kamenetsky - the classic of chemical kinetics theory [7]. It was derived for a slab slug of thickness "a", with no heat sources, except RRR, at a given periphery temperature T , but accounting for the Laplacian in the heat balance equation:

$$\frac{Q_R \cdot T_a \cdot a^2 K(T)n_R^2}{\lambda T^2} = 0.88. \quad (4)$$

Eq. (3) can be transformed into (4), except for the right term, provided that thermal conductivity is poor, because $1/\alpha \approx a^2/\lambda$ in that case.

A more detailed consideration of the classic approximation of the problem is given in a previous paper, Part I (published in Russian, JINR Communications, Dubna). Therein different approaches to solving Eqs.(2) can be found, which include those accounting for the space distribution of temperature due to the high density of energy release (it was neglected by the authors of [7-10], and causes the T value needed for Eqs.(3),(4) to remain unknown).

This paper, Part II, is devoted to different models of radical recombination in solid methane, apart from conventional theory. Both of the models presented share the common property that local non-uniformities (such as of radical concentration, track nature of energy deposition and others) have been accounted for.

2. CRITICISM OF THE CONVENTIONAL THEORY OF THERMAL INSTABILITY

Regretfully, the rigor and well-balanced theory of thermal explosion fails to explain the features of burps in solid methane. The experience of about 40 burps, observed during irradiation of solid methane samples at the IBR-2 reactor, Dubna, Russia, and of many burps at the IPNS solid methane moderator (SMM), ANL, USA, showed that burp performances are inconsistent with classical explanations. We will prove it with the following evidence:

1). Experimental data on the relationship of the critical concentration of radicals to ignition temperature have nothing to do with theoretical predictions. As shown in Fig.1, the experimental points on the plane (n,T) are concentrated near the horizontal line, whereas the function n(T), calculated from Eq.(4) with the parameters of RRR estimated from URAM-experimental data, shows a rather steep character. Moreover, the classical theory predicts no lower limit of concentration to ignite a burp, provided the ignition temperature is sufficiently high. On the contrary, experiments reveal a definite limit of about 0.3% molar concentration of radicals.

The experience of the IPNS SMM also confirms this conclusion. At IPNS SMM they daily observed self-ignited burps at 15K; thus the critical concentration of radicals was about 0.6-0.7%, whereas the calculated concentration was at least ten times as much, using Eqs.(3),(4) with the real parameters $K(15K) \cong 0.008 \text{ h}^{-1}$ and $T_a \cong 300K$ (this value of T_a was estimated from the saturation density of radicals in the 23-28K range by Eq.(2), [3]).

2) It is hard to understand the temporal dependence of the methane temperature during burps in the frame of the classical theory of combustion. In fig.2 the time dependence of temperature is shown for both a real burp and a calculated one, assuming that burning (more precisely, recombination of radicals) occurs simultaneously in the entire slug of methane. The temperature-time functions are quite different: for a real burp, the peak of the rate of heating is near the start, and, conversely, it is near the termination of the burp for the calculated one.

We get more information if we evaluate the value of the rate of RRR, K(T), in the process of RRR, from the experimental temperature dependence on time; the result of such a restoration is shown in Fig.3. For a great range of temperatures, the K(T) function appears to be only slightly temperature-dependent. Moreover, even at low temperatures,

this factor is several orders of magnitude greater than the value of the rate of RRR in the process of storing radicals that was estimated from the saturation condition:

$$K(26K) = R / n_{\text{sat}}^2 = 0.01 \text{ molCH}_4 / \text{molCH}_3 \text{ sec.}$$

Yet, the temperature dependence of the K-factor should obey the Arrhenius law:

$$K(T) = K_0 e^{-T_a/T}$$

The lack of such a dependence in a fast RRR, as one can judge from Fig.3, is evident.

An attempt was made to overcome this discrepancy (and problem 1), too) by considering the RRR process as being spatially extended. It could travel through the volume of a sample like a flame front in a combustible; radicals recombine for only a short time when the "flame" front passes that point. Sure enough, in this case the observed rate of RRR, K(T), would be actually consistent with the temperature near the maximal one at a burp, 55-56K, not with the low temperature of ignition. The real value of K(T) at T_{max} would be even more than the estimated one in Fig.3, if the size of the temperature sensor were larger than the depth of the flame front. If so, the K_2 value observed in a burp should be less than the value estimated at $T = T_{\text{max}}$ from the relation

$$K_2 = K_2(26K) \cdot \exp(T_a/26 - T_a/T_{\text{max}}) \cong 10 \text{ mol/mol sec,} \quad (5)$$

actually, it is $10^2 - 10^4 \text{ sec}^{-1}$.

A more conclusive way is to compare the estimated and observed values of the travelling speed of the front. The speed would be ruled by the known equation [7]:

$$v = 2 \cdot (D/\theta^3 \tau)^{1/2}, \quad (6)$$

where D is the temperature conductivity coefficient, $D \cong .003 \text{ cm}^2/\text{s}$; $\theta = T_a \cdot (T_{\text{max}} - T_0) / T_{\text{max}}^2$; $\tau = 1/K_2 \cdot n_R$ is the "life time" of radicals at $T = T_{\text{max}}$. One can calculate the speed of travel

of the front from (6) as equal to 0.005 cm/sec, whereas the flame front (if it exists) actually travels with a speed on the order of 1 cm/sec. The discrepancy between the theory prediction of the time dependence of temperature and experimental experience of as many as a hundred times, assures us of the inapplicability of either the conventional theory of thermal explosion or Eq.2 to describe burping in irradiated solid methane.

3) No strict repetition in the magnitudes of energy released in burp processes with adequate conditions was observed (see figures in [3]). The random, to some extent, number of radicals recombined during a burp cannot be understood in terms of the conventional thermal explosion theory.

4) And, finally, the inapplicability of the conventional theory is clearly demonstrated by one of the RRR, B8, observed at the SMM of the IBR-2 reactor (see Fig.4). This "abnormal" RRR was initiated within several hours following reactor shutdown at a uniform temperature as low as 21-22K whereas the space averaged irradiation temperature was as much as 25K-26K. The usual temperature for fast RRR initiation is in the range 25-30K. All attempts to find $K(T)$ values that would fit the critical conditions (3),(4) for the B8 thermal explosion have to fail in advance: you see, before methane exploded in the B8 case, both the temperature and concentration of radicals were well below those of the cases when no fast RRR had happened.

3. CONCEPTION OF A "HOT TRACK" RECOMBINATION OF RADICALS

The model of burps in irradiated solid methane discussed in this chapter is based upon the proposition that, in the cold phase of storing, radicals recombine only inside the hot proton track region. The rate of radical recombination by diffusion at low temperatures (<40K) is too slow. Only near

tracks are temperature conditions sufficient to provide for radical recombination. The differential equation for radical concentration then appears to be:

$$\begin{cases} \frac{dn_R(r,t)}{dt} = R(t) - R K_1(T) n_R^2(r,t) - K_2(T) n^2(r,t) \\ \rho C \frac{dT}{dt} = \lambda \nabla^2 T(r,t) + q(t) + Q K_3(T) n^2(r,t) \end{cases} \quad (7)$$

instead of Eqs.(2). In these equations $R K_1(T)$ means the rate of radical recombination induced with tracks, which is why it is proportional to the rate of radical generation R (more strictly, to the dose rate). The third term in the first equation has the common meaning of the rate of radical recombination caused by casual collision in the course of diffusion. The K_2 function is nothing other than the Arrhenius law with a real activation temperature; otherwise, $K_1(T)$ would appear to be a different function of temperature, generally speaking. The K_3 coefficient is a definition of the sum $R K_1 + K_2$.

The rate of radical recombination near a track can be calculated with a simple formalism. The number of radicals recombining after one track appears as:

$$\xi \approx \int K_2(T) n^2 dV dt \approx K_2(T_{mean}) n^2 V t,$$

where V is the effective volume for radicals to recombine and t is the effective time. As both V and t are dependent on the bulk temperature of the methane, T , and $T_{mean} = T + T_{tr}$ (T_{tr} is the effective overheating of volume V during time t), then we can write

$$\xi \approx K_2(T_{mean}) n^2 V t = K_1(T) n^2,$$

and the rate of radical recombination due to tracks (the second term) will be proportional to ξR .

It is easy to understand that in the restricted temperature range near the bulk temperature, $K_1(T)$ is close to the Arrhenius law, with the activation temperature being equal to

$$T_{a,eff} \approx T_a (T/T_{mean})^2,$$

that is, less than the real activation temperature T_a .

It is now possible to understand why the radical recombination process proceeds in different ways in the cold phase of RRR and in burps: the cold process is ruled by the second term, but the hot one (a burp) - by the third term, with different values of activation temperatures and rates of RRR.

It was calculated from the data of cold moderator experiments at IBR-2, that the discrepancy between the experimentally observed burp parameters and the expected ones can be eliminated if one accepts the real activation temperature to be equal to about 1000-1200K. In this case, the third term in Eq.(7) is negligible, at $T < 30-40K$, under the conditions of IBR-2 irradiation.

The concept of the propagation of fast RRR through the methane bulk like 'front of flame' becomes possible because there is nothing to prevent us from supposing a high activation temperature for the hot process in Eq.7. One may also suppose the τ -value in (6) to be as high as is needed to move the flame front with the speed actually observed.

Taking into account the preceding, we can understand the lack of dependence of the ignition temperature on the concentration of radicals (see Fig.1). It is evident that there should be a limit to the concentration of radicals for flame propagation through a bulk. If this condition is fulfilled, then a burp can appear at any moment, provided ignition of the RRR in a small volume of a definite size occurred.

Problems 1) and 2) listed in Chapter 2 are now resolved by this concept. Two others remain: the stochastic character of the number of radicals recombined during a burp, and the cause of ignition of fast RRR in the very "origin", the point at which a RRR flame starts. It might be the case discussed in the next chapter.

4. CONCEPTION OF A "DOUBLE-CHAIN" NATURE OF FAST RECOMBINATION OF RADICALS IN SOLID METHANE ("MATRYOSHKA MODEL")

A key to understanding all features of fast RRR in solid methane is in taking into account the non-uniformity of the space distribution of radicals and of the energy deposited. The radicals are generated in the tracks of recoil protons, and therefore they are arranged mainly in lines. The distance on a line between neighbouring radicals was estimated, with the value of the linear energy transfer characteristic for the fast neutron energy spectrum of a nuclear reactor and with the yield of radicals as was observed in the URAM experiment, to be nearly equal to the lattice parameter of the methane matrix. Accounting for this fact, and, in addition, for the fact that the diffusion of radicals at low temperatures is too slow to get them away from their origins, we come to the proposition about the possibility of a chain process of radical recombination along the line of a track. Acts of recombination could propagate quickly along a track, provided energy from a recombination act is transferred directly to the neighbouring pair of radicals through the excitation of molecules, not through the process of spreading heat.

There is a theory of the chain process of radical recombination in solid media by J.Jackson [11]. It has nothing to do with the non-uniformity of radicals or with tracks. The mechanism proposed [11] for propagation of the radical chain reaction was this: the heat from a recombination reaction frees "frozen" (i.e. trapped in the matrix) radicals within a sphere of some volume. These freed molecules could recombine with other trapped radicals. If the number of secondary recombinations is unity or more, then the chain of recombinations will continue. The critical condition of stability of radicals was derived by J.Jackson as

$$n_R^2 \approx 0.62 \cdot C_m \cdot (T_a - T_0) / \xi Q_R, \quad (8)$$

where C_m is the molar specific heat, ξ is the number of the nearest trap sites plus one (for the methane matrix, ξ is 13); other symbols are customized. He did not apply the Arrhenius law to the rate of recombination, but only considered a free radical reacting with its neighbour at once if there is one.

For solid methane and CH_3 radicals, Eq.(8) gives the critical value of radical molar concentration as about 4% for $T_a=340K$ and about 7% for $T_a=1000K$. Such a high concentration could hardly be achieved even inside a track region. Therefore, this can not be our case with $n_R=0.3-0.6\%$.

Nevertheless, a chain process of RRR propagation, similar to Jackson's, might occur at a appropriately arranged cluster of tracks. We postulate that the location of radicals replicates the structure of a track for hours. If a chain process of recombination reactions could propagate through a single track, then it would propagate through a cluster of intercrossing tracks as well. Such tiny regions filled with intercrossing tracks (we may call them "percolated regions") can be generated over time. One, or several, simultaneous acts of recombination in a percolated cluster could ignite recombinations of all radicals in the cluster. It could be called "the first-step chain process".

Percolated regions appear and disappear, without influence on each other, until the critical condition is satisfied. It means, that the increase in the local transient temperature, caused by bursting of the primary percolated region, and the duration of heating are both enough to cause a number of recombination reactions in neighbouring percolated regions, and to ignite at least one secondary cluster. Then, the RRR process will propagate through the sample, from one cluster to another, being "the second-step chain process".

The simplest case of a cluster of radicals is a single track. Then, the critical concentration of radicals can be approximately estimated from (8), if the heat of the recombination reaction Q_R is substituted by $N \cdot Q_R$, where N is the average number of stored radicals in a single track:

$$n_R^2 \cong 0.62 \cdot C_m \cdot (T_a - T_0) / \xi Q_R \cdot N(T, n_R). \quad (9)$$

For the IBR-2 neutron spectrum, the N -value amounts to 10^3-10^4 . Recombination of all radicals in a track could reduce the critical concentration by a factor 30-100: from 4-7% to 0.04-0.25%. Based on the experience of the IBR-2 solid methane moderator testing, n_R is within 0.3-0.6%. Therefore, the value of N in (9) should be settled to be about 100 - meaning that the radicals in a single track only partly recombine. This is evident, if stochastic character of the first-step chain process is taken into account. [Note: the number of recombined radicals in a cluster (track), N , depends on both the space-averaged radical concentration, n_R , and the irradiation temperature, because the conditions at which radicals are generated and recombine control the length of the tracks of stored radicals. That is why N is a function of T and n_R in (9)].

But, the theory of Jackson is not consistent with the Arrhenius law for rate of reaction. It is more accurate to derive a critical condition accounting for it. The critical condition should be derived from an expression something like this:

$$v \cdot n_R^2 \cdot \int_V dv \left(\int_0^\infty K_2(T(r,t)) dt \right) = 1, \quad (10)$$

where v is the average of the number of clusters surrounding each cluster; V is the volume occupied by one cluster; K_2 is the rate of the second-order reaction, and T is the transient temperature that is both N -value and T_0 -temperature dependent. So, Eq.(10) is sensitive to the temperature of irradiation, T_0 , and gives the key to applying the chain-process model to methane bursts at very low temperatures, as well.

The rate of RRR during a chain process should be ruled by an ordinary differential equation of decay; the relative rate

of RRR would be $\theta=(k-1)/\tau$, where k is the multiplication factor (the ratio of a number of secondary clusters ignited to the primary ones), and τ is the time duration of one step of a chain. From experiments, $\theta \cong 0.1-1\text{sec}^{-1}$ (see Fig.2). The value of τ can be estimated theoretically from $\tau \cong a^2/D$, if supposing the distance between clusters to be equal to the size of the clusters, a , and if estimating the last value from Eq.(10); τ appears to be in the interval of 10^{-8} to 10^{-10} sec. Then, $k-1$ is on the order of 10^{-8} to 10^{-11} . It is hard to expect that such a fine, delicate dk could maintain the same value throughout a sample. It is more realistic that the dk -values range widely in different regions of a sample. So, a sample burps when, for a single small region, the critical conditions are satisfied. After this region has burned, and the sample has been heated a little, the critical conditions for the neighbouring regions are satisfied, and they will burn also, perhaps, with other values of $k-1$. In other words, a sample of unstable solid methane represents many small regions, each of them being near critical in the terms of the "double-chain" process. When one initial region becomes supercritical, it burns. The burning of radicals starts to propagate through the methane bodies, separating this initial region from neighbouring near-critical ones, with low speed, determined by Eq.(6). When the temperature at the border of the neighbouring region increases slightly, it burns as well, and the process proceeds through the sample.

This challenging concept of burping irradiated solid methane would clarify all the features of the observed burps discussed in Chapter 2: very fast heating, spontaneous character, the intermediate value of the speed of burning propagation, discrepancy between the expected and real values of the ignition temperature. Because this model includes some serial steps of transferring energy from smaller objects to larger ones (radical molecule \rightarrow track (or cluster of tracks) \rightarrow near-critical volume, comprising some clusters \rightarrow and, finally, the sample of methane as a whole), we may call it "matryoshka", like a Russian folk doll.

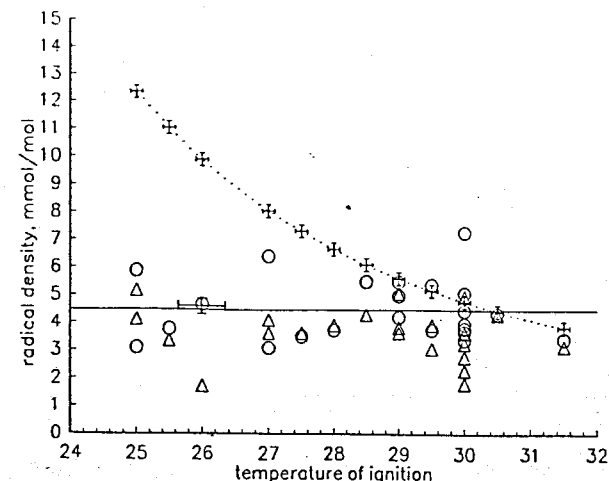


Fig.1. The temperature of ignition to concentration of radicals relationship of burps in solid methane: triangles - experimental points of the IBR-2 cold moderators with concentration, estimated at the given irradiation time; circles - ibid, but with concentration estimated from the energy yield of a burp; crosses - calculations based on the classic theory of thermal explosion (relation (4)).

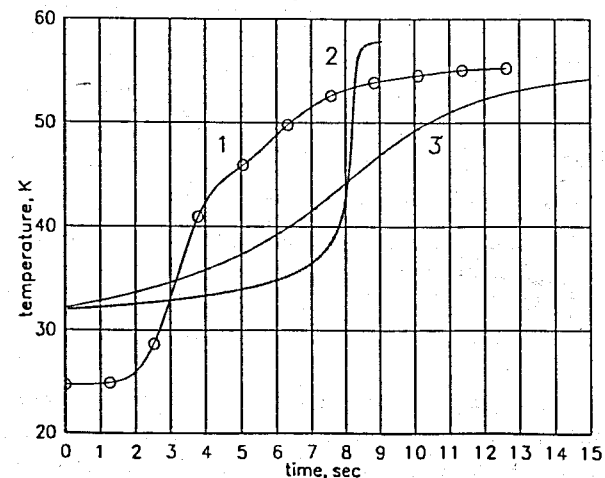


Fig.2. Experimental (curve 1) and calculated from equation (2) (curves 2 and 3) time diagrams of methane temperature during a burp; 2 - the "activation temperature" value T_a is set equal to 700K, 3 - $T_a = 340\text{K}$ with the time scale reduced ten times.

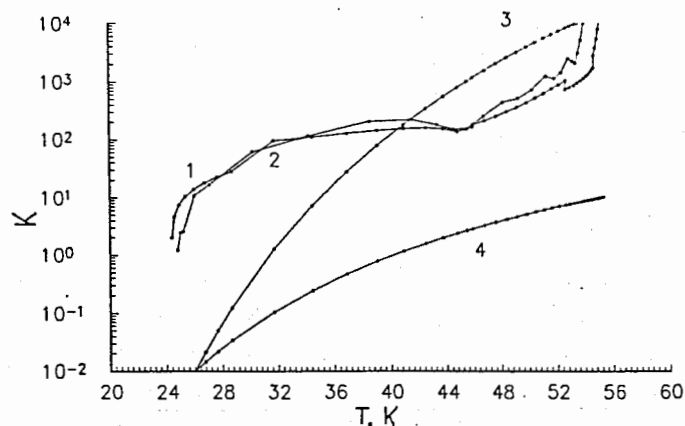


Fig. 3. Coefficient of the rate of the radical recombination reaction, K , $\text{molCH}_4/\text{molCH}_3 \text{ sec}$, versus methane temperature, degrees Kelvin, for a burp; curves 1, 2 - estimated from experimental data $T(t)$, 3, 4 - calculated from the Arrhenius law with "activation temperature" values set equal to 700K and 340K, respectively.

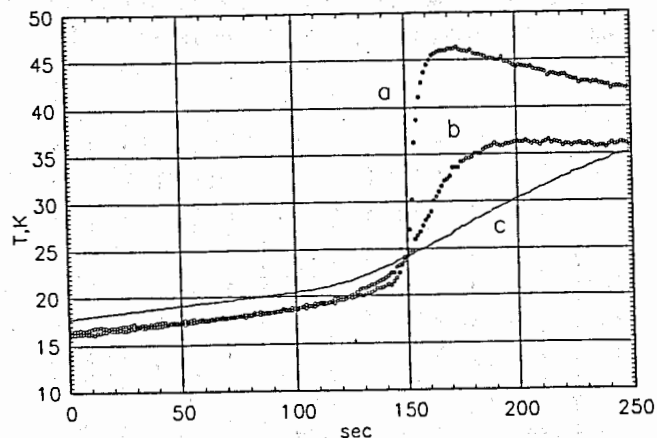


Fig. 4. Time diagrams of methane temperature at two points (a, b) and helium (coolant) temperature (c) of burp number B8, that occurred during the IBR-2 cold moderator tests at zero reactor power after 4 hours of preceding irradiation at 2 MW and 25K methane temperature.

CONCLUSION

In conclusion, the author should confess that both of the models presented are based on some assumptions not fully justified. So, a rigorous theory for the fast burning of radicals is desired. Maybe, a combination of both models should be used to explain all the features of the "burp" phenomenon in irradiated solid methane.

References:

1. S.Ya. Pshezhetski. Mechanisms & Kinetics of Radiation Induced Chemical Reactions (in Russian). Moscow, "Chimiya", 1968.
2. J. Carpenter. Cold moderator for pulsed neutron sources. In: Proc. of Intern. Workshop on Cold Neutron Sources. LANCE, Los-Alamos, US, 1990, LA-12146-C. p 131-153.
3. A.A. Beljakov, V.G. Ermilov, V.L. Lomidze et al. In: Proc. of ICANS--XII, RAL Report 94--025, v. II, p. 144--155
4. E.P. Shabalin, A.A. Beljakov, V.G. Ermilov, V.V. Melikhov. In: "Advanced Pulsed Neutron Sources". Proc. of PANS-II, Dubna, 14-17 June 1994. JINR-Communications, Dubna, 1995.
5. J. Carpenter. Thermally activated release of stored chemical energy in cryogenic media. Nature, 1987, # 330, # 6146, p. 358-360.
6. S. Ikeda, N. Watanabe, S. Satoh et al. In: Proc. of International Collaboration on Advanced Neutron Sources (ICANS-IX). PSI, Willigen, 1986, v. II, p. 18--22.
7. D.A. Frank-Kamenetski. Diffusion & Heat Transfer in Chemical Kinetics (in Russian). Moscow, "Nauka", 1969.
8. N.N. Semyenov. Chain Reactions (in Russian). Leningrad, ONTI, 1934.
9. F. Bowden, A. Yoffe. Fast Reactions in Solids. London, 1958.
10. W.C. Pimm, J.M. Carpenter. Mathematical Approaches to the Problem of "Burping" in the Solid Methane Moderator. IPNS Note 64, 1990. Argonne, ANL, USA.
11. J.L. Jackson. Dynamic Stability of Frozen Radicals. The Journal of Chemical Physics. V. 31, 1959, p. 154-157, p. 722-730.

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