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CHEMICAL REACTIVITY AT DEFECT SITES IN SOLIDS

by

Joseph Jach

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I. A Study was made

This work began as an extension of previous studies on the chemical reactivity at defect regions of a crystal.(1,2,3) The reactivity specifically studied was thermal decomposition ~~and the system was~~ of $NaBrO_3$ which thermally decomposes according to the equation

$$NaBrO_3 \xrightarrow{\text{yields}} NaBr + 3/2\ O_2 .$$

It is known that reactivity varies markedly from one crystal to another of the same substance and therefore a comparison between a normal crystal and one containing a large number of deliberately introduced defects is fraught with uncertainties especially since the act of studying the decomposition destroys the crystal.

The motivating idea behind this work was a direct comparison between reactivity of a normally situated bromate ion and one that is placed at a very disordered region of the <u>same</u> crystal. In this way an <u>in-situ</u> comparison is made for normal and defect regions. This has been achieved in the following way. A sample of polycrystalline $NaBrO_3$ is irradiated in a nuclear reactor. The nuclear reaction

$$^{81}Br + \text{neutron} \rightarrow {}^{82}Br^{*} + \text{gamma ray}$$

occurs (amongst others).(4) The emission of the gamma ray results, in most cases, in an energetic recoil of the $^{82}Br^{*}$ (of the order of hundreds of electron volts). This recoil a) is radioactively labelled - this is denoted by the asterisk and b) results in a highly damaged region in the vicinity of its resting place. The exact nature of the recoil species has not yet been established, but it is known that thermal treatment of the irradiated material results in the formation of $Br^{*}O_3^{-}$, the parent species with the Br labelled. This re-formation of parent material occurs at temperatures well below those at which thermal decomposition occurs. If the temperature is now raised, the decomposition of BrO_3^- and $Br^*O_3^-$ occur simultaneously and because of the fact that the bromate ion at the damaged region is labelled one may obtain decomposition rates of normal bromate and bromate situated at damaged regions in the SAME crystal under identical conditions.

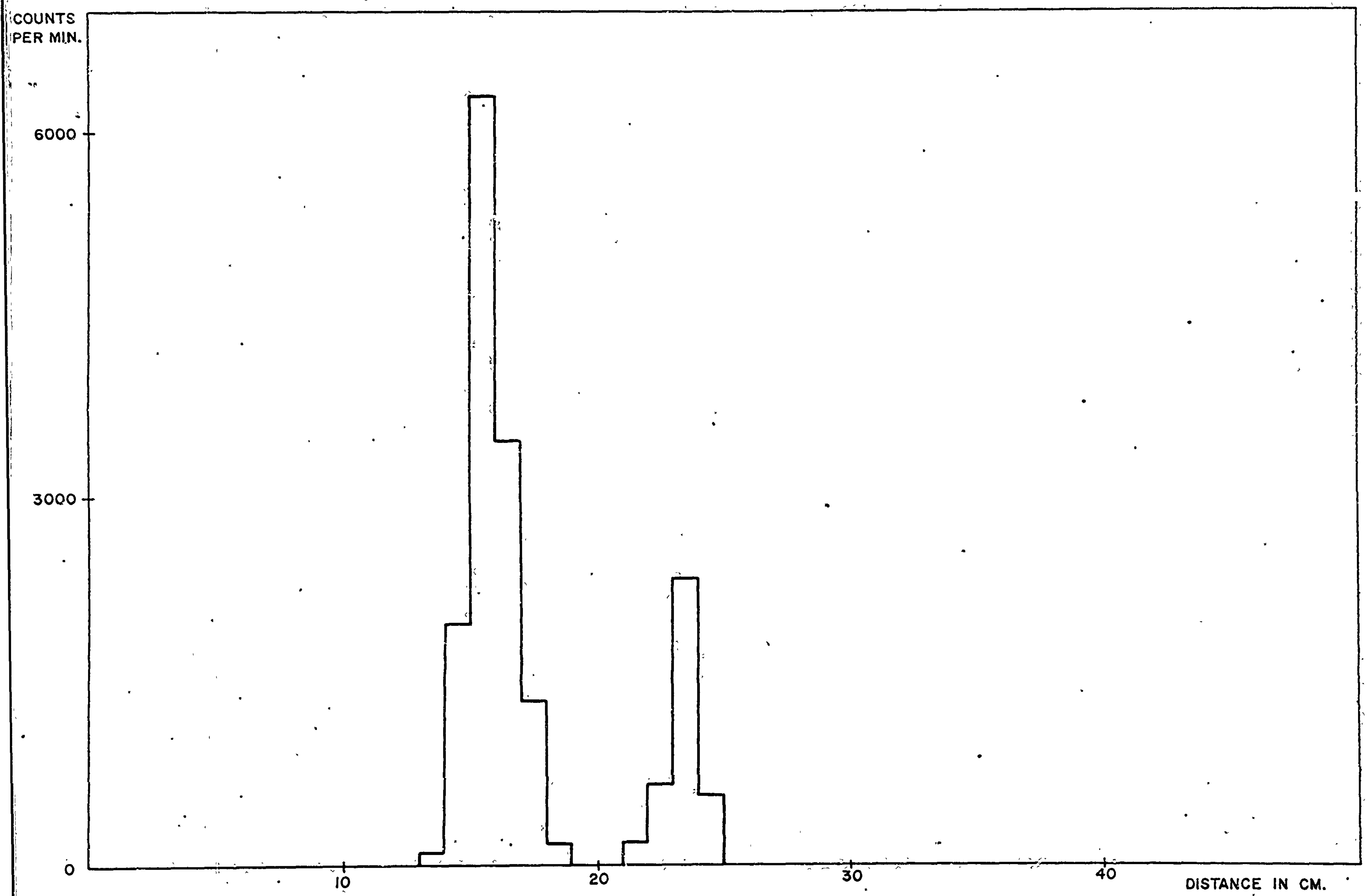
The experimental procedure was as follows. About 100 mgs. $NaBrO_3$ (A.R. Grade - polycrystalline)were irradiated in an evacuated quartz ampoule for one hour in the Brookhaven Graphite Research Reactor (flux approximately 10^{13} neutrons/cm^2/s). This sample was then opened and divided into eight approximately equal portions, each portion being placed in a quartz boat mounted on a metallic slug. All eight boats were placed at the end of a long quartz tube. This end of the tube was provided with a ground glass stopper. The same tube then passed through a 24" combustion type furnace. At the other side of the furnace the tube connected up with a high vacuum system. In this way it could be evacuated leaving the samples in a vacuum environment at room temperature. The boats, being situated on metallic slugs could be magnetically manipulated into and out of the furnace at will. In practice, the tube was evacuated and the desired furnace temperature set. The furnace was capable of being controlled (by a Leeds and Northrup C.A.T. controller - programmer) to $\pm 0.1^\circ C$. for long periods (weeks). All eight samples were then quickly inserted into that portion of the quartz tube situated in the flat zone of the furnace, the system being open to the pumps during the entire experiment.

It was decided not to first anneal below decomposition temperature (to re-form $Br^*O_3^-$) and then take the system to decomposition temperatures but rather to take the samples to decomposition temperatures directly. Most of the re-formation of $Br^*O_3^-$ is then very rapid. Warm-up times were generally around 15 minutes.

The eight samples were pulled out of the furnace one by one to freeze the reaction at desired time intervals. After all samples were removed the system was opened to atmosphere and each of the eight samples dissovled in 1 cc of an approximately 0.001 N KOH. Each solution was then analyzed for $Br^{*}O_3^-/Br^{*-}$ ratio using a paper electrophoresis technique already described(5). Briefly this technique separates bromate and bromide ions on a piece of chromatographic paper, 1cm width (moistened with dilute electrolyte solution) across which 1000 Volts is placed. After about 1 hr of this treatment the paper is dried and cut up into 1 cm^2 sections. Each section is counted for the gamma ray activity from ^{82}Br on a scinillation well counter. Figure 1 shows a typical histogram(7). The ratio $Br^{*}O_3^-/Br^{*-}$ is simply the ratio of the area of the first peak to that of the second. By duplicating this procedure for each of the eight samples one can follow the $Br^{*}O_3^-$ concentration as a function of time, i.e. the kinetics of the $Br^{*}O_3^-$ decomposition. It must be pointed out now that the BrO_3^- and $Br^{*}O_3^-$ from any given sample travel at the same rate on the chromatographic paper of course. By simply allowing the $^{82}Br^{*}$ activity (half-life 35.5 hrs) to decay to zero and then re-irradiating all the sections and re-counting for ^{82}Br it is possible to obtain the original BrO_3^-/Br^- ratios, it being borne in mind that the original number of bromine atoms activated by the first one hour irradiation is a negligable number compared to the total bromine atom concentration. The second irradiation is effectively an activation analysis and measures BrO_3^-/Br^-. This latter ratio is to be compared with the $Br^{*}O_3^-/Br^{*-}$ and corresponds to the identical crystal with the same thermal treatment. In practice the ratio bromate to bromate plus bromide was used in order to conform to current practice in the field of hot-atom chemistry. In order

FIGURE 1.

Typical Histogram for the $Br^{*}O_3^-/Br^{*-}$ Separation


COUNTS PER MIN.
6000
3000
0
10
20
30
40
DISTANCE IN CM.

to compare the decomposition of a bulk bromate ion and a bromate situated at the site of an original recoil, it is only necessary to plot, as a function of time, the quantities R and R* where

$$R = \frac{[BrO_3^-]}{[BrO_3^- + Br^-]} \quad \text{and} \quad R^* = \frac{[Br^*O_3^-]}{[Br^*O_3^- + Br^{*-}]}$$

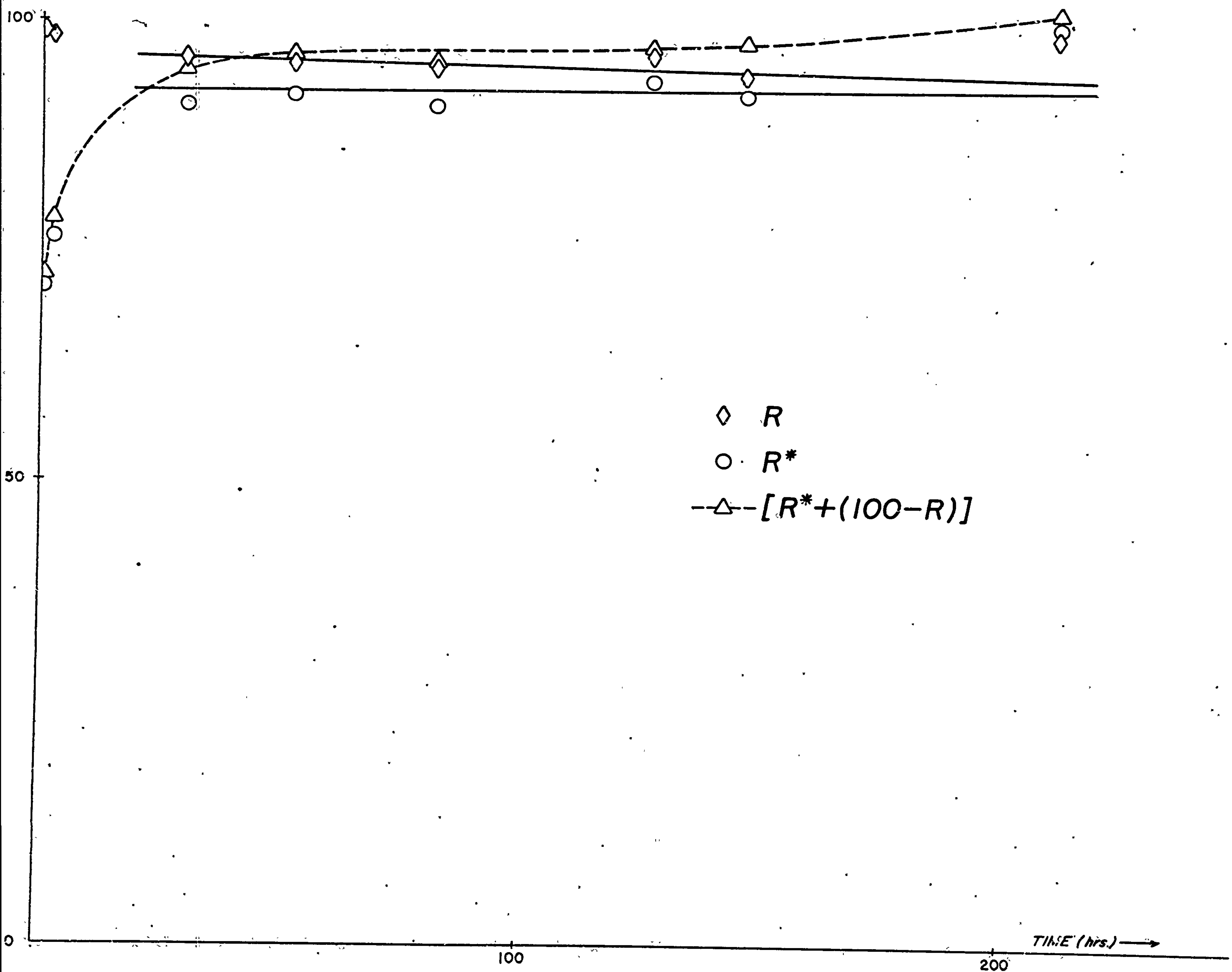
RESULTS

The results are contained in the R vs. time curves. Space prevents showing these curves for all the temperautres studied, but four typical ones, from the lowest to the highest temperatures are shown in Figures 2 through 5. Each figure represents an isothermal run and in each there are sets of eight points. The open circles are the R^* values and for each of these there is a corresponding R value (diamond shaped) at the same time (the time of withdrawal from the furnace). Note that in all the runs, the temperature dropped about 2°C. when all the eight samples were introduced into the furnace. It took about 15 minutes for the set temperature to be attained. All times were recorded after this temperature equilibration occurred.

Figure 2 shows results for the lowest temperature (319.2°C.). The diamond shaped points represent simple thermal decompositon of bulk bromate ion and show that the reaction is very slow at this temperature. The scatter is large for the last three points owing to the poor counting statistics (the run lasted more than a week). The R^* values show an initial steep rise and what is probably a pseudo-plateau. This curve is in fact almost a standard Szilard-Chalmers annealing curve. The latter generally show a sharp initial rise and a subsequent pseudo-plateau. Most of the Szilard-Chalmers annealing, i.e. the formation of $Br^*O_3^-$ from the recoil species, apparently occurs during the 15 minute warm-up time. It may be mentioned here that at 200°C., which is the highest temperature studied heretofore$^{(5)}$, the pseudo-plateau value of R^* was 52%. The dashed curve shown in the figure represents a plot vs. time of the quantity $[R^*+(100-R)]$. The purpose of this plot is the following: If it is assumed that the

<u>FIGURE 2</u>

R and R* vs. time (319.2°C)


100
50
0
100
200
TIME (hrs.) →
◊ R
○ R*
--△-- [R*+(100−R)]

re-formed $Br^{*}O_3^-$ ions in the crystal are subject to the same (thermal) decomposition as the normal bulk BrO_3^-, one may obtain some idea of what the classical Szilard-Chalmers annealing curve would have looked like in the absence of decomposition at these temperatures by adding to the R^{*} values that amount of decomposition that has occurred, i.e. (100-R). The dashed curve, shown in this Figure as well as Figures 3, 4 and 5, may thus be regarded as a standard Szilard-Chalmers annealing curve. The original motivating idea of these experiments, i.e. a possible difference in decomposition rate of BrO_3^- and $Br^{*}O_3^-$ is thus ignored in this analysis.

Figure 3 represents a temperature of 322.8°C. (The insert will be discussed later). Here the thermal decomposition is more in evidence. After about 20 hours both R and R^{*} appear to fall on straight lines. Despite the scatter, it is clear that

$$-\left(\frac{dR}{dt}\right) > -\left(\frac{dR^{*}}{dt}\right)$$

This relationship held for all the other (lower) temperature runs not shown.

A somewhat higher temperature is shown in Figure 4. Again the insert will be discussed later. The curves join up after about 20 hours and, within experimental error, remain joined for the rest of the run. This is typical of the higher temperatures where the curves always joined and never crossed over. Figure 5 is for one of the highest temperatures studied.

ARRHENIUS PLOTS

It is difficult to choose a parameter to obtain Arrhenius plots. One needs an idea of the activation energy for the decomposition of normal bulk bromate as well as that for the processes responsible for the annealing of $^{82}Br^{*}$ species, i.e. the Szilard-Chalmers annealing. For the bulk decomposi-

FIGURE 3

R and R* vs. time at 322.8°C.

(The insert is for the simple Br^-/BrO_3^- exchange at 325.0°C)

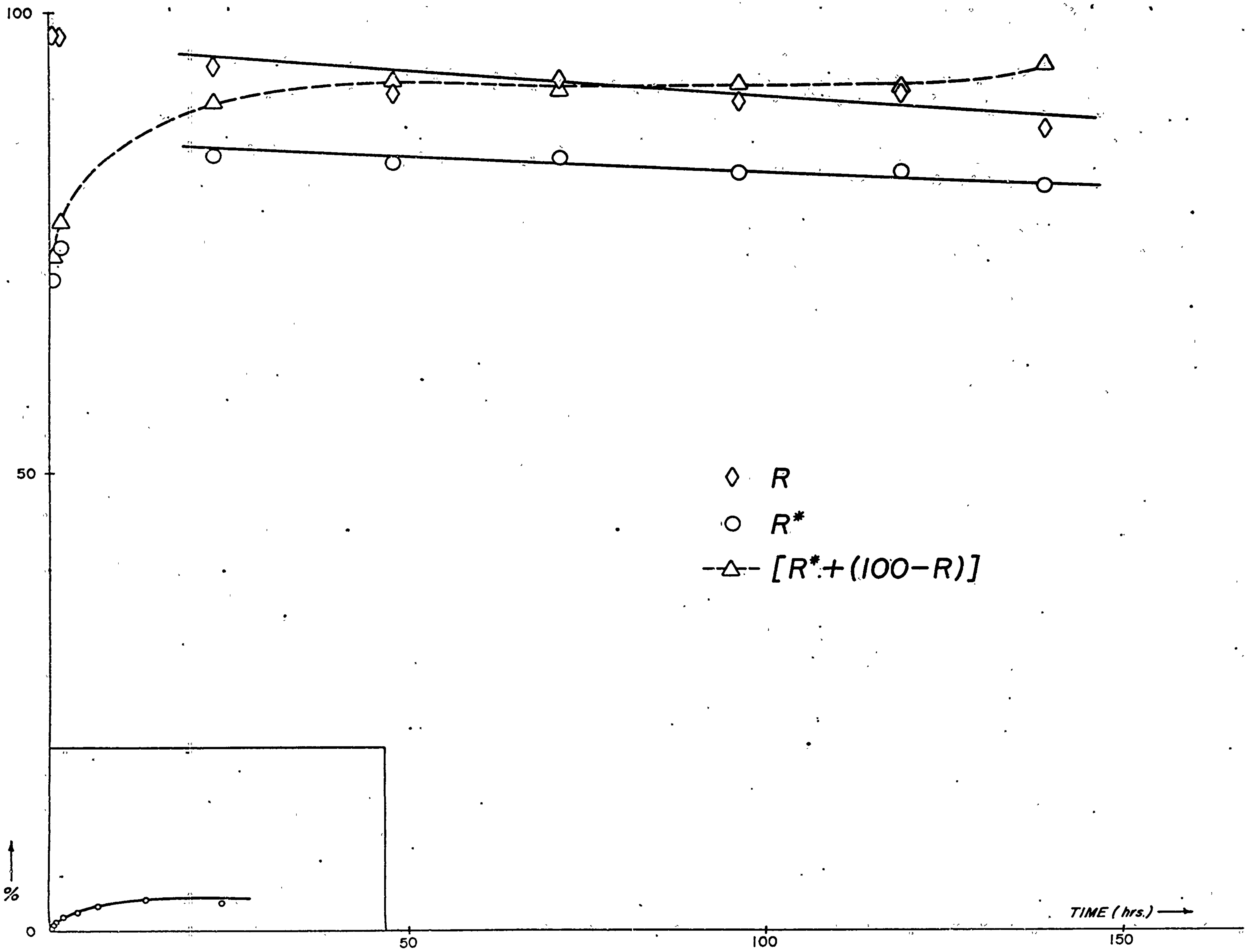

100
50
0
%
◊ R
○ R^*
-△- $[R^* + (100-R)]$
50
100
150
TIME (hrs.)

FIGURE 4

R and R^* vs. time at 336.8°C

(The insert is for the simple Br^-/BrO_3^- exchange at 336.0°C)

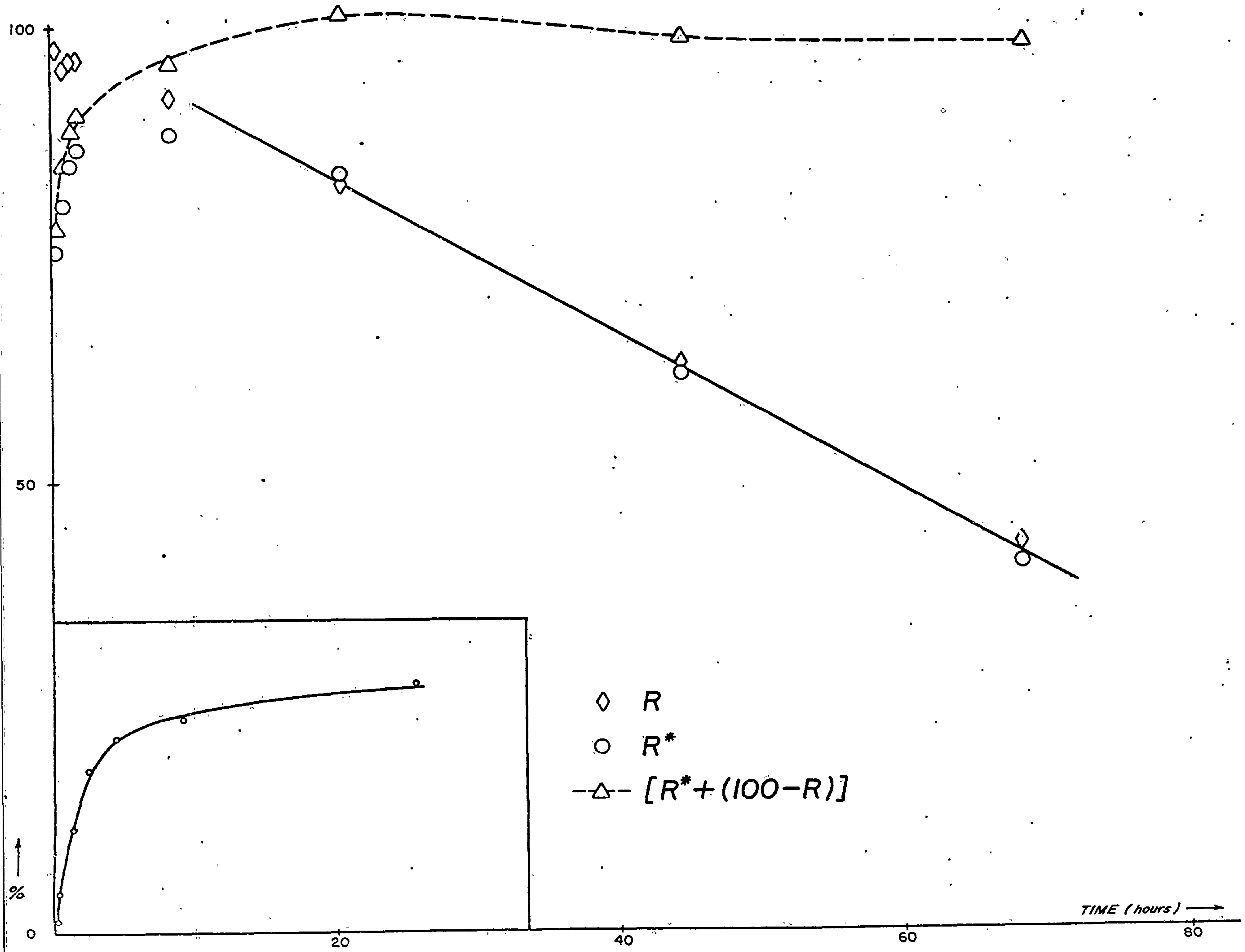
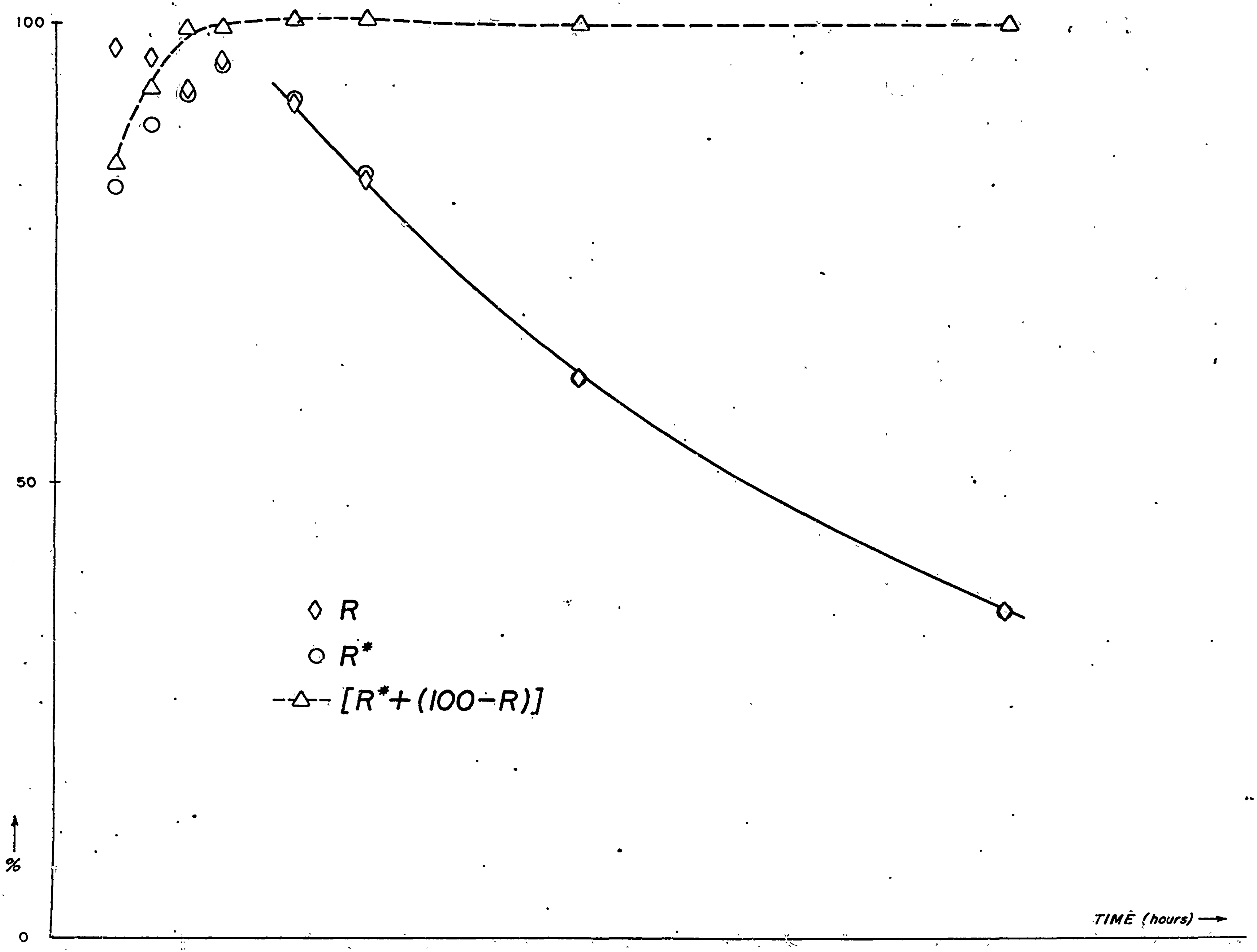

100
50
0
% ↑
0
20
40
60
80
TIME (hours) →
◇ R
○ R*
–△– [R*+(100–R)]

FIGURE 5

R and R* vs. time at 342.2°C


100
50
0
%
TIME (hours)
R
R*
[R*+(100−R)]

tion, the parameter ki was chosen. This is $\frac{-dR}{dt}$ for small t which conforms to the previous study(1). These experiments were not designed to obtain accurate values of the activation energy for bulk decomposition but rather to obtain an in-situ comparison of this quantity with the corresponding quantities for $Br^*O_3^-$. Figure 6 shows that at the lower temperatures the bulk decomposition occurs with an activation energy over 100 kcal/mole. Figure 7 is an Arrhenius plot for two parameters associated with Szilard-Chalmers annealing. They are 1) the reciprocal of the time to reach the maximum value of R^*, and 2) the reciprocal of the time corresponding to the beginning of the pseudo-plateau on the dashed curves of Figures 2 through 5. Both parameters yield some idea of the activation energy of the Szilard-Chalmers process toward the end of the annealing. As stated before the great bulk of the annealing occurs first and is extremely rapid. In fact the latter is completed within the warm-up period (15 minutes) and it is estimated that the activation energy for this process is well under 10 Kcal/mole. The particular technique employed in these experiments does not make possible the measurement of an accurate value for this quantity. It is clear that the plots in Figure 6 and 7 display the same general form but that the activation energy for the bulk decomposition at the lower end of the employed temperatures is at least a factor of 4 greater than the processes involved in the Szilard-Chalmers annealing at these temperatures.

FIGURE 6

Arrhenius plot for the bulk decomposition ki (hr^{-1}) vs $1/T \times 10^5$.

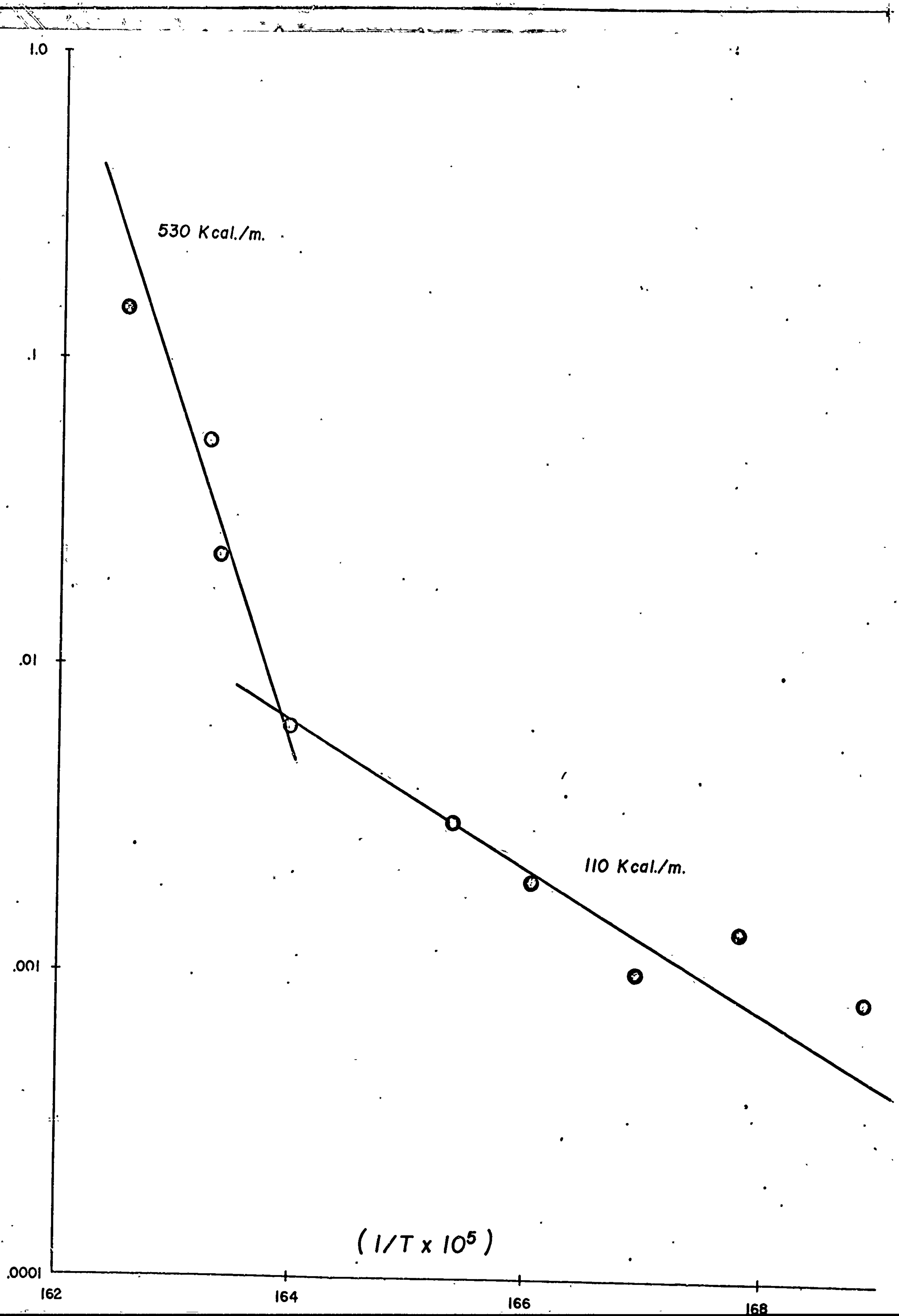
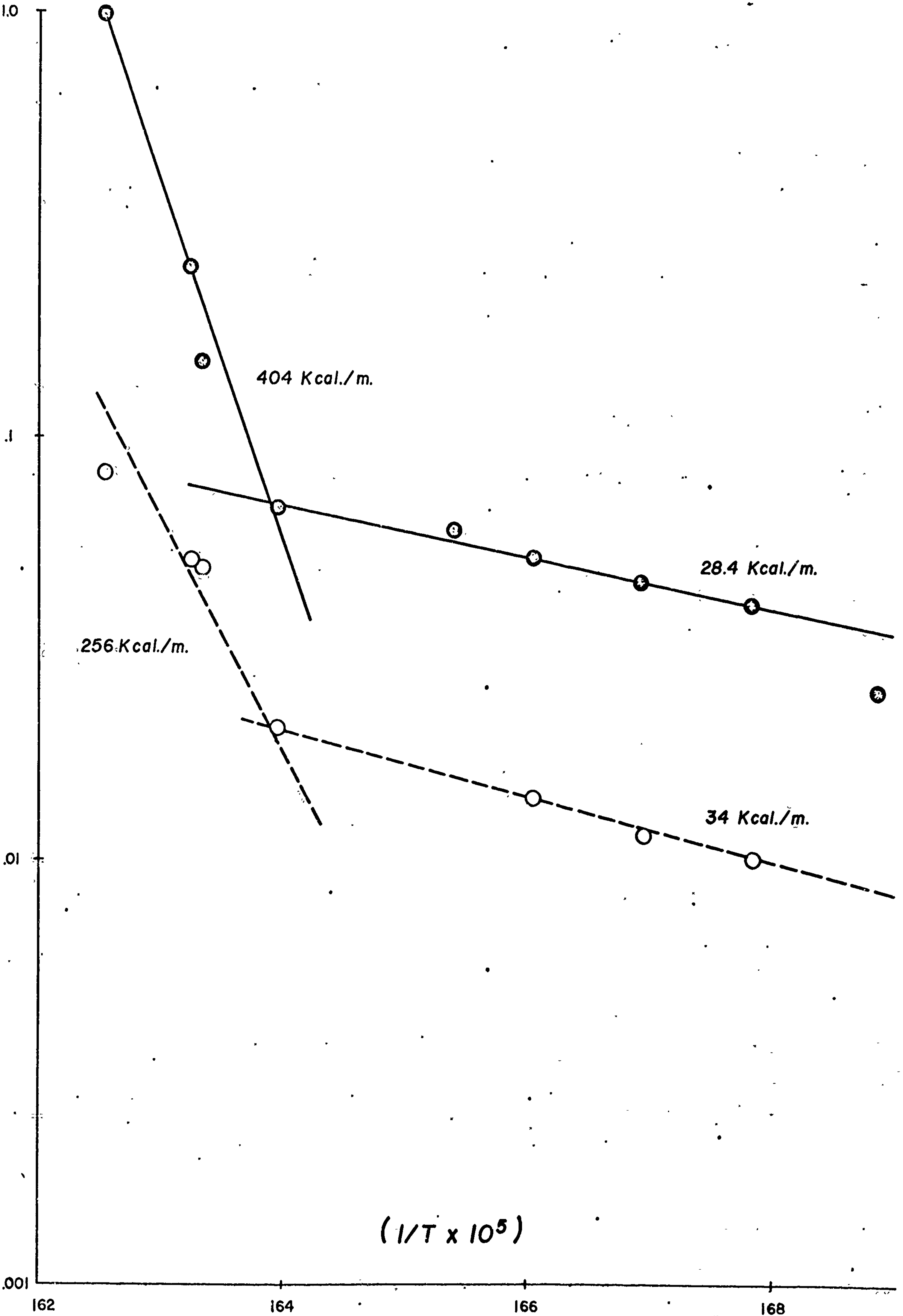

1.0
.1
.01
.001
.0001
530 Kcal./m.
110 Kcal./m.
(1/T x 10⁵)
162
164
166
168

FIGURE 7

Arrhenius Plots for Szillard-Chalmers annealing

(Closed circles are reciprocal of time in hours to reach the pseudo-plateau)

Open circles are reciprocal of time in hours to reach maximun $R^{*} \times 10^{-1}$).


1.0
.1
.01
.001
404 Kcal./m.
28.4 Kcal./m.
256 Kcal./m.
34 Kcal./m.
(1/T x 10^5)
162
164
166
168

DISCUSSION

Before proceeding to a discussion of these results, it is well to point out some of the features of the $NaBrO_3$ thermal decomposition. It is believed that the whole surface becomes nucleated immediately upon attainment of decomposition temperature(1). This applies to visible surfaces as well as sub-grain boundaries, etc. The nucleation thus creates an interface between reacted and un-reacted material and it is the advance into the crystallite of this envelope (the so-called contracting envelope) which determines the topochemical kinetic features of the decomposition or the overall observed fractional decomposition vs time. These kinetics usually yield little information about the ultimate atomic mechanisms involved in the decomposition. The presence of the product NaBr in contact with unreacted $NaBrO_3$ is believed to cause a eutectic type of melting above about 329°C., but that this melting and decomposition occur simultaneously. This is to be distinguished from ordinary melting in that it occurs below the thermodynamic melting point and the decomposition occurs concurrently with partial melting. Hence, at about 329°C., the decomposition rate rises very sharply since the liquid state of $NaBrO_3$ decomposes much faster than the bound state.

With these notions in mind one may examine the results of this experiment with two points of view in mind: a) there is present an interface where the reactivity is centered, and b) at the higher temperatures, the presence of a liquid phase must be included in the discussion.

SHAPES OF THE R AND R^* VS TIME CURVES

Some of the observed features of these curves are to be expected while others are quite surprising. The R vs time curve is simply a repetition of a simple thermal decomposition study, but these experiments were not designed to yield accurate kinetics of this decomposition but merely to provide a control so as to obtain a comparison between the decomposition of BrO_3^- and $Br^*O_3^-$. However, one feature is apparent that was never observed when the kinetics were measured by plotting oxygen evolved vs. times, namely, a jog in the curve near the beginning of the decomposition. The most likely cause is the annealing of the radiation products but it is strange that the oxygen pressure plots never showed this effect. The overall shape at lower temperatures is in agreement with previous measurements, as is the shape at higher temperatures.

The R^* vs. time curves also show, within very general limits, the expected behavior. A sharp initial rise is followed by a plateau or pseudo-plateau. At the higher temperatures the occurrence of the thermal decomposition of $Br^*O_3^-$ (newly formed) gives rise to the observed drop in R^* at larger times.

The surprising features are the following: 1) where the temperature was high enough, the values of R and R^* <u>always</u> merged and within experimental error the R and R^* vs. time plots never crossed over after becoming equal but always followed the same values until the end of the experiment. Where the temperature and therefore reaction rate was too low to observe this merging, the slopes of the R and R^* vs. time curves indicated an eventual join-up and, in fact, an Arrhenius plot of the time to merge, whether actually observed or extrapolated, showed apparent activation energies not too different from those in Figure 7. 2) the dashed curve, which one may assume to at least roughly represent Szilard-Chalmers annealing after decomposition is accounted for is a typical such curve except that the attainment of 100% retention is very unusual.

ARRHENIUS PLOTS

The activation energy plots invariably show two distinct portions. Whether these are two classical straight lines or merely a plot of continuously increasing slope is a difficult question to answer. Much more data would be required to yield an answer. However, it is perhaps not too serious a problem since either case more or less allows the same conclusions. For ease of discussion it will be assumed that there is a higher temperature region of large slope and a lower one of much lesser slope. The large slope region has previously been observed in the $NaBrO_3$ thermal decomposition study$^{(1)}$ and roughly corresponds to the same slope and temperature range observed here. Any differences might easily result from the fact that different starting material was used. In the thermal decomposition studies mentioned, the temperature range was extended beyond that used in this study and the Arrhenius plot at about 340°C. straightened out into a definitely classical one corresponding to an activation energy of about 45Kcal/mole. This is the temperature region of rapid liquefaction and will not be considered any further. The "large slope" region was considered to result from the melting of a eutectic type of mixture formed between the product (bromide) and parent (bromate) material, The large slope was not considered to yield a true activation energy since the onset of melting must have an enormous enhancing effect on the pre-exponential factor. The large slopes are quoted in Kcal/mole merely for reference sake.

It is apparent that the activation energies for processes measured by the labelled recoil ^{82}Br species are much lower than for processes involved in the bulk thermal decomposition. However, the shapes of the Arrhenius plots are similar.

CONCLUSIONS

The original purpose of these experiments was to measure the difference, if any, between the decomposition rate of normal bulk BrO_3^- and the $Br^*O_3^-$ at the damaged sites. While the experiments do show different values of the linear regions of $-\frac{dR}{dt}$ and $-\frac{dR^*}{dt}$ one may not assume that the re-formation of $Br^*O_3^-$ is complete in this region. Hence it may equally well be assumed that $-\frac{dR}{dt} > -\frac{dR^*}{dt}$ only because the Szilard-Chalmers annealing is not yet complete in this region. In other words, had the annealing been complete before this linear region, $-\frac{dR}{dt}$ would be equal to $-\frac{dR^*}{dt}$ but since $Br^*O_3^-$ are still being formed, their apparent decomposition rate is slightly lower than the bulk BrO_3^- rate. In fact this latter argument appears to the author to be the more plausible one. On the basis of this argument however, the fact that the values of $[R^* + (100-R)]$, (the dashed curves) reach 100% is very significant. One may now focus attention on the lower temperature region at the time when $[R^* + 100-R]$ reaches 100%. The crystallites have undergone some thermal decomposition, and if the present picture of the latter is correct, all crystallites consist of bromate surrounded by the appropriate amount of bromide. However, the original recoil sites must have been homogeneously distributed throughout the crystal. The re-formed $Br^*O_3^-$ originally in the region which is now bromide must also have decomposed (to Br^{*-}). Hence, the remaining undecomposed solid must consist of BrO_3^- and $Br^*O_3^-$ but no Br^{*-} (since dissolution of the whole system results in equal values of R and R^*). Thus the picture which emerges is a solid bromate crystallite in which the re-formation of $Br^*O_3^-$ goes to completion well before thermal decomposition has disrupted the crystal. If true, this has significant bearing on both the mechanism of thermal decomposition as well as Szilard-Chalmers annealing.

It now becomes interesting to examine this picture in the light of the Arrhenius plots. The Szilard-Chalmers annealing and the thermal decomposition BOTH show a vast change in slope of their respective Arrhenius plots. This renders more than likely that whatever is causing the slope change for the decomposition is also responsible for the slope change of the Szilard-Chalmers annealing. In the thermal decomposition study it had been assumed that the pre-melting previously referred to was responsible for the sharp rise in slope. However, the melting in the temperature range of these studies is only partial, i.e. there is solid bromate and a liquid phase always present. The fact that some of the bromate is in the liquid state is thought to be responsible for the vastly increased decomposition rate. This must then also be responsible for vastly increased Szilard-Chalmers annealing rate. The latter process however, is bound to be homogeneous since the original recoil fragments are homogeneously distributed (from the original neutron irradiation). It appears then that either the picture of a heterogeneous thermal decomposition or a homogeneous Szilard-Chalmers annealing must be in error.

The author believes that the heterogeneous picture of thermal decomposition may have to be modified. A possible clue as to how this comes about is provided by the fact that the re-formation of $Br^*O_3^-$ goes to completion. Such perfect annealing is rare and has been difficult to justify in terms of current theories. An answer is the possible existence of exchange reactions. Suppose that at these temperatures, the solid state exchange reaction

$$Br^- + BrO_3^- \leftrightarrow Br^- + BrO_3^-$$

becomes possible. Such a reaction would easily explain the attainment of a 100% re-formation of $Br^*O_3^-$ in the solid state. One need not even postulate that the recoil species is Br^{*-}. Suppose the species is not bromide and is denoted by (Br^*X). The reaction

$$(Br^*X) + BrO_3^- \rightarrow (BrX) + Br^*O_3^-$$

might occur but the reverse would be unlikely since the chance of (BrX) meeting a $Br^*O_3^-$ will be small compared to its meeting a BrO_3^-, and the latter will cause no overall changes. One is of course assuming fairly rapid diffusion and a minimal "cage" effect, which is not a bad assumption near the melting point.

The intervention of such exchange reactions in the thermal decomposition mechanism is also an interesting possibility. It is easy to imagine the decomposition of a bromate ion at the surface of a bromate crystallite. It is a little more difficult to visualise this decomposition at the interface formed by the two solids (bromate and bromide). However, one may suppose that bromide easily formed at the surface undergoes exchange with bromate beneath the surface. The net effect of such an exchange is to continuously bring bromate ions to the surface where steric factors render more easy the decomposition. Such a mechanism has (in effect) been previously proposed for thermal decompositions but has never been taken seriously(1,6). The decomposition may then be described neither as homogeneous or heterogeneous but as something between the two. It is as if the decomposition now permeates the whole crystal and a bulk disintegration ensues. At highest temperatures, the presence of Br^- throughout the crystal must cause a generalized bond loosening and/or partial melting. This gives rise to the sudden increase in slope of the Arrhenius plot for decomposition and Szilard-Chalmers annealing, since both processes involve steric factors, bond rupture, etc.

It is postulated that both thermal decomposition and $Br^*O_3^-$ annealing involve the exchange reaction. The decomposition occurs with much higher activation energy since it involves the additional (difficult) step of disruption of BrO_3^-. The exchange also involves bond rupture but this is partially offset by the attractive energy between the Br^- and the oxygens of the bromate with which it is exchanging.

The existence of a Br^-/BrO_3^- exchange reaction has been tested. The inserts in Figures 3 and 4 represent results for the following experiment. A few mgs. (about 3) of NaBr were irradiated with neutrons and dissolved in a solution containing about 100 mgs $NaBrO_3$. The solution was dried in vacuum oven at about 50°C. and the resulting powder given exactly the same thermal treatment as the irradiated $NaBrO_3$ in the main experiments described above, i.e. samples are withdrawn from a constant temperature oven at different times. It was found that, although the solid initially contains only $^{82}Br^{*-}$ and BrO_3^-, the thermal treatment results in the formation of $^{82}Br^*O_3^-$ the fraction of which is shown in the insert as a function of time. Apparently the reaction

$$Br^{*-} + BrO_3^- \leftrightarrow Br^- + Br^*O_3^-$$

occurs. Note that the temperature corresponding to the inserted graphs are close to those used in the main experiment on the same graph.

This experiment proves that Br^- exchanges with BrO_3^- in the solid state but does not proceed as rapidly as the reaction of recoil Br species. However the nature of the recoil species is unknown. It may not be bromide or if it is bromide it may be situated at an especially reactive site. It may be a bromide containing species that is much more capable of exchange with bromate than is bromide itself and yields bromide ion upon dissolution.

Clearly much more work is needed, but it seems likely that thermal decomposition and Szilard-Chalmers annealing reactions may throw light upon each others mechanisms. The simple exchange of Br^- and BrO_3^- is presently being studied in this laboratory. Probably the data on the variation of such a reaction with temperature as the solid passes through various stages of premelting might also throw some light on the as yet very little understood melting process.

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