STATE UNIVERSITY OF NEW YORK

AT STONY BROOK

COLLEGE OF
ENGINEERING

Report No. 9

THERMAL DECOMPOSITION

OF IRRADIATED   LEAD AZIDE

by

Joseph Jach

April, 1963

Thermal Decomposition of Irradiated α Lead Azide*

BY JOSEPH JACH †

State University of New York, Stony Brook, L.I., N.Y.

The thermal decomposition of unirradiated and heavily reactor irradiated colloidal α-PbN_6 has been studied between 195 and 253°C and 173 and 239°C respectively. The irradiation greatly reduces the induction and acceleratory periods found with unirradiated material and increases the maximum rate and the rate of the final decay. The maximum rate normally occurs at about 40 % decomposition but is shifted to approximately zero time on irradiation. The change in decay rate on irradiation is given by the two rate constants,

$$k \text{ (unirradiated)} = 10^{12 \cdot 0 \pm 1 \cdot 0} \exp(-36 \cdot 3 \pm 2 \cdot 3 \text{ kcal}/RT)$$

and

$$k \text{ (irradiated)} = 10^{7 \cdot 9 \pm 1 \cdot 0} \exp(-25 \cdot 7 \pm 2 \cdot 4 \text{ kcal}/RT).$$

The decrease in activation energy is possibly associated with changes in electronic excitation energies, while the decrease in frequency factor may result from gross structural changes accompanying the irradiation. The power laws observed in the acceleratory region are interpreted in terms of simultaneous surface and 3-dimensional reactions.

Garner and Gomm [1] found the decomposition of small single crystals of α-PbN_6 to obey a contracting envelope type of mechanism, and partially decomposed crystals contained a white undecomposed core surrounded by a black cover of lead. Later, Garner et al.[2] concluded that the acceleratory stage of the reaction was governed by a power law between linear and cubic. This they attributed to " normal growth " as opposed to branching which would have resulted in much higher values of the power. Griffiths and Groocock,[3] using a new technique, concluded that nucleation occurred on external surfaces at a rate proportional to time followed by three dimensional growth into the crystal. Nucleus formation and growth were explained in terms of positive hole production. Groocock [4] then studied the effect of various irradiations on the subsequent thermal decomposition but reached no definite conclusions. More recently Stamler, Abel and Kaufman [5] using thermogravimetric and X-ray techniques found evidence for a step-wise decomposition corresponding to different phases of PbN_6.

The object of the current investigation is to further understanding of this decomposition, especially in terms of irradiation effects. Other irradiation studies include the effects of fission product recoils on the subsequent decomposition of uranyl oxalate by Young [9] in which reaction appeared to occur around fission tracks resulting in expanding cylinders. Flanagan [19] in the decomposition of lead styphnate monohydrate found γ-rays to be ineffective but neutron irradiation provided many more nuclei from which decomposition could proceed. From a study of the effect of various irradiations on permanganates, Prout [18] concluded that extensive cracking occurs in irradiated crystals as a result of decomposition centres caused by preferential annealing and Wigner energy releases around point defects.

EXPERIMENTAL

The reaction $PbN_6 \rightarrow Pb + 3N_2$ was followed by pressure measurement in a closed system. Colloidal αPbN_6 from Picatinny Arsenal was used without any further processing. The average particle size was 7μ but ranged from 40μ downwards. Approximately 5 mg portions were dried for 3 h at 80°C and encapsulated under backing-pump vacuum into quartz vials. Some of the vials were irradiated simultaneously in the Brookhaven reactor. The reactions vessel was a horizontal quartz tube with a flat one inch depression in the middle and was heated by a furnace controlled to ± 0.1°C. The samples (whether irradiated or not) were emptied from the vials into a platinum bucket attached to a magnetically operated device which allowed the crystals to be introduced into the depression after evacuation. Reactions therefore took place on a surafce of lead left by previous reactions. This was shown to be reproducible with respect to a bare quartz surface. Pressures were measured by a Pirani gauge whose signal was recorded continuously on a pre-calibrated West recorder. The final pressure never exceeded 150μ. In low-temperature runs, final pressures were obtained by raising the temperature.

RESULTS

The decomposition of unirradiated material was studied between 195 and 253°C and irradiated material between 173 and 239°C. The samples were irradiated for 35 h in the Brookhaven reactor with a flux of approximately $7\text{-}8 \times 10^{12}$ neutrons/cm^2 sec of which approximately 2×10^{11} were epi-Cd.
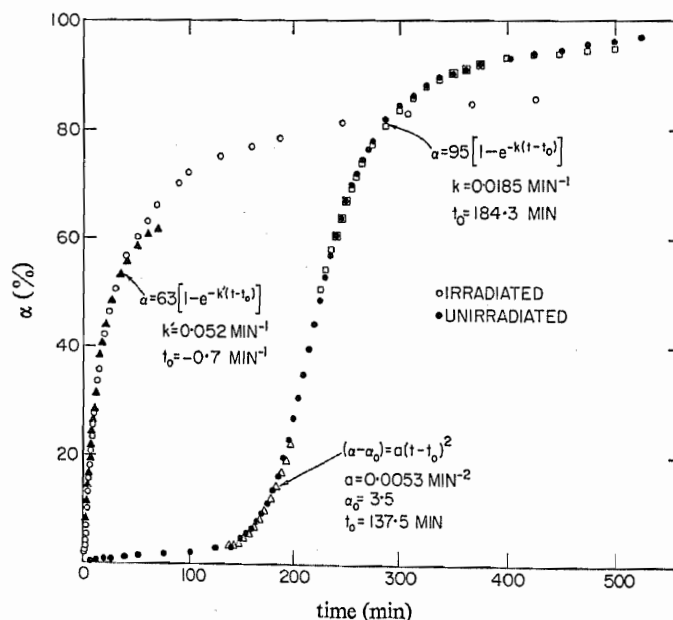

Fig. 1.—Fraction of total decomposition α against time. Full circles: expt. points for unirradiated material at 240·9°C; open circles: expt. points for irradiated material at 238·5°C; other points are the attempted fits indicated by arrows.

A typical α against t plot for unirradiated material is shown in fig. 1, where α is the fractional decomposition. The closed circles represent the experimental points for unirradiated material. An induction period is observed followed by an acceleratory, maximum rate and decay stage. Sometimes near the beginning of the reaction, a

small acceleratory region similar to that observed by Griffiths and Groocock [3] was seen. The rate before the main acceleration is essentially constant. The acceleratory region itself is well fitted (open triangles) to an expression

$$(\alpha - \alpha_0) = a(t - t_0)^2. \tag{1}$$

After the maximum rate, the decomposition follows closely an exponential decay of the form

$$\alpha = \alpha_\infty [1 - \exp\{-k(t - t_0)\}] \tag{2}$$

shown in fig. 1 as open squares and with $\alpha_\infty = 95\%$, from about $\alpha = 50\%$ to above 90%.

Irradiation significantly alters the decomposition kinetics. Fig. 1 also shows an α against t plot for irradiated material (open circles) at approximately the same temperature as the run on unirradiated material. The induction period is drastically reduced, and the acceleratory period is virtually absent. There is a short initial gas evolution ($< 1\%$ decomposition) during the induction period. After this, the rate rises to its maximum value and subsequently drops in the same way as the decay stage of the unirradiated material represented by eqn. (2). However, the fit (closed triangles) does not extend to as high values of α as with unirradiated material.
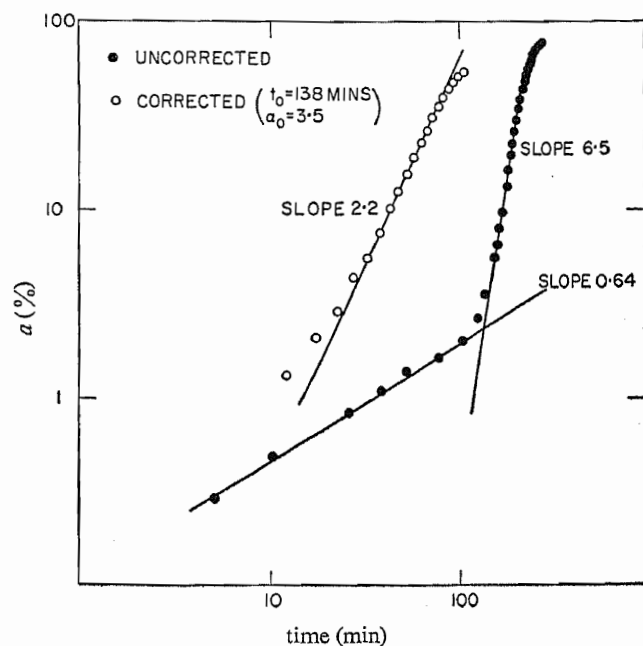

FIG. 2.—Logarithmic plot of α against time.

Attempts were made to fit the main acceleratory region of the unirradiated material to exponential and power laws as well as the Prout-Tompkins equation. The most satisfactory fits were the power laws, $\alpha = at^m$. Using the raw data shown in fig. 1, a log α against t plot gave two slopes as shown in fig. 2 by the closed circles. The initial slope is near unity and the slope during the acceleratory region is 6·5. It thus seems likely that a reaction is predominating near the beginning of the decomposition which then stops or is overshadowed by the reaction proceeding in the

main acceleratory region. Consequently, $\log(\alpha - \alpha_0)$ was plotted against $\log(t - t_0)$ where t_0 is a zero time correction and α_0 is the corresponding value of α at time t_0. The choice of α_0, t_0 was chosen as reasonably close to the acceleratory period as possible. The values of α_0 were in general about 4 %. The " corrected " plot is shown in fig. 2 as open circles. It has a slope of 2·2 in the region where the un-corrected plot showed a 6·5 slope. Hence the slope corresponding to the accelera-tory region is critically dependent on the correction ; this shows the danger of draw-ing conclusions from power laws. This dependence of the power on the correction is shown in table 1. In each case a good straight line over a substantial portion of

TABLE 1.—VALUES OF m OVER THE ACCELERATORY REGION FOR DIFFERENT t_0 CORRECTIONS

(The maximum rate occurs at $t = 220$ min)

t_0 (min)	0	28	56	84	112	138
m	6·5	5·0	4·3	3·7	2·7	2·2

the run could be obtained. The same general features were obtained with all the runs (at different temperatures) on unirradiated material. The slopes corresponding to the acceleratory period varied from 2·7 to 7·2 (uncorrected) to a value close to 2 for plots having the correction (table 2). The average value of 5·1 for the un-corrected plots is in agreement with Griffiths and Groocock, who obtained a slope of 4 for a $\log(d\alpha/dt)$ against $\log t$ plot. The true value of m in $\alpha = t^m$ is conjectural, but is small (five or less).

The irradiated material exploded at 255·7°C as compared to 258·3°C with un-irradiated material.

ACTIVATION ENERGY PLOTS

The following parameters were obtained from the α against t curves of the unirradiated material. (a) The induction period τ, arbitrarily defined as the intercept on the time axis of an extrapolation of the maximum rate. (b) The constant a of the equation $(\alpha - \alpha_0) = a(t - t_0)^2$, which holds over the acceleratory period, using 3 points well within this period. This gave a double check on the values of α_0 and t_0 used for obtaining table 2. (c) The maximum rate k_{max}. (d) The constant

TABLE 2.—UNCORRECTED AND CORRECTED VALUES OF THE POWER m FOR VARIOUS RUNS

uncorrected	3·7	5·2	6·5	4·7	2·7	6·1	6·0	4·3	5·4	7·2 average	5·1
corrected	2·0	1·1	2·2	2·6	1·8	2·0	2·2	1·7	2·0	2·4 average	2·0

k in the equation for decay, $\alpha = \alpha_\infty[1 - \exp\{-k(t - t_0)\}]$. For irradiated material, the only parameters obtainable were those corresponding to (a), (c) and (d). The Arrhenius plots for $1/\tau$ (unirradiated) and $1/\tau$ (irradiated) are shown together in fig. 3, $\sqrt{a}$ in fig. 4, k_{max} (unirradiated) and k_{max} (irradiated) in fig. 5, and k (unirradi-ated) and k (irradiated) in fig. 6. The reason for using $\sqrt{a}$ was that the square law suggests a two-dimensional growth. Therefore α is proportional to v^2t^2, and v^2 is proportional to a. An Arrhenius plot $\sqrt{a}$ will thus yield E, the activation energy for one-dimensional growth.

From fig. 3, it is evident that τ is not simple and is probably influenced by two or more concurrent events, whether the material is irradiated or not. The maximum rates give straight line plots but irradiation results in a marked decrease in the
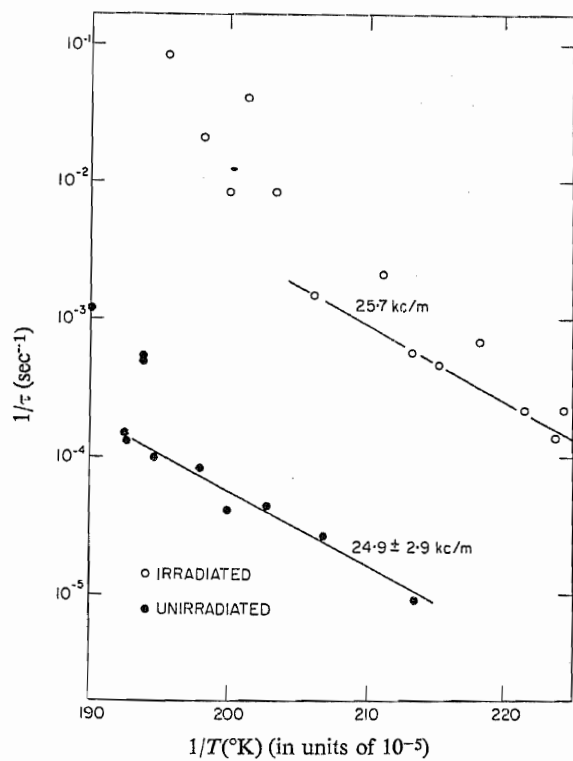
FIG. 3.—Arrhenius plot of $1/\tau$, unirradiated, full circles; and irradiated, open circles. In the lower straight line, no statistical weight is placed on the upper 3 points.
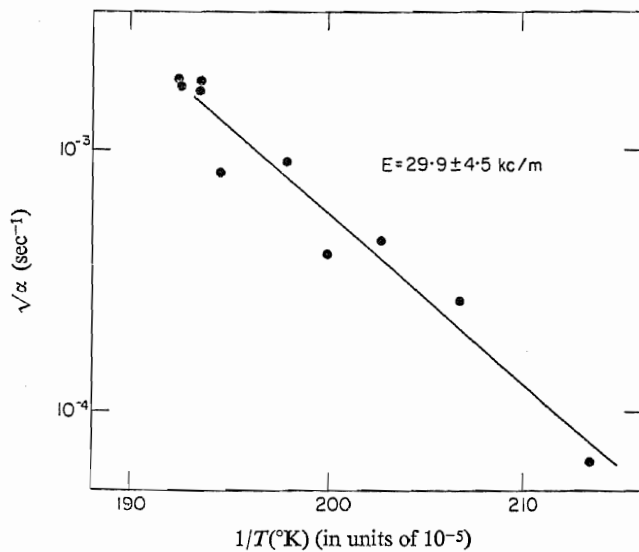

FIG. 4.—Arrhenius plot of $\sqrt{a}$.

activation energy and pre-exponential factor. The same remarks apply to the plots of k (irradiated) and k (unirradiated), which can be represented by the following:

$$k \text{ (unirradiated)} = 10^{12.0 \pm 1.0} \exp(-36.3 \pm 2.3 \text{ kcal}/RT), \qquad (4)$$

$$k \text{ (irradiated)} = 10^{7.9 \pm 1.0} \exp(-25.7 \pm 2.4 \text{ kcal}/RT). \qquad (5)$$
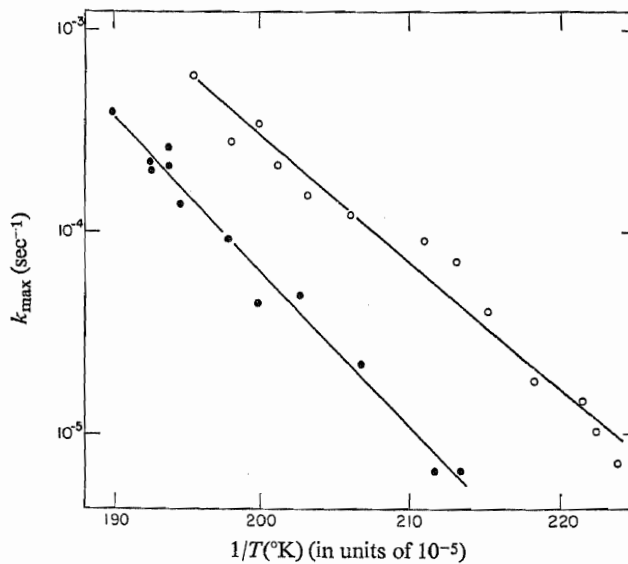

FIG. 5.—Arrhenius plot of k_{max}.

O irradiated $k_{max} = 10^{9.3 \pm 1.6} \exp[-(29.4 \pm 3.5 \text{ kcal})/RT] \text{ sec}^{-1}$

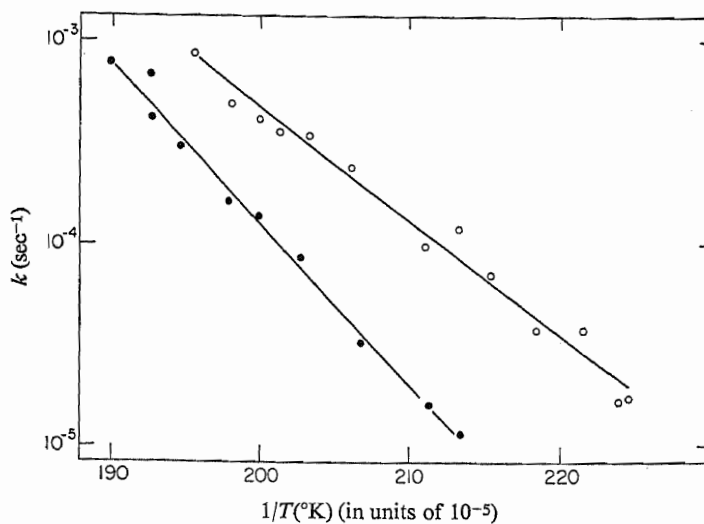● unirradiated $k_{max} = 10^{11.3 \pm 1.4} \exp[-(35.4 \pm 3.3 \text{ kcal})/RT] \text{ sec}^{-1}$

FIG. 6.—Arrhenius plot of k for the decay stage; fit with equation, $\alpha = \alpha_{\infty}\{1 - \exp[-k(t - t_0)]\}$.

O irradiated $k = 10^{7.9 \pm 1.1} \exp[-(25.7 \pm 2.4 \text{ kcal})/RT] \text{ sec}^{-1}$

● unirradiated $k = 10^{12.0 \pm 1.0} \exp[-(36.3 \pm 2.3 \text{ kcal})/RT] \text{ sec}^{-1}$

The overall rates after irradiation are increased over the whole decomposition range. Groocock [4] also observed a marked decrease in activation energy following X-ray and pile irradiation. His activation energy for irradiated materials agrees closely with that quoted here but his value for unirradiated material is a little higher.

The final pressures obtained from the unirradiated samples correspond, on average, to almost total theoretical decomposition. With irradiated samples, however, the final pressure/weight ratios were about 20 % lower, probably due to the irradiation decomposition since the irradiated crystals were black as compared to an off-white colour for the unirradiated crystals.

At very low temperatures the initial linear period extends to high α (30 %) over a period of 2 weeks. This percentage decomposition at higher temperatures corresponds almost to the value of α at the maximum rate. A similar phenomenon was observed with $NaBrO_3$.[6] It is possible that at very low temperatures, only those processes occurring with low activation energy such as decomposition along dislocation lines, etc., are fast enough to be observed and that at higher temperatures they are quickly masked by nucleation and normal growth, both of which have higher activation energies.

DISCUSSION

TOPOCHEMICAL ASPECTS

UNIRRADIATED MATERIAL

The initial stages are complex, but basically the reaction follows a linear rate with an activation energy somewhat lower than that found later. It is possible that initially reaction occurs preferentially at surfaces, cracks, dislocations, etc. At higher temperatures, these initial events are overshadowed by the reactions of higher activation energy, and the induction periods are shorter.

In the acceleratory region, the complexity of the log α against log t plots makes it difficult to draw any exact conclusions. Griffiths and Groocock concluded that the rate of nucleus formation was proportional to the first power of the time, on the basis of a value of $m = 4$, together with the assumption that the growth contributes a t^3 factor to t^m. They did not make any zero time corrections so that the true value of m is perhaps less than 4. Hence, the conclusion of a nucleation rate proportional to t is uncertain. In the acceleratory period m is between 2 to 5, although when t_0, α_0 corrections are made, it is between 2 and 3. For a reaction occurring only at the surface, the power should theoretically be 2 and for one occurring 3-dimensionally, it should be 3. This applies to non-interfering growths which is normally true at the beginning of the reaction. If the activation energy for nucleus formation is not too high, so that enough nuclei form during this growth period, the power will be higher depending on the rate law for nucleus formation.

There is some indication that a surface and a 3-dimensional reaction are occurring simultaneously. This would be true if their respective activation energies were not too different. Then, if $E_{surface} < E_{bulk}$, the bulk reaction will predominate at higher temperatures. The value of α at which $d\alpha/dt_{max}$ occurs will be higher for a predominantly 3-dimensional reaction than for a surface one; thus, for a 3-dimensional reaction starting from one nucleus on the surface of a sphere, $(d\alpha/dt)_{max}$ theoretically occurs at $\alpha = 16/27 = 59\cdot3$ %,[7] but if the surface reaction is instantaneous, and is followed by a 3-dimensional reaction, $(d\alpha/dt)_{max}$ occurs at $\alpha = 0$, this limiting case being the contracting envelope. Fig. 7 shows a plot of α_{max} against temperature; α_{max} rises with temperature, indicating that 3-dimensional and surface reactions are occurring simultaneously and that the 3-dimensional reaction with the

material, it is assumed that the period immediately following the maximum rates represent the same microscopic chemical event and that there are no other complicating effects of nucleation. This region, which can be represented by the equation

$$\alpha = \alpha_{\infty}[1 - \exp\{-k(t - t_0)\}]$$

for both irradiated and unirradiated material can then be used to compare the growth rates. The quantities

$$k \text{ (unirradiated)} = 10^{12.0 \pm 1.0} \exp(-36.3 \pm 2.3 \text{ kcal}/RT),$$

$$k \text{ (irradiated)} = 10^{7.9 \pm 1.0} \exp(-25.7 \pm 2.4 \text{ kcal}/RT),$$

are assumed proportional to rate of advance of an interface. An example in appendix 1 shows that this is so. Thus, irradiation effects two important changes : (i) the activation energy for interface growth is markedly reduced, (ii) the pre-exponential factor for interface growth is markedly reduced.

The drop in activation energy may be associated with a change in the excitation energy of the electrons, resulting from the excessive local strain induced by an irradiation decomposition of 20 %. The presence of one vacancy or foreign body per 5 lattice points must introduce large local strains which are not annealed, and these introduce electron traps sufficient to account for the observed decrease in activation energy. The act of decomposition is then determined by the untrapping of these electrons. The drop in activation energy is due to the greater depth of the traps after the straining and thus a lower energy for untrapping the electrons is obtained. However, after such heavy irradiation damage the entire structure of the crystal might be changed as in the more covalent types of crystals.[16] PbN_6 is more akin to AgN_3 than to KN_3 or NaN_3 in having more covalent character. Irradiation strains are not as easily removed by relaxation effects, and overall structural changes may result, consequently changes in electronic excitation energies may be expected. However, our results cannot distinguish between a homogeneous change in crystal structure or small, relatively undamaged regions in an amorphous matrix. Since the band structure is unknown, any statements about excitation or positive hole formation serves no useful purpose.

The change in the pre-exponential factor is more difficult to interpret; it appears to be related to a fundamental microscopic event rather than to a change in topochemical structure such as cracking, for example) accompanying irradiation (cp. appendix 2). An overall change in crystal structure might change the frequency factor, although it is difficult to account for a change of four orders of magnitude. A possible clue is the presence of an open structure brought about by vacancy introduction on irradiation. If the reaction is between two excitons or positive holes, then the presence of vacancies homogeneously distributed in large numbers would hinder the reaction between these two entities. A crude picture is that every 10^{-13} sec these two entities will react if they have sufficient activation energy. The partial relaxation at these vacancies could decrease this probability of reaction by three or four orders of magnitude, since these entities would be partially trapped by the vacancies. A probability factor, much the same as that introduced into bimolecular gas reactions might be operative, the increase of entropy in this case resulting from the presence of vacancies. This might be looked upon as a " cage effect " encountered in radiation chemical studies but the cage now hinders a reaction instead of helping. In the radiation decomposition of nitrates, for example, the primary act of decomposition into $NO_2^- + O$ is facilitated by the " free space " into which the O atoms can vibrate.[13, 14]

APPENDIX 1

RELATION BETWEEN THE DECAY CONSTANT AND THE INTERFACE VELOCITY

The decomposition proceeds by the advance into the crystal of an interface, and the parameter k is proportional to the velocity of penetration of this interface. Thus, suppose the decomposing particles are spheres of radius r' and particle size distribution $n(r')$ where

$$n(r') = A \exp(-ar').$$

In practice, $n(r') \to 0$ as $r' \to 0$, but over almost the whole range of r' the above equation is a sufficient approximation. Thus, in the real case, $n(r')$ will be zero at $r' = $ zero; it will then rise very sharply over a small range of r' and then fall exponentially. For the colloidal material used in this study, this is not unreasonable. Assume that at $t = 0$ all particles have intact interfaces which, as decomposition proceeds, penetrate the crystals at a velocity v cm/sec. Then, at any subsequent time t, the particle size distribution is represented by

$$n(r, t)_i = A \exp[-a(r+vt)],$$

which is equivalent to saying that particles of size vt at $t = 0$ will stop contributing to the reaction at time t. A particle of radius r contributes to $d\alpha/dt$ an amount proportional to its surface area, i.e., proportional to r^2. Hence,

$$d\alpha/dt = c \int_0^\infty r^2 n(r, t)dr = c' \int_0^\infty r^2 \exp[-a(r+vt)]dr$$

$$= c'(2/a^3) \exp(-avt) = C \exp(-avt).$$

Therefore $\alpha = a_\infty[1 - \exp(-avt)]$ ($\alpha = 0$ at $t = 0$). This is the same as eqn. (2) with $k = av$. Hence k is related to the interface penetration velocity by a constant of the system a with dimensions L^{-1}. Thus the slope of the Arrhenius plot for k represents the true activation energy for the velocity of interface penetration and the corresponding frequency factor will be directly related to that for the interface penetration velocity (see appendix 2). In the above argument, the assumption of any other solid form instead of spheres does not alter this conclusion, since the term $\exp(-avt)$ always remains. A particular particle size distribution might well explain the kinetics of decay of many observed first-order reactions. Even if the crystallites are of the same dimensions, the random cracking which occurs with most thermal decompositions even down to sub-grain levels probably ensures some exponential form of particle size distribution (cp. the $KBrO_3$ decomposition [17]).

APPENDIX 2

RELATIONSHIP BETWEEN THE MOLECULAR VIBRATION FREQUENCY AND THE OBSERVED PRE-EXPONENTIAL FACTOR FOR k

Let the molecules vibrate with frequency v_0 sec^{-1}. Then the fraction of any layer of molecules reacting per sec $= v_0 \exp(-E/RT)$, where E is the activation energy. The velocity of penetration of the reaction is therefore $v = hv_0 \exp(-E/RT)$, where h is the thickness of one molecular layer. Now $k = av = ahv_0 \exp(-E/RT)$. Hence the observed pre-exponential factor is ahv_0 where ah is a constant of the system. The decrease of the observed frequency factor with irradiation is $\sim 10^4$.

The thickness h cannot be much affected by irradiation and the effect on a would be to increase it (subdivision by cracking) which would imply an even lower v_0. It is thus not possible to relate the decrease in frequency factor to either a or h.

[1] Garner and Gomm, *J, Chem. Soc.*, 1931, 2123.
[2] Garner, Gomm and Hailes, *J. Chem. Soc.*, 1933, 1393.
[3] Griffiths and Groocock, *J. Chem. Soc.*, 1957, 3380.
[4] Groocock, *Proc. Roy. Soc. A*, 1958, **246**, 225.
[5] Stamler, Abel and Kaufman, *Picatinny Arsenal Monograph*, no. 72.
[6] Jach, to be published.
[7] Garner, *Chemistry of the Solid State* (Butterworths), p. 203.
[8] Bowden and Yoffe, *Fast Reactions in Solids* (Butterworths), p. 6.
[9] Young, *J. Chem. Soc.*, 1960, 877, 4533.
[10] Hall and Walton, *J. Inorg. Nucl. Chem.*, 1958, **6**, 288.
[11] Todd and Parry, *Nature*, 1960, **186**, 543.
[12] Keating and Krasner, *J. Physics Chem. Solids*, 1961, **20**, 150.
[13] Cunningham, *J. Physic. Chem.*, 1961, **65**, 628.
[14] Johnson, *J. Amer. Chem. Soc.*, 1958, **80**, 4460.
[15] Cunningham and Heal, *Trans. Faraday Soc.*, 1958, **54**, 1355.
[16] Binnington and Crawford, *Radiation Damage in Solids* (Princeton University Press), p. 234.
[17] Jach, *Proc. 4th Int. Symp. Reactivity of Solids* (Elsevier Publishing Co., Amsterdam), p. 334.
[18] Prout, *J. Inorg. Nucl. Chem.*, 1958, **7**, 368.
[19] Flanagan, *Nature*, 1958, **181**, 42.