Office of Naval Research
Contract No. Nonr-4673(00)
Task No. NR 056-467

Technical Report No. 2

THE THERMAL DECOMPOSITION OF IRRADIATED MATERIALS

by

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Prepared for Publication in

"Studies in Radiation Effects" Vol 2
Editor, G. J. Dienes
Gordon and Breach 1966

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March 1, 1966

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1. INTRODUCTION

The field which may broadly be called Solid State Chemistry is a relatively new one and parallels the rapidly advancing Solid State Physics field. It is however a very sad fact that chemical applications of the new solid state principles have been very few when one considers the vast scope of the chemical problems associated with solids. One such problem is the reactivity of the solid state and more particularly the thermal instability of certain solid chemical compounds. The subject of this article is the influence of irradiation on the thermal decomposition of solid compounds. These compounds and their decomposition at elevated temperatures have of course been known since the beginning of chemistry but an attempt to examine the mechanisms of their decompositions has only been initiated in the past few decades. Sadly, very little progress has been made. One promising tool is nuclear and other radiations. Irradiation effects are of course interesting and important per se but in the context of this article it is the <u>use</u> of irradiation as a tool in the study of these decompositions that is more emphasized. The usefulness of the irradiation "tool" derives mainly from the fact that irradiation tends to disrupt the natural orderliness of a solid and it is precisely such disruptions which favor heterogeneous processes such as decompositions. Thus, for example, if a decomposition begins from a special defect site on the surface which is normally difficult to create thermally (if the activation energy for the formation of this "nucleus" is high, say) then one would expect irradiation to enhance this process. Such an irradiation effect is an example of an obvious one. Others are less obvious.

This article will, broadly speaking, be divided into three sections. The first is a summary of present day knowledge of decompositions of unirradiated solids. These are the basic control experiments and the main purpose of this section is to familiarize the reader with the basic language of the field. The second section deals with the influence of irradiation itself, while the third section examines very briefly some related topics.

The intention is to select certain typical decompositions rather than describe all the published works. In this way it is hoped that the reader may acquire a feeling for the subject rather than a detailed knowledge of it. It is particularly designed for graduate students working in the broad field of chemical reactivity problems who wish to "read around" their subject.

(2) BASIC FEATURES OF DECOMPOSITION KINETICS

Jacobs and Tompkins(1) present an excellent review of this subject prior to 1955. Before proceeding to irradiation effects it is necessary to outline briefly the present knowledge of decomposition of normal unirradiated solids. The field is a very restricted one so that familiarity with the language becomes essential. The discussion will be limited to exothermic reactions belonging to the class

$$A_{solid} \rightarrow B_{solid} + C_{gas} \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

since it is almost exclusively on this type of (irreversible) reaction that irradiation effects have been studied.

(a) The α vs t curve

Most of the studies have been concerned with salts like azides, permanganates, oxalates, bromates, etc. In all cases a gas is evolved and a solid residue remains. The composition of the solid residue is in general known. Two main measuring techniques have been used to determine decomposition rates. The first involves determination of the amount of gas (pressure) released in a closed volume as a function of time while the second method merely involves weight loss of a reactant solid "A" as a function of time. These involve direct observations of, say, the number of nuclei formed as a function of time and also the rate of advance of a reaction front between reactant and product. However, only in rare cases can quantitative kinetic results be obtained from microscopic observations. The extent of reaction

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The isothermal decompositions of solids described by equation I may be conveniently divided into a few types by means of the distinct forms which the α vs. t curves display. Four of the most typical types are shown in fig. 1. For the moment, no distinction will be made between decomposition of one single crystal or a batch of polycrystalline material, but unless otherwise stated, all discussions in this chapter refer to the latter. Basically the curves are sigmoidal and most of the forms encountered in these decompositions are merely variations of the sigmoidal type. For example, curve (a) in fig. 1 shows a symmetrical type where the point of inflexion occurs at $\alpha = 0.5$, but such behavior is not typical. In general, the value of α at the point of inflexion, which will throughout this chapter be referred to as α_{max} , is not 0.5. This is shown in (b). In (c), the maximum rate occurs right at the beginning of the reaction. The discussion below shows that there is justification in regarding

FIGURE 1

Typical α vs t curves in the

thermal decomposition of solids

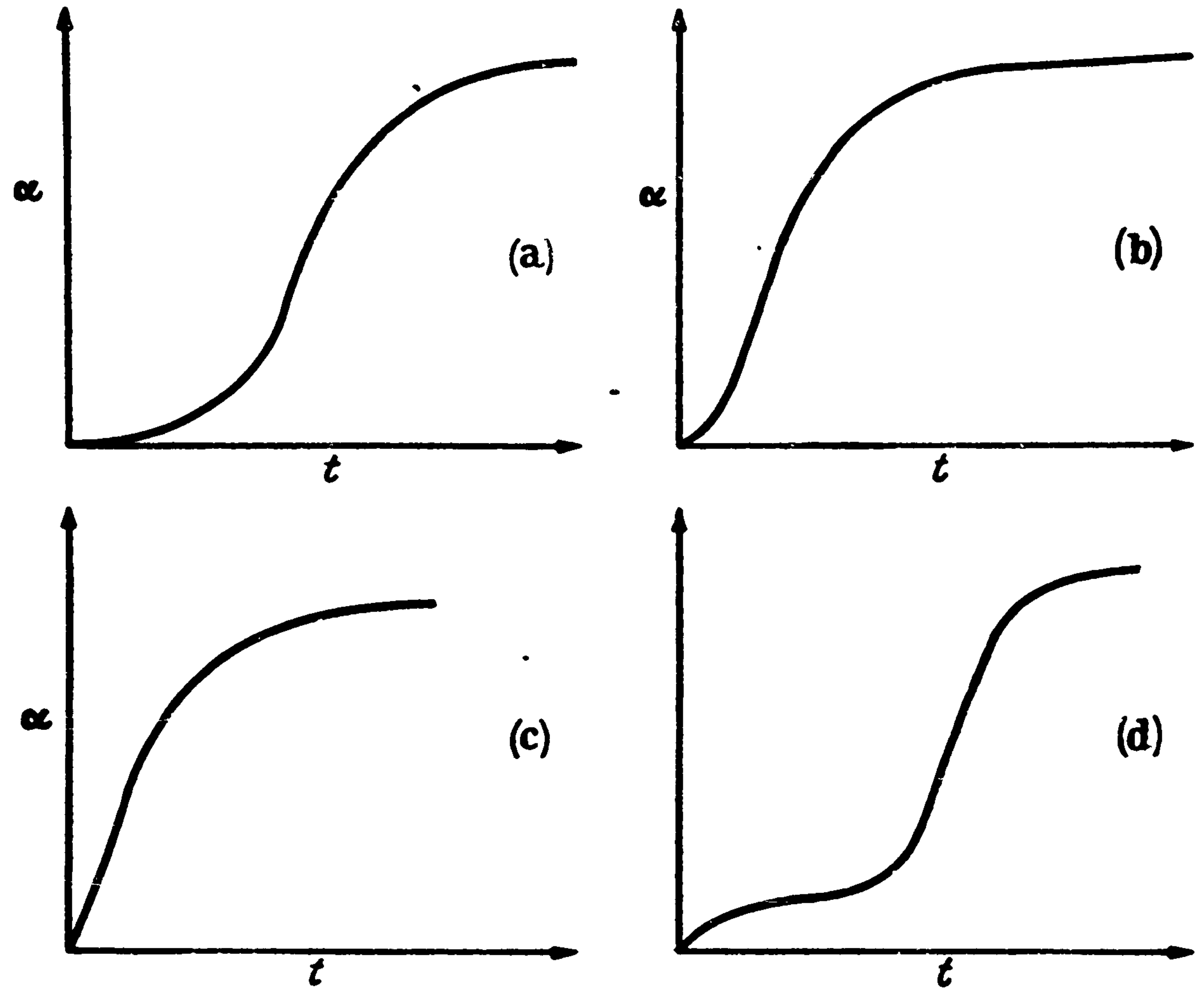


FIG. I

curve (c) as a special case of the sigmoidal type (a) with $\alpha_{max} = 0$. Curve (d) is again basically sigmoidal, but an initial reaction, which soon dissipates, is superimposed upon a "normal" sigmoidal type.

Many variations of these basic forms occur, with some or all of these features remaining. The existence of α vs. t curves of sigmoidal shape is not surprising. It is now well established that reaction invariably begins at nuclei which are generally located at discontinuities in the regular crystalline array. The most common such discontinuity is of course the external surface, but nuclei also appear at grain boundaries, dislocations and other imperfections. The nuclei are small regions of product B located in the matrix of A. Once formed they generally grow radially outwards. From a simple minded point of view it is clear that if the reaction front penetrates at a constant rate from the nucleus, the bulk of material which has reacted,will be related to a power of the time which is greater than unity since more than one dimension is involved in the growth. The <u>rate</u> is therefore an increasing function of time. When solid A becomes somewhat depleted it is equally clear that growing nuclei will begin to overlap and a deceleratory state must set in. However, a decomposition mode such as depicted by (c) in fig. 1 usually indicates that as soon as the reaction temperature is attained, the whole surface of a crystal instantly nucleates. Reaction can then only proceed into the crystallite as if the unreacted crystallite were surrounded by a contracting envelope. In this case nuclei "overlap" at t = 0 and no induction period is present. Such behavior might be expected when the activation energy for nucleus formation is less than or not too different from that for nucleus growth. If the activation energy for nucleus formation is substantially greater than for the growth process, only a relatively small number of nuclei will form and then only at energetically favorable places such as defects. Most of the decomposition will then occur by growth to large sizes of these limited number of nuclei. This behavior will be reflected in the sigmoidal curves. If the material is subjected to heavy grinding, irradiation or other mechanical working, it is generally found that the number of nuclei is greatly enhanced. The net effect is then to shorten the induction period since it is during this period that simultaneous formation of nuclei are occurring.

The importance of these families of α vs. t curves is thus self-evident. For example an Arrhenius plot of a parameter such as the length of the induction period (the definition of which is arbitrary) will be of significance in deciding just how easy nucleus formation is. Also, if it can be established that the initial few percent of the reaction is dominated by the formation of new nuclei rather than by the growth of existing ones, the activation energy for nucleus growth can be obtained from an Arrhenius plot of this initial rate. This may be compared to, say, the Arrhenius plot for some parameter associated with the decay region which usually describes the activation energy for the pure growth process since at this point the influence of new nuclei is negligible.

(b) Topochemical Kinetics

The topochemical kinetics describes the geometric forms which the unreacted crystal and/or the product solid display during decomposition. It is often possible to deduce these geometries from the rate equations which seem to fit the data plots. Thus, the α vs t curves are the basic raw data from which topochemical models are built. It is necessary to formulate laws which govern both nucleus formation and nucleus growth and then to see if together these laws predict some of the observed α vs t curves. This topic has been well reviewed by Jacobs and Tompkins(1). What follows is a summary.

(i) Nucleus formation. Nuclei are formed at special regions of a crystal where the activation energy required for the process is low. Suppose there are N_o such potential sites. Then the rate of formation of active nuclei, N, is

$$\frac{dN}{dt} = k_1(N_o - N) \qquad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where k_1 is the probability per unit time of the site becoming active. If the nucleation simply involves the decomposition of a single molecule, then $k_1 = \upsilon \exp(-\Delta G/RT)$ where υ = lattice vibration frequency and ΔG = free energy of activation for nucleus formation.

From (2),
$$N = N_o \left[1 - \exp(-k_1 t)\right] \qquad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

and

$$\frac{dN}{dt} = k_1 \cdot N_o \exp(-k_1 t) \text{ or simply } (k_1 \cdot N_o) \text{ for small t} \quad \ldots \quad (4)$$

However, nucleation may involve more than one simple step.

Suppose a stable nucleus is formed by a bimolecular combination of two active intermediaries each of which is formed at a constant rate. Neglecting the reverse reaction and assuming a small disappearance rate, the number of active species at time t = k't. The rate of nucleus formation is therefore

$$\frac{dN}{dt} = k(k't)^2 \qquad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

and

$$N = \frac{(k\ k')^2}{3} \cdot t^3 \qquad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

In general, if (β-1) entities are required to form a stable nucleus, then

$$N = \left[\frac{k\ k'^{(\beta-1)}}{\beta}\right] \cdot t^{\beta} = Dt^{\beta} \qquad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

Alternatively, several successive decompositions may be required to form a stable nucleus. Bagdassarian$^{(2)}$ showed that if β such successive events are necessary to form the nucleus and the probability of each event is k_1, then

$$N = \frac{N_0 (k_1 t)^{\beta}}{\beta\ !} = Dt^{\beta} \quad \text{again.}$$

The other possibility, already mentioned, is instantaneous nucleation (upon reaching reaction temperature). Here $N = N_0$ simply. There are thus constant, linear, exponential and power relationships for nucleation. Distinction between the two power laws can sometimes be made from energetic considerations. (An example of this is the BaN_6 decomposition$^{(3)}$.

(ii) Nucleus Growth

The nucleation rate is only half the story. From their instant of formation, nuclei begin to grow and a final expression for the amount of material decomposed can be very complex depending upon how this growth occurs. A general expression, using the nucleation formation law together with a generalized law for the nucleus growth rate may be obtained thus: - Let r be a size parameter. Thus, if the nucleus can only grow in one dimension, r would represent the length of a line of decomposed molecules. (The thickness of this line can, incidentally, be more than one molecule). For isotropic two-dimensional growth r would be the radius of a circular patch of decomposed material (of any thickness) while for 3 dimensional growth r might be the radius of a sphere or side of a cube etc., etc. Let the growth rate be represented by the function G. Then the size of a nucleus at time t which began its growth at time t = y is determined by the parameter r which itself is given by

$$r(t,y) = \int_y^t G(x)dx \qquad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

The size (volume) of a nucleus which commenced growth at t = y is, at time t,

$$v(t,y) = \sigma[r(t,y)]^\lambda \qquad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

where σ is a shape factor (e.g. $\sigma = 4\pi/3$ for a spherical nucleus) and $\lambda = 1$, 2 or 3 depending on whether the nucleus grows in 1, 2 or 3 dimensions. The total size (volume) of all nuclei at time t is then

$$v(t) = \int_0^t v(t,y).\left[\frac{dN}{dt}\right]_{t=y}.dy$$

$$= \int_0^t \sigma \left[\int_y^t G(x)dx\right]^\lambda . \left[\frac{dN}{dt}\right]_{t=y}.dy \qquad \ldots\ldots\ldots \quad (10)$$

where $\left(\frac{dN}{dt}\right)_{t=y}$ is the rate of nucleus formation at $t = y$.

The fractional decomposition α at any time t is then given by V(t) divided by the volume of product B at completion of the reaction. It is thus possible to derive the form of the α/t curve if the appropriate nucleation formation and growth rate laws are known or assumed. As a simple example, suppose nucleation proceeds according to a power law

$$\frac{dN}{dt} = D\beta t^{\beta-1}, \text{ where } \beta \text{ is an integer.}$$

Suppose the growth rate is constant, which is normally the case and that only the early stages of the reaction are considered. (This is to avoid accounting for overlap of nuclei as they grow). Then

$$v(t,y) = \sigma[k_2(t-y)]^\lambda$$

where k_2 represents the (constant) growth rate. Hence,

$$V(t) = \int_0^t \sigma[k_2(t-y)]^\lambda \cdot D\beta\, y^{\beta-1} \cdot dy$$

or

$$V(t) = \sigma k_2^\lambda \cdot Dt^{\beta+\lambda} \left[1 - \frac{\lambda\beta}{\beta+1} + \frac{\lambda(\lambda-1)}{2\,!} + \frac{\beta}{\beta+2} \ldots\right], \lambda \leq 3$$

or

$$\alpha = C' \cdot t^n \text{ where } n = (\beta+\lambda) \qquad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

This power law holds well for barium azide(4), where n = 6 to 8. A fuller discussion is found in the review paper of Jacobs and Tompkins(1) but basically this approach has proved satisfactory in explaining the acceleratory region of many decompositions. It has to be modified if the region beyond α_{max} is considered since here nuclei have already begun to overlap. Some of the modifications are described by Jacobs and Tompkins.

The possibility exists that in its passage through the crystal, a growing nucleus can activate potential nuclei in its path. This leads to branching chains which may take many different forms. The rate of formation of additional nuclei by this branching mechanism will greatly overshadow the original rate of formation of fresh nuclei. It can then be shown that $\frac{dN}{dt}$ is proportional to N(1). This leads to a nucleus formation rate (and ultimately also an α) which is exponential with time, i.e. proportional to exp (const. x time). The many variations on this basic theme are described by Jacob and Tompkins(1).

The above discussion then will serve as an outline of the manner in which the topochemical decomposition kinetics are obtained. It answers the question - <u>where</u> is reaction occurring? From rates and activation energies it is possible also to say something about <u>how</u> the reaction is occurring i.e. to formulate the ultimate atomic mechanism. However, experience has shown that severe limitations exist when attempting mechanism formulations from purely topochemical data. In practice much corroboratory information is necessary. Examples of these are electron microscope observations, diffraction, photo-chemical behavior, electrical conductivity, etc. It will become apparent in the main discussion of irradiation effects, which now follows, where and how this extra information is applied.

3. POST-IRRADIATION DECOMPOSITION STUDIES

It should be mentioned at the outset that work in this field has been limited and uncorrelated. Very little contact has existed between the small number of workers there have been. This has resulted in a few isolated schools each concentrating on one type of compound and an almost complete lack of unifying theories. It is mainly for this reason that the following discussion is divided into sections each of which deals with a specific type of compound, e.g. azides, oxalates, etc. The azides have perhaps been studied most thoroughly and will be discussed first. A summary of irradiation effects is given at the end of this chapter.

(a) Azides

The thermal decompositions of irradiated azides were investigated as far back as 1933 when Garner and Moon(5) found a slight acceleration of decomposition growth rate of existing nuclei in barium azide when exposed to radium irradiation but saw no enhancement of nucleus formation. Since then much work has been devoted to the azides, the first sizeable attack being on Barium Azide(4-12).

(i) Barium Azide

The thermal decomposition of $Ba(N_3)_2$ at about 100°C in vacuo displays certain features which are more capable of theoretical interpretation than most other compounds. The overall reaction is very simply

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

A relatively small number of large, roughly circular patches of Ba nuclei are formed and the α vs t curve is sigmoidal. Since the nuclei can be visually observed under the microscope, it is possible to measure rates (and activation energies) of their formation and growth separately. Photographic methods have shown that the growth rate is constant(7) i.e. $\frac{dr}{dt} = B$, a constant, where r is the radius of a nucleus. Since the growth is 3 dimensional, the amount of decomposed material associated with one nucleus varies as r^3 and hence as t^3. The rate of formation of nuclei was found to vary as t^2 and hence their number as t^3 (i.e. $N = At^3$). The total amount of material decomposed (proportional to α) should therefore vary as t^6 during the acceleratory period when nuclei overlap can be neglected. Although the raw data yield powers a little higher than 6, there is reason to believe that the true power is 6. The justification is based on the belief that small nuclei (too small to observe under an ordinary microscope) grow somewhat more slowly than larger ones. This idea was put forward by Thomas and Tompkins(8) who found that the equation $p = C(t-y)^6$ adequately represented the acceleratory period of the decomposition. This is shown in fig. 2. Here p is the pressure of N_2 released, t the time, C a constant and y is related to the time required for small nuclei to become "normally" growing larger ones. The activation energies corresponding to A, B, C were determined by Wischin(4) who found the values 74, $23\frac{1}{2}$ and 166

FIGURE 2

Plot of log (pressure) vs log (t-y), t is time, y is slow growth correction. The slope of these log-log plots is 6.0.

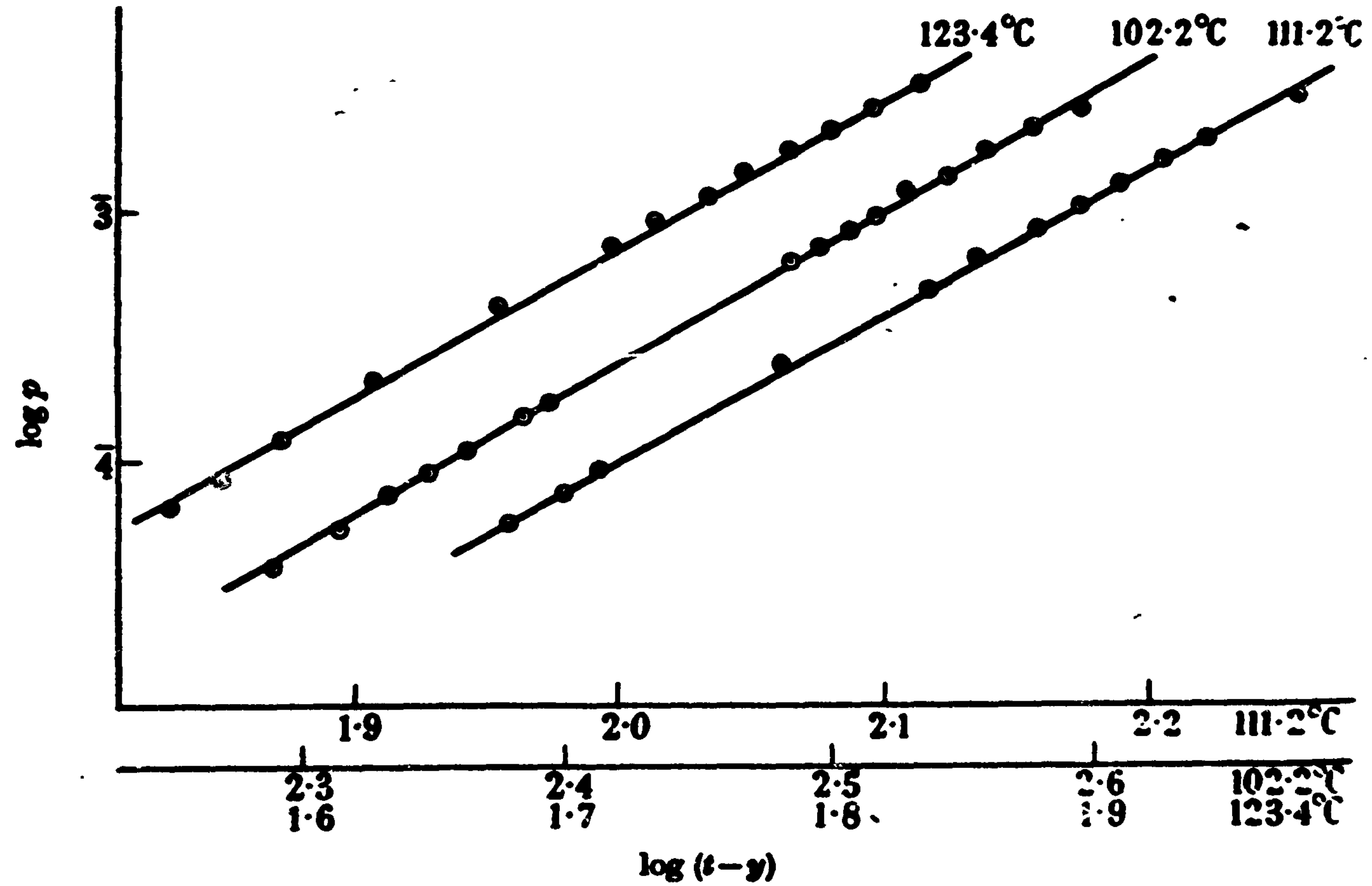

123·4°C
102·2°C
111·2°C
log p
$\bar{3}$
$\bar{4}$
1·9
2·0
2·1
2·2
111·2°C
2·3
2·4
2·5
2·6
102·2°C
1·6
1·7
1·8
1·9
123·4°C
log (t−y)

FIG. 2

Kcal/mole respectively.

Mott(11) irradiated $Ba(N_3)_2$ with U.V. light and found the topochemical kinetics to be much the same as for unirradiated material except for much larger values of C and many more nuclei. The explanation offered was that irradiation increased A while the growth rate (B) remained unaffected. The irradiation thus appeared to create many new potential nucleation centers. For very extended periods of irradiation the exponent 6 in the overall power law tended to the value 3. This would be explained if irradiation itself produces nuclei (as opposed to thermal production from potential sites) so that the only power reflected in the overall equation is the 3 from the pure nucleus growth (new nuclei are still formed thermally but their contribution to α is completely masked by the large number formed by irradiation). In order to understand some of the irradiation effects observed later it is necessary now to delve a little into the atomic mechanisms proposed by Mott and others for the $Ba(N_3)_2$ decomposition. This should perhaps also give a little background into the type of arguments involved in this field. Mott's mechanism for nucleus <u>formation</u> is analagous to that for latent image formation in photographic emulsions. In emulsions, the sensitivity is increased if on its surface the grain has specks of silver sulphide (sensitivity specks). The function of the speck is to catch an electron for a time long enough to attract an interstitial metal ion. If this "nucleus" remains intact long enough another electron can be captured and the nucleus will have a chance to build itself up to a large stable size. In azide, nucleus formation is structure sensitive so that probably the existence of surface electron traps renders possible the formation of nuclei in a similar way by trapping an electron, attracting interstitial barium ions, trapping more electrons and forming stable metal nuclei.

The theory begins with the assumption that following the decomposition of surface azide ions, there is an initial N_2 evolution too slow to be observed (in other compounds e.g. KN_3 it it observed(13)). The Ba atoms formed can then go into solid solution leaving an excess of free electrons in the crystal (this is analogous to the heating of ZnO which, when the O_2 is liberated, displays a very enhanced conductivity). He assumed that the number of electrons increases linearly with time during this slow N_2 emission stage. Thus, if n = electron concentration, S = crystal surface area, V = crystal volume, then $\frac{dn}{dt} = \frac{SQ}{V}$, where Q is a constant presumably given by $Q = Q_0 \exp(-q/kT)$. The energy q is that required to move an electron from a surface ion into the conduction band i.e. the energy to free an azide radical. Therefore $n=(SQ/V)t$. The mechanism of nucleus formation then involves the trapping of an electron at some surface trap for a time long enough for another one to be trapped. The probability per unit time that an electron is trapped is proportional to n while the probability of a second electron coming along before the first escapes is also proportional to n. If σ electrons are necessary to form a stable nucleus, the probability of formation of the nucleus in a given time is thus proportional to n^{σ}.

Hence,

$$\frac{dN}{dt} = \text{const} \left[\frac{SQt}{V}\right]^{\sigma}$$

or

$$N = \text{const}\ (SQ/V)^{\sigma} \cdot t^{\sigma+1} \qquad \text{.............} \quad (12)$$

For $Ba(N_3)_2$ at 100°C, $N \alpha t^3$, therefore $\sigma = 2$. This means that 2 electrons are sufficient to form a stable nucleus. Since $A = (SQ/V)^{\sigma}$, powders should have values of A much bigger than single crystals. This is the case. Also, since $\sigma = 2, (SQ/V)^{\sigma} = (S^2Q^2_0/V^2) \exp(-2q/kT)$. The measured value of 2q is 74 Kcals/mole so that the activation energy to free an azide radical would be 37 Kcals/mole. The traps may be anion vacancies on the surface. The increase in the quantity A upon irradiation would then be ascribed to these anion vacancies formed by the irradiation. The above process is then the fundamental step in the production of a nucleus.

Mott's theory of nucleus growth (as distinct from formation) begins with the assumption that N_2 can be liberated at the surface only since any gas liberated at the interface between Ba nuclei and unreacted azide could not escape. Hence the physical picture for nucleus growth is as follows: Occasionally an azide ion adjacent to the metal nucleus receives enough thermal energy to lose an electron to the metal (W in fig. 3). The azide radical cannot break up since it is not situated at the surface. However, an adjacent azide ion will transfer its electron to the azide radical. The latter positive hole is then capable of rapid diffusion to the surface where it can break up and escape as N_2 gas. The metallic nucleus is then negatively charged and

FIGURE 3

Energy levels of barium azide in contact with metal.

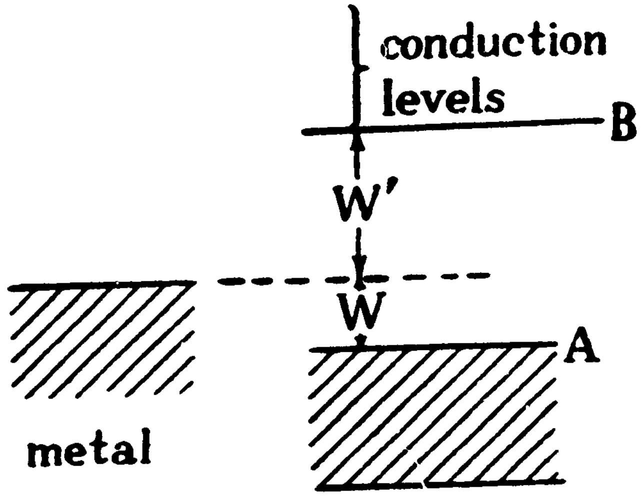


FIG. 3

attracts interstitial barium ions (assumed to be present in equilibrium with the crystal) and grows. On this picture, it is W (fig. 3) which is associated with the activation energy for growth ($23\frac{1}{2}$ Kcal/m). This mechanism then involves growth of metallic nuclei by diffusion of interstitial ions through the crystal and escape of N_2 gas from some surrounding free surface.

Mott's theory has been challenged by Tompkins and co-workers(12) on a theoretical basis as well as on further experimental work. They argue 1) that the energy required to form a cation vacancy is much less than that to form an interstitial cation and therefore the concentration of the latter will be small compared to the former. Any mechanism involving mobile cations will depend on vacancies. 2) Although transport numbers are not known, it is fairly certain that the azide ion is the mobile species (by-analogy with barium halides which are all anionic conductors). 3) Specific conductance measurements of barium azide show that the observed growth mechanism is 10^6 to 10^8 times as great as would be the case if the mobility of an interstitial barium ion is involved. In formulating a mechanism, they point to the following corroboratory experimental results a) when the azide is irradiated with UV (predominantly the 2537Å line) at room temperature, the rate of N_2 evolution during irradiation varies as the square of the radiation intensity, The primary process of photolysis is therefore regarded as the excitation of 2 adjacent azide ions. In support of this they state that (by analogy with gas phase data) the reaction $N_3 \rightarrow N_2 + N$ is certainly highly endothermic whereas $2N_3 \rightarrow 3N_2$ is highly exothermic, hence two azide groups are involved. b) Photoconductance and absorption experiments strongly suggest the formation of excitons. They therefore propose the following mechanism for nucleus formation: Two adjacent surface azide groups receive sufficient thermal energy to react. This needs a high overall energy and since the activation energy for nucleus formation is as low as 74 Kcal/mole, they suppose that one azide ion is excited first and remains so for a long time and therefore becomes rate-determining. The process envisioned is the formation of an exciton which can acquire sufficient additional energy to allow the ejection of the electron into the conductance band. Subsequently this electron is deeply trapped, probably at an impurity center. The positive hole formed is mobile and it gets trapped at some surface defect. Now an azide ion adjacent to this trapped positive hole (or azide radical) may receive sufficient thermal energy to react with the positive hole. This yields nitrogen and a complex remains which is an F-center associated with a vacant anion site. This complex can later be thermally dissociated into an F-center and anion vacancy. Although F-centers have no intrinsic mobility, by a process of association with a mobile anion vacancy and a subsequent dissociation, they may move through the lattice at a rate determined mainly by the mobility and concentration of such vacancies. When two F-centers "collide", aggregation to double F-centers results because such aggregates are more stable than single F-centers, since the electrons in the two identical

defects may "resonate". A double F-center aggregate corresponds to a barium atom in the lattice and is regarded as a nucleus. Growth of this nucleus proceeds predominantly by a process involving the transference of electrons from azide ions adjacent to the nucleus, this transference requiring much less energy than that required to eject an electron from the azide ion to the conduction band. The positive hole remaining reacts with an excited azide ion adjacent to it and also to the nucleus, giving nitrogen. Further F-centers are thereby produced which aggregate to the nucleus which thus grows. This mechanism is also consistent with observed kinetics and activation energies as follows. The rate of formation of double F-centers (or nuclei) = $e^{-E/kT}[F]^2$ .... (13)
where [F] = F-center concentration and E = activation energy for mobility of anion vacancies. The F-centers are produced at a constant rate and hence [F] = const $(e^{-E_1/kT})t$ .... (14)
where t is time and E_1 is the energy to eject an electron from the full band to the conduction band. The rate of formation of nuclei is thus = const. $(e^{-E/kT}) \cdot (e^{-E_1/kT})^2 \cdot t^2$ .... (15)
This is the correct expression, i.e. $\frac{dN}{dt} \propto t^2$ or $N \propto t^3$ (c.f. eqn.6). Note that only at small times will F-center formation rate be constant, so that equation 14 only applies for low times. Equation 15 is consistent with measured values (74 Kcal/m) of the activation energy for nucleus formation as well as the mobility energy of anion vacancies and thermal excitation to the conduction band.

The effect of irradiation on this decomposition is shown to strengthen their conclusions regarding their mechanism. The N_2 pressure released in the thermal decomposition is given by $P = C(t-y)^6$. They find the effect of pre-irradiation with U-V is to merely increase C without changing its activation energy. This increment of C is proportional to irradiation intensity times irradiation time (I T) i.e. total energy received during pre-irradiation. The effect of the pre-irradiation is thus to merely increase the number of places at which nuclei may be formed in the subsequent thermal decomposition. As regards the product of the pre-irradiation they note the following: 1) It is stable for long periods (3 to 4 weeks). 2) It is produced with the evolution of N_2. 3) It is presumably present in the unirradiated salt. 4) The increase in their number is proportional to the amount of energy received during pre-irradiation. The simplest process, they consider, is that an electron is moved from the full to the conduction band and is then trapped. For small irradiation (small I T) it is considered that the electrons are trapped at ferric ion impurities (which are known to be included in most azides in minute quantities). The vacant anion site left after decomposition of two adjacent azide groups increases the nucleation rate in the subsequent thermal decomposition because such sites are necessary for mobility of F centers and it is the aggregation of 2 F-centers that provides a stable nucleus which then grows. However, the number of Ferric ion traps is limited so at higher I.T the conduction electrons will instead become increasingly trapped at vacant anion sites forming actual F centers. In the thermal decomposition then, the rate of formation of double F centers will depend on a power lower than 6. When all ferric ions are used up and F centers only are produced (so that nucleation is complete before thermal decomposition begins) only the growth phenomena will be registered in the pressure increase i.e. pressure should be proportional to $(t-y)^3$. This fall of power from 6 to 3 is shown in fig. 4 which is a log-log plot of irradiation dose (IT) vs. induction period. Note that the fall in power from 6 to 3 is a necessary but not sufficient condition for supporting the details of the mechanism they propose. Whenever nucleation is enhanced from whatever cause, the power must ultimately reflect the domination of the growth process on the kinetics.

Tompkins et al extended the UV irradiation work to the effect of electron bombardment(14). Accelerating potentials of 100 to 200 Volts were used and the rates of subsequent thermal decompositions measured. Basically, the kinetic form of the decomposition is unchanged, but the value of the constant C is increased markedly (by a factor of 500 for the electron exposures used). They conclude that the centers created by UV and electron irradiation are the same as is the subsequent thermal decomposition. However, two differences show up: 1) With electron bombardment, C increases as the square of the electron flux and later saturates for a very high flux. For UV irradiation, C increases somewhat faster than linearly. 2) The power 6 in the equation $P = C\,(t-y)^6$ is unchanged no matter how much electron bombardment is given previous to the thermal decomposition (for UV, the power changes from 6 to 3). The explanation

FIGURE 4

Plot of log (intensity X time of irradiation) vs log (induction period). The numbers give the slope of log P vs log (t-y) plots. Circles 10 sec. irradiation. Squares, 90 sec. irradiation.

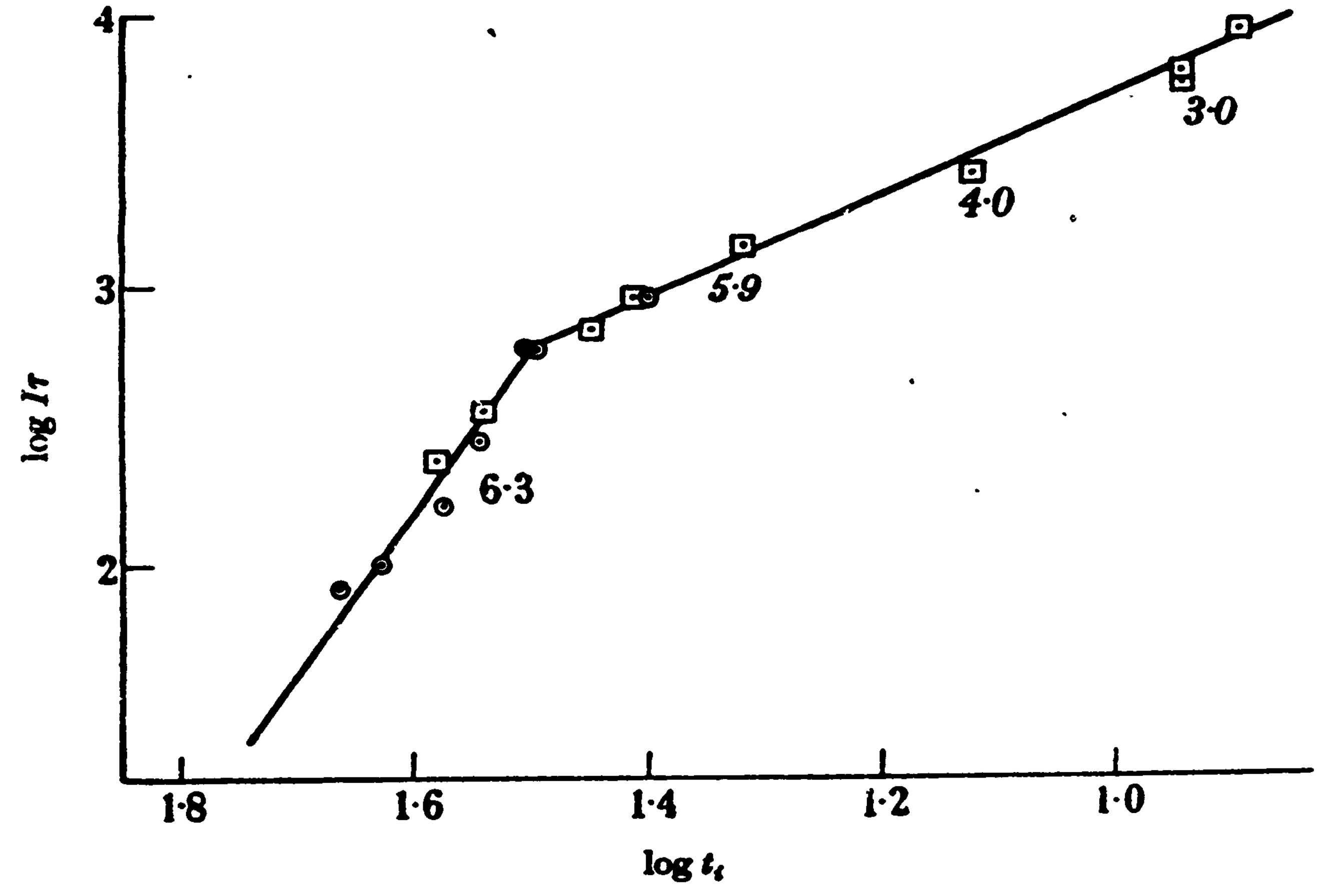


FIG. 4

advanced by Groocock and Tompkins is as follows. Since the exponent 6 is retained upon electron bombardment no nuclei are created during pre-treatment. The initial act of the beam is probably to eject electrons from azide ions but with sufficient energy for photoemission. Also, since there is now a high excess of electrons, surface anion vacancies can now be converted to F-centers which are immobile since their mobility rests on the presence of anion vacancies. Hence nucleation formation during bombardment is improbable. During the warm up period for the thermal decomposition the F-centers and positive holes regenerate azide ions and vacancies. The latter assist in nucleus formation thereby accelerating the thermal process. However, it is difficult to see why electron bombardment does not itself produce nuclei. Electrons are ejected from azide ions and nitrogen is released from what were originally 2 adjacent azide ions. The vacancies left are converted to F-centers by the electron bombardment. The two adjacent F-centers complex is precisely what is regarded as a nucleus. It is difficult to see why the electron bombarded solid does not undergo a subsequent thermal decomposition with a power less than 6. One is tempted to think that in the much accelerated decomposition which follows the irradiation the exact power becomes a very difficult quantity to measure. The fact that C saturates for high values of the electron flux is explained by assuming that when the F-center concentration becomes high enough, some surface Ba^{2+} ions are surrounded by four F-centers. Under these conditions, electron transfer from the F-center to

Ba^{2+} can take place during warm-up. This leaves a Ba atom surrounded by vacancies and so the atom can evaporate thus rendering it useless as a nucleus. The rapid change from C dependent on (electron flux)^2 to a constant C is explained by saying that the probability of evaporation depends on a very high power of the surface F-center concentration hence a very high power of the electron flux. The truth of the above supposition would lend substance to the argument that many Ba nuclei must exist at the beginning of the thermal decomposition. It thus seems difficult to accept their hypothesis that the $(t-y)^6$ law does not hold upon electron bombardment because no nuclei are formed during the bombardment or increased upon warm up.

(ii) Lead Azide

The decomposition of irradiated BaN_6 has been described in fair detail since theoretical interpretations are more possible in this case. However, many other azides have been irradiated and their subsequent thermal decompositions studied. Some of these will now be described but space will only permit limited detail. One of the most widely studied compounds has been lead azide, PbN_6, particularly in view of its use as a detonator. Much of the work has been of an applied nature, but many military installations both in Britain and the U.S.A. have concentrated some of their efforts on fundamental studies. Two forms of PbN_6 exist, the α and β. Groocock(15) studied the effect of high energy x-rays and pile irradiation on the thermal decomposition of batches of very small single αPbN_6 crystals between 253 - 292°C. The kinetics exhibit the usual acceleratory, maximum rate and decay stages. X-irradiation (up to about 10^7 r) produces a progressive fall in the activation energies of the decomposition (with dose) but also results in certain complex kinetic behavior. For example, with increasing X-irradiation dose the maximum rate first increases then passes through a minimum (below the value for unirradiated material) and then rises (to above the "unirradiated" value) to a maximum. The time required to reach maximum rate is much reduced by irradiation. Groocock considers that the complexity of the irradiation effects and subsequent thermal decomposition do not render any speculation as to detailed reaction mechanisms worthwhile. However, he compares the effects of X and pile irradiation by calculating the energy deposition in both cases. He concludes that pile irradiation is slightly less effective than high energy x-rays in altering the subsequent thermal decomposition kinetics.

Jach(16) studied the effect of extensive reactor irradiation doses on colloidal αPbN_6 over a much wider temperature range (173-253°C). A typical α vs t plot for normal and irradiated material is shown in fig. 5. The acceleratory region of the unirradiated material is well fitted to the equation.

$$(\alpha - \alpha_o) = a(t-t_o)^2 \qquad \ldots\ldots\ldots\ldots\ldots \quad (16)$$

where α_o, t_o are corrections which take into account certain unspecified surface reactions which occur before the main acceleratory region. Fig. 5 shows that the irradiation drastically reduces the induction period and increases the maximum rate and decay rate. The α_{max} for unirradiated materials is normally around 0.4. Irradiation reduces this practically to zero i.e. the reaction now begins almost with its maximum rate. Since the irradiations may be described as "heavy" and the change in kinetics rather severe, Jach points out that care must be exercised in choosing a parameter with which to compare kinetics and activation energies for irradiated and unirradiated material. Since the decay stage almost certainly only involves growth processes (the contribution from newly formed nuclei being practically nil) the parameter chosen was k in the equation

$$\alpha = \alpha_{\infty}[1-\exp\ \{-k(t-t_0)\}] \quad \ldots\ldots\ldots\ldots\ldots \quad (17)$$

which fits the decay stage of both irradiated and unirradiated material. α_{∞} (which is not necessarily unity) and t_0 are constants. The change in decay rate is indicated in the following two rate expressions obtained:

$$k(\text{unirradiated}) = 10^{12\cdot0\pm1\cdot0}\ \exp(-36\cdot3\pm2\cdot3\ \text{kcal}/RT)$$

$$k(\text{irradiated}) \quad = 10^{7\cdot9\pm1\cdot0}\ \exp(-25\cdot7\pm2\cdot4\ \text{kcal}/RT) \quad \ldots \quad (18)$$

and is shown in the Arrhenius plot figure 6. Groocock also noted a substantial decrease in activation energy following X and pile irradiation.

In the same paper, Jach points out the dangers involved in drawing far-reaching conclusions from the power laws of the type $\alpha = at^m$, especially in cases like PbN_6 where there is

FIGURE 5

Fraction of total decomposition of PbN_6 vs 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.

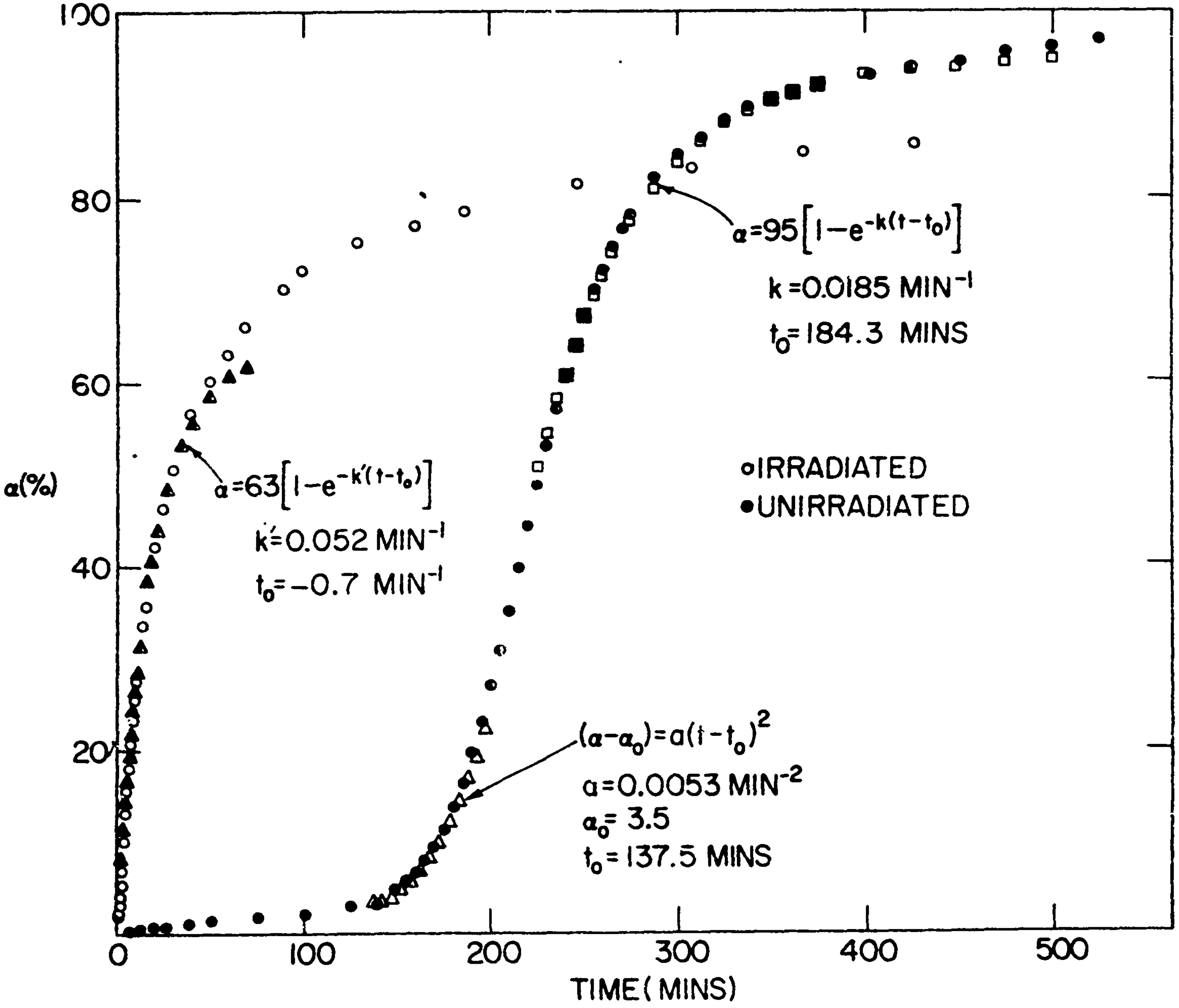

100
80
60
40
20
0
α(%)
0
100
200
300
400
500
TIME (MINS)
α=95[1−e^{−k(t−t₀)}]
k=0.0185 MIN⁻¹
t₀=184.3 MINS
○IRRADIATED
●UNIRRADIATED
α=63[1−e^{−k′(t−t₀)}]
k′=0.052 MIN⁻¹
t₀=−0.7 MIN⁻¹
(α−α₀)=a(t−t₀)²
a=0.0053 MIN⁻²
α₀=3.5
t₀=137.5 MINS

FIG. 5

FIGURE 6

Arrhenius plot of k for the decay stage; fit with equation

$$\alpha = \alpha_\infty \left[1 - \exp[-k(t-t_o)]\right]$$

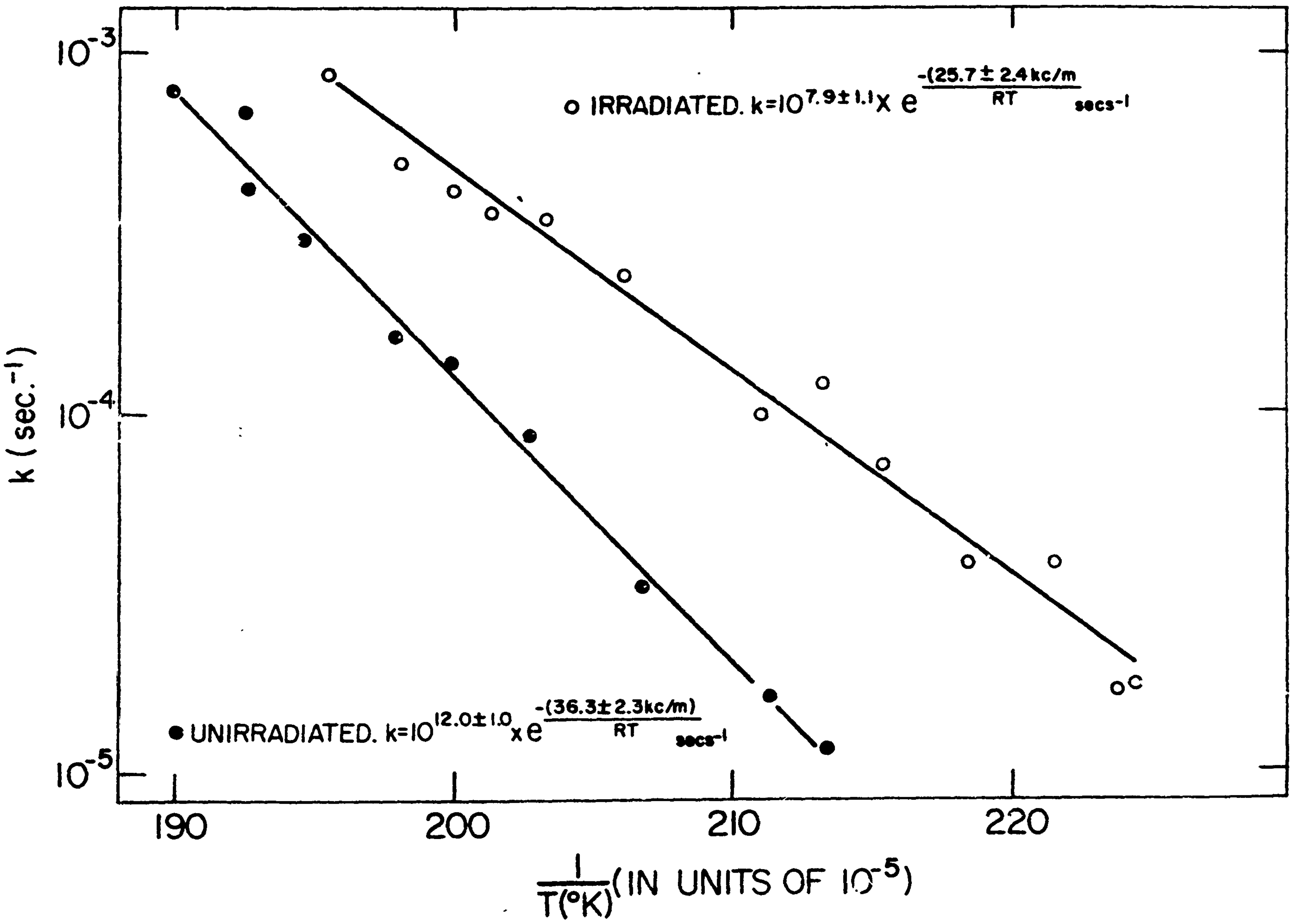
k (sec.$^{-1}$)
10^{-3}
10^{-4}
10^{-5}
190
200
210
220
$\frac{1}{T(°K)}$ (IN UNITS OF 10^{-5})
○ IRRADIATED. $k = 10^{7.9 \pm 1.1} \times e^{\frac{-(25.7 \pm 2.4 \text{kc/m}}{RT}} \text{secs}^{-1}$
● UNIRRADIATED. $k = 10^{12.0 \pm 1.0} \times e^{\frac{-(36.3 \pm 2.3 \text{kc/m})}{RT}} \text{secs}^{-1}$
C

FIG.6

obviously some initial reaction which obscures the main one. The equation $(\alpha - \alpha_o) = a(t-t_o)^2$ reduces this objection somewhat since α_o, t_o may be regarded as a correction to α and t which tends to "eliminate" the obscuring reaction. However, it is possible to draw some generalized topochemical conclusions from these power laws if some trend in the power is observed with a variation in temperature, irradiation conditions, etc. The reader is referred to the original paper for details, but evidence exists for assuming that a two and a three dimensional reaction occur simultaneously. The two dimensional reaction probably involves decomposition at grain-boundaries, dislocations, etc. while the 3 dimensional reaction is simply growth into the more perfect regions of the crystal. However, as regards irradiation, Jach concludes that irradiation vastly increases the concentration of potential nuclei. On attaining furnace temperature, a rapid two dimensional reaction occurs which surrounds all "perfect" areas of crystal with Pb, the decomposition product. From then on, the reaction naturally follows contracting envelope kinetics.

The decay rate is shown to reflect the rate at which this interface penetrates the "perfect" crystallites. If it is assumed that the growth mechanism in some way involves the excitation of an electron from the full band to an electron trap below the conduction band then the decrease in activation energy upon irradiation might result from a possible change in this excitation energy after 20% irradiation decomposition which has occurred prior to the thermal decomposition. The presence of one foreign body for every 5 lattice points must introduce large local strains which are not annealed and these can introduce electron traps. These traps are probably deep so that thermal excitation from the full band is easier. The act of decomposition is assumed, in a general way, to depend upon the untrapping of these electrons. The large decrease in pre-exponential factor is more difficult to interpret. It is difficult to see how cracking, faulting, etc. can cause such a major change in the pre-exponential factor. Jach tentatively suggests the following. The irradiation decomposition leaves behind what must be a fairly open structure. If decomposition is governed by the reaction between two entities such as azide radicals, or an azide ion plus an azide radical (as has been put forward many times in connection with azide decompositions) then the presence of vacancies homogeneously distributed would hinder the reaction between these entities. A simple minded picture is these two entities coming together every 10^{-13} secs. and reacting if they have sufficient excitation energy. The partial relaxation into these vacancies could decrease the reaction probability by the four orders of magnitude observed. This is akin to a probability factor operative in bimolecular reactions where the probability is strongly influenced by steric factors. It is, so to speak, a reverse cage effect.

From the point of view of irradiation effects, the two compounds described above, PbN_6 and BaN_6 are the most important since they have been the most widely studied. Many others have been studied but very little has been said of these regarding irradiation. Only PbN_6 has practical use. The alkalie azides have proved more difficult to study mainly because the volatility of the product metal (K,Na,etc.) destroys the reproducibility. Irradiation studies then become meaningless. Perhaps a more important reason is that the heavy metal azides are more slow to nucleate. This results in an induction period and sigmoidal kinetics. It is in such cases that irradiation has its largest and most obvious influence, namely the production of more nuclei or potential nuclei. If unirradiated material were to nucleate instantly (resulting in contracting envelope kinetics) it is clear that an irradiation effect of the type just considered will be lost, since the effect of any irradiation produced nuclei will be swamped by those already present. However, irradiation can produce marked effects even when nucleation is normally instantaneous (see later - Bromates) but reproducibility is a necessary prerequisite. Mention should nere be made of a study by Jacobs and Tompkins of the KN_3 thermal decomposition(13) in which pre-irradiation with U.V. was carried out. They conclude that U.V. create more nucleus centers and one effect of this is to eliminate irreproducibility otherwise obtained. A similar influence occurs with $KBrO_3$ (see later). Also, an enhancement of rate is found.

(b) Oxalates

The thermal decompositions of metal oxalates have been studied with particular emphasis on the silver and nickel compounds. The α vs t curves are always sigmoidal but a duality of the type of acceleratory region exists, namely the "exponential" and "power law" type. Basically, these are $\alpha = A\exp(kt)$

and $\alpha = Bt^m$ respectively. The exponential law is generally regarded as indicative of a chain reaction i.e. the branching of a growing nucleus whereas the power law indicates a fixed topochemical scheme in which "m" depends on whether nuclei grow in 1, 2, or 3 dimensions and on the law governing their rate of increase.

(i) Silver Oxalate

Haynes and Young(17) conducted an extensive kinetic investigation of the effect of small reactor doses on the subsequent thermal decomposition of silver oxalate. They found it was not possible to reproduce results for fresh unirradiated material. The acceleratory region sometimes followed the exponential and other times a cubic law kinetic picture. The decay period, however, was reproducible if the period below $\alpha = 0.5$ was "eliminated" by translating the runs to a common time at $\alpha = 0.5$. The decay period followed "contracting cube" kinetics given by

$$\alpha = 1 - (1 - kt)^3 \tag{19}$$

The freshly prepared material was irradiated for times between 5 and 40 minutes in the B.E.P.O. core (thermal flux 1.2×10^{12} neutrons/cm^2/sec). The subsequent thermal decomposition was still found to be irreproducible, but in a different way. Now the α vs t curves for the acceleratory region were "predominantly cubic", since $\alpha^{1/3}$ vs t were "moderately straight plots." By introducing a time correction to the data and then multiplying each of the α values for a given run by a given factor it was possible to superimpose all the curves for irradiated fresh material. It indicates that although the results are irreproducible, they all appear to have the same kinetic form, namely an approximately cubic acceleratory region followed by a "contracting cubic" decay period. Since both irradiated and unirradiated material display the contracting sphere kinetics it is assumed that an interface is established which after the maximum rate stage, moves into the crystal at a constant rate. The irreproducibility below the maximum rate is associated with differences in the way in which this interface is established, namely, the radiolysis results in different numbers of "growth nuclei".

Haynes and Young draw the following conclusions. For fresh unirradiated material, the kinetic form depends on the nature of the external and internal surfaces exposed during the reaction. Cracking, probably due to the release of occluded solvent takes place irregularly throughout the early stages of the reaction. At the maximum rate cracking has ceased and each crystallite is covered by product. This coverage could be achieved by an "exponential" branching process (which would give interconnected compact nuclei) or by a simple first order nucleus formation law (the latter should theoretically yield $\alpha \propto t^4$ law) whereas Haynes and Young only mention the power obtained in one run, namely, 3.7. For irradiated fresh material they suggest that the light irradiation dose poisons the branching process by converting the branching points from "germ" to "growth" nuclei after which the only possibility is the growth of a constant number of compact nuclei from sites determined by the nature and extent of the pre-irradiation and by cracking. However, it is not clear why irreproducibility should still exist after irradiation. If their mechanism were operative it would seem that a higher irradiation dose would enhance the number of compact nuclei in a manner proportional to the dose. Furthermore, it is generally accepted that branching occurs at grain boundaries if at all. Here reactivity is higher than in bulk material. It is difficult to see how irradiation, especially such light doses, can change this picture. If the branching points were converted from "germ" to "growth" nuclei, the only effect would seem to be a systematic enhancement of the (exponential) growth rate with irradiation dose.

The number of new (growth) nuclei created by irradiation will not be enough to change the kinetics, since, by its very nature, the exponential process will very shortly after furnace temperature has been attained, overshadow the effect of new irradiation produced nuclei. Only a very large dose, which would create <u>many</u> growth nuclei at the surface and in the bulk might be expected to change an exponential to a cubic law. But then α_{max} would be close to zero, which it is not.

After annealing they find that the irreproducibility was eliminated and that now a systematic irradiation effect occurs with increasing dose. Basically, they find an increase in the acceleratory rate with increasing irradiation and a simultaneous <u>increase</u> in α_{max} $(0.4 \rightarrow 0.7)$. Also, the acceleratory region is now more closely fitted to a cube law while the decay stage deviates from the contracting cube expressions for high doses

($4 \cdot 3 \times 10^{15}$nvt). They explain these results by assuming that in heavily irradiated material, compact growth nuclei can be established in loci where they do not readily overlap with other nuclei. Then they would contribute to the t^3 dependence but since they do not overlap as readily the maximum rate would occur at higher values of α than for unirradiated material. At the same time, there are still regions of high nucleus density at the surface.

Again, it is difficult to reconcile these speculations with experiment or theory. It is generally accepted that reaction within the bulk of a near perfect crystallite is unlikely since escape of only the very smallest gas molecules is possible. It seems just as likely that irradiation induced strain leads to a larger number of smaller crystallites and if it is assumed that the number of growth nuclei is proportional to the newly exposed surface area, then the larger crystals will exhibit lower α_{max} than the smaller ones produced by irradiation. Experience has shown that distinction between an exponential and power law can be a very difficult task if at all possible. It would seem that such distinctions are valuable only when very definite trends occur with such variables as temperature, irradiation, etc.

(ii) Nickel Oxalate

The decomposition of nickel oxalate has received some attention. The irradiation effect for dehydrated nickel oxalate has been studied by Jach and Griffel(18). They used polycrystalline material and worked in the range 253-360°C, a quite large span for this material. Fig. 7 shows some of the observed irradiation effects. Curve B shows a typical α vs t plot for unirradiated material. An acceleratory region is present and is represented by an $(\alpha - \alpha_o) = a(t - t_o)^m$ type expression with m = 2, while the decay stage closely fits an "exponential" type of decay. The thermal decomposition of irradiated material (390 hrs. in the Brookhaven Graphite Research Reactor, flux about 1×10^{13} neutrons/cm^2/sec overall and 4×10^{11} epi-Cd) at almost the same temperature is shown in curve A which is on the same scale as B while curve C represents the irradiated material curve on an expanded time scale to display more details of the acceleratory region. Three irradiation effects are at once evident. a) The time required to reach the maximum rate is drastically reduced. b) The maximum rate is not affected and c) α_{max} is reduced. The temperature effects on the "unirradiated" reaction are complex but basically they find that irradiation has no effect on the rate or activation energy in the region <u>above</u> the maximum rate, while in the early stages the activation energy is reduced and the rate increased. The effect of temperature and irradiation on α_{max} is shown in figure 8. The following topochemical model is introduced. Reaction begins at the surface of each crystalline from a certain number of potential nuclei which become activated by chance thermal fluctuations. Growth then proceeds two-dimensionally into the crystallite probably along certain planes (nickel oxalate has been shown to have a layer like structure). This accounts for the power m = 2. (Jacobs and Kureishy(19) find the same power and draw the same

FIGURE 7

Fractional decomposition α vs time for dehydrated nickel oxalate.

Open circles: unirradiated material at 279.9°C.

Closed circles: irradiated material at 282.7°C.

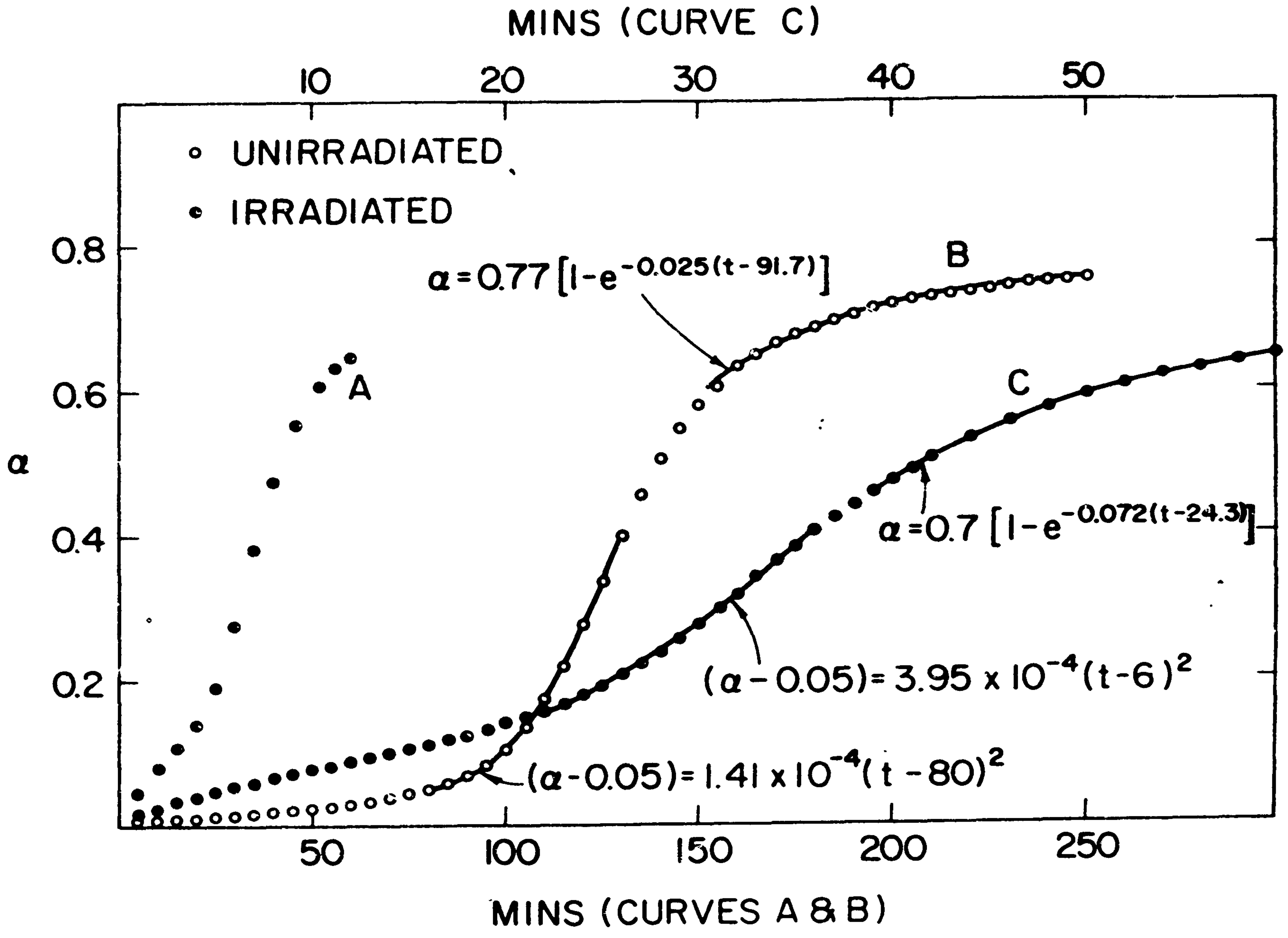
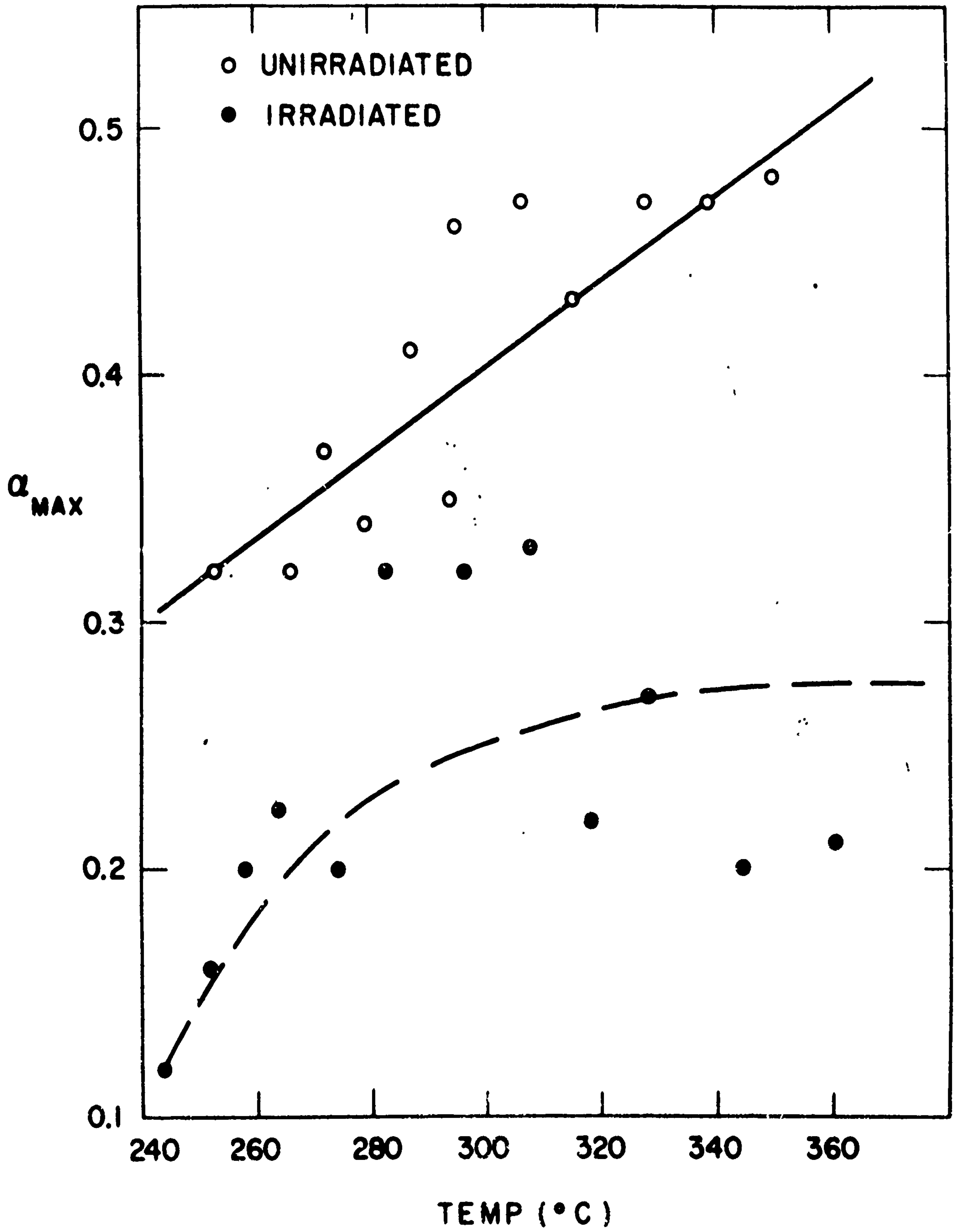

MINS (CURVE C)
10
20
30
40
50
○ UNIRRADIATED
● IRRADIATED
0.8
0.6
0.4
0.2
α
A
B
C
$\alpha = 0.77\left[1 - e^{-0.025(t-91.7)}\right]$
$\alpha = 0.7\left[1 - e^{-0.072(t-24.3)}\right]$
$(\alpha - 0.05) = 3.95 \times 10^{-4}(t-6)^2$
$(\alpha - 0.05) = 1.41 \times 10^{-4}(t-80)^2$
50
100
150
200
250
MINS (CURVES A & B)

FIG. 7

conclusion. The activation energy for nucleus formation is a little lower than for growth and irradiation greatly enhances the number of potential nuclei but does not affect the growth rate. The justification for this model is as follows. The complexity of the Arrnenius plots indicate that nucleation and growth are occurring simultaneously at the beginning of the reaction but at elevated temperatures the growth process is enhanced relatively more than the nucleation (since it has the higher activation energy). This is reflected in the "clean" $m = 2$ law at lower temperatures. After irradiation this "clean" $m = 2$ law holds even at lower temperatures. This is because large numbers of potential nuclei exist so that growth of existing nuclei predominate. This agrees with the behavior of α_{max} (fig. 8). The argument is that any condition favoring enhanced nucleation leads to a lower value of α_{max}. This condition is realized by lower temperatures (lower activation energy for nucleation) and irradiation (increased number of potential nuclei). A simple-minded topochemical model shown in fig. 9 might clarify this argument. The figure shows how randomly formed nuclei have grown after a certain time. If conditions were such that only two nuclei were able to grow, the picture b) might apply. Now α_{max} occurs when nuclei overlap. In case a) α_{max} would clearly be lower than case b). On the basis of this picture, it is shown why the maximum rate is not increased upon irradiation even though the number of nuclei is increased. The reader is referred to the original paper. The fact that the decay stage is uninfluenced by irradiation is simply due to the fact that at this

FIGURE 8

α_{max} vs temperature.

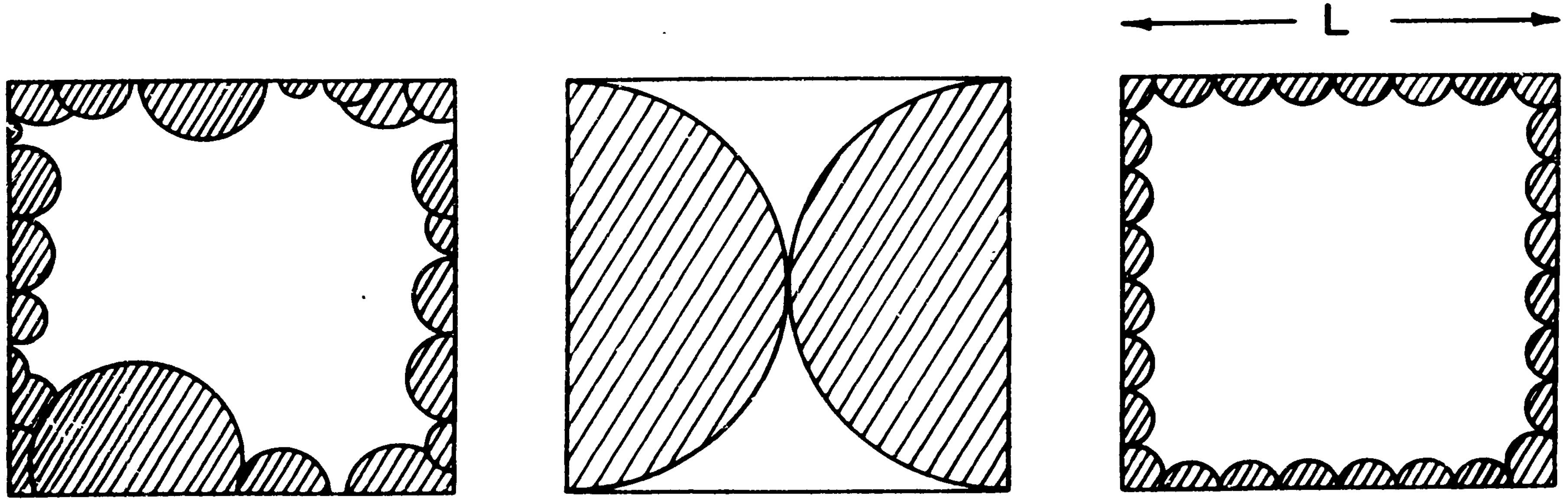


○ UNIRRADIATED
● IRRADIATED
α_{MAX}
0.1
0.2
0.3
0.4
0.5
240
260
280
300
320
340
360
TEMP (°C)

FIG.8

FIGURE 9

Simplified topochemical model.



(a) (b) (c)

FIG. 9

stage the interfaces have been completely established. This stage merely reflects the growth of this interface into the crystal. To summarize, it appears that irradiation increases the number of nuclei but not the growth rate.

(iii) Other Oxalates

Numerous irradiation effects on other oxalates have been described in the literature. These will be described briefly. Young(34) studied the radiation decomposition of uranyl oxalate which also included a brief study of the subsequent thermal decomposition after small irradiation doses (about 4×10^{14} thermal neutrons/cm^2/sec). The fission fragment damage so produced leaves a fixed number of linear imperfections which are also lines of chemical inhomogeneity where the nucleation requirements have already been established. As soon as reaction temperature is reached, the reaction propagates radially outwards at a constant rate thus forming cylinders of product. This should lead to a t^2 law, which is observed.

Finch, Jacobs and Tompkins(20) briefly studied the effect of UV on the subsequent thermal decomposition of silver oxalate during the course of a photolysis study. The acceleratory region of the "unirradiated" decomposition could be represented by the exponential law $\alpha = Ce^{kt}$. The only effect of pre-irradiation was to increase the value of C. There is evidence for a high activation energy for nucleation, which process consequently occurs at rather special surface sites corresponding to low activation energy. Reaction therefore consists of growth from a few fixed sites. The effects of irradiation is explained simply by assuming an increased number of these surface sites. Space does not permit a fuller description of their work but they conclude that reaction starts at places where pre-irradiation has decomposed a whole patch of oxalate ions leaving anion vacancies. The nucleation activation energy then corresponds to the energy required to transfer an electron from an oxalate ion into an anion vacancy.

The thermal decomposition of irradiated lead oxalate has been studied by Prout et al(21) but since the effects are so similar to those on permanganates studied by Prout the reader is referred to the following discussion of the permanganates.

(c) Permanganates

The subsequent thermal decompositions of irradiated permanganates have been thoroughly studied by Prout and co-workers(22-25). The results and conclusions are basically similar for all and so only a typical one, $KMnO_4$ will be described. The effect of the various typical irradiations are shown in fig. 10. Increasing irradiation doses have the following effects. a) Vast reduction of the induction period and b) an increase in the maximum rate. Comparison of the results obtained after thermal column and x-ray irradiation indicated that x-rays were the effective agents. Prout considers that the displacements of significance are those of K^+ ions into interstitial positions by Compton recoil electrons. These will be no more than 4 or 5 atomic distances from the vacancies created and will be randomly distributed throughout the crystal. At thermal decomposition temperatures (∿225°C) annealing of these point defects and the

FIGURE 10

Effect of pre-irradiation on thermal decomposition at 215°C.

Whole Crystals: A-unirradiated; C - 15 hr. in BEPO;

D - 15 hr. in γ - hot-spot; G - 3 min. in cyclotron.

Ground Crystals: B - unirradiated; E - 15 hr. in BEPO,

F - 15 hr. in γ - hot-spot.

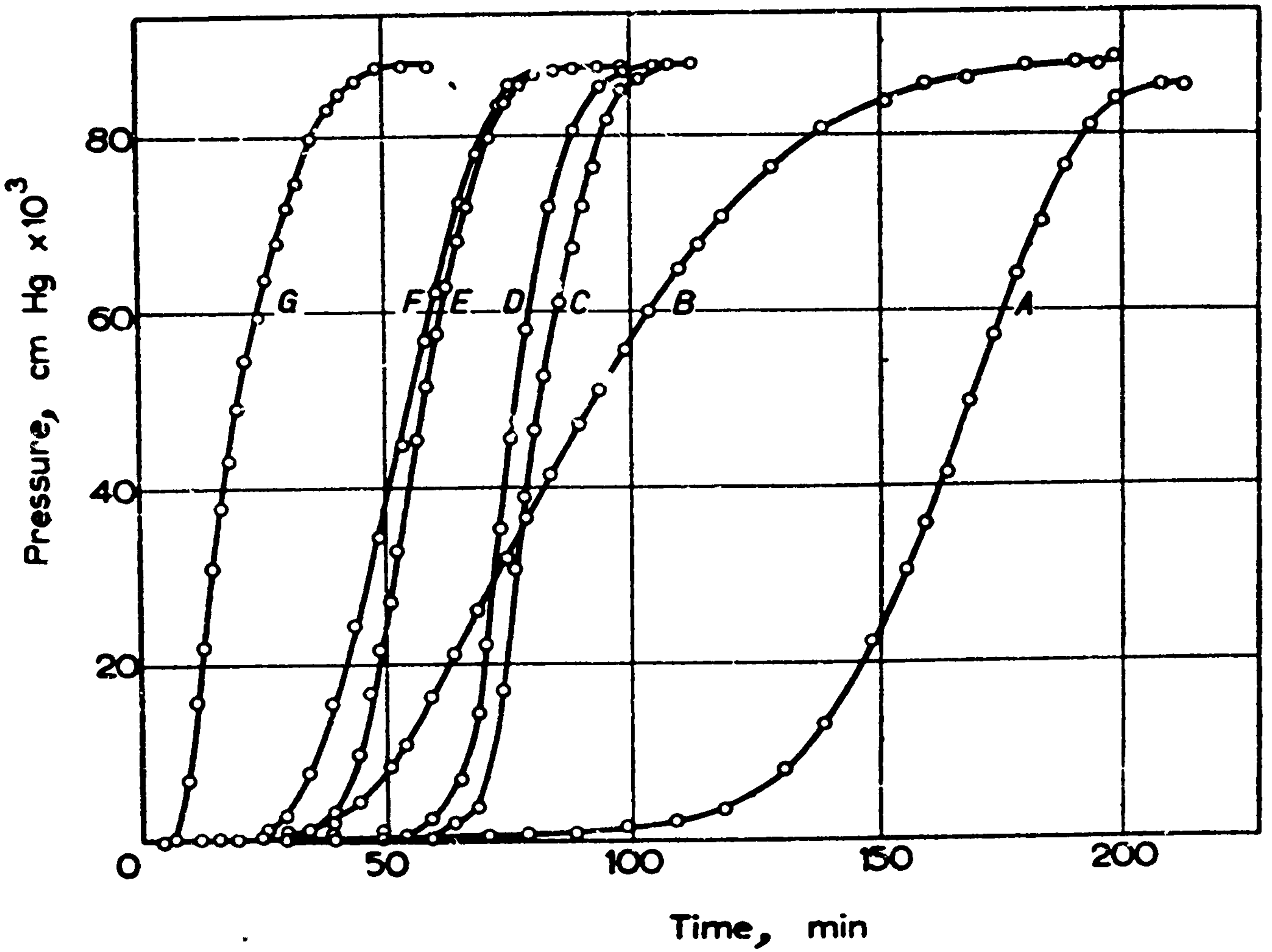

Pressure, cm Hg x10^3
80
60
40
20
0
50
100
150
200
Time, min
G
F
E
D
C
B
A

FIG. 10

associated Wigner energy release can cause bond rupture in adjacent permanganate ions resulting in a "decomposition center." Prout further considers the "decomposition center" to be a region of strain which may result in a lower activation energy for vacancy jumps. Thus, preferential annealing around this region may give rise to a "decomposition spike". A steady accumulation of strain results which produces physical fracture at the end of the induction period followed by a general bulk disintegration. With moderate and heavy doses the fracture process occurs even after the induction period. With heavy doses fracture produces an instantaneous breakup of the crystal. The very low value of α_{max} is the result.

In support of his mechanism, Prout quotes the following evidence a) A plot of log I against 1/T where I is the length of the induction period, should yield an activation energy for vacancy migration if his mechanism holds (this is equivalent to comparing annealing times during which the same degree of annealing occurs as a function of temperature). The value found is 1.31 eV. By comparison with vacancy migration in cold worked Cu and Mo Prout assigns his energy to vacancy migration. b) Proton bombardment virtually eliminates the induction period. This he feels is due to the greater damage done by fast particles in creating a larger number of secondary knock ons. Annealing will be rapid due to the high concentration of defects and shortening of jump times caused by lattice distortions. c) Ground and whole crystals irradiated for the same time and decomposed at the same temperature have different induction periods, the ground case being shorter. This he attributes to the greater number of close pairs and vacancies in irradiated ground material. However he also finds a saturation effect where after grinding, ever increasing irradiation doses have no effect. He considers that instantaneous recovery of displaced atoms occur at these high doses.

Prout's hypothesis has been challenged by V.V. Boldyrev.(26) and co-workers. Bolydrev points out that the minimum electronic energy to cause Ag^+ displacement in silver permanganate is about 0.7 MeV based on a 25 eV displacement energy. Prout indeed finds that preliminary Co^{60} γ-irradiation (1.33 MeV) of $AgMnO_4$ does accelerate the decomposition, whereas U-V (10-100 eV) leaves the decomposition unchanged. However, Bolydrev's experimental data do not support Prout's mechanism. Such experiments include irradiation of $AgMnO_4$ with 0.2 MeV x-rays (i.e. less then a third of the threshold energy) which resulted in a marked increase in the rate of thermal decomposition, even though the radiation doses were an order of magnitude smaller than those used by Prout. In addition, Boldyrev points out that the decomposition of Barium azide is appreciably accelerated after decomposition by relatively soft x-rays (50-70 KeV). This again does not support Prout's mechanism. However, Boldyrev does consider the possibility that it is not Prout's mechanism which is at fault but rather the calculation for its verification. Thus, for example, the value 25 eV for ion or atom displacement may be quite in error for such positions as at a dislocation, etc.

Unlike Prout, Boldyrev and co-workers consider the most probable cause for the acceleration of thermal decomposition subsequent to irradiation is the radiolytic inclusion of a solid product into the lattice of the initial substance. The acceleration then results from deformation of the initial substance layer at the interface with the radiolytic product and the ease with which electronic and ionic processes occur in this region. A similar idea has already been proposed by Jach for the αPbN_6 decomposition(16).

(d) Bromates

Very little, if any, irradiation studies have been done on the thermal decomposition of compounds of the type that are instantly nucleated. It would appear that since the primary irradiation effect is nucleation enhancement, any effect of irradiation would be masked in such compounds. This is largely true, but there do exist some subtler effects. An early study on potassium bromate(27) revealed that irradiation has a marked effect on the decomposition even though this compound is nucleated instantly and displays its maximum rate at $t = 0$. An Arrhenius plot showed a marked discontinuity over which a tenfold increase in rate occurred in unirradiated material. This is believed due to melting of a eutectic formed between the product KBr and $KBrO_3$, The bromate in the liquid phase decomposing much faster than in the solid state. The interesting effect of irradiation here was to remove this discontinuity (or rather, if there was a discontinuity with irradiated material it was displaced to a temperature too low to be observed).

This was interpreted as enhanced melting due to strain imposed by irradiation products. However, these bromate studies were followed by a more extensive and meaningful study of $NaBrO_3$ (28,29). Jach has shown that there might possibly be irradiation effects other than enhanced nucleation. The thermal decomposition of polycrystalline $NaBrO_3$ was studied in the temperature range 323-430°C. The only products are NaBr and oxygen. A typical decomposition is shown in fig. 11. Such behavior is typical of decompositions in which the surface of a crystallite becomes nucleated the instant the temperature is attained. Following this, the reactant-product interface advances into the crystal at a constant rate. The rate is therefore a maximum at the beginning and falls off according to a definite topochemical scheme. Various attempts to fit the curves with a mathematical expression failed except for the cubic expression

$$\alpha = at^3 - bt^2 + ct \qquad \ldots\ldots\ldots\ldots\ldots \quad (20)$$

where a, b, c are positive quantities. If the original crystallite is a cube of side A and the interface advances at a rate k (length/time) then clearly

$$\alpha = \frac{A^3 - (A - kt)^3}{A^3} = 8\left(\frac{k}{A}\right)^3 \cdot t^3 - 12\left(\frac{k}{A}\right)^2 \cdot t^2 + 6\left(\frac{k}{A}\right) \cdot t \quad \ldots \quad (21)$$

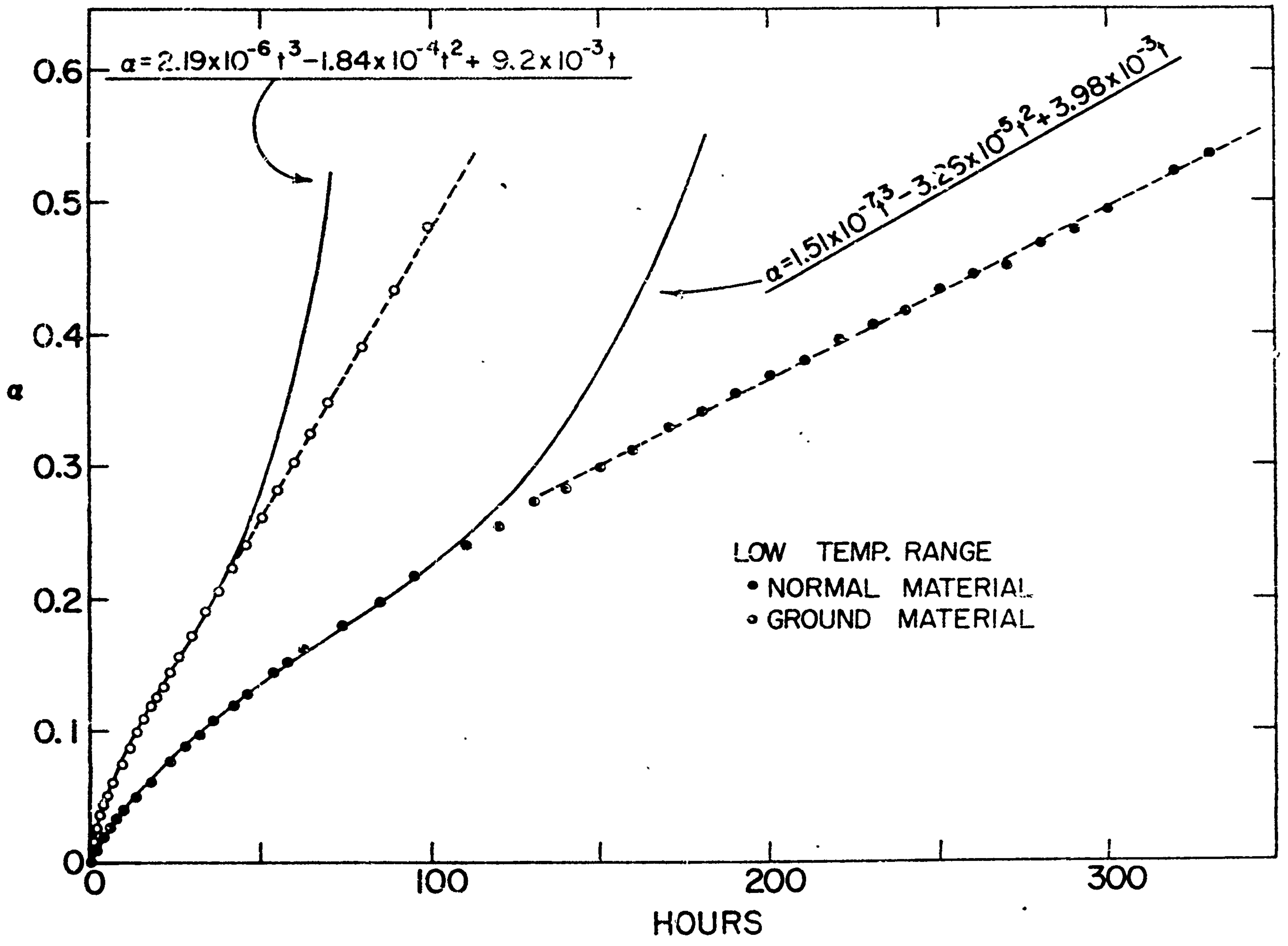
or

$$\alpha = 8\, r^3t^3 - 12\, r^2t^2 + 6\, rt \qquad \ldots \quad (22)$$

where $r = k/A$.

FIGURE 11

α vs time in low temperature region for $NaBrO_3$ at 330°C.



α = 2.19x10^-6 t^3 - 1.84x10^-4 t^2 + 9.2x10^-3 t
α = 1.51x10^-7 t^3 - 3.25x10^-5 t^2 + 3.98x10^-3 t
LOW TEMP. RANGE
• NORMAL MATERIAL
∘ GROUND MATERIAL
α
0
0.1
0.2
0.3
0.4
0.5
0.6
0
100
200
300
HOURS

FIG. 11

The cubic fit to the experimental points is therefore consistent with the "contracting cube" type of kinetics. However, it should be mentioned that over most of the temperature range studied decomposition is preceded by some incipient form of melting. This is shown in fig. 12. which shows an Arrhenius plot of the initial rate $(\frac{d\alpha}{dt})_{t=o}$. The large discontinuity is due to the onset of what is probably the melting of a eutectic between $NaBrO_3$ and product NaBr. It is different to ordinary melting of a pure substance in that only the surface layers (in contact with newly forming NaBr) melt and the system is well below the thermodynamic melting point. At temperatures below the discontinuity, the decomposition is presumably of the purely solid type. However, in this region the rates are so slow that a systematic investigation was impossible. Now, the "melting" does not invalidate the contracting cube kinetics since decomposition is faster than this melting process otherwise complete liquidation would occur. Comparison of equations 20 and 21 shows that it is possible to extract from the experimental cubic expressions three values of the parameter r (or k/A), one from each term. If $r_c \cdot r_s \cdot r_1$ are the values of r obtained from the cubic, square and linear term respectively, then $r_c = (a/8)^{1/3}$, $r_s = (b/12)^{1/2}$ and $r_1 = (c/6)$. ...... (23) Clearly, equality of these 3 quantities must strengthen the assumption of cubic kinetics. An Arrhenius plot of these three quantities is shown in fig. 13 together with the corresponding values for γ-ray irradiations which are discussed below. Two features are worth noting with unirradiated material. a) At

FIGURE 12

Arrhenius plot of $k_i = \left[\frac{d\alpha}{dt}\right]_{t=o}$.

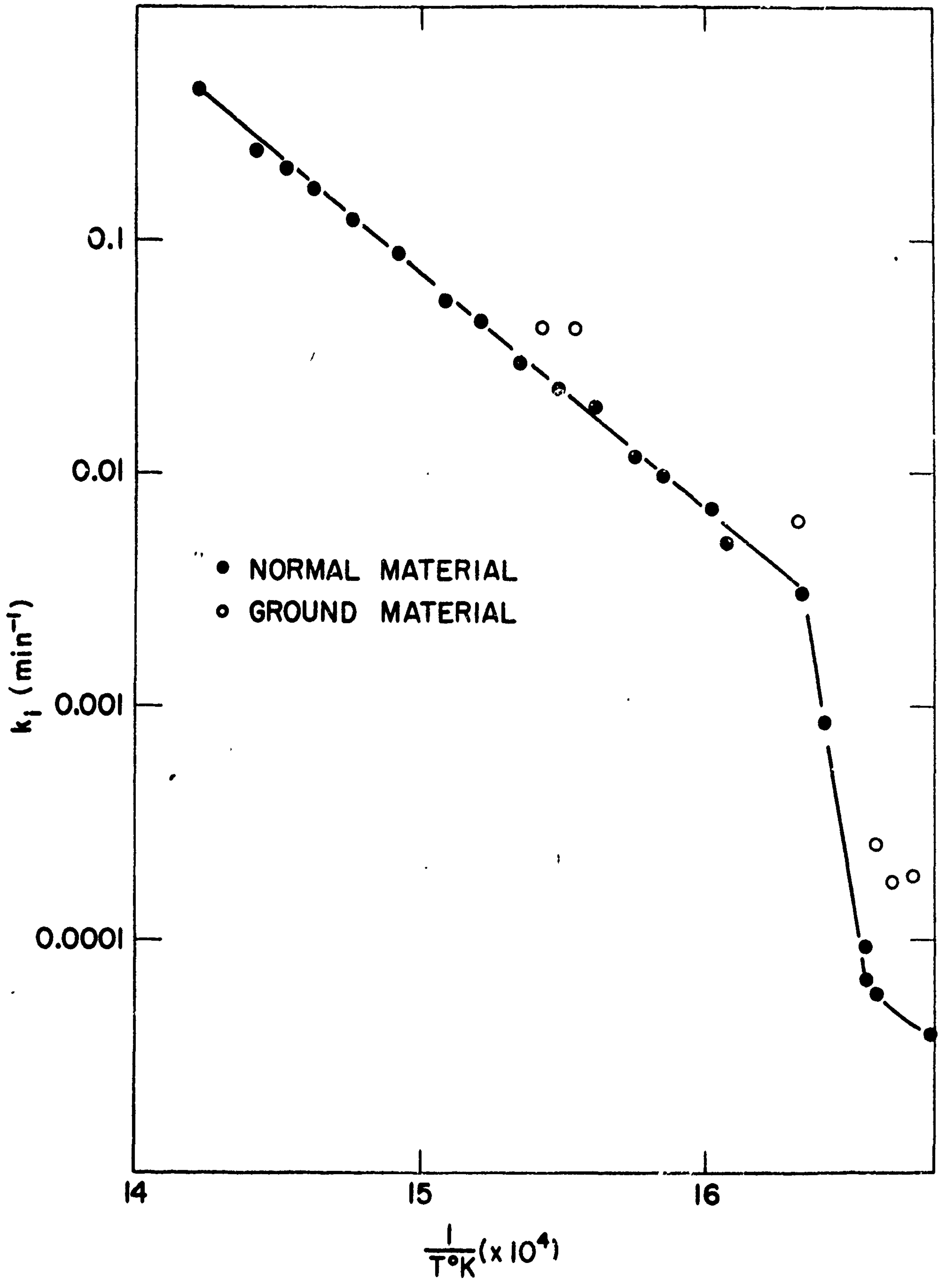

0.1
0.01
0.001
0.0001
k_1 (min^{-1})
● NORMAL MATERIAL
○ GROUND MATERIAL
14
15
16
$\frac{1}{T°K}$ (x 10^4)

FIG. 12

high temperatures the three quantities are practically equal b) At lower temperatures (but still above the discontinuity) they begin to diverge somewhat and below the discontinuity they are widely divergent.

The basic contention arising out of this study is that these observed divergencies of r can be explained in terms of preferential reaction at "abnormal" sites such as sub-grain boundaries, dislocations, etc. As an example, Jach considers the kinetic equations corresponding to reaction at sub-grain boundaries which will be more in evidence at lower temperatures since he presumes that the activation energy for this mode of decomposition will be relatively low. Thus instead of a contracting envelope around a crystallite, low temperature might favor a situation where reaction begins at all sub-grain boundaries followed by contracting cubes around all the subgrains. Suppose then, that the original crystallite cube, side A, is divided up into "m" subgrains of size "L". The equation corresponding to equation 22 is now

$$\alpha = 8r^3t^3(1+m) - 12r^2t^2(1+m\theta) + 6rt(1+\theta^2 m) \quad \ldots\ldots \quad (24)$$

where $\theta = L/A$. This equation only differs from equation 22 in that extra terms are introduced into the coefficients of the t, t^2 and t^3 terms. These extra terms result in the divergences seen in figure 13. It is possible to solve for r, θ and m and the "activation energy" of these quantities are self-consistent. (The reader is referred to the original paper).

FIGURE 13

Arrhenius plot of cube law parameters (showing γ-ray effects).

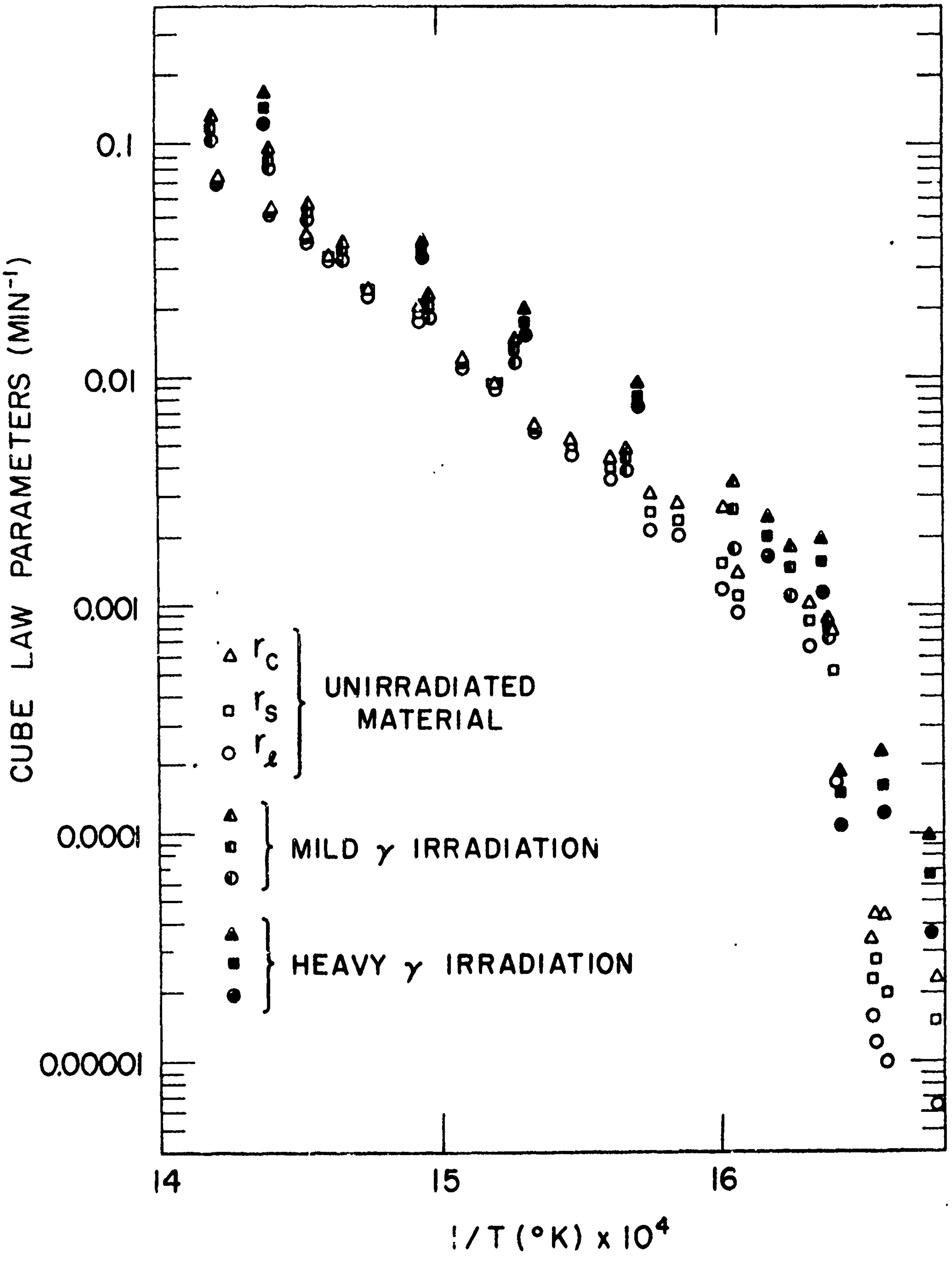

CUBE LAW PARAMETERS (MIN⁻¹)
0.1
0.01
0.001
0.0001
0.00001
14
15
16
1/T (°K) x 10⁴
△ r_c
□ r_s
○ r_ℓ
UNIRRADIATED MATERIAL
MILD γ IRRADIATION
HEAVY γ IRRADIATION

FIG. 13

However, it is pointed out that any reaction other than the normal contracting cube around a crystallite will introduce extra terms in the coefficients and might therefore also explain the divergences. For example, preferential reaction along a dislocation might result in an expanding cylinder of product (with dislocation line as axis of cylinder) and might therefore introduce a strong extra term in the t^2 coefficient, the volume of the cylinder being proportional to t^2. The kinetic analysis merely demonstrates that the assumption of preferential reaction (at lower temperature) at "abnormal" sites can explain the divergences of the cube law parameters.

One of the main purposes of introducing this kinetic analysis was to demonstrate any possible influences of irradiation. Arrhenius plots of these parameters after x-ray irradiations are also shown in figure 13. Clearly the divergences are more pronounced. At high temperature divergences do occur which is not the case for unirradiated material. Jach considers this to be evidence for preferential reaction at defects, the number of such defects being enhanced upon irradiation. One might, for example, consider sub-grain boundaries. At high temperature, the "normal" contracting cube around a crystallite will move fast. Although reaction at the sub-grain boundaries must occur as well, the latter will be masked by the "normal" reaction. However, this will not be the case after extensive irradiation damage. The introduction of defects at the sub-grain boundaries can enhance reaction there to such an extent that this mode will no longer be masked. The same conclusions can be drawn about the ground material and reactor irradiated material which exhibits effects similar to those already described. One must add one important observation here. The wording preferential reaction might in the case of bromates have to be replaced by preferential melting, since a relationship between melting and decomposition obviously exists here. It is possible to explain the irradiation and grinding effects by postulating preferential melting rather than preferential decomposition. However, the importance of the kinetic analysis still remains since in its most general terms the reaction is still occuring preferentially at defects. Or, looking at it from another viewpoint, one should perhaps be constantly aware of the possibility of preferential melting in discussing possible reactivity problems. Jach points out that these postulates are speculative but at the same time demonstrates the need for further work along these lines. Far too little is known about preferential chemical reaction at defects.

(e) Other Compounds

(i) Mercury Fulminate

As part of an extensive study on the mercury fulminate decomposition, Bartlett, Tompkins and Young(30) irradiated this compound with mercury resonance radiation (2537Å). When mercury fulminate is heated to about 100°C it evolves mainly CO_2 and N_2 leaving a solid residue of uncertain composition. There apparently exists a very strong aging effect in this material. The kinetics of thermal decomposition of freshly prepared crystals differs markedly from aged crystal. Basically freshly prepared material exhibits an acceleratory period which fits an exponential law ($\alpha \propto e^{kt}$) while aged material fits a cubic law ($\alpha \propto t^3$), after the usual t_o corrections are made for initial reactions. They present evidence for preferential reaction at sub-grain boundaries. In fresh material these boundaries are intact and an advancing reaction front can branch where these boundaries intersect. This would lead to exponential kinetics. In aged material, the crystals become separated into largely independent blocks. Before the acceleratory region a gas is evolved by a reaction of low activation energy. This they feel is a gaseous product from a slow prolonged room temperature decomposition which also changes the crystals from a white to a brown color. The cubic reaction then describes processes which occur within the individual blocks. The effect of irradiation on fresh material is to change the kinetics from the exponential to the cubic type. A similar effect is obtained after crushing fresh material. They believe that the effect of irradiation (and crushing) is therefore to break up the crystals by rupture at sub-grain boundaries. Photographs of irradiated material do indeed show crack formation. The effect of irradiation on aged material is to reduce α_{max} from 65 to 50% and to enhance the maximum rate. This is not explained.

(ii) Lead Styphnate

Flanagan(31) studied the effects of x-ray and neutron irradiation on the thermal decomposition of lead styphnate monohydrate in the range 197-228°C. An initial gas evolution and small linear period are followed by the typical acceleratory region. A series of Co^{60} gamma irradiations at room temperature up to 1.8×10^8r did not significantly alter the subsequent thermal decomposition. Reactor irradiation, however, greatly affects the subsequent thermal decomposition. This is shown in fig. 14. The maximum rate for the longest irradiation (curve A) is nearly three times that of the unirradiated sample. Note that the results for irradiated material are unaffected by storage of samples between irradiation and decomposition. The damage appears to be of a permanent type. Flanagan suggests that the irradiated material is decomposing at a large number of evenly distributed sites formed from fast particle damage in the crystal while the "unirradiated" decomposition proceeds from a smaller number of more localized regions, e.g. cracks, grain boundaries, etc. It is difficult to see why α_{max} is increased upon irradiation. One possible explanation is that irradiation has no effect other than allowing the crystal to fracture into more crystallites upon decomposition as compared to the unirradiated state. Then if it is assumed that nucleation centers exist in numbers merely proportional to exposed crystal surface area then on average the smaller crystallites have fewer nucleation centers than the original larger (unirradiated) ones. This will lead to a larger α_{max} (see nickel oxalate section) but at the same time the rate is increased due to the larger number of crystallites (and therefore nuclei). Clearly, further work is needed, especially direct microscopic observations.

FIGURE 14

The thermal decomposition curves of reactor-irradiated lead styphnate monohydrate (222.5°C).

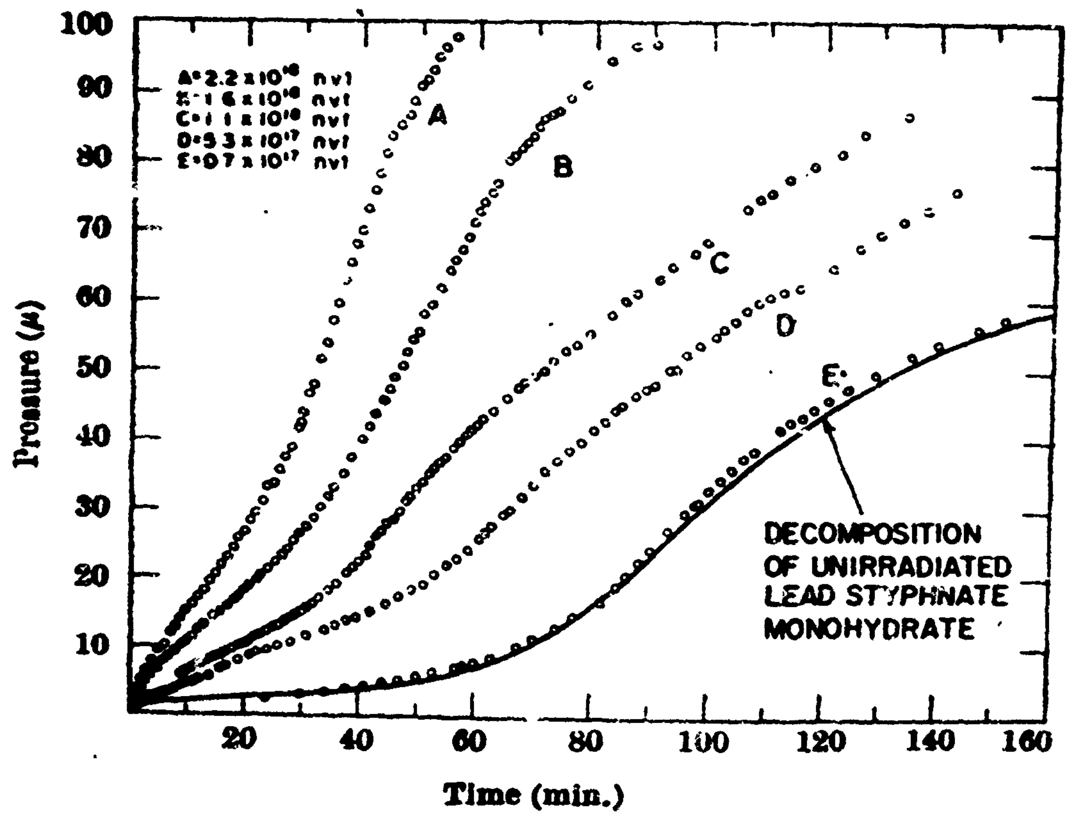

A=2.2 x 10^18 nvt
B=1.6 x 10^18 nvt
C=1.1 x 10^18 nvt
D=5.3 x 10^17 nvt
E=0.7 x 10^17 nvt
A
B
C
D
E
DECOMPOSITION
OF UNIRRADIATED
LEAD STYPHNATE
MONOHYDRATE
Pressure (μ)
100
90
80
70
60
50
40
30
20
10
Time (min.)
20
40
60
80
100
120
140
160

FIG. 14

4. RELATED TOPICS

(a) Thermal decomposition at dislocations

Although this topic might better be suited to a review related to unirradiated material, certain instances have arisen in which a correlation to irradiation effects appears. Jach(32,49) has reported that during some recent thermal decomposition studies, linear kinetics ($\alpha = kt$) were observed in three normally different (kinetically) materials under certain special conditions. These conditions included a) a very low relative temperature where reaction may take a week or two for 10% decomposition, and b) cold-working or pre-irradiation. The three compounds referred to are $NaBrO_3$, αPbN_6 and dehydrated nickel oxalate. As mentioned previously, the $NaBrO_3$ decomposition proceeds by a rapid surface nucleation followed by a contracting envelope. This causes the maximum rate to occur at $t = 0$. αPbN_6 exhibits the classical sigmoid curve while the nickel oxalate decomposition, although sigmoidal, differs very much in detail to αPbN_6.

It is difficult to imagine how a decomposition, growing as it does 3-dimensionally into the crystal, can result in linear kinetics. (Linear kinetics due to one-dimensional growth have been observed in certain dehydration reactions, but these have no relation to the present discussion). Jach proposed that at very low relative temperature, reaction occurs preferentially at dislocations in a manner similar to Franks crystal growth theory at the step of a screw dislocation but in the reverse sense. Thus, if it is assumed that at the step decomposition proceeds with lower activation energy then at very low temperature such a mechanism is favored. The decomposition might occur at the surface step which appears when a screw dislocation meets a surface. The crystal may be described as one atomic plane in the form of a spiral ramp. Decomposition at the step results in successive layers being "peeled" off without destroying the step. This would yield linear rates. Pre-irradiation and grinding enhances this effect by increasing the limits of over which linearity occurs or by increasing the temperature at which it occurs. Both these processes are known to increase the dislocation density. The possible existence of the phenomenon outlined by Jach has been strengthened by recent electron microscope observations(33) on decomposition of Cadmium iodide.

(b) Radiolysis of Solids

As a result of the enormous strides made during the past 15 years in the field of Solid State Physics much interest has been generated in the fundamental processes responsible for chemical changes in solid substances. It is unfortunate that only in a few instances has the attack on such problems been concerted. Chemists have until now paid relatively little attention to solid state phenomena and have approached the problem only when specific practical answers were needed. Historically, chemists have shied away from reactions that were either heterogeneous or irreversible. Studies of reactions that exhibit both disadvantages have naturally suffered severely. The availability of strong sources of irradiation have not greatly improved this situation but now irradiation effects are beginning to spark some enthusiasm. Two end goals are evident. Firstly, irradiation is being used as a tool in the fundamental studies of chemical effects in solids. Secondly, irradiation effects themselves are of interest from a theoretical and practical point of view. In this connection might be mentioned the quest for radiation resistant materials, the use of solid dosimeters, the production of radioisotopes, etc. Several recent reviews have appeared (ionizing radiation effects - Forty(35), Boldyrev and Bystrykh(36), Davids and Weiss(37), Heal(38) and heavy particle radiolysis - Dominey(39). Slow progress has been made over the years in understanding some of the fundamentals in the mechanism of radiation induced changes. The primary processes of irradiation are ionization, excitation without ionization and displacement. Nuclear reactions such as capture, spallation, etc. may also occur. The chemical consequences of these processes in turn depend on the substance being bombarded. The mechanism of displacement by ionizing radiation is still in question. Varley(40) has suggested that multiple ionization of the halogen ions occurs with recombination times sufficiently long to allow ejection of the now positively charged entity by electrostatic repulsion of the positively charged neighbors. One objection to this mechanism is that the recombination time is probably shorter than the natural period of the ion in the crystal lattice rendering displacement before recombination unlikely. Klick(41) proposed a modification in which double ionization of the halide ion occurs followed by transfer of an electron from a neighboring halide. Two neighboring positive holes are formed which react to give a halogen molecule. This molecule occupies one vacant halogen ion site. The other site can move away and later be converted to an F-center while the molecule can after electron capture be converted to an H center. Both centers have been observed simultaneously. Smoluchowski and Wiegand(42) suggest that after multiple ionization the Cl^+ is driven to a neighboring Cl^- forming Cl_2, the de-excitation of the latter providing sufficient repulsive energy to force one of the atoms away creating a vacancy and an interstitial Cl atom. The latter might be formed many lattice distances away from the vacancy by transmission through focusing collisions. What follows these events is a complex sequence of phenomena depending on crystal structure, methods of preparation of the materials (including impurity effects), ionization potentials and bond strengths, etc. As an example of crystal structure effects, one may cite the "cage effect." The primary products of x-ray and electron irradiation of nitrates is nitrite and oxygen. The yield depends on the extent of recombination of these two species which in turn depends on the free volume available within the lattice. The free volume is the difference between the volume of a unit cell and the volume of the ions in it. A higher free volume favors a removal of the oxygen from the influence of the nitrite ion and thus tends to limit recomination. The free space is usually the predominant influence but, as Boldyrev and Bystrykh(36) point out, the ionization potentials of the ions involved may play a determining role. Thus, the free volumes in silver and sodium nitrates are about the same but the ionization potential of the cations differ strongly (7.54 and 5.1 respectively). The radiation stability of silver nitrate is therefore far less than that of sodium nitrate since the silver ion will exert a stronger polarizing action on the nitrate ion than will the sodium ion. Bond strengths in complex ionic salts must also be considered. For example, the energy of the Cl-O and N-O bonds in the chlorate and nitrate ion is respectively 2.38 and 3.65 eV. The corresponding radiation yields are 4 and 0.8 mole O_2 per 100 eV. The presence of water of crystallization in a nitrate, for example, enhances the radiolytic probability as a result of the competitive radiolysis of the water as well as the removal by the water of the oxygen thus reducing the recombination processes. Last, but not least, is the major electronic and structural role played by all types of defects. These may act as trapping centers for excitons and electrons thus enabling reaction to occur where otherwise de-excitation or electron-hole recombinations would occur instead. They may structurally also be centers for preferential decomposition resulting from "cage" type effects. Thus, radiolysis might be favored around the site of an edge dislocation where room is available for decomposition as compared to the smaller, normal lattice site.

The above discussion is merely an attempt to point out some of the current ideas and problems involved in the field of radiolysis of solids. No unifying theory exists nor is it reasonable to assume that one is possible. While the action of irradiation on one chemical compound might be predominantly electronic the action on another may be mostly structural.

An important body of work which may have significant bearing on thermal decomposition subsequent to irradiation has been under way for the past few years by Forty and co-workers who have been examining the decomposition of various compounds by electron bombardment. Lead iodide has been extensively investigated by them and the work has proved most interesting. Forty et al(43) followed the decomposition of thin platelets (about 1/10 mm diameter and a few angstroms thick) in an electron beam of an electron microscope. The ultimate product is metallic lead and iodine. Usually three stages are involved in this decomposition. The first is the rearrangement of the existing dislocation configuration to form isolated loops of dislocations. In the intermediate stage bright patches appear which probably represent cavities in the crystal. This is followed by a stage in which small lead crystallites are nucleated by precipitation in the cavities and grow by local decomposition of the surrounding lead iodide. It is deduced that point defects are created near the center of the irradiated area which subsequently condense in the cooler parts of the crystal, either on existing dislocations to cause climb or in disk-like aggregates to form dislocation loops. The formation of cavities is actually seen only with high electron intensities (10^{17} electron cm^{-2} sec^{-1} at 80 keV) but they may also be formed at lower intensities but may not be easily recognizable. Finely dispersed particles of lead do appear at the lower intensities (10^{14} electrons cm^{-2} sec^{-1}). The cavities represent an important step in the decomposition.

They are mobile and drift outward from the center of irradiation at rates as great as 1 μm sec^{-1} for a cavity 1 μm diameter, 50 Å thick. Thin platelets of lead form in the cavities with the (111) plane of the parent crystal. The cavities often break away from the precipitates during irradiation and spread further into the undisturbed crystal to provide sites for further decomposition. In the final stage of the decomposition isolated precipitates thicken into stable crystallites by local decomposition of surrounding lead iodide. They calculate that, on the average, there is at least one ion vacancy formed for each electron passing through the crystal. This greatly exceeds the rate expected from a pure heating effect of the beam, even if temperatures close to melting are achieved. They conclude that probably ionization displacement plays a predominant role in damaging the crystals and thereby causes decomposition. The displacement mechanism envisaged by Forty is a simple one and is peculiar to the special structure of lead iodide which consists essentially of hexagonal close-packed I^- ions with Pb^{2+} ions placed in the octahedral holes. At higher temperatures the Pb^{2+} ions can quite readily be shifted to the other available interstitial sites. An I^- ion can readily be stripped of an electron by an ionizing particle or photon. The resulting I atom will be very weakly bound and can be displaced by a small amount of recoil or thermal energy. The I^- vacancy which carries a net positive charge can exert sufficient repulsive force on a neighboring Pb^{2+} to displace it simultaneously to another interstitial site. The vacancy thus created will be firmly bonded to the I^- vacancy.

"Aggregation of these vacancy pairs and individual I^- vacancies can account for both the climb of dislocations and the formation of cavities. The precipitation of lead in the cavities during the later stage of decomposition occurs by the trapping and interaction of the interstitial Pb^{2+} ions and free electrons."

A similar investigation of KCl was reported by Tubbs and Forty(44). The behaviour is similar to PbI_2 except that the cavities do not appear to be mobile. In the final stage dark speckles appear which are thought to represent a dispersion of small colloidal particles of potassium. Forty concludes that in general then this type of decomposition proceeds by the formation of cavities followed by the precipitation of the new metallic phase, usually within the cavities. "The formation of cavities is possible only if a high degree of supersaturation of vacancies exist', and this may be taken to mean that there is some form of interaction creating vacancies other than that associated with the heating of the crystals."

Studies similar to those of Forty et al have been conducted by Sawkill(45), McAuslan(46) and Camp(47) who sought a direct examination of the development of metallic nuclei in an electron microscope. Some of this work has been summarized in Bowden and Yoffe's book "Fast Reactions in Solids"(48). Sawkill decomposed a single crystal of Silver Azide in the electron beam of an electron diffraction camera. Starting with the normal diffraction pattern of silver azide, Sawkill observed various stages in the decomposition ending up with the pattern for silver, thus following the collapse of the silver azide lattice. It is found that two forms of silver are formed during decomposition. One is randomly oriented and the other highly oriented with respect to the silver azide lattice. The random form consists of single crystals of silver while the highly oriented form comprises a network of silver. The diffraction patterns show that the lattice of silver azide does not collapse directly to silver. It is suggested that the silver atoms diffuse and add themselves to the lattice in special positions and some reshuffling of silver atoms already on the lattice takes place but without changing the lattice dimensions. This silver lattice collapses to a face centered cubic lattice of dimension greater than normal silver. This then collapses further to the normal silver lattice. The randomly oriented silver crystals are probably formed in the surface at defects, and there grow down into the crystal. Bowden and Yoffee then summarize some other interesting means of observing this decomposition.

(c) Irradiation of Explosive Materials

A large number of explosives have to date been irradiated with α particles, electrons, x-rays, fission fragments, etc. The object of these experiments was to test a) whether explosions could be initiated by these irradiations and b) whether the explosion rate or time to explode are affected. As regards the first possibility, it has now been fairly well substantiated that initiation of an explosion depends on the creation of a hot-spot sufficiently large to begin the chain reactions. All the known methods of inducing explosions such as impact and friction have been shown quite convincingly to be thermal in origin. The size of the hot-spot depends on the material of course but it is thought to be in the neighborhood of 10^{-3} - 10^{-5} cm in diameter. Only very intense irradiation sources can satisfy such thermal requirements and for practically all the known explosives no irradiation initiated explosions have been observed. The notion that the activation of a small group of adjacent molecules will cause explosion has thus been discredited. A full review of this topic appears in a book by Bowden and Yoffee(48). As regards the second point, irradiation has been shown to shorten induction periods and time to explode in a manner which is generally consistent with observations on "slow" thermal decompositions already discussed in this chapter. The reader is again referred to Bowden and Yoffee's book for more details.

5. SUMMARY

It is clear that as a field of scientific research the influence upon decomposition of irradiation is still in its early stages. By and large the work to date has been small in volume, almost completely uncorrelated and with no unifying theories. Only one assertion can be made with any degree of certainly. Irradiation almost always enhances a decomposition. This enhancement is generally manifested as a sharp reduction of the induction period when sigmoidal kinetics occur but may also take the form of an enhanced maximum rate. Another feature which seems fairly general is that although the initial and intermediate stages are enhanced, the final or decay stage is rarely affected. In general terms these observations are perhaps exactly what one might expect. The fact that the initiation of a solid state decomposition occurs at regions of imperfections makes it reasonable to suppose that a change in the number or kind of such imperfections readily influences the reaction. On the other hand, the fact that the growth of the reaction, especially towards the end when the more easily excited imperfect regions have already reacted must take place in the more ordered and undamaged bulk regions, makes very reasonable the supposition that in this stage irradiation damage effects will exert their smallest influence.

However, when one ventures past these fairly obvious features there remains little that one may describe in a general.

way. Here it seems that each worker has uncovered an effect here and an influence there but with little depth and often with less substantiation. Irradiation can be a powerful tool but its potential has been barely used. It does seem obvious also that irradiation by itself may be capable of yielding only limited information. This was early realized by Tompkins et al in the azide studies where other information such as electrical conductivity, absorption spectra, etc. were effectively brought to bear on these problems. More physical tools such as ESR, electron microscopy, field ion microscopy, etc. should be used in combination with irradiation studies in solid state chemical problems as indeed they have been used in solid state physics.

One particular feature, in the opinion of the author, deserves further study and that is the measurement of activation energies at abnormally low temperatures. It is in this temperature region that the low activation energy processes can be sorted out. By and large, it is these processes which initiate the decompositions. More careful temperature control over long periods of time are required but it seems certain that useful information will emerge.

REFERENCES

1. Jacobs and Tompkins, "Chemistry of the Solid State", Chapt. 7, Butterworth, 1955.
2. Bagdassarian, Quoted from reference 1.
3. See P. 189, reference 1.
4. Wischin, Proc. Roy. Soc. (London) A172, 314 (1939).
5. Garner and Moon, Chem. Soc. (London) Part II, 1398(1933).
6. Harvey, Trans. Faraday Soc. 653, 29 (1933).
7. Thomas & Tompkins, Proc. Roy. Soc. (London), A209, 550 (1951).
8. Thomas & Tompkins, Proc. Roy. Soc. (London), A210, 111 (1951).
9. Tompkins & Young, Discussions Faraday Soc., 23, 202 (1957).
10. Garner & Maggs, Proc. Roy. Soc., A172, 299 (1939).
11. Mott , Proc. Roy. Soc., A172, 325 (1939).
12. Tompkins, Indust. and Eng. Chem., 44, 1336 (1952).
13. Jacob & Tompkins, Proc. Roy. Soc., A215, 265 (1952).
14. Groocock & Tompkins, A223, 267 (1954).
15. Groocock, Proc. Roy. Soc. A246, 225 (1958).
16. Jach, Trans. Faraday Soc., 59, 947 (1963).
17. Haynes & Young, Trans. Faraday Soc., (1961).
18. Jach & Griffel, J. Phys. Chem., 68, 731 (1964).
19. Jacobs & Kurinsky, Trans. Faraday Soc., 58, 551 (1962).
20. Finch, Jacobs & Tompkins, J. Chem. Soc., 2053, (1954).
21. Prout and Herley, Nature 184, 445 (1959).
22. Prout, J. Inorg. Nucl. Chem. 7, 368 (1958).
23. Prout, Nature, 183, 884 (1959).

23a. Prout and Solc, J. Inorg. Nucl. Chem. 9, 232 (1959).

24. Prout and Brown, Nature, 203, 398 (1964).

25. Prout and Herley, J. Inorg. Nucl. Chem. 16, 16 (1960).

26. Boldyrev, Proc. of the Second All-Union Conf. on Radiation Chem Trans. from Russian. Israel Program for Sci. Translations, Jerusalem, 1964).

27. Jach, 4th Int. Symp. on Reactivity of Solids, Amsterdam, May 1960, Elsevier, p. 334.

28. Jach, J. Phys. Chem. Solids, 24, 63 (1963).

29. Jach, J. Phys. Chem. Solids, 24, 75 (1963).

30. Bartlett, Tompkins and Young, J. Chem. Soc., 3323 (1956).

31. Flanagan, Nature, 181, 42 (1958).

32. Jach, Nature, 196, 827 (1962).

33. Bristow and Rees, Nature 198, 178 (1963).

34. Young, J. C. S., 4533 (1960).

35. Forty, J. Appl. Phys., 14, 3 (1963).

36. Boldyrev and Bystrykh, Russian Chem. Rev., Vol. 32, No. 8, 426(1963).

37. Daniels and Weiss, Research 10, 341 (1957). 10, 396 (1957).

38. Heal, Atomics, 1955, 205 and 241.

39. Dominey, A Review of the Heavy Particle Radiolysis of Solids, AERE-R4505.

40. Varley, Nature, 174, 886 (1954).

41. Klick, Phys. Rev. 120, 760 (1960).

42. Smoluchowski and Wiegand, Disc. Faraday Soc. 31, 151 (1961).

43. Forty, Phil. Mag. 5, 787 (1960). 6, 587 (1961). 6, 895 (1961).

44. Tubbs and Forty, Phil. Mag. 2, 709 (1962).

45. Sawkill, Proc. Roy. Soc., A229, 135 (1955).

46. McAuslan, Ph.D. Thesis, Cambridge (1957).

47. Camp, 1957 Ph.D. Thesis (Univ. of Cambridge).

48. Bowden & Yoffee, Fast Reactions in Solids, Butterworths, 1958.

49. Jach, "Reactivity of Solids", (5th International Symposium, Munich 1964), G. M. Schwab (Editor), P. 422. Elsevier Publishing Co. Amsterdam 1965.

ACKNOWLEDGMENTS

This work was supported in part by the Office of Naval Research.