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THE HOT-ATOM CHEMISTRY OF SULFUR(35) PRODUCED BY THE CHLORINE-35(NEUTRON,PROTON)SULFUR-35 REACTION IN MIXED CRYSTALS OF POTASSIUM CHLORIDE AND POTASSIUM BROMIDE

JOHN ROBERT HOBBS

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BY THE $^{35}$Cl(n,p)$^{35}$S REACTION IN MIXED
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BY

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[Signatures]

Date: October 10, 1968
This thesis is dedicated to my parents.
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61. Luminescence Intensity of Vₖ Band in Mixed KCl-KBr vs. Mole Percent KBr
The hot-atom chemistry of recoil $^{35}$S from the $^{35}$Cl(n,p)$^{35}$S reaction in mixed crystals of KCl-KBr has been investigated. The oxidation states of the $^{35}$S were separated by dissolution of one-half of a sample in a basic carrier solution of sulfide and sulfate ions and the other half in a basic solution without carriers. In the presence of sulfide carrier, neutral sulfur radioactivity ($S^0$) is rapidly converted to sulfide; in the absence of sulfide, it is converted by water to sulfate and/or sulfite. The sulfide was precipitated as cadmium sulfide centrifuged, oxidized to sulfate with hypochlorite ion in basic solution, and the sulfate precipitated as barium sulfate. The difference between the relative sulfide yields of the aliquots dissolved by the two dissolution procedures gave the relative neutral sulfur yield.

The results indicate that in the 0-30 mole percent KBr region there are competing oxidation and reduction reactions. This behavior is explained by the following reactions between $F$(reducing)-centers and $V$(oxidizing)-centers and the stabilized sulfur species $S^+$, $S^0$, and $S^-$. 

$$S^+ + [F\text{-red}] \rightarrow S^0$$
\[
\begin{align*}
S^0 + [F\text{-red}] & \rightarrow S^- \quad (2) \\
S^0 + [V\text{-oxd}] & \rightarrow S^+ \quad (3) \\
S^- + [V\text{-oxd}] & \rightarrow S^0 \quad (4)
\end{align*}
\]

The oxidation-reduction reactions occurring in the low KBr region are thought to be due to changes in the concentration and nature of defects resulting from changes in structure upon mixed crystal formation. These conclusions are consistent with independent studies of the properties of the alkali halides and their mixed crystals. Differences in the nature and concentrations of defects in the low KBr region of the mixed crystals have been observed.

Thermal annealing studies have shown that very little annealing takes place at 75°C except for samples with 0-20 mole percent KBr. Increasing the annealing temperature to 215°C promoted reactions (2) and (3), increasing the \( S^+ \) and \( S^- \) yields and decreasing the \( S^0 \) yield. These observations are consistent with the known behavior of defects in alkali halides upon thermal annealing.

Thus, the chemical stabilization of the recoil atom has been found to be dependent upon the composition of mixed crystals of KCl-KBr. The stabilization is related to the environment in which the recoil atom loses its excess energy and this energy loss is determined by the nature of the defects in the crystal.
I. INTRODUCTION

Hot-atom chemistry, in the sense used here, denotes the chemical behavior of atoms activated by nuclear transformations. As shown in Chapter III, atoms resulting from nuclear processes are often electronically excited and usually possess kinetic energy well in excess of chemical bond energies. As a result of such a high energy the atoms can undergo chemical reactions not observed by ordinary means. If, as is often the case, the transformed atoms are radioactive, they can be easily detected and their ultimate chemical states determined.

The first study of the chemical consequences of atoms produced by a nuclear transformation was reported by Szilard and Chalmers\textsuperscript{1} in 1934. They irradiated ethyl iodide with neutrons and found that a fraction of the radioactive iodine could be extracted into water in an inorganic form. Since that time considerable effort has been made to understand the chemical changes induced by nuclear transformations and the effects of various experimental parameters on the nature of these changes.

For many years the chemical behavior of $^{35}\text{S}$ atoms produced from the $^{35}\text{Cl}(n,p)^{35}\text{S}$ reaction in the alkali halides has been the object of investigation. This is a particularly interesting system since the radioactive atom formed is not isotopic with the target atom. In alkali chlorides the possibility for radiation decomposition of an oxyanion does not exist, thus the number of possible oxidation states of the recoil sulfur is reduced. Also, the possibility of isotopic exchange between $^{35}\text{S}$ and other atoms in the matrix is eliminated. In the alkali chlorides one is then investigating
one of the simplest systems for solid state hot-atom chemistry. Finally, much experimental data is available concerning the properties and behavior of the alkali chlorides.

In early work Koski and Wilk found that all of the \(^{35}\)S radioactivity was in the sulfate form when neutron irradiated KCl was dissolved in water containing sulfate, sulfite, and sulfide carriers. Koski and Willard found that 95 percent of the \(^{35}\)S radioactivity was in the sulfide form if the crystals were thoroughly degassed prior to irradiation. But Croatto and Maddock found all the \(^{35}\)S radioactivity in KCl as sulfate even after degassing, although RbCl contained 50 percent of the \(^{35}\)S radioactivity in the sulfide form.

Milham irradiated potassium chloride crystals which were sublimed in vacuum and found 90 percent of the \(^{35}\)S activity in the sulfide form when the sample was dissolved in de-areated aqueous solutions of sulfide carrier. When the sulfide carrier was added after dissolution of the irradiated potassium chloride in de-areated water, only 30 percent of the \(^{35}\)S activity was found as sulfide; the remaining activity was found as sulfate. According to the author the difference was due to a very reactive species \(S_1^2\), which underwent immediate oxidation to sulfate upon dissolution in water.

Koski suggested that this behavior was due to the permeability of the alkali halides to gaseous oxygen which caused the direct oxidation of the elemental sulfur to sulfate. Maddock and Pearson found strong influences of introduced defects on the final state of the \(^{35}\)S recoil atoms in neutron irradiated alkali chlorides and argued that Koski's explanation was probably not correct. They
found that doping of the KCl with CaCl₂ or CdCl₂ increased the yield of \(^{35}\)S in the sulfide form by 57 percent after irradiation in air; a control sample of pure KCl gave less than 1 percent in the sulfide fraction.

Chiotan, Zamfir, and Szabo\(^9\) were able to extract 65 percent of the \(^{35}\)S in the elementary form with trichloroethylene and interpreted this as evidence for the existence of elemental sulfur in irradiated KCl crystals.

Yoshihara, Ebihara, and Shibata\(^10\) studied the chemical states of \(^{35}\)S in neutron irradiated KCl and proposed that chlorine atoms produced during the neutron irradiations acted as strong "oxidants" in the neighborhood of the recoil atom at the moment of dissolution of the crystals for analysis.

By various dissolution procedures Milham, Adams, and Willard\(^11\) showed that at least 60 percent of the \(^{35}\)S radioactivity in neutron irradiated KCl could be attributed to elemental sulfur. They proposed that upon dissolution in 0.3 M NaOH solution containing sulfide, sulfite and sulfate carriers the following reaction takes place:

\[
^{35}\text{S}^0 + \text{S}^- \rightarrow ^{35}\text{SS}^- \rightarrow ^{35}\text{S}^- + \text{S}^0 \quad (1)
\]

If the irradiated KCl is dissolved in degassed 0.3 M NaOH solution, and the carriers added afterward, the following reactions are postulated to take place:

\[
^{35}\text{S}^0 + 3 \text{H}_2\text{O} \rightarrow \text{H}_2^{35}\text{SO}_3 + 2 \text{H}_2 \quad (2)
\]

\[
^{35}\text{S}^0 + 4 \text{H}_2\text{O} \rightarrow \text{H}_2^{35}\text{SO}_4 + 3 \text{H}_2 \quad (3)
\]
They suggested that defects produced during irradiation or by doping affect either the chemical state of the $^{35}\text{S}$ recoil atom in solid KCl or the reactions it undergoes on various dissolution procedures.

Maddock and Mirsky$^{12}$ studied the oxidation states of $^{35}\text{S}$ in neutron irradiated potassium chloride and showed that increased density of point defects and, possibly, dislocations tend to increase the proportion of $^{35}\text{S}$ found in the sulfide form. In all forms of annealing experiments, with the exception of bleaching, they observed conversion of some of the $^{35}\text{S}$ to the sulfate precursor. They also found that degassing did not change the proportion of $^{35}\text{S}$ in the sulfide form.

Recently Freeman, Kasrai, and Maddock$^{13,14}$ investigated the nature of atomic sulfur in an alkali halide matrix. They concluded that the $^{35}\text{S}$ in neutron irradiated potassium chloride is present in four distinguishable forms. These comprised sulfide ions, atomic sulfur, and two kinds of S-Cl complexes, formed by the interaction of the sulfur with V-centers and their derivatives in the crystals. Their experiments suggested that the formation of these four species is not peculiar to the $^{35}\text{S}$ produced by the (n,p) reaction. They introduced $^{35}\text{S}$ into sodium chloride crystals by ion implantation using a 40 Kev beam of $^{35}\text{S}^+$ and obtained very similar results to those obtained with the (n,p) reaction in KCl.

Cifka and Bracokova$^{15}$ investigated the chemical states of $^{32}\text{P}$ and $^{35}\text{S}$ in neutron irradiated potassium chloride. They observed that the water content of potassium chloride had no significant effect either in oxidation or reduction of either product. They found that the ionizing radiation damage of the crystal substantially influenced both the initial distribution and the post-irradiation
changes of the $^{32}$P and $^{35}$S recoil atoms. The initial distributions of $^{32}$P and $^{35}$S recoils were very similar in their dependence on the absorbed dose of ionizing radiation; on the other hand some differences were observed in the annealing behavior of these two isotopes. They found also that the oxidation processes for the $^{35}$S recoils are strongly dependent on the absorbed doses of radiation, while for $^{32}$P recoils the oxidation level reached after five hours of heating remained nearly constant in a dose range of $3 \times 10^{12} - 7 \times 10^{13}$ neutrons/cm$^3$. Finally they observed that the results of the analyses were strongly influenced by the exposure of the samples to sunlight.

Cifka and Kliment$^{16}$ investigated the chemical states of $^{35}$S in neutron irradiated ammonium chloride. They studied the influence of the conditions of preparation of the target material on the distribution of $^{35}$S between the respective valence states. A substantial fraction, 70 percent, of the $^{35}$S radioactivity was found in the sulfide fraction. However, these authors did not distinguish between sulfide present initially in the crystal from the recoil process and sulfide that could come from the exchange between sulfide and elemental sulfur in solution as observed by Milham, Adams, and Willard.$^{11}$ Their results showed only a small influence of oxygen or water present in the crystals on the initial content of $^{35}$S in the sulfide fraction. An oxidation of $^{35}$S atoms occurred during thermal annealing; a short initial reduction period was noted for some samples. Increasing the temperature and the duration of the neutron irradiation caused a decrease in the proportion of $^{35}$S activity in the sulfide fraction.

Campbell and Butterworth$^{17}$ studied the oxidation states of $^{32}$P recoil atoms resulting from the $^{35}$Cl(n,$\alpha$)$^{32}$P reaction in potassium chloride crystals. They performed
pre- and post-gamma radiation annealing experiments and presented evidence from bleaching experiments which suggested that F-centers may have been responsible for the reducing reactions which were observed.

Cifka\(^{18}\) studied the distribution of \(^{32}\)P atoms resulting from the \(^{35}\)Cl(n,a)\(^{32}\)P reaction in potassium chloride. He found a higher percentage for \(^{32}\)P of lower valance in crystals doped with Ca\(^{+2}\) and Cd\(^{+2}\) ions. An initial oxidation was observed during thermal annealing in pure potassium chloride while a short initial period of reduction was found in the doped crystals. Cifka proposed that the \(^{32}\)P recoil species could react with both V-centers and F-centers produced during the neutron irradiation and suggested these centers as explanations for the oxidation and reduction reactions found.

Kronrad and Kacena\(^{19}\) studied the chemical effects of the \(^{35}\)Cl(n,p)\(^{35}\)S reaction in silver chloride. They investigated the influence of thermal and light annealing on silver chloride crystals prepared by various means (by precipitation, melting and single crystal growth) and in plastically deformed crystals. The fraction of \(^{35}\)S activity associated with the sulfide fraction as a function of annealing time showed a general pattern of several maxima and minima regardless of the preparation. The individual plots differed only in their quantitative characteristics such as the number of the maxima and minima and the distance of these maxima and minima from the origin. The authors interpreted the results by postulating that excitons play a major role in the annealing experiments. They did not attempt to separate neutral sulfur from the sulfide fraction.

Kronrad and Kacena\(^{20}\) investigated the chemical changes of sulfur atoms in silver chloride doped with sulfide-\(^{35}\)S and sulfate-\(^{35}\)S. The doped samples were heated to 460-480°C for
15 minutes and the initial distribution of the radioactivity in the sulfide-$^{35}\text{S}$ and the sulfate-$^{35}\text{S}$ doped samples was identical. They concluded that the chemical state of the sulfur in an AgCl matrix is related to the concentration ratio of oxidizing and reducing defects in the crystals. During thermal annealing sulfur atoms were found to undergo changes similar to those produced by the $^{35}\text{Cl}(n,p)^{35}\text{S}$ reaction. They did not determine the amount of neutral sulfur in these experiments.
II. STATEMENT OF THE PROBLEM

Since various kinds of defects have been shown to be the principal reactants encountered by recoil $^{35}$S in solid alkali chlorides, a study of $^{35}$S behavior in a system in which the concentrations of defects can be continuously varied should be of interest. Solid solutions of KCl-KBr constitute such a system.

It is therefore the purpose of this thesis to investigate the chemical behavior of recoil $^{35}$S in solid solutions of KCl-KBr. In addition to the effect of composition at room temperature, the effects of thermal annealing on the chemical distribution of the $^{35}$S will be of concern.
III. GENERAL CONSIDERATIONS

A. Chemical Activation by Nuclear Reactions

(1) Origin and types of excess energy

Nuclear reactions leave the resulting radioactive atoms with excess energy which is of one or more of three kinds: kinetic, ionization, and excitation.

Kinetic energy results from the conservation of momentum in the nuclear reaction. For reactions initiated by thermal neutrons, the recoil atom has a momentum equal to the resultant of the other products of the nuclear reaction.

For the case of a nuclear transformation involving the emission of high energy particles such as alpha particles, protons, neutrons, and neutrons, Libby has developed formulas to calculate the energy of the recoil atom. For cases in which a single particle is emitted, Libby has derived the following equations for the average recoil energy, $\tilde{E}_M$, and the spread, $2A$.

$$E_M = \tilde{E}_M - A \cos \theta$$  \hspace{1cm} (4)

$$\tilde{E}_M = \frac{E M \mu}{(M+m)^2} + \frac{E m (m+M-\mu)}{(m+M)^2} \left[ 1 + \frac{Q E \mu}{m+M-\mu} \right]$$  \hspace{1cm} (5)

$$2A = \frac{4 E \mu}{(M+m)^2} \left\{ M \mu (M+m-\mu) \left[ 1 + \frac{Q E \mu}{m+M-\mu} \right] \right\} \frac{1}{2}$$  \hspace{1cm} (6)
where

\[ \mu = \text{mass of the incident particle in amu} \]
\[ M = \text{mass of the recoil atom in amu} \]
\[ m = \text{mass of emitted particle in amu} \]
\[ E_M = \text{energy of recoil atom in MeV} \]
\[ E_\mu = \text{energy of incident particle in MeV} \]
\[ Q = \text{internal energy released in MeV} \]

assuming that all angles are equally probable

\[ E_M = \bar{E}_M \pm A \quad (7) \]

Thus, for the $^{35}\text{Cl}(n,p)^{35}\text{S}$ reaction produced by thermal neutrons (0.025 eV), $Q = 0.614$ MeV, and the average recoil energy calculated by equation (5) is approximately 17,600 eV. Thus, the recoil energy of the $^{35}\text{S}$ atom is many times greater than normal chemical bond energies (1-5 eV).

Ionization energy may result from several processes: (1) internal conversion, (2) shake off processes, (3) direct ionization, and (4) autoionization. In internal conversion excess nuclear energy interacts with electrons within the atom causing one or more of them to be ejected. This produces a vacancy in the K or L shell of the atom permitting electrons from outer shells to drop into this vacancy. The electron energy released in this transition may also be internally converted; the result is the ejection of several so-called Auger electrons. The resulting change in the atom has been measured in a few cases. Wexler and Carlson\textsuperscript{22} have measured the charge spectrum of halogen atoms as a result of the $(n,\gamma)$ processes or from isomeric transitions and have shown that the distribution of charges ranges from $+1$ to $+15$ with a maximum at $+8$. 
The shake-off process\textsuperscript{23} may result from the sudden change in nuclear charge on emission of a nuclear particle which produces considerable disturbance in the atomic electron configuration. Thus, on beta ray emission from an atom of atomic number $Z$, the electrons must take up new equilibrium positions which are on the average nearer the nucleus of the daughter (charge $Z+1$) than in the parent (charge $Z$). The electrons still have the same quantum numbers, but their energies are now different from their normal state due to the disturbance in the atomic configuration. This energy may be released in two different ways. First, if the speed of the nuclear particle is slow in comparison with the speed of the orbital electrons, the energy may be transferred to the emitted particle. On the other hand, if the nuclear particle is so fast that the nuclear process is essentially non-adiabatic, the daughter atom must take up the excess energy by ionization excitation. A nuclear process is said to be adiabatic if there is no exchange of energy between the incoming or emerging particle and the electron distribution around the nucleus.\textsuperscript{24} Direct ionization may occur if the emitted particle "knocks out" some orbital electrons as it passes through them, but this process is usually $1/1000$ as important as the other process considered here. Autoionization may occur if the atom recoils with energy such that its velocity is greater than that of the peripheral electrons. That is, the slow electrons will simply be left behind.

Excitation energy may occur in nuclear transformations in which the nuclear charge of an atom changes from $Z$ to $Z + dZ$. As a result of this process the energy of the atom will change by an amount $dE(Z)$ which is given by

$$\frac{dE(Z)}{dZ} = e\Phi(Z)$$

(8)
where \( \phi(Z) \) is the electrostatic potential produced by the atomic electrons at the surface of the nucleus that undergoes the nuclear transformation and \( e \) is the elementary charge.  

If in any nuclear reaction the charged particles entering or leaving the nucleus have velocities considerably greater than the velocities of the orbital electrons of the target atom, the electron cloud cannot adjust adiabatically to the sudden change in nuclear charge. Thus a certain amount of electronic energy is available for atomic excitation, which in an adiabatic process would be absorbed by the incoming or emerging charged particles. Following the approach of Serber and Snyder\(^{26}\), Steiger\(^{25}\) shows that this energy, \( \Delta E \), is given by the difference between the energy absorbed by the charged particle in a reorientation of the electronic cloud in an adiabatic transition, and the energy absorbed in the actual non-adiabatic process. Carrying through this process Steiger shows that the average energy of excitation of a heavy nuclear reaction product, following a change in nuclear charge from \( Z \) to \( Z' \) is

\[
\Delta E = 22.85 \, Z^{2/5} \,(Z' - Z)^2 \, (\text{eV}) \quad (9)
\]

Serber and Snyder\(^{26}\) have calculated that for the transformation

\[
^{32}\text{Si} \rightarrow ^{32}\text{P} + \beta^- + \nu, \quad E_{\text{exc}} = 59 \, \text{eV}.
\]

For the \(^{35}\text{S} \) decay reaction:

\[
^{35}\text{S} \rightarrow ^{35}\text{Cl} + \beta^- + \nu
\]

\( E_{\text{exc}} \) is approximately 66 \, eV. Electronic excitation may also occur as a result of charge neutralization as has been shown by McGee and Gurnee\(^{27}\) for the reaction
They estimated that as much as 30-40 eV may be available for the excitation of the electrons. Thus, atoms ionized by the nuclear process may become electronically excited upon partial neutralization.

(2) Chemical consequences of excess energy

A nuclear reaction leaves the newly formed atom in a highly energetic state; in addition to electronic excitation, the atom usually possesses kinetic energy, a result of conservation of momentum, many times greater than chemical bond energies. The consequence of this highly energetic state is the rupture of the chemical bonds in the compound and subsequent recoil of the radioactive atom through the surroundings.

The recoil atom loses a considerable portion of its energy through collisions and interactions with the electrons of the atoms and molecules in the matrix environment. When the energy of the recoil atom has been degraded to near the range of normal bond energies, the recoil atom may again form chemical bonds.

The new bonds formed are likely to be different from the original for the following reasons: (1) the atom by recoiling through its surroundings will find itself in a different chemical environment; (2) numerous reactive fragments will have been produced by the recoil of the atom, and these may play a part in the chemical bonds formed; and (3) the bonds quite likely will be formed when the atom still has considerable kinetic energy.

Such investigations provide an opportunity to study chemical reactions in an energy range inaccessible by ordinary means. For the most part ordinary chemical reactions are studied at energies slightly greater than the
threshold energy, i.e., the minimum energy required for the reaction. As the energy of the reactants increases, the probability (or rate) of the reaction increases. However, it is known that there is an upper limit of energy beyond which atoms cannot remain bonded to each other, and thus the probability (or rate) of a reaction cannot continue to increase indefinitely, but necessarily must go to zero.

The study of reactions of energies much above the threshold energy is hindered by the experimental problems encountered in attaining and controlling the high temperature required. The maximum energy at which bonding may occur is thought to correspond to a temperature of about 100,000°C (∼ 10 ev). Normal methods available to the kineticist do not yield such high temperatures and so one must find other methods. One of the most successful methods of obtaining atoms with kinetic energies in this range is by recoil from nuclear reactions.

In hot-atom chemistry studies there are two energy regions of interest; (1) the hot region in which all reactions take place before the recoil atom obtains thermal equilibrium with its environment, i.e., $E > 0.025$ ev; and (2) the thermal region where $E \sim 0.025$ ev and in which the recoil atom can diffuse through the environment to participate in the usual chemical reactions of addition, substitution, recombination, and exchange.

B. Chemical Stabilization of Activated Atom

1. Hot Zone Model

There are two major differences between hot-atom reactions in solids and those in gases and liquids. In solids the recoil range is shorter than in liquids and gases, and hence the probability for repeated collisions is higher in solids than in liquids or gases. Also, in solids there
are long range interactions which are absent in gases and which probably occur very rapidly in liquids. These long range interactions are probably very slow in solids at ordinary temperatures, but may become very important at higher temperatures.

The results of hot-atom chemistry studies in the solid state have been best interpreted by the hot zone theory of Harbottle and Sutin. This theory is based upon the displacement spike theory of Seitz and Koehler used in studies of radiation damage in materials. When solids are irradiated by neutrons or high energy particles there is considerable energy transfer and excitation within a small region of the solid. If the excitation is high enough that many atoms in the small region are displaced from their normal lattice positions and wander about, the disturbance is called a displacement spike. The main features of the hot-zone theory are:

a) The recoil atom slows down to an energy less than that required for the production of displacements ($\approx 25 \text{ ev}$) in approximately $10^{-13}$ sec. During this slowing down period approximately six displacements are produced in molecular crystals by atoms with recoil energies of $\approx 300 \text{ ev}$ and about sixteen such displacements in ionic crystals. The displaced atoms represent "hot spots" and lie within a sphere of approximate radius $5r_s$, where $r_s$ is the atomic radius of the recoiling atom and is given by equation (11):

$$4/3\pi r_s^3 = 1/n_o$$

(11)

where $n_o$ is the number of atoms/cubic centimeter.
b) The hot spots coalesce in approximately $10^{-12}$ seconds to give a hot-zone of relatively uniform high temperature.

c) The temperature of the hot-zone falls below the melting point of the crystal in $10^{-11}$ seconds.

d) There is good probability for reactions between a recoil atom and any reactive fragments in its vicinity during the lifetime of the hot-zone in spite of the fact that these reactions may require a moderate activation energy.

e) Since recoil atoms have been shown to undergo recombination reactions during annealing, the reactions in the hot-zone are quenched by thermal cooling before going to completion. These reactions may subsequently be studied further by observation of the effects of thermal heating or of radiation.

Seitz and Koehler consider the formation of the hot spot in the following manner. Consider an atom in a lattice that has been struck hard enough to vibrate with a large amplitude, but not large enough to dislodge the atom from its lattice site. An atom in this excited state rapidly transfers energy to its neighboring atoms which then become abnormally excited. This transfer of energy continues in a similar manner and thus a localized excitation region develops and then dies out. This region of excitation is called the displacement spike, the thermal spike or the hot-zone. This condition is analogous to the situation that would exist if the lattice had suddenly been heated to a high temperature in a localized region. Thus, one visualizes the formation and loss of the excitation as a form of heat conduction.

On the basis of the displacement theory one considers the energy $Q$, transmitted to a lattice atom as heat energy.
localized in the lattice and spreading according to the laws of heat conduction. The medium is considered to have a thermal diffusion coefficient \( D \) and a temperature \( T(r,t) \) at each point \( r \) and time \( t \). The diffusion coefficient is given by equation (12):

\[
D = \frac{C}{cd}
\]

where \( C \) is the thermal conductivity, \( c \) the heat capacity, and \( d \) the density of the medium.

The temperature of the thermal spike obeys equation (13):

\[
\nabla^2 T = \frac{1}{D} \left( \frac{\partial T}{\partial t} \right)
\]

The solution of this equation at a distance, \( r \), from the origin \((t=0)\) at time \( t \) is:

\[
T(r,t) = T_o + \frac{Q}{(4\pi)^{3/2} cd} \frac{1}{(Dt)^{3/2}} e^{-r^2/4Dt}
\]

where \( T_o \) is the initial temperature and \( Q \) is the heat liberated at the origin. For the present case \( Q = 17,600 \) eV, the heat capacity of KCl is 0.162 cal/gm-\(^\circ\)C\(^{30}\) or \( 4.3 \times 10^{18} \) eV/gm-\(^\circ\)C, the density of KCl is 1.984 gm/cm\(^3\)\(^{31}\), the time \( t \) is the initial time of the formation of the hot-zone and is \( \approx 10^{-13} \) sec\(^{28}\), the radius of the sulfur atom is approximately 2.0 \( \times \) 10\(^{-8} \) cm, and the diffusion coefficient is \( \approx 10^{-3} \) cm/sec.\(^{28}\) By equation (14) the initial temperature of the hot-zone 10\(^{-13} \) seconds after formation is \( \approx 17.5 \times 10^6 \) \(^\circ\)C.

The displacement spike theory of Harbottle and Sutin has as an important feature the provision for specific chemical effects in the hot zone. Thus, the chemical state and composition of the hot zone should have a pronounced effect on the final chemical state of the recoil atom.
(2) **Factors Affecting Stabilized Form**

a) **Recoil energy**

As yet experiments have not been devised to determine conclusively whether recoil energy affects the stabilized form. Herber\(^{32}\) carried out experiments to determine the effect of high energy deposition in the compound nucleus on the chemical fate of the sulfur activity produced in various targets using 300 Mev alpha particles and 550 and 680 Mev protons. In the alpha particle bombardments the distribution of 87.1 day \(^{35}\)S produced by the \(^{37}\)Cl \((\alpha,\alpha pn)^{35}\)S and \(^{35}\)Cl \((\alpha,3pn)^{35}\)S reactions were directly compared to the 172 min \(^{38}\)S produced by the \(^{37}\)Cl \((\alpha,3p)^{38}\)S reaction. The targets were subjected to standard aqueous radiochemical procedures for sulfur isotopes. A sulfate \((SO_4^2-\)) fraction and a non-sulfate \((S)\) fraction were recovered and converted to barium sulfate for counting. The data obtained is shown in Table I.

Herber inferred that the amount of energy transferred to the recoiling sulfur atom does not in itself decisively affect the final chemical fate of the recoiling atom. There are many examples of differences in the hot-atom behavior of isotopes. However, it is not clear whether these differences are due to differences in recoil energy or to differences in the nuclear properties of the isotopes themselves and to their modes of deactivation in the sample matrix.\(^{33}\) It is generally regarded that the effect of recoil energy as such is small.

b) **Mode of deactivation**

The maximum energy at which chemical reactions can occur certainly cannot be in the high energy region of the energy spectrum of the recoil atom since the atoms possess too much energy to remain bonded together and hence
**TABLE I**

$^{35}\text{S}$ and $^{38}\text{S}$ Distributions from High Energy Bombardments

<table>
<thead>
<tr>
<th>Target</th>
<th>Particle</th>
<th>Energy (MeV)</th>
<th>Fraction</th>
<th>$^{38}\text{S}$</th>
<th>$^{35}\text{S}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$Cl</td>
<td>$\alpha$</td>
<td>300</td>
<td>S</td>
<td>11.3</td>
<td>18.8</td>
<td>30 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td>88.7</td>
<td>81.2</td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>$\alpha$</td>
<td>300</td>
<td>S</td>
<td>37.4</td>
<td>15.1</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td>62.6</td>
<td>84.9</td>
<td></td>
</tr>
<tr>
<td>NaClO$_4$</td>
<td>$\alpha$</td>
<td>300</td>
<td>S</td>
<td>1.3</td>
<td></td>
<td>single crystal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td></td>
<td>98.7</td>
<td></td>
</tr>
<tr>
<td>NaClO$_4$</td>
<td>$^{1}\alpha$</td>
<td>300</td>
<td>S</td>
<td>1.7</td>
<td></td>
<td>single crystal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td></td>
<td>98.3</td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>$^{1}\text{H}$</td>
<td>680</td>
<td>S</td>
<td>84.3</td>
<td>15.5</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>$^{1}\text{H}$</td>
<td>680</td>
<td>S</td>
<td>82.1</td>
<td>17.9</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>$^{1}\text{H}$</td>
<td>550</td>
<td>S</td>
<td>24.6</td>
<td>75.4</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>$\alpha$</td>
<td>550</td>
<td>S</td>
<td>15.7</td>
<td>12.9</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
move apart. In the high energy region (\( \sim 25 \text{ Kev} \)) the only interactions which are probable are ionization reactions such as reaction (15)

\[
T^+ + \text{CH}_4 \rightarrow \text{CH}_4^+ + T + e^- \tag{15}
\]

and charge exchange reactions such as reaction (16)

\[
T^+ + \text{CH}_4 \rightarrow \text{CH}_4^+ + T \tag{16}
\]

It is only when the recoil atom has reached the region in which elastic and inelastic collisions are operative (10 - 1000 ev) can one begin to discuss the possibility of chemical reactions. Evidence from the study of hot-atom reactions in inorganic solid systems indicates that chemical reactions occur only at the end of the recoil path, i.e., when the recoil atom has been degraded in energy by interaction with its environment.

There is at least one way in which the mode of energy loss can affect the stabilization of the recoil atom. Some nuclides undergo de-excitation by delayed emission of gamma rays, beta particles, etc., after having initially entered chemical combination. This can lead to a different chemical state than that of one of its isotopes which is completely de-excited before entering chemical combination.

c) Temperature

The study of hot-atom chemistry has relied heavily upon nuclear reactors for the production of particles with very high energies, i.e., from the recoil from nuclear reactions. The energy of the hot-atom is supplied by the nuclear reaction and this process is independent of the environmental temperature. Therefore, hot-atom reactions
should be temperature independent. However, reactions of hot-atoms which have been thermalized (those which have lost their energy but have not yet undergone reaction) and other molecules may be affected by temperature as are most of the ordinary reactions of diffusion, recombination, exchange, and substitution. Since observed results are usually a combination of hot (temperature independent) and thermal (temperature dependent) reactions, temperature control and variation are important in the interpretation of such results.

d) **Pressure**

Andersen and Maddock\(^{34}\) reported quantitative data on the annealing (see D below) of recoil damage by compression for potassium chromate. It thus appears that pressure on the system (even solid systems) is important to the ultimate fate of the recoil atom, either by influencing the volume of the hot zone, or by creating new reaction sites at bulk defects, or by influencing the rate of diffusion in the bulk of the solid.

e) **Physical matrix**

Since the stabilization of the recoil atom in the crystal is dependent on the particular environment of the recoil atom as it loses its excess energy, one would expect the composition of the crystal to be an important factor. Also affecting the stabilization is the nature of the defects in the crystal prior to irradiation and the defects produced in the crystal upon irradiation. Therefore, it is important that possible effects of different structures, compositions, and defect concentrations be considered in investigations of the recoil behavior of atoms in solids.
f) **Impurities**

The usual number of atoms of high energy produced by recoil from nuclear reactions is of the order $10^{12}$. The level of impurities in a very pure solid system is usually much higher than this value, but often below the limit of detection. Usually the identity of the impurities is not known and there is no possibility of designing a purification procedure with absolute certainty that it will give a pure product; it may introduce more impurities than it removes. Upon irradiation such impurities may yield fragments which could affect the energy loss of the hot-atom or could react with the hot-atom to change the distribution of the species in the crystal. There are several criteria which may be applied as indicative of the fact that impurities have been reduced to a level where they do not influence the results. They are: (a) identical results are obtained with reagents purified by widely different methods; (b) a number of different but related compounds give identical results; and (c) the products are characterized and found to be such that they could not have been formed by reaction with any conceivable impurity.

g) **Radiation damage accompanying activation**

The production of a recoil atom necessarily involves the interaction of particles of electromagnetic radiation with the material. In order to produce one recoil atom much energy must be supplied to the system and as a result the system receives a large dose of irradiation, which may introduce defects and displacements in the crystals. These defects and displacements affect the rate of energy loss and can also diffuse through the crystal and react with the recoil species thereby changing the distribution. Care must be taken to separate the hot-atom chemistry from the
radiation chemistry.

C. Defects in Alkali Halides and Their Mixed Crystals

An imperfection in the solid state is considered to be any deviation from a perfect regular lattice of structure. All crystals are in some respect imperfect and the nature of these imperfections are fairly well understood in some classes of compounds such as the alkali halides. Much research effort in solid state physics today is directed towards an understanding of the nature of these imperfections in nearly perfect crystals. This may be explained by the fact that a great many of the important properties of solids are controlled far more by the nature of the imperfections in the crystals than by the nature of the bulk crystal which contains these imperfections. Some of the properties of crystals which are found to depend upon the imperfections are the conductivity, color, luminescence, diffusion, mechanical and plastic properties, and the rate and mechanism of growth of crystals themselves.

In general there are two basic types of point defects in crystals. The first are Schottky defects which are lattice vacancies, coupled pairs of lattice vacancies, or divalent ions present substitutionally in the crystal with their associated positive ion vacancies. The second class of point defects are Frenkel defects in which an atom has been transferred from a lattice site to an interstitial site. The production of Schottky defects lowers the density of the crystal because the volume increases while the mass remains the same. There is no accompanying density change with the production of Frenkel defects.
Frenkel pairs (vacancies and associated interstitials) are not generated in the alkali halides as a result of normal thermodynamic equilibrium processes since their energy of formation is high (~3.0 ev) compared to that for Schottky defects (1.9-2.0 ev). In the alkali halides Schottky defects may be produced by doping with divalent cations using mixtures of the alkali halide and divalent salts such as CdCl$_2$ or CaCl$_2$. Frenkel defects may be produced in the alkali halides by the action of ionizing radiation since the interaction of radiation with the crystals is not a process occurring in thermodynamic equilibrium. $^{35}$

Ionizing radiation may also produce defects in crystals by mechanisms which are thought to be quite different from that for direct displacement of atoms by bombarding particles. Radiation damage experiments performed on the alkali halides at room temperature indicate that a large number of different defect configurations exist. $^{35}$ These defects seem to be associated with vacancies, aggregations of vacancies, and several interstitial configurations produced by the displacement of ions from their normal lattice sites. The damage produced at this temperature is sensitive to the previous history of the crystal and to its impurity content. As the temperature of irradiation is reduced the sensitivity of the damage to the structure of the sample decreases and at liquid helium temperatures the initial rate of production of defects appears to be independent of sample history. $^{36}$

The best understood Frenkel defect produced by ionizing radiation at room temperature is the color center designated as the F-center. The simultaneous production of halide ion vacancies and interstitials in the alkali halides sub-
jected to ionizing radiation was first suggested by Varley. His experiments on the high energy electron irradiation of the alkali halides at room temperature led him to postulate an indirect mechanism for the formation of an F-center by high energy electrons in which a halide ion is multiply ionized in a single electron impact. The strong repulsion caused by the six nearest neighbor alkali ions then ejects the positive halogen ion to an interstitial site, leaving the halide ion vacancy which can then trap an electron to become an F-center.

At liquid helium temperatures the negative ion vacancy exists in two charge states: (1) the $\alpha$-center which is a negative ion vacancy without an associated electron, and (2) the F-center which is a negative ion vacancy with an associated trapped electron. The other member (anti-center) of the Frenkel pair has been identified for each of these centers. The H-center has been considered to be the anti-center of the F-center, and Kanxig and Woodruff have shown that in KCl, KBr, and LiF this anti-center is an $X_2^-$ molecule sitting on a lattice site and sharing its hole with the two neighboring $X^-$ ions. The H-center is a neutral interstitial associated with a vacancy containing an electron, charge conservation thus being assured. The $\alpha$-center should be associated with a negative ion interstitial and Gerhardt and Itoh have identified such a center in the optical absorption spectrum of KBr. This so-called I-center is considered to be a negative ion interstitial occupying a body-centered site rather close to the site of the $\alpha$-center.

The H-center is not the only possible anti-center of the F-center. The $V_{K}^-$-center is also found in low temperature irradiations and is apparently a self-trapped hole. A
self-trapped hole is a hole (chlorine atom) trapped at an alkali metal ion vacancy. V-centers can also be formed by heating alkali halides in excess halogen vapor. A chlorine atom is incorporated in the lattice. The halogen atom has a deficit of one electron with respect to the halide ion and is thus attracted to a cation vacancy.

Varley has given an excellent review of some of the postulated mechanisms for the formation of F-centers in the alkali halides. However, several objections have been raised to the Varley mechanism, and various authors have proposed mechanisms which involve the transfer of energy to the electronic system of the halogen ion, which is then displaced to an interstitial position as a result of its altered electronic environment.

The data available for the production of F-centers at room temperature suggest that the final equilibrium array of defects in a lattice at a given temperature is the result of a series of complex reactions taking place during and immediately after the radiation exposure. The fact that some of these transient centers have the same configurations as stable defects found at low temperatures suggests that the mechanism of radiation affects the annealing processes which give rise to the final equilibrium array of stable (center-anti-center) configurations.

The experimental and theoretical aspects of the mechanism of production of the defects are still in an early stage and the exact mechanism of formation is not clear. However, it would seem that the mechanism of F-center formation is probably the same between 4°K and room temperature. The factor causing the observed differences in the optical
absorption spectra, volume expansion and lattice parameter data, luminescence, formation efficiency, etc., at various temperatures would therefore seem to be the stability of the anti-center associated with the vacancy.\textsuperscript{50} Also the available experimental data indicate that at all temperatures the F-center is an electron trapped in a halide ion vacancy.

In general irradiation of the alkali halides with ionizing radiation has been shown to produce the following types of centers: F, F', V\textsubscript{1}, V\textsubscript{2}, V\textsubscript{3}, V\textsubscript{4}, V\textsubscript{5}, V\textsubscript{6}, V\textsubscript{7}, V\textsubscript{K}, R\textsubscript{1}, R\textsubscript{2}, M, and possibly others. The F-center has been shown to be an electron trapped in a halide ion vacancy. The F'-center is generally regarded as two electrons situated at the same halide ion vacancy. The R- and M-centers are formed when crystals containing F-centers are irradiated with light of the F-band wavelength or are heated to the appropriate temperature. The exact structures of these centers are not known, but they are believed to be F-centers which have coagulated to yield colloidal particles of alkali metals.\textsuperscript{51} There are several V-centers, only one of which has been well characterized. Kanzig\textsuperscript{52} identified the V\textsubscript{1}-center (stable at liquid helium temperatures) as a halide molecule-ion, apparently formed from two neighboring halide ions by removing one electron during irradiation in such a manner that the resulting electron deficiency is shared equally by the two ions. The V\textsubscript{1}-center was found not to be associated with any other type of imperfection and has been regarded as a self-trapped hole. V\textsubscript{2}- and V\textsubscript{3}-centers have been found in alkali halides x-ray irradiated at room temperature. These centers are also believed to be electron deficient centers, but their structures are not known.
The above centers have all been experimentally observed in alkali halides that have been irradiated at liquid helium or liquid nitrogen temperature.\textsuperscript{51} Many of them are not stable at room temperature and hence are not observed after room temperature irradiations although they may have been produced initially. Irradiation of the alkali halides at room temperature has been shown to yield F, M, V_2, and V_3 centers in the ratio of F:V:M = 22:5:1.\textsuperscript{89}

Recently Ritz\textsuperscript{54} determined the F-center production efficiencies in potassium bromide, potassium chloride, sodium chloride, and lithium fluoride. The production efficiency is defined as the ratio of the total dose received by the sample to the number of centers produced by that dose, i.e., electron volts/F-center. The doses were determined by the Fricke dosimeter and the concentration of F-centers was determined spectrophotometrically and calculated by equation (17) developed by Smakula.\textsuperscript{55}

\[ N = (2.97 \times 10^{17} / t) \left[ n \frac{D w_{1/2}}{(n^2 + 2)^2} f \right] \] (17)

where

- \( N \) = number of F-centers/cm\(^3\)
- \( t \) = thickness of the crystal specimen
- \( n \) = index of refraction of the crystal
- \( D \) = optical density of the absorption peak
- \( w_{1/2} \) = half-width of the absorption peak (eV)
- \( f \) = oscillator strength

A typical absorption spectrum for the F-center in potassium chloride is shown in Figure 1.\textsuperscript{56} The results obtained for potassium chloride and potassium bromide are shown in Table II.
Figure 1. Absorption Spectrum of F-center in KCl
TABLE II
F-Center Production Efficiencies (ev/F-center)\(^{54}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>2.0 Mev electrons</th>
<th>50 kv X-rays</th>
<th>50 kv X-rays unfiltered</th>
<th>15 kv X-rays</th>
<th>10 kv X-rays</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr</td>
<td>4700</td>
<td>2740</td>
<td>1700</td>
<td>3300</td>
<td>4600</td>
</tr>
<tr>
<td>KCl</td>
<td>3750</td>
<td>2900</td>
<td>2400</td>
<td>4600</td>
<td></td>
</tr>
</tbody>
</table>

These results indicate that at liquid helium temperatures using 2.0 Mev electrons it takes less energy to produce an F-center in potassium chloride than in potassium bromide.

Some work has been carried out to determine the effect of the composition of mixed crystals of potassium chloride-potassium bromide on the production of F-centers in these mixed crystals. Smakula, Maynard, and Repucci\(^{57}\) studied the defects produced in mixed crystals of potassium chloride-potassium bromide by irradiation with 3.0 Mev electrons at -190°C. They found that the absorption maximum of the F-band for a potassium chloride-potassium bromide mixed crystal was between that for pure potassium chloride and pure potassium bromide. This data indicates that at a given dose and temperature the concentration of F-centers is greatest in pure potassium chloride, lower in pure potassium bromide and lowest in a mixed crystal of potassium chloride-potassium bromide.

More recently, Arends, den Hartog, and Dekker\(^{58}\) studied the composition dependence of the colorability (F-centers) of mixed alkali halide crystals after X-ray irradiation at room temperature. They found that the peak intensity of the F-band at 300°K as a function of composition
of the mixed crystal of potassium chloride-potassium bromide exhibited a minimum at the equimolar concentration. They also found that the F-center growth curves for the potassium chloride-potassium bromide mixed crystals were lower than those for pure potassium chloride or pure potassium bromide and that the largest portion of the F-centers in the mixed crystals was produced in the early stages of the coloration. However, the F-center growth curves given by Arends, et al., are graphs of log $I_0/I$ versus the absorbed dose and do not represent the exact concentration of F-centers in accordance with Smakula's equation which takes into account the crystal thickness. Therefore, there is no data available for the concentration of color centers in mixed crystals of KCl-KBr as a function of composition. The available data tends to indicate that the concentration of F-centers in the mixed crystals would be intermediate between the pure components and would exhibit a minimum at the equimolar concentration.

D. Effect of Post Irradiation Treatment

During the lifetime of the hot-zone, initial chemical reactions are believed to occur, but are quenched when the hot-zone cools. Therefore, annealing or further irradiation should permit the reactions to proceed further. Recent evidence has shown that annealing reactions occur below room temperature as well as above. The processes taking place above room temperature have activation energies in the region of 1 to 2 electron volts. There are other annealing processes which have activation energies from 0 to 1 electron volts, but which are observed only if the sample is irradiated at low temperatures and maintained at the low temperature until the time of analysis.
By reference to equation (14) one can see that if \( T_0 \) is lowered, then \( T(r,t) \) must necessarily be lowered since \( Q \), the recoil energy, is a product of the nuclear reaction and is independent of the temperature of the sample. Since the annealing or thermal reactions are temperature dependent, i.e., the reactions depend upon the diffusion of the recoil atom through the matrix, these reactions will be slowed down because the environmental temperature \( T(r,t) \) has been lowered. Thus, a large part of the necessary activation energy is not available for the diffusion controlled replacement and recombination reactions, and hence the reactions will not go as far to completion as the reactions which would have been produced had the sample been irradiated at higher temperatures.

Since some of the initial chemical reactions of the recoil species are quenched when the hot-zone cools, annealing will permit the reactions to proceed further. Studies of annealing reactions may give information as to the activation energies for recombination. The effect of changes in the crystal environment upon annealing reactions may be studied and this work may lead to a better understanding of the nature of the primary recoil species.

Williams\(^{65}\) found that increased irradiation of crystals containing a recoil atom produced a "back reaction" which returned the once-free recoil atom to a form inseparable from the parent. Green and Maddock\(^{66}\) found that the same type of back reaction could also be induced simply by heating the irradiated crystals in the laboratory. Since these introductory annealing experiments, thermal annealing reactions of recoil atoms in many crystals have been reported. It is now known that annealing can be produced not merely by heat and ionizing radiation, but also by light\(^{67,68}\) and even by pressure.\(^{34}\)
The isothermal annealing curve in which the yield of a particular recoverable species is plotted against time of heating, generally shows an initial rapid change followed by a plateau in which the change is very slight. Figure 2 shows a series of hypothetical annealing curves. At a higher temperature the plateau is reached at the same time as that of heating at a lower temperature, but the plateau is at a higher level. Neutron irradiated crystals can be annealed isothermally up to the plateau for that temperature and a new phase of rapid growth can take place, if the temperature is increased and a new plateau characteristic of the higher temperature is obtained. A typical hypothetical case is shown in Figure 3.

Maddock and de Maine found that the increase in yield of a product from the beginning of the plateau could be described by the empirical rule $\Delta R \propto \frac{1}{T}$, where $\Delta R$ is the change in yield of the species.

There are three factors which affect the rate and the extent of annealing. First, we have seen that the temperature is important in determining the rate of the annealing reactions as expected for processes which have moderate activation energies.

A second factor of importance in annealing is the concentration and kinds of defects in the crystals. These effects have been studied by Maddock and his co-workers and the results summarized as follows: the introduction of defects into a crystal through grinding, irradiation with gamma rays, or by doping with aliovalent "foreign" cations, has a strong effect on the subsequent course of the thermal annealing reactions. In general, this effect is acceleration, i.e., the annealing reactions proceeds more rapidly, or to a higher plateau in the yield. Recent studies seem to
Figure 2. Hypothetical Annealing Curves
Figure 3. Hypothetical Interrupted Annealing Curves
indicate that the cation vacancy is one of the most important of these active defects.\textsuperscript{76}

A third factor in annealing is the nature of the nuclear transformation which has occurred and which led to the recoil atom whose annealing reactions are being studied. Neutron capture (n,\gamma) reactions are likely to lead to ionization or electronic excitation by internal conversion. Both the extent of charging and the average recoil energy of the atom depend upon the nuclear reaction and this is different for every nuclide. When the annealing reactions of different isotopes in the same crystal are studied isotopic differences are found. The hot zone model explains this behavior on the basis that the nuclear reactions produced atoms in different states and produced different degrees of radiation damage in the hot zone. As the hot zone cools down (in $10^{-11}$ seconds), some of the radiation damage is frozen in. The extent and kind of the damage affect the chemical reactions of the trapped recoil species and the annealing reactions thus depend on the particular mode of nuclear production of the recoil species.

The interpretation of thermal annealing requires the use of some model to describe the rate of the annealing process. The assumption is usually made that thermal annealing is the recombination of pairs of interstitials and vacancies. For hot-atom purposes a vacancy in a complex crystal may be regarded as a trap consisting of a fragment or any species capable of reacting chemically with the displaced recoil atom. In some cases this might consist of an oxygen atom or oxide ion which could be capable of diffusion in the crystal. In other cases the trap might be a defect such as an F-center or an electron deficient hole.
One of the simplest models of annealing is that of the recombination of initially correlated pairs. This is a recombination of the recoil atom with a collision fragment or with one of its originally bonded partners and it is assumed that this pair has a small initial separation. Close to the vacancy there is an elastic deformation of the lattice which results in a lowering of the potential barrier to the jumping of the interstitial atom from one interstitial position to the next as it nears a vacancy. The frequency $v_j$ of jumps of the recoil atom of type $j$ from one interstitial to another is

$$v_j = v_o \exp(-E/kT) \tag{18}$$

where $v_o$ is the typical frequency for the vibration of atoms in the lattice and $E$ is the energy required by the interstitial to jump to the adjacent interstitial site. The rate of recombination is then

$$-\frac{dn}{dt} = v_j n \tag{19}$$

where $n$ is the number of uncombined pairs which are correlated. This equation leads to the first order law

$$n_t = n_o \exp(-v_j t) \tag{20}$$

in which $n_t$ and $n_o$ are the number of uncombined pairs at times $t$ and zero, respectively. Provided the isothermal annealing leads to retention (re-formation of the parent compound, or a species which produces the parent compound upon chemical analysis), equation (20) may be expressed as

$$\ln (R_{oo} - R_t) = \ln (R_{oo} - R_o) - v_j t \tag{21}$$
where $R_t$ and $R_{oo}$ are the retentions at time $t$ and at infinite time of isothermal annealing. These quantities are shown plotted in Figure 4.

If there are several classes of fragments in the same, or different zones which have different activation energies for annealing, then

$$n_t = n_{01} \exp(-v_{j1} t) + n_{02} \exp(-v_{j2} t) + \ldots \quad (22)$$

where $n_0 = n_{01} + n_{02} + \ldots$, and $v_{j1}$ is the jump frequency of the atom in the $i$th locus from its initial position.

Maddock and de Maine$^{69,78}$ have modified the model of the recombination of initially correlated pairs by introducing electrostatic interactions which deal with the diffusion of interstitial atoms in the neighborhood of a correlated defect. After irradiation but prior to annealing they assumed the distribution of correlated pairs (recoil atom-vacancy) distances ($X$) in the crystal to be as shown in Figure 5. There are no distances less than $X_0$, because partners having this separation would have recombined even at room temperature and contributed to the $R_o$ term. There are no distances greater than $X_{oo}$, a distance equal to the maximum range of the recoil atom. The distribution is assumed to be uniform between $X_0$ and $X_{oo}$. The rate of recombination of partners is given by

$$-dn/dt = n v \exp(-U/kT) \exp(V/kT) \quad (23)$$

where $n$ is the number of possible pairs, $U$ is the activation energy barrier opposing recombination, $v$ is the frequency of vibration of the vacancy $T$, is the absolute temperature, $X$ is the smallest separation of partners at time $t$, and $V$ is an electrostatic potential term containing the charges of the defects or ions, dielectric constant, and crystal parameters.
Figure 4. Hypothetical Illustration of Quantities in Equation (21)
Figure 5. Distribution of Recoil Atom-Vacancy Distances in the Maddock-de Maine Model
The model pictures the increase in retention on annealing as the recombination of partners having increasingly greater values of $X$, the process visualized as slow movement of the vertical line $X_o$ to $X_{oo}$, the area lying to the left of the line as the number of the pairs that have already recombined. The change in retention, $\Delta R$, is a linear function of $X$ and appears in the rate expression

$$\frac{1}{(R_{oo}-R)} \frac{dR}{dT} = v \exp(-U/kT) \exp[V/ckT(\Delta R+S)]$$

(24)

where $S$ is a constant and $c$ is a constant which relates the retention to $X$. When annealing is begun, $\Delta R$ is small and the second exponential term is large and dominates the reaction. As annealing proceeds the second exponential becomes effectively unity and the rate of increase in retention becomes controlled by the first exponential. The value of $\Delta R$ (equal to $\Delta R_e$) for which the second exponential becomes unity is taken from the expression

$$V/ckT(\Delta R_e+S) = \alpha$$

(25)

where $\alpha$ is a number such that $e^{\alpha} = 1$. It can be seen that the values of $\Delta R_e$ characteristic of the plateaus at different temperatures obey the equation

$$\Delta R_e = C'/T$$

(26)

where $C' = V/ck$. Hence one can see that on the basis of the Maddock-de Maine model the increase in retention upon annealing to the plateau should be a linear function of $1/T$ which is what has been experimentally observed.
There are some additional models based upon the recombination of initially correlated pairs, but these approximate the experimental annealing data only under certain conditions. These will be discussed only briefly.

Harbottle and Sutin\textsuperscript{70} discussed the recombination of initially correlated pairs with electron transfer as the rate determining step. This may be important for some hot-atom reactions, but the activation energies for annealing processes do not in general fit this model. There are examples of annealing reactions which do not proceed at all, or only very slowly, at 0°C, but go very rapidly at temperature around 100-200°C. This would imply an activation energy of 1-2 ev which is of the order of magnitude of the activation energies for diffusion in ionic crystals, but too large for electron transfer reactions.\textsuperscript{70}

Fletcher and Brown\textsuperscript{77,79,80} have discussed a model based on the recombination of initially correlated pairs after a random walk process. For the interstitials located outside the deformed region the probability of jumping in any direction is the same. These interstitials wander according to a random walk process. Those that wander back into the deformed region are subsequently captured by their original partners, and the rest wander off through the crystal. In some cases the data predicted by the model introduces an inflection point near the origin of the annealing curve, a phenomenon which has not been experimentally observed. Also the linear relation between $\Delta R$ and $1/T$ is not observed.

Harbottle and Sutin\textsuperscript{70} also discuss a model based upon the recrystallization of the hot zone, but again the data fits the model only under certain specific conditions.
Annealing may also take place by diffusion controlled bimolecular recombination of initially randomly distributed pairs.\textsuperscript{70} This process would follow second order kinetics. If the number of fragments of the two recombining types is the same, then the rate expression is

\[-\frac{dn}{dt} = kn^2\]  

where \(n\) is the number of uncombined fragments at time \(t\), and \(k\) is the bimolecular rate constant. The variation with temperature is given by

\[k = k_0 \exp(-E/kT)\]  

where \(k_0\) is a constant roughly independent of temperature and \(E\) is the activation energy. If bimolecular processes are important in a Szilard-Chalmers system, it seems likely that the recombination rate would depend upon the extent of radiation damage in the crystal before and during annealing. Bimolecular kinetics leads to the retention expression

\[R_t = R_0[1 - 1/(1+kR_\infty t)]\]  

where the symbols have their usual meaning and the retentions are measured from \(R_0\).

The thermal exchange model\textsuperscript{70} would be another mechanism in which activity could be returned to the parent form. It can be argued that the activation energy for such processes are too high to account for annealing at moderate temperatures. But just as the activation energies for diffusion are lowered in the presence of defects, so may the activation energy for exchange.
If exchange between X* and any of its C neighboring groups is equally probable, the retention should follow the law

\[
\frac{(R_{oo} - R_t)}{(1 - R_{oo})} = c \exp\left[-(c+1)vt/c\right]
\]

(30)

where v is the frequency of the exchange process. This model predicts that the log of \( \Delta R \) should yield a straight line when plotted against time. This has not been experimentally observed.

Recently, Harbottle\textsuperscript{81} reviewed the theory of annealing of processes occurring with different activation energies. The general expression for the disappearance of annealable species in a particular reaction is

\[
-dn/dt = cn^\gamma
\]

(31)

\[
-dn/dt = [A \exp(-E/kT)]n^\gamma
\]

(32)

where \( n \) is the number of recoil fragments of a certain type, participating in a particular annealing reaction, \( c \) is a rate constant compounded of A, the frequency factor, and \( \exp(-E/kT) \), the usual Arrhenius term for the activation energy E, and \( \gamma \), the order of the reaction. If several different fragments participate, then higher orders may result

\[
-dn_1/dt = c n_1^{\gamma_1} n_2^{\gamma_2} \ldots \ldots
\]

(33)

where \( n \) refers to the fragments, the reactions of which increase the retention, i.e., \( \Delta n \) is proportional to \( \Delta R \). If an initial correlation between fragments followed by a random walk of one of the partners is assumed, an equation involving the error function results for integration of the
rate expression. If initial correlation and reaction only between those correlated fragments is assumed, then first order kinetics should hold. There appears to be varied opinion as to the order of annealing reactions and zero, first, and second order kinetics have been used.

Equation (32) gives the rate of disappearance of the recoil species as a function of the activation energy and the order of the reaction. Fletcher and Brown\textsuperscript{77} constructed composite annealing curves for the annealing out of $\text{Co(NH}_3)_5\text{Br}^{++}$ by $^{82}\text{Br}$ recoils in $\text{Co(NH}_3)_6\text{Br}_3$ from the annealing data of Yoshihara and Harbottle.\textsuperscript{82} Fletcher and Brown attempted to fit the experimental data by theoretical curves which assumed a particular order or mechanism of reaction and a single activation energy. Their results are shown in Figure 6. From the data shown there are some obvious conclusions. The annealing process begins earlier in time and lasts longer than it would for any single activation energy process. This suggests that the observed annealing reactions are governed by a distribution of many activation energies. This is not a contradiction since there will be a distribution of atomic recoil energies after neutron capture and a variety of radiation damage sites, both in degree and range.

Vand\textsuperscript{83} and Primak\textsuperscript{84} developed a mathematical analysis to determine the spectrum of activation energies provided isothermal annealing data is available which covers a wide range of temperature and time. They assumed a distribution of activation energies, $n(E,0)$, where $n(E,t)$ is the number of particles with energy $E$ at time $t$, then each differential slice of the initial distribution $n(E,0)dE$, will have isothermally
Figure 6. Composite Annealing Curve of $\text{Co(NH}_3\text{)}_5\text{Br}^{++}$ in $\text{Co(NH}_3\text{)}_5\text{Br}_3$. Ref. (82)
annealed at temperature $T$ and time $t$ to the extent

$$f(t) = n(E,0) \exp(-Kt) \, dE$$  \hspace{1cm} (34)

where $K$ is the first order rate constant for that particular slice of the distribution. $K$ must be dependent on the activation energy and temperature as given by

$$K = v \exp(-E/kT)$$  \hspace{1cm} (35)

where $v$ is the frequency vibration of atoms in the lattice. Integrating over all activation energies

$$F(t) = \int_0^\infty f(t) \, dE = \int_0^\infty n(E,0) \exp[v t \exp(-E/kT)] \, dE$$  \hspace{1cm} (36)

to obtain the function $F(t)$ of all the annealing processes which remain after that time at that temperature. The retention would then be $100\{1-F(t)\}$ in percent.

Two types of distributions, $n(E,0)$, were tried. First a simple Block distribution in which $n(E,0) = 0$ up to a certain value of $E$, and then $n(E,0) = 1$ to a higher value. By integrating equation (36) numerically, isothermal annealing curves were obtained which agree quite well with the experimental data and which follow Maddock's empirical $\Delta R \sim 1/T$ rule.

The second distribution used was the Gaussian distribution for which

$$n(E,0) = \frac{1}{\sigma \sqrt{2 \pi}} \exp \left\{ -\frac{1}{2} \frac{(E-M)^2}{\sigma^2} \right\}$$  \hspace{1cm} (37)

where $M$ is the position of the center of the distribution and $\sigma$ is the width, on the activation energy scale. The desired integral for $F(t)$ is
\[
F(t) = \frac{1}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} \exp \left\{ -\frac{1}{2} \frac{(E-M)^2}{\sigma} \exp \left[ -vt \exp \left( -\frac{E}{kT} \right) \right] \right\} dE
\]

The integration of this equation also yielded isothermal annealing curves which agree quite well with experimental data and which also follow Maddock's empirical \( \Delta R \propto 1/T \) rule. Vand and Primak concluded that no matter how complete the knowledge of the activation energy spectrum one has, one still does not know anything about the mechanism of annealing. The mechanisms proposed, however, must be consistent with the activation energies found experimentally, and with the measured order of reaction.

Annealing may also be produced by radiation such as gamma rays, X-rays, fast neutrons, and even light in some cases. The interpretation of these processes are not well established, but there are some possible explanations.

For gamma rays and X-rays there are three possibilities: (1) interaction of the radiation with the crystal produces thermal spikes and these occur close enough to the recoil atom to permit "thermal annealing"; (2) lattice vibrations excited by the electrons liberated by the radiation pass through the crystal until they encounter a defect, where they give up some of their energy, again supplying the recoil atom with enough energy to overcome its potential barrier for recombination; and (3) the recoil atom combines with fragments or free electrons produced by the radiation.

Fast neutrons, on the other hand, do not produce ionization and they lose their energy entirely by nuclear interactions, producing "knocked on" atoms whose energy is given by equation (39)

\[
E_{\text{max}} = \frac{4 M E}{(M+1)^2}
\]
where M is the mass of the "knocked on" atom and E is the neutron energy. A neutron of only 325 ev can displace an atom of mass 50 (assuming a displacement energy of 25 ev). Each such energetic atom will initiate a hot zone which its attendant thermal effect and thermal annealing may take place in these zones.

Maddock and co-workers\textsuperscript{85,86} studied the first effects of photochemical bleaching and found results which indicate that annealing may take place via light as well as by temperature. However, no mention was made of the mechanism of such annealing.

Butterworth and Campbell\textsuperscript{17} found that the change in the fraction of $^{32}\text{P}$ in the lower valance state as a function of the annealing temperature and the decrease in the concentration of F-centers in NaCl as a function of temperature showed similar behavior as the temperature was increased. From this data it was concluded that since the F-center concentration decreased as the annealing temperature increased, the effect is due to the release of F-centers, yielding electrons which then react with the recoil species to produce the observed retention.

Recently Cifka\textsuperscript{87} studied in detail the photo-annealing and thermal annealing of $^{32}\text{P}$ recoils in neutron irradiated KCl. A careful study was performed of the concentrations of the F, M, R\textsubscript{1}, and R\textsubscript{2} centers as a function of optical bleaching after neutron irradiation. The F-center concentration fell off exponentially with increasing length of exposure to light while the M-center concentration went through a maximum and then tapered off exponentially. The R\textsubscript{1} and R\textsubscript{2}-center curves increased rather slowly with exposure time until the concentration reached a plateau value. Using this color center concentration data and the data for the
retentions due to optical bleaching, Cifka proposed the following set of reactions:

\[ \text{F-center} \xrightarrow{h\nu} e^- + \alpha \] \hspace{1cm} (40)
\[ \alpha = \text{negative ion vacancy} \]
\[ e^- + \text{hole} \rightarrow \text{Cl}^- \] \hspace{1cm} (41)
\[ e^- + \text{F-center} \rightarrow \text{F'}-\text{center} \] \hspace{1cm} (42)
\[ e^- + \alpha \rightarrow \text{F-center} \] \hspace{1cm} (43)
\[ e^- \text{ } 32p^{n+} \rightarrow 32p^{(n-1)+}, \text{ etc.} \] \hspace{1cm} (44)

where \( h\nu \) = photon absorbed in the F-band. The accompanying secondary reactions are

\[ \text{F'}-\text{center} \rightarrow \text{F-center} + e^- \] \hspace{1cm} (45)
\[ \text{F'}-\text{center} + \text{F-center} \rightarrow \text{M-center} \] \hspace{1cm} (46)
\[ \text{F'}-\text{center} + \alpha \rightarrow \text{M-center} \] \hspace{1cm} (47)

plus additional reactions which lead to the \( R_1 \) and \( R_2 \) centers. Thus the optical bleaching is explained on the basis of the conversion of color centers into defects and electrons which then continue to react with the recoil atom to give the observed retention.

It is well known that the F-centers in the alkali halides can be annealed out by the application of heat or by irradiation with light of the wavelength of the F-center absorption band. Harrison\(^{88}\) found that bleaching of the F-band with 558 mp light produced an initial growth of the M-absorption band which was followed by a growth of the more complex centers. The F-band intensity decreased as the irradiation continued. The reactions proposed are the following:

\[ \text{F-center} \xrightarrow{h\nu} e^- + \alpha \]
\[ e^- + \text{hole} \rightarrow \text{Cl}^- \]
\[ e^- + \text{F-center} \rightarrow \text{F'}-\text{center} \]
\[ e^- + \alpha \rightarrow \text{F-center} \]
\[ e^- \text{ } 32p^{n+} \rightarrow 32p^{(n-1)+}, \text{ etc.} \]
F-center $\xrightarrow{\text{hv}(\text{F-band})}$ e$^-$'s + anion vacancy + F$^-$-center (48)

F$^-$-center + anion vacancy $\rightarrow$ M-center (49)

M-center + anion vacancy $\rightarrow$ R-center (50)

2 F-centers $\rightarrow$ M-center (51)

Kobayashi$^{89}$ found that thermal annealing of color centers in NaCl proceeded in three stages. The first stage occurs from room temperature to 150°C during which the electrical conductivity was found to decrease. During this stage of annealing, the $V_3$-band and the F-band decreased in intensity while the M-band increased in intensity. The second stage was between 150°C and 250°C during which time the resistivity of the specimen exhibited a minimum. The $V_3$, F, M, R$_2$ and 840 $\mu$m bands decreased in intensity while a band at 578 $\mu$m increased in intensity. In this interval almost all of the F-centers were found to go to the increase of the 578 $\mu$m band which was designated as the F-center coagulation band. The third stage of annealing occurs between 250°C and 400°C in which there is a complete absence of color centers.

Damm and Tompkins$^{90}$ have concluded that thermal bleaching and optical bleaching in KCl proceed by the mechanism which is shown below.

F-center $\Delta$ or $\text{hv} \rightarrow$ halide ion vacancy + free electron (52)

Free electron + V$_2$-center $\rightarrow$ halide ion (53)

This reaction sequence is dependent upon the relative concentration of the V$_2$-centers. Damm and Tompkins have shown that if the V$_2$-center concentration is low, then the reaction which is predominant is the formation of more complex centers as shown by the following equation.
They observed that in crystals in which the $V_2^-$-center concentration is high ($\text{KCl: Sr}^{2+}$) the $V_2^-$-centers initially trap the electrons released from the excited F-centers. Thus for a short time, trapping of the electrons by the $V_2^-$-center proceeds preferentially to the formation of the M-center; however, the trapping rate decreases with the time of bleaching so that the rate of formation of M-centers, though slow, becomes the predominant reaction.

**E. Exchange Reactions**

In order for valid conclusions to be drawn from a hot-atom chemistry study, it is necessary to know whether isotopic exchange reactions occur between the various forms. In this study the species of interest are $S^0$, $S^-$, $S_0^-$, and $SO_4^-$. 

(1) $S^-$ and $SO_4^-$

Voge$^{91}$ and King and Levy$^{92}$ report no sulfur exchange between $S^-$ and $SO_4^-$ in alkaline solution after 36 hours at 100°C or in aqueous solutions of AgS in $^{35}S$ labeled Ag$_2$SO$_4$.

(2) $SO_3^-$ and $SO_4^-$

Daudel, Daudel and Martin$^{93}$ indicated that there is no sulfur exchange between $SO_3^-$ and $SO_4^-$. Voge$^{91}$ reported no sulfur exchange between $SO_3^-$ and $SO_4^-$ in alkaline or acidic solution after 36 hours at 100°C. Ames and Willard$^{94}$ in a study of the exchange between $SO_3^-$ and $S_2O_3^-$, postulated that there may be oxygen exchange between $SO_3^-$ and $SO_4^-$. 

F-center (low $V_2^-$-center concentration) $\rightarrow$ (M, $R_1$, $R_2$-centers) 

(54)
(3) $S^-$ and $SO_3^-$

There is no direct data available on the exchange of sulfur between $S^-$ and $SO_3^-$. However, the following information may allow a prediction of the probability of this exchange. Ames and Willard found that exchange between $SO_3^-$ and $S_2O_3^-$ occurs by exchange of the outer sulfur atom in $S_2O_3^-$ according to equation (55). The outer sulfur atom of $S_2O_3^-$ designates the sulfur atom which is not located at the center of the $S_2O_3^-$ tetrahedron.

$$SO_3^- + S^{35}SO_3^- \leftrightarrow 35SO_3^- + SSO_3^- \quad (55)$$

They investigated the exchange in the pH range 5-14 and temperatures between 60-100°C. Voge also found that exchange takes place between $SO_3^-$ via the outer sulfur of $S_2O_3^-$ as shown in equation (56). The exchange is complete after one hour at 100°C in basic solution.

$$^{35}SO_3^- + SSO_3^- \leftrightarrow S^{35}SO_3^- + SO_3^- \quad (56)$$

Ames and Willard also found that $S^-$ exchanges with $S_2O_3^-$ by way of the outer sulfur atom of $S_2O_3^-$ according to equation (57).

$$S^- + ^{35}SSO_3^- \leftrightarrow ^{35}S^- + SSO_3^- \quad (57)$$

Since $S^-$ does not exchange with $S_2O_3^-$ through the inner sulfur atom of $S_2O_3^-$, exchange between $S^-$ and $SO_3^-$ is not likely.

(4) $S^0$ and $SO_3^-$ and $S^0$ and $SO_4^-$

There is no data to indicate whether exchange takes place in the $S^0$-$SO_3^-$ and the $S^0$-$SO_4^-$ systems. The data of Milham, Adams, and Willard show that if $S^-$ is present
in either of the systems, the $S^0$ exchanges with the $S^-$; if $S^-$ is absent, the $S^0$ is oxidized to $SO_3^-$ or $SO_4^-$. Therefore, exchange between $S^0$-$SO_3^-$ and $S^0$-$SO_4^-$ is not an important consideration in this work.

F. Some Properties of Pertinent Nuclides.

(1) Sulfur-35

Sulfur-35 is a radioactive isotope of sulfur having a half-life of 87.1 days. It is a pure beta emitter (no gamma rays) with the maximum energy of the beta rays equal to 0.167 Mev.95

Sulfur-35 may be prepared by a variety of reactions such as the (n, $\gamma$) reaction on $^{34}S$, by the (d,p) reaction on $^{34}S$, by the (d,$\alpha$) reaction on $^{37}Cl$, and by the (n,p) reaction on $^{35}Cl$. It is the last process, the (n,p) reaction on $^{35}Cl$, which will be of interest in this work. The thermal neutron cross section for this reaction is $400 \pm 100$ mb.96

(2) Other Nuclides

Various other nuclides will also be produced by the (n, $\gamma$) reaction on various target atoms in the mixed KCl-KBr. These include $^{42}K$, $^{80}_{35}Br$, $^{80m}_{35}Br$, $^{82}_{35}Br$, $^{38}Cl$, $^{36}Cl$, and $^{32}P$. The half-lives and modes of decay of these isotopes are listed in Table III.95
### TABLE III
Properties of Pertinent Nuclides

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Mode of Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{42}$K</td>
<td>12.36 hours</td>
<td>beta, gamma</td>
</tr>
<tr>
<td>$^{80}$Br</td>
<td>17.6 minutes</td>
<td>beta, gamma</td>
</tr>
<tr>
<td>$^{80m}$Br</td>
<td>4.5 hours</td>
<td>gamma</td>
</tr>
<tr>
<td>$^{82}$Br</td>
<td>35.3 hours</td>
<td>beta, gamma</td>
</tr>
<tr>
<td>$^{38}$Cl</td>
<td>37.3 minutes</td>
<td>beta, gamma</td>
</tr>
<tr>
<td>$^{36}$Cl</td>
<td>$3.0 \times 10^5$ years</td>
<td>beta</td>
</tr>
<tr>
<td>$^{32}$P</td>
<td>14.3 days</td>
<td>beta</td>
</tr>
</tbody>
</table>

Interference by short-lived nuclides ($^{42}$K, $^{80}$Br, $^{80m}$Br, $^{82}$Br, and $^{38}$Cl) was avoided in this work by allowing them to decay completely before counting of the $^{35}$S radioactivity. The maximum contribution of long-lived nuclides to the total radioactivity can be estimated by equation (64), Chapter IV. The calculated contribution of $^{36}$Cl is $10^{-6}\%$ and that of $^{32}$P is 0.04% of the $^{35}$S radioactivity. The detailed calculation for $^{32}$P is shown in Chapter IV. In addition, the chemical procedures used further reduced the interference of these nuclides.
IV. EXPERIMENTAL DETAILS

A. Materials

The KCl used in these experiments was Matheson, Coleman, and Bell reagent grade crystals for calomel cells. The KBr was Fisher reagent grade crystals. These were used without further purification.

The Na$_2$S$_2$.9H$_2$O used to prepare the sulfide carrier solution was Fisher reagent grade crystals. The crystals as received were very hygroscopic and non-weighable. To produce a form that was weighable, the Na$_2$S$_2$.9H$_2$O was placed in a 100 ml boiling flask equipped with a socket joint for connection to a high vacuum system. The crystals were dried at room temperature under vacuum for 48 hours during which time the pressure in the system was $< 1 \times 10^{-3}$ mm Hg. The crystals which were produced by this procedure were white and appeared to be very dry. The sample formula weight of the dried sodium sulfide was determined as follows. Using the analytical separation scheme discussed in part G of this section, it was found from data on the weight of Na$_2$S$_2$.9H$_2$O taken and from the weight of the BaSO$_4$ precipitates obtained from the oxidation of sulfide to sulfate, that the correct formula weight for the dried sodium sulfide was 136 ± 5 corresponding to a formula of Na$_2$S$_3$.3H$_2$O. The data for these determinations are shown in Table IV.

The data were taken in two separate determinations. In the second determination the sodium sulfide solution was allowed to stand one day before the aliquots were taken. The first series of determinations were performed immediately after the carrier solution was prepared. It may be that allowing the solution to stand may affect the results.
<table>
<thead>
<tr>
<th>grams of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ taken</th>
<th>grams of $\text{BaSO}_4$ found</th>
<th>apparent molecular weight of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2669</td>
<td>0.4650</td>
<td>138</td>
</tr>
<tr>
<td>0.2669</td>
<td>0.4460</td>
<td>139</td>
</tr>
<tr>
<td>0.2669</td>
<td>0.4350</td>
<td>143</td>
</tr>
<tr>
<td>0.2669</td>
<td>0.4538</td>
<td>137</td>
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<td>0.2669</td>
<td>0.4488</td>
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<td>0.2669</td>
<td>0.4617</td>
<td>135</td>
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<td>0.2669</td>
<td>0.4682</td>
<td>133</td>
</tr>
<tr>
<td>0.2666</td>
<td>0.4610</td>
<td>139</td>
</tr>
<tr>
<td>0.2666</td>
<td>0.4514</td>
<td>142</td>
</tr>
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<td>0.2666</td>
<td>0.4896</td>
<td>131</td>
</tr>
<tr>
<td>0.2666</td>
<td>0.4991</td>
<td>128</td>
</tr>
<tr>
<td>0.2666</td>
<td>0.4908</td>
<td>130</td>
</tr>
<tr>
<td>0.2666</td>
<td>0.5015</td>
<td>128</td>
</tr>
</tbody>
</table>

average value $136 \pm 5$
It should be pointed out that these determinations have several sources of error. First, the weight of the Celite filtering air used is accurate to ± 0.001 gm. Secondly, the dried material is hydroscopic and does pick up some water during weighing. However, in the BaSO₄ ppt determinations, the carrier solutions were used immediately after preparation and a formula weight of 132 gms was used as the formula weight of the dried sulfide in all experiments.

For the BaSO₄ precipitates, the BaCl₂·2H₂O, and NaOH were Fisher reagent grade and were used without further purification. The NaOCl solution used for the oxidation of sulfide to sulfate was a Fisher 4-6% solution and was used as received. The Celite used in aiding the layering down of the BaSO₄ precipitates was Johns Manville Analytical Filter Aid. The water used in the solution preparation was de-mineralized water from a Lab-flow demineralizer.

B. Preparation of Mixed Crystals of KCl-KBr

The mixed KCl-KBr crystals were prepared by fusion of the weighed amounts of the pure components in a covered platinum crucible in a Cenco electric furnace at 900 ± 10°C for one half hour. The temperature was measured with a Pt-13% Rh-Pt thermocouple against room temperature using a Rubicon portable precision potentiometer. The platinum crucible was cleaned with nitric acid and sodium pyrosulfate prior to initial use when received. Prior to each sample fusion the crucible and cover were rinsed with demineralized water and then heated to redness in a Meeker burner to oxidize any materials left on the crucible.

After the fusion the oven was turned off and the sample was allowed to cool slowly to slightly above room
temperature at which time the crucible and contents were removed from the furnace. The fused sample was removed from the crucible and stored in a vacuum desiccator over magnesium perchlorate. The crystals were broken into large pieces when the crucible was taken from the oven. This was probably due to the strains that developed as the melt cooled. The crystals were transparent resembling single crystals.

The verification of the formation of mixed crystals was done with the aid of X-ray diffraction. The X-ray diffraction patterns for the powdered mixed crystals were taken on a Siemens Crystaloflex IV X-ray generator and associated electronics for obtaining graphical recording of the data. The lattice parameters were obtained for both sets of mixed crystals from the experimental X-ray data, using the formula for cubic systems in which the lattice parameter is related to the d-value by equation (58), where \( a_0 \) is the lattice parameter in angstroms, \( d_{hkl} \) is the d-value for reflections from the crystal planes given by the Miller indices \( h \), \( k \), and \( l \). The lattice parameters

\[
d_{hkl} = \frac{a_0}{(h^2 + k^2 + l^2)^{1/2}} \tag{58}
\]

were then treated by the technique of Nelson and Riley to obtain the best value of the lattice parameter. For treatment of data taken by a diffractometer the method of Nelson and Riley calls for careful alignment of the instrument prior to analysis and adjustment of the specimen surface to coincide as closely as possible to the diffractometer axis. The correction for absorption by the sample is given by Nelson and Riley as equation (59) in which \( \Delta d \) is the change in the d-value

\[
\Delta d/d = K(\cos^2 \Theta / \sin \Theta + \cos^2 \Theta / \Theta) \tag{59}
\]
caused by absorption, $\Theta$ is the angle of reflection from the $d_{hkl}$ plane, and $K$ is a constant. This equation holds quite accurately at both high and low values of $\Theta$. The best value of the lattice parameter can be found by plotting the experimental values of $a_0$ as calculated by equation (64) against $(\cos^2 \Theta / \sin \Theta + \cos^2 \Theta / \Theta)$ which approaches zero as $\Theta$ approaches 90°.

C. Preparation of Sample for Irradiation

The samples were pulverized to a fine powder in an agate mortar and pestle and approximately 0.1 gram of the material was placed into a 4 mm (O.D.) quartz tube which had been sealed off at one end and which had been rinsed in distilled water and evacuated to a pressure of $1 \times 10^{-3}$ mm Hg at 400°C for one half-hour. The sample tube was then connected to a high vacuum system via a Beckmann connector and a Fischer and Porter 4 mm Teflon needle valve. The samples were then heated in a small electric furnace to 400°C for one hour under a pressure of < $1 \times 10^{-3}$ mm of Hg. The temperature was measured as before. The samples were sealed off under vacuum.

The samples analyzed by the precipitation method were sealed off by a somewhat different procedure. The sample tubes were first evacuated without any sample in order to be sure that they were very dry. The sample was then placed into the tube and the tube and contents connected to the high vacuum system. The sample was then evacuated to a pressure of $1 \times 10^{-4}$ mm of Hg and sealed off without heating. Preliminary experiments showed that heating the samples to 400°C for 1, 2, 4, and 8 hours had no effect on the distribution of the recoil species when analyzed by the electrophoretic method.
D. Irradiation of Samples

The samples were irradiated at ambient temperature (100°C) in slant tubes ST-3 and ST-4 of the U. S. Army Materials and Mechanics Research Center Reactor. The neutron fluxes were approximately $4 \times 10^{12}$ neutrons/cm$^2$-sec in ST-4A, $1 \times 10^{12}$ neutrons/cm$^2$-sec in ST-3C, and $5 \times 10^{12}$ neutrons/cm$^2$-sec in ST-3A at a power level of 2 megawatts. The samples irradiated in ST-4 were irradiated for 15 minutes while those in ST-3 were irradiated for 10 minutes. The attendant gamma ray dose at the core of the reactor was approximately 140 megarads/hour.

Other samples were irradiated at ambient temperature (100°C) in the Graphite Research Reactor at Brookhaven National Laboratory. The samples were irradiated in PN-4 for 20 minutes at a neutron flux of $1 \times 10^{13}$ neutrons/cm$^2$-sec at a power level of 15 megawatts. The attendant gamma ray dose in this irradiation position was 10 megarads/hour.

The samples irradiated in ST-3C and ST-3A of the Army Materials and Mechanics Research Center reactor were wrapped in aluminum foil in order to keep bleaching by the light to a minimum. The samples irradiated in ST-4A of the same reactor were not wrapped in aluminum foil. The samples irradiated at the Brookhaven reactor were also not wrapped in aluminum foil.

E. Post-Irradiation Treatment of Samples

Thermal annealing studies were made at temperatures above room temperature. For these annealing studies the samples were irradiated at room temperature and stored at room temperature in the dark until the beginning of the annealing process. The thermal annealing was carried out in a Cenco electric furnace at $75.0 \pm 0.5^\circ$C and $215 \pm 2^\circ$C
with the temperature measured with a mercury thermometer (uncorrected). The individual samples were withdrawn after 3, 6, 12, and 24 hours of annealing and stored in a dewar in dry ice until the time of analysis.

F. Separation of the Oxidation States of Radiosulfur

1. Electrophoretic separation

The apparatus consisted of plate glass sheets 30" x 12" x 1/4" on a wooden support. The paper was cut into strips 1" wide and 61 cm long and placed between the glass plates with the ends dipping into the electrolyte trays at each end of the apparatus. Pressure was applied to the glass plates by placing a tray containing ice cubes and a 5 pound weight on top of the apparatus. This arrangement also permitted cooling of the electrophoretic papers during the separations. The electrolyte trays were constructed of Plexiglas and contained four individual compartments so that four samples could be analyzed at the same time. A Plexiglas cover prevented the evaporation of the electrolyte from the trays.

Whatmann 3MM paper was used in the separations. The paper was soaked with the electrolyte, blotted and allowed to equilibrate between the glass plates for 15 minutes prior to an electrophoretic separation. Voltage gradients of 16.4 volts/cm were supplied by a Harrison Laboratories Model 6525A high voltage power supply. The total current varied from 20 to 30 milliamperes. The electrolyte used was a 0.1 M \((\text{NH}_4)_2\text{CO}_3\) solution (pH 8.9). During the electrophoretic separations a small rise in the current was noted followed by a decrease to near its original value. The effect may have been due to the increased saturation of the paper during the separation.
Separation times were 3 hours. Under the above conditions the following migration rates were obtained using test solutions of sulfide, sulfite, and sulfate ions: sulfite (30.5 cm), sulfide (41.0 cm), and sulfate (41.9 cm).

The following procedures were used to identify the migration of the ions. Sulfide was detected by spraying the paper with a lead acetate solution which produced the characteristic black spot indicating lead sulfide. Sulfite was detected by a method outlined by Fiegel. This involved spraying the paper first with a saturated zinc sulfate solution followed by a sodium ferrocyanide solution (10 gm/10 ml) and a sodium nitroprusside solution (1%). This produced a rose colored spot characteristic of the reaction of sulfur dioxide and zinc nitroprusside. Sulfate ion was detected by using a solution containing $^{35}$S-labeled sulfate ions. An electrophoresis strip was run with this solution and the sulfate located by means of its radioactivity.

A separation of a mixture of the three ions from a test solution confirmed that a poor separation would be obtained if based upon the ion migration rates noted above. Sulfate and sulfite could easily be separated from one another using the above experimental conditions, but these two ions could not be separated from sulfide ion.

The electrophoretic procedure was then modified to permit the separation of sulfide ion from sulfate and sulfite ions. The sulfide activity was precipitated at the beginning of the electrophoretic strip with an excess of 0.1 M cadmium chloride solution. The cadmium sulfide precipitate remained at the origin during the entire electrophoretic separation. The complete separation scheme was then checked using the test mixture of the three ions. A good separation was found with the sulfide at the origin and the sulfite and sulfate
ions having migrated their characteristic distances noted above. However, the sulfite and sulfate peaks showed considerable spreading and overlap. Since the yield of sulfide and neutral sulfur was of interest, the lack of separation of sulfite and sulfate presented no interference and thus the sulfite and sulfate data were combined. In these separations using the test solutions which contained the $^{35}S$-labeled sulfate ions, counting of the electrophoretic strips revealed that all the radioactivity was located in the sulfite-sulfate peak and none remained at the origin where the sample was spotted and the cadmium sulfide precipitate was located. This observation also supports the absence of isotopic exchange between sulfide and sulfate ions.

The procedure used to analyze an irradiated mixed crystal is described below. The exchange between neutral sulfur and sulfide ion reported by Adams, Milham and Willard\textsuperscript{12} was used as the basis for the separation of sulfide and neutral sulfur from sulfite and sulfate. The irradiated crystal was divided into two nearly equal portions, the first of which was dissolved in 0.50 mls of 0.1 M sodium sulfide trihydrate in 0.1 M ammonium carbonate which was delivered from a graduated one milliliter pipet. This portion was labeled "carrier" sample. The second portion of the same sample was dissolved in 0.50 mls of 0.1 M ammonium carbonate delivered from a one milliliter graduated pipet. This solution was labeled "no carrier" solution. To the "no carrier" solution was added 50 $\mu$l of a 1.0 M sodium sulfide trihydrate solution so that the concentration of sulfide ions in both the "carrier" and "no carrier" solutions was approximately the same. Three to four drops of the above solutions were spotted on the appropriate electrophoretic paper marked "carrier" or "no carrier". The strips were treated with an excess of the cadmium chloride solution prior to the deposition of the sample solutions. These spots were allowed to
stand for about five minutes to allow for equilibration in the mixtures, and then the glass plates were carefully placed over the electrophoretic paper and the electrophoretic run begun.

When the electrophoretic run was completed the strips were removed from the apparatus and hung horizontally to dry. This method of drying prevented any running of the spots on the strips. The electrophoretic apparatus was then thoroughly cleaned with soap and Radicwash solution and dried before being used for another electrophoretic run.

It was found from the analysis of a large number of irradiated potassium chloride samples that the electrophoretic method was not reproducible. The calculated values were obtained as in section H part b of this chapter. The data for these samples is shown in Table V. It should be pointed out that these samples were not wrapped in aluminum foil and hence the large non-reproducibility may be due in part to varying degrees of light bleaching of the samples.

Other possible reasons for the lack of reproducibility are the incomplete exchange between neutral sulfur and sulfide, spreading of the cadmium sulfide precipitates causing poor separation, and reaction of neutral sulfur with the electrophoretic paper. In regard to the exchange between neutral sulfur and sulfide, Adams, Milham and Willard reported that a sulfide concentration of $1 \times 10^{-3}$ moles/liter or greater was sufficient for complete exchange between neutral sulfur and sulfide. However, the sulfide concentration was increased to 1.0 M for some experiments and the separation and the reproducibility did not improve. Because of the lack of reproducibility of the electrophoretic method of analysis, it was decided to develop a different method of analysis for the radiosulfur products.
TABLE V
Results for the Electrophoretic Analysis
of Irradiated Potassium Chloride

<table>
<thead>
<tr>
<th>sample number</th>
<th>% $S^{O} + S^{-}$</th>
<th>% $S^{-}$</th>
<th>% $S^{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>124-A</td>
<td>67.1</td>
<td>38.4</td>
<td>28.7</td>
</tr>
<tr>
<td>124-B-1</td>
<td>72.7</td>
<td>37.4</td>
<td>35.3</td>
</tr>
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<td>124-B-2</td>
<td>72.1</td>
<td>47.0</td>
<td>25.1</td>
</tr>
<tr>
<td>124-B-3</td>
<td>74.2</td>
<td>38.3</td>
<td>35.9</td>
</tr>
<tr>
<td>124-C</td>
<td>65.3</td>
<td>47.0</td>
<td>18.3</td>
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<tr>
<td>124-D-1</td>
<td>76.0</td>
<td>39.9</td>
<td>36.1</td>
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<td>124-D-2</td>
<td>76.8</td>
<td>29.3</td>
<td>47.5</td>
</tr>
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<td>82.2</td>
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<td>124-F-1</td>
<td>61.8</td>
<td>48.4</td>
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<td>124-F-2</td>
<td>72.8</td>
<td>44.2</td>
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<td>124-G</td>
<td>75.5</td>
<td>49.3</td>
<td>26.2</td>
</tr>
<tr>
<td>124-H-1</td>
<td>75.5</td>
<td>48.8</td>
<td>26.7</td>
</tr>
<tr>
<td>124-H-2</td>
<td>74.0</td>
<td>65.0</td>
<td>9.0</td>
</tr>
<tr>
<td>average values</td>
<td>72.8</td>
<td>45.1</td>
<td>26.7</td>
</tr>
<tr>
<td>standard deviation</td>
<td>5.4</td>
<td>7.8</td>
<td>10.2</td>
</tr>
</tbody>
</table>
2. Barium Sulfate Precipitations

The procedure finally adopted for the separation of the oxidation states of the radiosulfur was that of barium sulfate precipitations. This is a common radiochemical method for determining sulfur and was used by Adams, Milham, and Willard\textsuperscript{11} and with modifications also by Maddock and Mirsky\textsuperscript{12}.

The sample to be analyzed was divided into two nearly equal portions. To the first portion of the sample was added a basic carrier solution containing sulfate and sulfide carrier in 0.1 M ammonium carbonate (pH \textless 8.9). The weights of the carrier components (Na\textsubscript{2}SO\textsubscript{4} and Na\textsubscript{2}S.3H\textsubscript{2}O) were accurately known and the carrier solutions were used immediately after preparation. This sample solution was designated as the "carrier" portion. The second portion of the sample was dissolved in 0.1 M ammonium carbonate and was designated a "no carrier" solution. To the "no carrier" solution was added a 10 ml aliquot of the same carrier solution that was added to the "carrier" portion.

In the "carrier" aliquot elemental sulfur exchanged with sulfide according to equation (60) while in the "no carrier" portion the neutral sulfur reacted according to equations (61) and (62). Therefore, the difference in the

\[
\begin{align*}
35S^0 + S^\equiv & \rightarrow 35S^\equiv \rightarrow 35S^= + S^0 \quad \text{(60)} \\
35S^0 + 3H_2O & \rightarrow H_235SO_3 + 2H_2 \quad \text{(61)} \\
35S^0 + 4H_2O & \rightarrow H_235SO_4 + 3H_2 \quad \text{(62)}
\end{align*}
\]
the sulfide yield between the "carrier" and "no carrier" portions gave the yield of neutral sulfur present in the irradiated sample.

The "carrier" and "no carrier" solutions were treated identically throughout the remaining analysis. To each of the solutions 45 mls of a 0.6 M cadmium chloride solution were added to precipitate the cadmium sulfide. After allowing the cadmium sulfide to precipitate, cadmium chloride was added dropwise to test for the completeness of the precipitation. The solutions containing the cadmium sulfide precipitates were then centrifuged, the cadmium sulfide precipitate removed, and the water layer and washings placed in a beaker. To the water layer and washings was added 10 mls of concentrated hydrochloric acid and 25 mls of a 0.2 M barium chloride solution in order to precipitate barium sulfite and barium sulfate. These precipitates were placed on a hot-plate to digest overnight.

The cadmium sulfide precipitate was resuspended in distilled water and 10 mls of 0.3 M sodium hydroxide and 125 mls of 4-6% sodium hypochlorite solution added. These reagents served to oxidize the sulfide ion to sulfate ion according to equation (63).

\[ S^{2-} + 4ClO^- \rightarrow SO_4^{2-} + 4Cl^- \quad (63) \]

to stand for approximately two hours or until the characteristic yellow color of cadmium sulfide was absent. Concentrated hydrochloric acid (15 mls) was then added to dissolve any cadmium carbonate and to convert the excess hypochlorite to chlorine gas which could then be boiled off. After the solution was boiled and the characteristic yellow-green color of chlorine gas absent, 10 mls of concentrated hydro-
chloric acid and 25 mls of 0.2 M barium chloride solution were added. The barium sulfite-barium sulfate precipitates were allowed to digest overnight. The pH of these solutions in which the barium sulfite-barium sulfate precipitates were formed was approximately 2 as measured by pHydrion paper. A flow diagram of the $\text{BaSO}_4$ separation scheme is shown in Figure 7. $S^+$ denotes the precursor of $\text{SO}_3^-$ and $\text{SO}_4^-$, $S^-$ represents the precursor of $\text{S}^-$ and $\text{S}^0$ is neutral atomic sulfur.

The barium sulfate-barium sulfite precipitates were layered down using a Nuclear-Chicago sample preparation set Model PM-5. The set as used consisted of a plastic chimney funnel, porous stainless steel discs, copper planchets, and a water suspension of Celite ($\text{SiO}_2$) of concentration 4 mg/ml. The chimney funnel fitted into a suction flask for vacuum filtration. The steel discs were secured in the chimney and first coated with approximately a 11.8 mg/cm$^2$ layer of Celite and the barium sulfite-barium sulfate solution added. In doing this the supernatant was first poured through the filter and then the precipitate was resuspended in distilled water and poured into the chimney with the suction off. The solution containing the precipitate was allowed to stand in order to allow the precipitate to settle in the chimney in a uniform layer, before the suction was applied. The barium sulfite-barium sulfate was filtered onto the Celite. The precipitates were washed with 250 mls of demineralized water and acetone and allowed to dry in air for about two minutes with the suction still on. The precipitates and steel discs were then removed with the suction still on and dried in an oven at 105°C. for about five minutes. The precipitate was then counted. Several checks were made on the discs to assure that they were radiochemically clean before reuse.
Figure 7. Flow Diagram of the BaSO₄ Precipitation Method
The area of the precipitates was 5.1 cm$^2$. The maximum range of the ray of $^{35}$S is about 15.0 mg/cm$^2$. Therefore, a precipitate of thickness equal to or greater than 15.0 mg/cm$^2$ is infinitely thick. The concentrations of the carrier solutions were such that a minimum of 0.1500 grams of barium sulfite-barium sulfate precipitate was obtained in order to guarantee infinitely thick precipitates.

The chemical yields were determined for the analytical separation scheme to determine whether all the sulfate carrier could be recovered as barium sulfate. A chemical yield could not be determined for the sulfide since it was assumed to be 100 percent recovered in determining the formula weight of the dried sulfide. Known amounts of sodium sulfate in a 0.1 M ammonium carbonate solution were taken. A 10 ml aliquot from this solution was used. The analytical scheme described above for the barium sulfate precipitations was used and the weights of the barium sulfate precipitates for the sulfate fraction were obtained. The weights of the precipitates are shown in Table VI.

There is some error in the weights shown due to the fact that a small amount of the barium sulfate precipitates stuck to the "0" rings used to secure the steel discs in the plastic filter chimney. Also, the mass of Celite used to aid the filtration could only be estimated.

The Celite was taken from a suspension containing 4 mg/ml. To determine the approximate weight of the Celite layer, four discs were coated with 15 mls of the above Celite suspension and dried and weighed. The weights of the Celite in each case were: 0.0600, 0.0590, 0.0588, and 0.0598 grams with an average weight of 0.0594 gms. Hence, the approximate weight of the Celite layers formed by the three 5 ml aliquots was taken as 0.0594 grams.
TABLE VI

Results for the Chemical Yield Determinations for the Barium Sulfate Precipitation Method

<table>
<thead>
<tr>
<th>Grams of Na₂SO₄ taken</th>
<th>Grams of BaSO₄ precipitate</th>
<th>Equivalent grams of Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1643</td>
<td>0.2682</td>
<td>0.1613</td>
</tr>
<tr>
<td>0.1643</td>
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<td>0.1654</td>
<td>0.2709</td>
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</tr>
<tr>
<td>0.1654</td>
<td>0.2641</td>
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</tr>
<tr>
<td>0.1654</td>
<td>0.2652</td>
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</tr>
<tr>
<td>0.1654</td>
<td>0.2461</td>
<td>0.1500</td>
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<tr>
<td>0.1654</td>
<td>0.2463</td>
<td>0.1480</td>
</tr>
<tr>
<td>0.1654</td>
<td>0.2690</td>
<td>0.1640</td>
</tr>
<tr>
<td>0.1654</td>
<td>0.2614</td>
<td>0.1590</td>
</tr>
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</table>
Checks were made on the reproducibility of the barium sulfate precipitation method by analysis of five irradiated potassium chloride samples. The results and the standard deviations for these five samples are shown in Table VII. These results indicate that the barium sulfate precipitation method is fairly reproducible and superior to the electrophoretic method of analysis.

As mentioned before, the possible radioactive interferences with this method would be from $^{42}$K, $^{80}$Br, $^{82}$Br, $^{38}$Cl, and $^{32}$P. The $^{42}$K, $^{80}$Br, $^{82}$Br, and $^{38}$Cl have half-lives which are short enough to allow them to decay away prior to the analysis. Phosphorous-32, on the other hand, has a half-life of 14.3 days and a maximum Bray energy of 1.7 Mev and thus would be a definite interference, if present. However, the cross section for the $^{35}$Cl(n,$\alpha$)$^{32}$P reaction is 0.08 mb $\pm$ 0.04 mb\textsuperscript{96} while the cross section for the $^{35}$Cl(n,p)$^{35}$S reaction is 400 mb $\pm$ 100 mb\textsuperscript{96}. Using this data, the ratio of the number of $^{32}$P atoms to the number of $^{35}$S atoms can be calculated using equation (64).

$$A = \frac{N_o}{M} \phi \sigma f w (1 - e^{-\lambda t})$$

(64)

where

- $A$ = activity in disintegrations per second
- $\phi$ = the neutron flux in neutrons/cm\textsuperscript{2}-sec
- $M$ = the molecular weight of the atom
- $\sigma$ = the neutron activation cross section in cm\textsuperscript{2}
- $f$ = percent abundance of the bombarded isotope
- $w$ = weight of the substance used
- $N_o$ = Avogadro's number
- $\lambda$ = decay constant for the isotope
- $t$ = the irradiation time
| Sample | $\% \text{S}^0 + \text{S}^- | \% \text{S}^- | \% \text{S}^0 | \% \text{S}_3^= + \text{S}_4^= |$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.0</td>
<td>7.1</td>
<td>37.9</td>
<td>55.0</td>
</tr>
<tr>
<td>2</td>
<td>45.0</td>
<td>6.2</td>
<td>38.8</td>
<td>55.0</td>
</tr>
<tr>
<td>3</td>
<td>45.9</td>
<td>5.6</td>
<td>40.3</td>
<td>54.1</td>
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<tr>
<td>4</td>
<td>42.8</td>
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<td>34.8</td>
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<td>41.2</td>
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<td>1.9</td>
<td>1.3</td>
<td>2.9</td>
<td>1.9</td>
</tr>
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</table>
after cancelling out common terms in equation (64) we can write the ratio of the $A_{P32}$ to the $A_{S35}$ as

$$\frac{A_{P32}}{A_{S35}} = \frac{\sigma_{P32} (1-e^{-\lambda_{P32} t})}{\sigma_{S35} (1-e^{-\lambda_{S35} t})}$$

(65)

The decay constants can be calculated from the relationship $\lambda = 0.693/t_{1/2}$. Carrying out this calculation for the sulfur and phosphorous isotopes of interest gives $\lambda_{S35} = 7.95 \times 10^{-3}$ days$^{-1}$ and $\lambda_{P32} = 4.85 \times 10^{-2}$ days$^{-1}$. Placing these values with the neutron cross sections into equation (65) gives

$$\frac{A_{P32}}{A_{S35}} = \frac{4 \times 10^{-4}}{1} = 0.04\%$$

Thus, assuming that most of the $^{32}P$ activity to be produced by thermal neutrons, the amount of $^{32}P$ produced is approximately $0.04\%$ of the amount of the $^{35}S$ produced at the same activation process and is negligible.

In addition, the chemical procedures used discriminate against $^{32}P$ activity in the form of phosphate, as shown below. Assuming that the majority of the $^{32}P$, causing an interference would probably be in the form of phosphate ion, 10 mls of the sodium sulfate and sodium sulfide trihydrate carrier solution was treated with 10 $\mu$l of a $^{32}P$-labeled sodium phosphate solution containing 5 mc of $^{32}P$/ml. Thus, the carrier solution contained approximately $1.1 \times 10^{12}$ dpm of $^{32}P$. The carrier solution was treated by the barium sulfate precipitation separation method and the barium sulfate precipitates obtained counted. The sulfate fraction barium sulfate precipitate showed an activity of 160 cpm above background while the sulfide fraction barium sulfate
precipitate showed an activity of 10,800 cpm above background. The sulfide fraction barium sulfate precipitate probably showed high activity because of the small number of the $^{32}\text{P}$ atoms in comparison to the number of sulfide ions in the carrier solution. When the sulfide ions were precipitated with cadmium ion, the $^{32}\text{P}$-labeled phosphate ions probably were co-precipitated. However, assuming a counter efficiency of 3 percent and calculating the percent of the $^{32}\text{P}$ atoms that reached the final barium sulfate precipitates out of the total amount of $^{32}\text{P}$-labeled phosphate ions added gives

\[
\frac{10,800 \times 99}{1.1 \times 10^{12}} \approx \frac{10^6}{10^{12}} \times 10^{-6} \times 10^{-4}\% 
\]

Thus, only a very small fraction of the $^{32}\text{P}$ activity would survive the analytical separation and be present in the barium sulfate precipitates as an interference.

A check was made to see if an irradiated potassium chloride sample contained any $^{32}\text{P}$ activity. The barium sulfate precipitates of an irradiated potassium chloride sample were counted using an aluminum absorber of thickness 34.4 mg/cm$^2$ which would eliminate all of the $^{35}\text{S}$ activity and permit approximately 80% of the $^{32}\text{P}$ activity to be counted. With the absorber it was found that there were no counts above background in either the sulfide or sulfate fraction barium sulfate precipitates.

G. Counting Procedures

Various counting arrangements were used for the paper electrophoretic strips, all of which employed the Geiger-Muller tube. Backgrounds were between 20-30 counts/min.
Manual sample counting of the paper electrophoretic strips was done by cutting the strips into 2 cm x 1 in pieces. These were glued onto aluminum discs and placed in planchets for counting in a manual sample changer using an end window Geiger-Muller tube of thickness of 1.4 - 2.0 mg/cm$^2$. Each piece was counted for fifteen minutes. The scalers used in these counting procedures were a Tracerlab 132M scaler and high voltage supply and a Nuclear-Chicago Model 181A scaler and high voltage supply.

An automatic counting system used consisted of a Nuclear-Chicago 186 Scaler and high voltage power supply, a Model C-110B sample planchet changer, and a Model C-111B printing timer. Here again, the electrophoretic strips were cut into 2 cm x 1 in pieces, glued to aluminum discs and placed in planchets. Each piece was counted for a preset count of 1000 and the time required for this count was printed by the printing timer.

An additional counting apparatus was employed which consisted of a Geiger-Muller tube mounted horizontally and perpendicular to a paper chromatogram moving device. The paper chromatogram device pulled the electrophoretic strip in front of the Geiger-Muller tube at a constant rate. The chromatogram moving device was connected to the strip chart recorder so that the chart paper and the electrophoretic paper moved at the same rate. The Geiger-Muller tube was connected to a Tracerlab Model 231 ratemeter and high voltage supply. The output of the rate meter was then fed to the strip chart recorder and the radioactivity recorder on the chart paper as a function of distance down the electrophoretic paper.

The barium sulfite-barium sulfate precipitates were counted on a Beckmann Instruments Wide Beta II low background
counter using Matheson high purity methane as the counting gas. The counts were recorded at either a preset count rate of 10,000 counts or a preset time of 20 min. The background of this counter was between 1.0 and 2.0 counts/min.

H. Calculation of the Percent of Radiosulfur in the Various Oxidation States

1. Paper electrophoresis
   a) Cut strips

   The count in the sulfide peak minus background and the sulfate-sulfite peak were added to obtain the total count. The fraction of sulfide-$^{35}$S was found by dividing the counts in the sulfide peak by the total counts. The percent sulfate-sulfate was found by subtracting sulfide percent from 100. The yield of $S^-$ in the samples was given by the sulfide yield for the "no carrier" strip. The yield of $S^-$ plus $S^0$ was given by the sulfide yield from the "carrier" strip. The yield of $S^0$ was obtained from the difference between the sulfide yields for the "carrier" and the "no carrier" strips. The yield of $S^+$ was found from the sulfate-sulfite fraction of the "carrier" sample.

   b) Scanned strips

   The areas under the sulfide and sulfate-sulfate peaks for both the "carrier" and "no carrier" strips were found using a planimeter. From the areas of the peaks the yields were calculated as in the above method.

2. Barium sulfate method

   In the calculations for the $\text{BaSO}_4$ precipitation samples the counts per minute for the sulfide and the sulfate-sulfate fractions were multiplied by the number of moles of sulfide and sulfate carriers added normalized to $10^{-3}$ moles of carrier. Thus, if $1.158 \times 10^{-3}$ moles of sulfide carrier and $2.018 \times 10^{-3}$ moles of sulfate carrier were added then the correction factors would be 1.158 for the sulfide
fraction and 2.018 for the sulfite-sulfate fraction. This, in effect, compensates for the effect of differing amounts of carrier on the infinite thickness activity of the BaSO$_4$.

The yields of $S^-$, $S^0$, and $S^+$ were calculated as in 1a above.

I. Determination of Concentration of Color Centers in Mixed KCl-KBr Crystals

1. Preparation of samples for gamma ray irradiation

The fused mixed crystals were pulverized in an agate mortar and pestle for two minutes. The pressed pellets were made in a Carver laboratory press equipped with an evacuable die. The die was heated to approximately 60°C prior to use. The powdered sample was added to the die and lightly compacted in the die with the die push rod. The upper part of the die was inserted and the die and contents evacuated to 0.5 mm of Hg as a little pressure was placed on the die. The pressure on the die was then raised to 20,000 psi in small increments and the pressure was allowed to remain on the die for two minutes. The pressure was released and the die and contents were removed from the press and placed in an oven at 100°C for six to seven hours. The pellets were then removed from the die and placed in individual polyethylene bags and stored in a vacuum desiccator over magnesium perchlorate. The pellets were transparent but slightly foggy. Approximately 0.10 grams of the material produced a pressed pellet of approximately 1 mm thickness and a diameter of 13 mm.

2. Gamma irradiation of pellets of mixed KCl-KBr crystals

The samples were wrapped in 2 1/2 x 2 1/2" sheets of black paper and positioned in a cardboard sample holder with marked sample positions. This cardboard sample holder served to locate the samples in reproducible positions. The
cardboard sample holder was placed inside of a metal can 2 1/2" in diameter and 5" tall, in such a manner that its position in the can could be repeated in other irradiations. The can plus the samples were then placed on a sample base in the irradiation facility. The sample base was connected to a motor which turned the sample base plus the irradiation can at 4 rpm. The sample base also maintained the irradiation can in the same position with respect to the irradiation source which was then lowered into place inside the irradiation can. Using this technique, the irradiation can received the same total dose during an irradiation. Four samples of each mixed crystal were irradiated at the same time so that an average value could be taken. The pellets of mixed KCl-KBr crystals were irradiated for 24 hours in a 62 Curie cobalt-60 source. This source is composed of cobalt pellets enclosed in a rectangular brass container, 3/4" x 3/4" x 2", which is attached to the end of a brass rod which can be raised or lowered in the shielded compartment. A description of this source has been given elsewhere. The dose rate of this source is approximately 80,000 R/hr (6 x 10^{16} ev/gm min).

The irradiated samples and holder were removed from the irradiation source at night and transferred in a light tight cardboard box to the laboratory for further experiments. In this manner the bleaching of the color centers was kept to a minimum.

3. Visible spectra of irradiated pellets

The visible spectra of the irradiated pellets were taken immediately after irradiation on a Cary Model 15 spectrophotometer. The spectrophotometer baseline was adjusted using two non-irradiated pressed pellets of the same composition as the irradiated pellet whose spectra was being
taken. The spectra of the irradiated pellet was then taken against one of the un-irradiated pellets of the same composition in the reference beam. The spectra were taken from 8000 Å to 3000 Å.

4. **Calculation of the F-center concentration of mixed KCl-KBr pellets**

A typical spectrum of a gamma irradiated mixed crystal is shown in Figure 8. As the composition of the mixed crystal changed, the position of the maximum shifted from 5550 Å for pure KCl to 5950 Å for a mixed crystal of 85.0 mole percent KBr and finally to 6220 Å in pure KBr.

The calculation of the concentration of F-centers was made using the optical density from the spectra and Smakula's equation (17). The optical densities of the peaks were measured by drawing a baseline on the absorption curve between the extensions of the peaks. This produced a Gaussian shaped peak in most cases. The half-widths were measured at one-half the height and a line was drawn at this point parallel to the baseline and intersecting the peak on both sides. The wavelengths from the intersection of this half-width line with the peaks were noted, converted to an energy by the Einstein relationship, \( E = hc/\lambda \), and the difference between these two values taken. This procedure gave the half-thickness in electron volts. The index of refraction for the mixed crystals were taken from the literature values given by Wood.\(^{104}\) The value used for the oscillator strength was 0.80 which is the value of the oscillator strength for KCl. No data is available for the oscillator strength of the mixed crystals or for KBr. Ritz\(^{59}\) assumed the oscillator strength to be the same for all the alkali halides. Therefore, for lack of a correct value the assumption was made that an oscillator strength for the mixed crystals was 0.80.
Figure 8. Typical Absorption Spectrum for Mixed KCl-KBr Crystal, 12.7 Percent KBr
V. RESULTS AND DISCUSSION

A. Introduction

In order to discuss hot-atom results, it is convenient to present a model with which to explain the data. In the previous studies of the hot-atom chemistry of $^{35}$S in the alkali halides, it was observed that the defects present in the crystal were important in determining the chemical stabilization of the hot-atom in the matrix.

Data for irradiated potassium chloride$^{51,53}$ suggest that the defects present in potassium chloride at room temperature irradiations are mostly F-centers, V-centers of various types, and possibly small amounts of complex centers. The initial distribution of $^{35}$S in potassium chloride is believed to be in the $S^0$, $S^+$, and $S^-$ oxidation states.$^{14}$

The F-center is an electron rich center and may be regarded as a reducing center while the V-centers are electron deficient centers and may be regarded as oxidizing centers. The proposed model includes possible reactions between the precursors $S^0$, $S^-$, and $S^+$, and the defect centers. For simplicity the reducing F-center will be denoted by $[\text{F-red}]$ and the oxidizing V-center by $[\text{V-oxd}]$. Other oxidizing and reducing centers could also react, but the predominant centers to be considered are the F- and the V-center. The reactions proposed in the model used to explain the observed data are shown in equations (66) to (69).

\begin{align*}
S^+ + [\text{F-red}] & \rightarrow S^0 \quad (66) \\
S^0 + [\text{F-red}] & \rightarrow S^- \quad (67) \\
S^0 + [\text{V-oxd}] & \rightarrow S^+ \quad (68) \\
S^- + [\text{V-oxd}] & \rightarrow S^0 \quad (69)
\end{align*}
The experimental results to be presented will be discussed in terms of these reactions.

B. Verification of Mixed Crystal Formation

The mixed system potassium chloride-potassium bromide forms a complete series of solid solutions over the entire composition range as pointed out by Havinghurst, Mack and Blake. The phase diagram for the potassium chloride-potassium bromide system is shown in Figure 9. From the X-ray data the \( d_{hkl} \) values were obtained and the best values of the lattice parameters were calculated by the interpolation method of Nelson and Reiley and were found to be a linear function of the composition in accordance with Vegard's Law.

A sample Nelson and Riley plot is shown for pure KCl in Figure 10. The best values of the lattice parameters as calculated by the method of Nelson and Riley are shown tabulated in Table VIII and are plotted in Figures 11 and 12. It can be seen that both the curves are practically identical and both are linear functions of the composition in agreement with Vegard's law indicating that these crystals are indeed true mixed crystals. The best values of the lattice parameters obtained by this method are accurate to \( \pm 0.0005 \) Å.

C. Concentration of F-centers as a Function of Composition of the Mixed Crystals

The data for the concentration of F-centers as a function of composition are shown tabulated in Table IX. The data are plotted in Figure 13. The data indicate that the F-center concentration goes through a small maximum at 12.7 percent KBr, passes through a minimum at the equimolar concentration, and then rises to a higher value at 100
Figure 9. Phase Diagram for the Potassium Chloride-Potassium Bromide System. Data from Reference (108)
Figure 10. Typical Nelson and Riley Plot, Sample 114
TABLE VIII
Best Values of the Lattice Parameters for Mixed KCl-KBr Determined by the Method of Nelson and Riley

<table>
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<tr>
<th>Sample</th>
<th>Mole Percent KBr</th>
<th>Best Value of Lattice parameter</th>
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<td>114</td>
<td>-</td>
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<td>133</td>
<td>100.0</td>
<td>6.596</td>
</tr>
<tr>
<td>144</td>
<td>-</td>
<td>6.293</td>
</tr>
<tr>
<td>145</td>
<td>6.4</td>
<td>6.321</td>
</tr>
<tr>
<td>146</td>
<td>13.5</td>
<td>6.338</td>
</tr>
</tbody>
</table>
Figure 11. Best Value of the Lattice Parameter vs. the Mole Percent of KBr, Samples (114-123)
Figure 12. Best Value of the Lattice Parameter vs. the Mole Percent of KBr, Samples (124-133)
### TABLE IX

Concentration of F-centers as a Function of the Composition of the Mixed KCl-KBr

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole Percent KBr</th>
<th>Concentration of F-Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>-</td>
<td>$3.11 \times 10^{15}$ (a)</td>
</tr>
<tr>
<td>115</td>
<td>6.9</td>
<td>$1.60 \times 10^{15}$ (b)</td>
</tr>
<tr>
<td>116</td>
<td>12.7</td>
<td>$2.37 \times 10^{15}$ (c)</td>
</tr>
<tr>
<td>119</td>
<td>37.3</td>
<td>$5.17 \times 10^{14}$ (d)</td>
</tr>
<tr>
<td>121</td>
<td>59.5</td>
<td>$8.20 \times 10^{13}$ (c)</td>
</tr>
<tr>
<td>123</td>
<td>85.0</td>
<td>$1.20 \times 10^{15}$ (c)</td>
</tr>
<tr>
<td>KBr</td>
<td>100.0</td>
<td>$9.45 \times 10^{14}$ (c)</td>
</tr>
</tbody>
</table>

(a) average value of 20 determinations  
(b) only one determination  
(c) average of 3 determinations  
(d) average of 2 determinations  

The expected error is $\pm$ 10 percent of the value shown.
Figure 13. Concentration of F-Centers in Mixed KCl-KBr as a Function of Mole Percent KBr
percent KBr. The value for the pure KCl is higher than the value for the pure KBr. Except for the maximum at 12.7 percent KBr, the data are in agreement with that of Smakula, Maunard, and Repucci57 and with that of Arends, den Hartog, and Dekker.58 It was not expected that the data would be agreeable since the other experiments used single crystals. As mentioned previously, the nature of the defects present in the crystal prior to exposure to ionizing radiation affect the concentration of F-centers produced.

D. Chemical States of $^{35}$S in Mixed KCl-KBr Crystals

It should be pointed out that great variations in results are expected from the different conditions of irradiation, post-irradiation treatment, and analysis. The data for the results of the hot-atom studies of the mixed KCl-KBr crystals are tabulated in Tables X to XXIX along with the pertinent data for the irradiation and analysis conditions used for the various samples.

The data were accumulated under varying conditions as can be seen from the Tables. Two sets of the Mixed crystals were unavoidably exposed to light for a short period of time; the exact length of time is not accurately known but is approximately somewhere around 10-40 minutes. These sets of crystals were then thermally annealed at 75° and 215°C. Another set of mixed crystals was exposed to light for times of the order of days. Finally, one set of mixed crystals was not exposed to light and was thermally annealed at 75°C and 215°C.

The data will be discussed in essentially three sections: Series I samples with short light exposure, Series II with long light exposure, and Series III no light exposure.
The error bars shown on the graphs are the standard deviations for the different analysis as listed in Tables V and VII.

1. Series I, Electrophoretic Analysis, Short Light Exposure

The samples studied in this series of samples were exposed to light approximately 10-40 minutes in room light. However, the exact length of light exposure is not known and there is probably some variation from sample to sample within the series.

a) Room temperature data

The room temperature data for the samples exposed to light 10-40 minutes is shown in Table X and in Figure 14. The yield of $S^+$ rises sharply to a maximum at 6.4 percent KBr, passes through a minimum at 13.5 percent KBr, and then increases slowly to a limiting value as the KBr content is increased. The $S^0$ yield slowly rises to a maximum at 13.5 percent KBr and then decreases to a plateau value. The $S^-$ yield decreases rapidly up to 6.4 percent KBr, goes through a maximum at 13.5 percent KBr and then levels off to a limiting value. In the lower percent KBr solutions reactions (68) and (69) occur rapidly until after 6.4 percent KBr when reactions (66) and (67) dominate. At 13.5 percent KBr and greater, reactions (68) and (69) again play the major role.

b) Thermal annealing at 75°C

(i) Yield vs. Composition, Annealed 3 Hours at 75°C

The data for these samples are shown in Table XI and in Figure 15. The $S^0$ yield passes through a slight minimum at 6.4 percent KBr, a maximum at 13.5 percent KBr,
TABLE X

Series I, Mixed KCl-KBr, Brookhaven Irradiation, Room Temperature, Analysis by Electrophoretic Method

Irradiated 20 min at $1 \times 10^{13}$ neutrons/cm$^2$/sec in PN-4
Samples in evacuated quartz vials degassed 1 hour at 400°C
Exposed to light approximately 10-40 min

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0 + S^-$</th>
<th>% $S^-$</th>
<th>% $S^0$</th>
<th>% $SO_3^-$</th>
<th>$SO_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>124-9</td>
<td>0</td>
<td>51.1</td>
<td>33.5</td>
<td>17.6</td>
<td>49.9</td>
<td></td>
</tr>
<tr>
<td>125-9</td>
<td>6.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>126-9</td>
<td>13.3</td>
<td>54.2</td>
<td>30.3</td>
<td>23.9</td>
<td>45.8</td>
<td></td>
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<tr>
<td>128-9</td>
<td>29.4</td>
<td>29.4</td>
<td>11.7</td>
<td>17.7</td>
<td>70.6</td>
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<td>130-9</td>
<td>48.5</td>
<td>27.1</td>
<td>11.2</td>
<td>15.9</td>
<td>72.9</td>
<td></td>
</tr>
<tr>
<td>132-9</td>
<td>72.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>124-10</td>
<td>0</td>
<td>62.8</td>
<td>38.2</td>
<td>24.7</td>
<td>37.2</td>
<td></td>
</tr>
<tr>
<td>125-7</td>
<td>6.4</td>
<td>33.5</td>
<td>8.3</td>
<td>24.7</td>
<td>66.5</td>
<td></td>
</tr>
<tr>
<td>126-10</td>
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<td>58.7</td>
<td>22.6</td>
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<td>41.3</td>
<td></td>
</tr>
<tr>
<td>128-10</td>
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<td>34.6</td>
<td>14.4</td>
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<td>65.4</td>
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<tr>
<td>130-10</td>
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<td>22.1</td>
<td>17.7</td>
<td>60.2</td>
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<tr>
<td>132-10</td>
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<td>34.4</td>
<td>23.3</td>
<td>11.1</td>
<td>65.6</td>
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</table>
Figure 14. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Room Temperature, Electrophoretic Analysis, Short Light Exposure, Average Values for Two Runs (Series 9 and 10)
TABLE XI
Series I, Mixed KCl-KBr, Brookhaven Irradiation,
Annealed for 3 Hours at 75.0 ± 0.5°C,
Analysis by Electrophoretic Method

Irradiated for 20 min at $1 \times 10^{13}$ neutrons/cm$^2$/sec in PN-4
Samples in evacuated quartz vials degassed for 1 hr at 400°C
Thermally annealed for 3 hours at 75.0 ± 0.5°C
Exposed to light for 10-40 min
Average values of two determinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>$% \text{SO}_2$</th>
<th>$% \text{S}^-$</th>
<th>$% \text{SO}_4$</th>
<th>$% \text{SO}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>124-125</td>
<td>0</td>
<td>56.6</td>
<td>28.1</td>
<td>28.5</td>
<td>43.4</td>
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<td>125-17</td>
<td>6.4</td>
<td>61.6</td>
<td>35.7</td>
<td>25.9</td>
<td>38.4</td>
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<td>58.4</td>
<td>26.5</td>
<td>31.9</td>
<td>41.6</td>
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<tr>
<td>128-15</td>
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<td>66.6</td>
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<tr>
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<td>18.8</td>
<td>19.3</td>
<td>61.9</td>
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<tr>
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<td>72.1</td>
<td>28.3</td>
<td>17.9</td>
<td>10.4</td>
<td>71.7</td>
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</table>
Figure 15. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed for 3 Hours at 75.0 ± 0.5°C Electrophoretic Analysis, Short Light Exposure
and then decreases to a limiting value at 29.4 percent KBr. The yield of $S^+$ passes through a minimum at 6.4 percent KBr and the increases to a limiting value after 29.4 percent KBr. The $S^-$ yield passes through a maximum at 6.4 percent KBr and decreases slowly with increasing composition of KBr. Between 0 and 6.4 percent KBr, reactions (66) and (67) take place to increase the $S^-$ yield. From 6.4 percent KBr to 13.5 percent KBr, reactions (68) and (69) occur to increase both the $S^+$ and $S^-$ yields. After 13.5 percent KBr, reactions (68) and (69) are occurring with reaction (68) being faster than (69).

(ii) Yield vs. Composition, Annealed 6 Hours at 75°C

The data are shown in Table XII and in Figure 16. The curves are in general the same as for the samples annealed 3 hours at this temperature. The maxima and minima in the yields are more pronounced than at 3 hours of heating. In general the same processes are occurring as after 3 hours of heating. The minimum in the $S^+$ yield is absent indicating that reaction (66) is not occurring.

(iii) Yield vs. Composition, Annealed 12 Hours at 75°C

The data for these samples is shown in Table XIII and in Figure 17. The yield of $S^+$ is initially higher and that of $S^0$ lower than at 6 hours of heating. The yield of $S^+$ passes through a minimum at 6.4 percent KBr while the $S^0$ yield passes through a sharp maximum at the same composition. The $S^+$ yield slowly increases after 13.5 percent KBr as the KBr concentration is increased. The $S^0$ yield decreases rather quickly after passing through the maximum at 6.4 percent KBr. The $S^-$ yield increases only slightly from 0 to 6.4
TABLE XII
Series I, Mixed KCl-KBr, Brookhaven Irradiation, Annealed 6 Hours at 75.0 ± 0.5°C, Analysis by Electrophoretic Method

Irradiated for 20 min at $1 \times 10^{13}$ neutrons/cm$^2$/sec
Samples in evacuated quartz vials degassed 1 hour at 400°C
Thermally annealed for 6 hours at 75.0 ± 0.5°C
Exposed to light approximately 10-40 min
Average value of two determinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0 + S^\equiv$</th>
<th>% $S^\equiv$</th>
<th>% $S^0$</th>
<th>% $SO_3^\equiv + SO_4^\equiv$</th>
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</thead>
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<td>29.1</td>
<td>34.0</td>
<td>36.9</td>
</tr>
<tr>
<td>125-18</td>
<td>6.4</td>
<td>62.1</td>
<td>38.5</td>
<td>23.6</td>
<td>37.9</td>
</tr>
<tr>
<td>126-16</td>
<td>13.3</td>
<td>56.4</td>
<td>24.8</td>
<td>31.5</td>
<td>43.6</td>
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<tr>
<td>128-16</td>
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<td>38.9</td>
<td>18.7</td>
<td>20.2</td>
<td>61.1</td>
</tr>
<tr>
<td>130-16</td>
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<td>37.4</td>
<td>16.6</td>
<td>20.8</td>
<td>62.6</td>
</tr>
<tr>
<td>132-16</td>
<td>72.1</td>
<td>38.8</td>
<td>20.4</td>
<td>18.4</td>
<td>61.1</td>
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</table>
Figure 16. Percent of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed 6 Hours at 75.0 ± 0.5°C, Electrophoretic Analysis, Short Light Exposure
TABLE XIII
Series I, Mixed KCl-KBr, Brookhaven Irradiation,
Annealed 12 Hours at 75.0 ± 0.5°C,
Analysis by Electrophoretic Method

Irradiated 20 min at $1 \times 10^{13}$ neutrons/cm²/sec in PN-4
Samples in evacuated quartz vials degassed 1 hour at 400°C
Thermally annealed for 12 hours at 75.0 ± 0.5°C
Exposed to light approximately 10-40 min
Average value of two determinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0+S^-$</th>
<th>% S-$</th>
<th>% $S^0$</th>
<th>% $SO_3^-+SO_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>124-17</td>
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<td>17.2</td>
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<td>54.2</td>
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<tr>
<td>125-19</td>
<td>6.4</td>
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<td>21.8</td>
<td>41.4</td>
<td>36.8</td>
</tr>
<tr>
<td>126-17</td>
<td>13.3</td>
<td>47.8</td>
<td>21.6</td>
<td>26.2</td>
<td>52.2</td>
</tr>
<tr>
<td>128-17</td>
<td>29.4</td>
<td>40.7</td>
<td>23.0</td>
<td>17.7</td>
<td>59.3</td>
</tr>
<tr>
<td>130-17</td>
<td>48.5</td>
<td>35.2</td>
<td>20.7</td>
<td>14.5</td>
<td>64.8</td>
</tr>
<tr>
<td>132-17</td>
<td>72.1</td>
<td>33.2</td>
<td>22.8</td>
<td>10.4</td>
<td>66.8</td>
</tr>
</tbody>
</table>
Figure 17. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed 12 Hours at 75.0 ± 0.5°C, Electrophoretic Analysis, Short Light Exposure
percent KBr and remains constant as the KBr content increases. Reaction (66) occurs between 0 and 6.4 percent KBr, with a small contribution from (69). From 6.4 to 72.1 percent KBr, reaction (68) is the most important reaction occurring.

(iv) Yield vs. Composition, Annealed 24 Hours at 75°C

The data for these samples are shown in Table XIV and in Figure 18. The yield of $S^+$ shows identical behavior to the $S^+$ yield at 12 hours of annealing data. The $S^-$ yield passes through a sharp maximum at 6.4 percent KBr and decreases to a limiting value at 29.4 percent KBr. The $S^0$ yield remains constant until 13.5 percent KBr and then decreases slowly to a limiting value after 29.4 percent KBr. Between 0 and 6.4 percent, KBr reactions (66) and (67) are taking place. After 6.4 percent KBr reactions (68) and (69) are the important reactions.

(v) Yield vs. Hours of Annealing at 75°C, Pure KCl

The data for these samples are taken from the yield vs. composition curves for the various times of annealing and are shown in Figure 19. The yield of $S^0$ increases slowly up to 6 hours of annealing where it reaches a limiting value. The $S^-$ yield is initially higher than the $S^0$ yield but decreases slowly to a limiting value. The $S^+$ yield is constant until 3 hours of annealing, passes through a small minimum at 6 hours, and then increases to a limiting value after 12 hours. Reaction (69) occurs from 0 to 3 hours of heating. Between 3 and 6 hours of heating, reactions (66) and (69) are taking place. After 6 hours of heating reactions (68) and (69) are occurring and are complete after 12 hours.
### TABLE XIV

Series I, Mixed KCl-KBr, Brookhaven Irradiation,  
Annealed 24 Hours at 75.0 ± 0.5°C,  
Analysis by Electrophoretic Method

Irradiated for 20 min at $1 \times 10^{13}$ neutrons/cm$^2$/sec in PN-4  
Samples in evacuated quartz vials degassed for 1 hour at 400°C  
Thermally annealed for 24 hours at 75.0 ± 0.5°C  
Exposed to light approximately 10-15 min  
Average values of two determinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0 + S^\equiv$</th>
<th>% $S^\equiv$</th>
<th>% $S^O$</th>
<th>% $SO_3^{\equiv} + SO_4^{\equiv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>124-18</td>
<td>0</td>
<td>45.1</td>
<td>18.2</td>
<td>26.9</td>
<td>54.9</td>
</tr>
<tr>
<td>125-20</td>
<td>6.4</td>
<td>60.4</td>
<td>34.1</td>
<td>26.3</td>
<td>39.6</td>
</tr>
<tr>
<td>126-18</td>
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<td>53.0</td>
<td>25.8</td>
<td>27.2</td>
<td>47.0</td>
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<td>29.4</td>
<td>40.3</td>
<td>21.8</td>
<td>18.5</td>
<td>59.7</td>
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<tr>
<td>130-18</td>
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<td>34.2</td>
<td>23.9</td>
<td>10.3</td>
<td>65.8</td>
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<tr>
<td>132-18</td>
<td>72.1</td>
<td>42.0</td>
<td>12.9</td>
<td>29.1</td>
<td>58.0</td>
</tr>
</tbody>
</table>
Figure 18. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed 24 Hours at 75.0 ± 0.5°C, Electrophoretic Analysis, Short Light Exposure
Figure 19. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 100% KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
(vi) Yield vs. Hours of Annealing at 75°C, 6.4 percent KBr

The data for these samples are taken from the yield vs. composition curves for the various times of annealing and are shown in Figure 20. The yield of $S^+$ falls off rapidly with heating and reaches a plateau after 3 hours of heating. The yield of $S^-$ increases rapidly to a plateau value after 3 hours of heating. The $S^0$ yield increases only slowly with time of annealing. These curves would suggest that reaction (66) is rapid in the earlier stages of annealing and that reaction (69) is taking place at a slower rate since $S^0$ increases only slightly with heating. There is no indication of either reaction (67) or (68).

(vii) Yield vs. Hours of Annealing at 75°C, 13.5 percent KBr

The data for these samples are taken from the yield vs. composition data for the various hours of heating and are shown in Figure 21. The most striking feature of these annealing curves is that the yields are almost independent of time of annealing with the $S^0$ yield showing only a slight increase and $S^+$ a small decrease. This would indicate that at this composition only reaction (66) is important, and it is essentially complete after 3 hours of annealing.

(viii) Yield vs. Hours of Annealing at 75°C, 29.4 percent KBr

Data for these curves are taken from the yield vs. composition curves for the various hours of annealing and are shown in Figure 22. The yield of $S^+$ is higher for all times of heating then the data for the previous
Figure 20. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 6.4 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
Figure 21. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C, for 13.3 Mole Percent of KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
Figure 22. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 29.4 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
composition. The yield of $S^+$ decreases only slowly with time of annealing to a limiting value after 6 hours of heating. The $S^-$ yield increases slowly between 0 and 3 hours of heating and reaches a limiting value after 6 hours. The yield of $S^0$ remains constant with time of heating. There is very little annealing taking place and the only reactions which seem to take place are reactions (66) and (67).

(ix) Yield vs. Hours of Annealing at 75°C, 48.5 percent KBr

Data are taken from the yield vs. composition curves for various times of annealing and are shown in Figure 23. The $S^+$ yield behaves as in the previous composition, but now there is a very slight increase after 6 hours of heating. The $S^-$ yield shows a gradual increase while the $S^0$ yield shows a slight decrease with increasing time of annealing. This suggests that reactions (67) and (68) are becoming more important after 6 hours.

(x) Yield vs. Hours of Annealing at 75°C, 72.1 percent KBr

Data are constructed from the yield vs. composition data for the various hours of heating and are shown in Figure 24. The $S^+$ yield is essentially constant with time of heating. The $S^-$ yield decreases slowly to a limiting value after 6 hours and the $S^0$ yield increases to a limiting value after 6 hours. Reaction (69) is taking place and is complete after 6 hours of heating.

c) Thermal annealing at 215°C

(i) Yield vs. Composition, Annealed 3 Hours at 215°C

The data are shown in Table XV and in Figure 25.
Figure 23. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 48.5 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
Figure 24. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 72.1 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
### TABLE XV

Series I, Mixed KCl-KBr, Brookhaven Irradiation, Annealed 3 Hours at 215 ± 2°C, Analysis by Electrophoretic Method

<table>
<thead>
<tr>
<th>Sample</th>
<th>% KBr</th>
<th>% SO₂⁺SO₄⁻⁻</th>
<th>% S²⁻</th>
<th>% SO²⁰⁺SO²⁻²</th>
<th>% SO₃⁻³⁺SO₄⁻⁻</th>
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</thead>
<tbody>
<tr>
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<td>38.4</td>
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<td>36.8</td>
<td>17.7</td>
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<td>50.2</td>
<td>37.6</td>
<td>12.6</td>
<td>49.8</td>
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<tr>
<td>128-11</td>
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<td>39.5</td>
<td>29.7</td>
<td>9.8</td>
<td>60.5</td>
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<tr>
<td>130-11</td>
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<td>31.3</td>
<td>30.6</td>
<td>1.7</td>
<td>68.7</td>
</tr>
<tr>
<td>132-11</td>
<td>72.1</td>
<td>38.7</td>
<td>28.7</td>
<td>10.0</td>
<td>61.3</td>
</tr>
</tbody>
</table>

Irradiated 20 min at $1 \times 10^{13}$ neutrons/cm²/sec in PN-4

Samples in evacuated quartz vials degassed 1 hour at 400°C

Thermally annealed for 3 hours at 215 ± 2°C

Exposed to light approximately 10-15 min

Average values of two determinations
Figure 25. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed 3 Hours at 215 ± 2°C, Electrophoretic Analysis, Short Light Exposure
The data show the same general shaped curves as the corresponding curves for the 75°C data. However, the S⁻ yield is initially higher than at 75°C and decreases slowly with composition. The S⁰ yield on the other hand shows a much lower initial value than for 3 hours of annealing at 75°C and the maximum in the yield occurs at 6.4 percent KBr, after which the yield decreases slowly with increasing composition. The yield of S⁺ is higher and shows the same general shape as that for the 3 hours of annealing at 75°C, but the minimum is more pronounced. Between 0 and 6.4 percent KBr, reaction (66) is taking place with a small contribution from reaction (69). Above 6.4 percent KBr reaction (68) and (69) are the important reactions. The data suggest that at the higher temperature reactions (67) and (68) are more important than at 75°C.

(ii) Yield vs. Composition, Annealed 6 Hours at 215°C

The data for these samples are shown in Table XVI and in Figure 26. The S⁻ yield is about two times that in the corresponding data at 75°C. The yield of S⁻ decreases slowly with composition. The yield of S⁰ is lower by a factor of three from the corresponding data at 75°C and is essentially constant with composition showing a slight maximum at 6.4 percent KBr. The S⁺ yield is constant up to 13.5 percent KBr and then increases slowly with composition. These data suggest that reaction (69) occurs between 0 and 6.4 percent KBr. After this composition the main reactions are reactions (69) and (68).
TABLE XVI
Series I, Mixed KCl-KBr, Brookhaven Irradiation,
Annealed 6 Hours at 215 ± 2°C,
Analysis by Electrophoretic Method

Irradiated for 20 min at $1 \times 10^{13}$ neutrons/cm$^2$/sec in PN-4
Samples in evacuated quartz vials degassed 1 hour at 400°C
Thermally annealed for 6 hours at 215 ± 2°C
Exposed to light approximately 10-15 min
Average values of two determinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0 + S^=$</th>
<th>% $S^=$</th>
<th>% $S^0$</th>
<th>% $SO_3^= + SO_4^= $</th>
</tr>
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<tbody>
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<tr>
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<td>72.1</td>
<td>40.7</td>
<td>27.9</td>
<td>12.8</td>
<td>69.3</td>
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Figure 26. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed 6 Hours at 215 ± 2°C, Electrophoretic Analysis, Short Light Exposure
(iii) Yield vs. Composition, Annealed 12 Hours at 215°C

The data for this series of samples are shown in Table XVII and in Figure 27. The yield of \( S^0 \) is initially higher than at 6 hours of annealing at 215°C, but decreases slowly with increasing composition. The yield of \( S^- \) is initially lower than that for 6 hours of heating at 215°C and exhibits a slight minimum at 6.4 percent KBr, goes through a small maximum at 13.3 percent KBr and then slowly decreases to a limiting value at 29.4 percent KBr. The yield of \( S^+ \) is initially about the same as the value for 6 hours of annealing and increases to a limiting value at about 29.4 percent KBr. Compared to 12 hours of heating at 75°C, the \( S^- \) yield has increased for all compositions. However the \( S^0 \) yield shows a sharp decrease in the 0 to 13.3 percent KBr region compared to the data for 12 hours of annealing at 75°C, and remains constant for all compositions after 29.4 percent KBr. Also the maximum in the yield of \( S^0 \) is absent at this temperature and time of annealing. The increased temperature has had the effect of promoting reactions (67) and (68) in the 0 to 13.3 percent KBr region such that both the \( S^- \) and \( S^+ \) yields have increased in this region.

(iv) Yield vs. Composition, Annealed 24 Hours at 215°C

The data for this set of samples are shown in Table XVIII and in Figure 28. The yield of \( S^0 \) is approximately constant for all compositions; in contrast to the same data for the 75°C annealing, the maximum at 6.4 percent is absent. The \( S^+ \) yield passes through a minimum at 6.4 percent KBr and the increases to a limiting value at 29.4 percent KBr. The effect of the increased temperature has been
TABLE XVII

Series I, Mixed KCl-KBr, Brookhaven Irradiation,
Annealed for 12 Hours at 215 ± 2°C,
Analysis by Electrophoretic Method

Irradiated for 20 min at $1 \times 10^{13}$ neutrons/cm$^2$/sec in PN-4
Samples in evacuated quartz vials degassed 1 hour at 400°C
Thermally annealed for 12 hours at 215 ± 2°C
Exposed to light approximately 10-15 min
Average values of two determinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>% KBr</th>
<th>% S$^0$+S$^-$</th>
<th>% S$^-$</th>
<th>% S$^0$</th>
<th>% SO$_3^-$+SO$_4^{2-}$</th>
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<td>70.0</td>
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<td>5.2</td>
<td>59.3</td>
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<tr>
<td>132-13</td>
<td>72.1</td>
<td>38.4</td>
<td>36.5</td>
<td>1.9</td>
<td>-61.6</td>
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</table>
Figure 27. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed 12 Hours at 215 ± 2°C, Electrophoretic Analysis, Short Light Exposure
TABLE XVIII
Series I, Mixed KCl-KBr, Brookhaven Irradiation,
Annealed 24 Hours at 215 ± 2°C,
Analysis by Electrophoretic Method

Irradiated 20 min at $1 \times 10^{13}$ neutrons/cm$^2$/sec in PN-4
Samples in evacuated quartz vials degassed 1 hour at 400°C
Thermally annealed for 24 hours at 215 ± 2°C
Exposed to light approximately 10-15 min
Average values of two determinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0+S^-$</th>
<th>% $S^-$</th>
<th>% $S^+$</th>
<th>% $SO_3^-=SO_4^-$</th>
</tr>
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<tr>
<td>126-14</td>
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<td>42.6</td>
<td>6.3</td>
<td>51.1</td>
</tr>
<tr>
<td>128-14</td>
<td>29.4</td>
<td>32.8</td>
<td>25.8</td>
<td>7.0</td>
<td>67.2</td>
</tr>
<tr>
<td>130-14</td>
<td>48.5</td>
<td>37.4</td>
<td>34.4</td>
<td>3.0</td>
<td>62.6</td>
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<tr>
<td>132-14</td>
<td>72.1</td>
<td>34.6</td>
<td>34.1</td>
<td>0.5</td>
<td>65.4</td>
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</table>
Figure 28. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Brookhaven Irradiation, Annealed 24 Hours at 215 ± 2°C, Electrophoretic Analysis, Short Light Exposure
to decrease the yield of $S^0$ and to increase the yield of $S^+$ and $S^-$ indicating that reactions (67), (68), and possibly (69) are important at 215°C.

(v) Yield vs. Hours of Annealing at 215°C, Pure KCl

The data for these samples, taken from the yield vs. composition curves for the appropriate times of annealing, are shown in Figure 29. The yield of $S^+$ increases to a maximum at 3 hours and then decreases to a limiting value after 6 hours. The yield of $S^0$ decreases quickly to a limiting value also after 3 hours of annealing in contrast to the 75°C data in which the $S^0$ yield went through a maximum after 6 hours of annealing and then decreased. The yield of $S^-$ increases slowly to a limiting value after 6 hours. The increased temperature of annealing has increased the yield of $S^-$ and decreased the yield of $S^0$ after 3 hours. Reactions (67) and (68) are important from 0 to 3 hours of heating. After 3 hours of heating and up to 6 hours, reactions (66) and (67) take place. After 6 hours of annealing reactions (69) and (68) occur to a small extent.

(vi) Yield vs. Hours of Annealing at 215°C, 6.4 percent KBr

The data are taken from the yield vs. composition curves for the various times of annealing and are shown in Figure 30. The yield of $S^+$ decreases rapidly with increasing time of annealing to a limiting value after 3 hours, but not as rapidly as at 75°C for the same composition. The yield of $S^0$ decreases with increased time of heating instead of slowly increasing as at 75°C. The $S^-$ yield increases rapidly with heating to a constant value after 3 hours of heating. This data suggest that reaction (66) occurs to a small extent with the major reaction being reaction (68).
Figure 29. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for Pure KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
Figure 30. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 6.4 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure.
The annealing reactions appear to be almost complete after 12 hours. The main reaction seems to be the conversion of $S^0$ to $S^-$.  

(vii) Yield vs. Hours of Annealing at 215°C, 13.3 percent KBr

The data are constructed from the yield vs. composition data for the various times of annealing and are shown in Figure 31. The $S^+$ yield increases very slowly to a plateau value very similar in behavior to that for the 75°C data. The $S^-$ yield increases rapidly to a plateau value after 6 hours of annealing while the $S^0$ yield decreases to a limiting value. This suggests that reaction (67) is the only important reaction at this composition.

(viii) Yield vs. Hours of Annealing at 215°C, 29.4 percent KBr

Data are taken from the yield vs. composition data for the various times of annealing and are shown in Figure 32. The yield of $S^+$ is almost identical to that at 75°C and decreases very little with increased time of heating. The yield of $S^-$ increases to a limiting value after 6 hours of heating and the $S^0$ yield decreases to a limiting value after 6 hours. These data suggest that reaction (66) occurs, but is complete after 3 hours of heating. Reaction (67) also occurs and is complete after 6 hours of annealing.

(ix) Yield vs. Hours of Annealing at 215°C, 48.5 percent KBr

The data are taken from the yield vs. composition curves for the various times of heating and are shown in Figure 33. The yield of $S^+$ is essentially constant with
Figure 31. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 13.3 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
Figure 32. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 29.4 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
Figure 33. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 48.5 Mole Percent KBr in KCl, Brookhaven Irradiation, Electrophoretic Analysis, Short Light Exposure
time of heating. The $S^0$ and $S^-$ yields behave as in the previous composition indicating that the same processes occur. Reaction (67) appears to be the main reaction and is complete after 6 hours).

\[(x)\] Yield vs. Hours of Annealing at $215^\circ C$, 72.1 percent KBr

The data are taken from the yield vs. composition data for various times of annealing and are shown in Figure 34. The curves of the yields show basically the same general shape as the preceding composition. The same process is occurring with reaction (67) being the most important reaction.

Some generalizations about these data are possible keeping in mind the conditions and the errors involved. The yield vs. composition curves for various times of annealing at $75^\circ C$ show the same behavior in the 0 to 30 percent KBr region. That is, the yield of $S^-$ goes through a maximum and the $S^0$ yield go through a maximum and a minimum while the $S^+$ yield goes through a minimum. After approximately 30 percent KBr there seems to be little effect of composition on the yields, (in some cases there may be a maximum in the $S^+$ yield at about 50 percent KBr).

The curves of the yields vs. the hours of annealing at $75^\circ C$ for the various compositions indicate that there is very little effect of thermal annealing at $75^\circ C$ in these samples. Only for 6.4 percent KBr is there evidence for any appreciable annealing. The $S^+$ yield decreased rapidly and the $S^-$ yield increased rapidly to limiting values after 6 hours of annealing. The data show that annealing at $75^\circ C$ tends to increase the yield of $S^0$ and $S^-$ and decrease the yield of $S^+$. In the region of 0 to 48.5 percent KBr the yield of $S^0$ is greater than the yield of $S^-$ at the same time...
Figure 34. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 72.1 Mole Percent KBr in KCl, Brookhaven Irradiation. Electrophoretic Analysis. Short Light Exposure.
of annealing; above 48.5 percent KBr the yield of $S^0$ falls below that of $S^-$. The yield vs. composition curves for various hours of annealing at 215°C show the same general trends as at 75°C. The yield vs. hours of annealing curves at 215°C for the various compositions are for the most part similar to those for annealing at 75°C. There appears to be more thermal annealing taking place at 215°C than at 75°C. There is a small conversion of $S^+$ to $S^0$, with the major reaction being conversion of $S^0$ to $S^-$. One marked difference in the annealing at 215°C as compared to thermal annealing at 75°C is that at 215°C the yield of $S^-$ is always greater than the yield of $S^0$ for all compositions.

2. **Series II electrophoretic analysis, long light exposure**

The room temperature data for the mixed crystals of KCl-KBr which were exposed to light for times of the order of days are shown in Tables XIX and XX and the average values of the yields are plotted in Figure 35. It should be emphasized that the exact amount of light exposure was not accurately known, but it is known that it far exceeds the amount of light that the previous set of samples received. Also the irradiation conditions for these samples were entirely different than those for the other light bleached set. Hence, one should be cautious in comparing the data obtained under the varying conditions. From this data it is seen that the yield of $S^+$ shows an increase from the initial value to a plateau value at approximately 30 percent KBr. The $S^-$ yield decreases rapidly from 0 to 10 percent KBr, then remains constant for the remaining compositions. The $S^0$ yield goes through a maximum at 6.9 percent KBr, decreases
TABLE XIX
Series II, Mixed KCl-KBr-I, Watertown (AMRA) Irradiation, Room Temperature, Analysis by Electrophoretic Method

Irradiated for 15 min at $4 \times 10^{12}$ neutrons/cm$^2$/sec in ST-4A
Samples in evacuated quarts vials degassed for 1 hour at 400°C
Large amount of light bleaching, but not accurately known

<table>
<thead>
<tr>
<th>Sample</th>
<th>% KBr</th>
<th>% S$^0$+S$^-$</th>
<th>% S$^-$</th>
<th>% S$^0$</th>
<th>% SO$_3$+SO$_4^{2-}$</th>
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<td>10.2</td>
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</tr>
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</table>
TABLE XX

Series II, Mixed KCl-KBr-II, Watertown (AMRA) Irradiation,
Room Temperature, Analysis by Electrophoretic Method

Irradiated for 15 min at $4 \times 10^{12}$ neutrons/cm$^2$/sec in ST-4A
Samples in evacuated quartz vials degassed for 1 hour at 400°C
Large amount of light bleaching, but exact amount not known

<table>
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<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $SO_4^-$</th>
<th>% $SO_3^-</th>
<th>% S^=</th>
<th>% S$^O$</th>
<th>% $SO_3^-+SO_4^-$</th>
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<tr>
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<td>70.6</td>
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Figure 35. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Watertown Irradiation, Room Temperature, Electrophoretic Analysis, Long Light Exposure
to a plateau value at 30 percent KBr and remains constant for all the remaining compositions. The large amount of light bleaching has removed the characteristic behavior of the $S^+$ and the $S^-$ yields in the lower KBr region. The yield of $S^-$ decreases very rapidly while the yield of $S^+$ increases only slowly suggesting that reaction (69) probably contributes to the maximum in the $S^0$ yield. At compositions other than 6.9 percent KBr, reaction (68) becomes important, as shown by the increase in the yield of $S^+$. This reaction is complete after 13.5 percent KBr and there is no further evidence for reaction (66) at all. Reaction (68) appears to be complete at approximately 25 percent KBr. Reaction (69) is complete at 6.4 percent KBr.

3. Series III BaSO$_4$ precipitation analysis, no light exposure

It should be noted again that the irradiation conditions for these samples are different than those for the preceding two sets of samples as indicated in Tables XXI to XXIX. It should also be re-emphasized that the BaSO$_4$ precipitation method is far more precise than the electrophoretic method. The circles and error bars shown on the curves indicates the standard deviations for this analysis as shown in Table V.

a) Room temperature data

The data for the room temperature analyses are tabulated in Table XXI and the average values shown in Figure 36. The yield of $S^0$ is constant until 6.4 percent KBr after which it decreases quickly and passes through a minimum at 40-50 percent KBr and increases slowly until 85.0 percent KBr is reached. The $S^-$ yield decreases through a shallow
TABLE XXI
Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation, Room Temperature, Analysis by the BaSO$_4$ Precipitation Method

Irradiated for 10 min at $1 \times 10^{12}$ neutrons/cm$^2$/sec in ST-3C
Samples in evacuated quartz vials wrapped in aluminum foil
No light bleaching

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0 + S^-$</th>
<th>% $S^-$</th>
<th>% $S^0$</th>
<th>% $SO_3^- + SO_4^-$</th>
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Figure 36. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Watertown Irradiation, Room Temperature, Analysis by BaSO₄ Precipitation Method, No Light Bleaching, Average Values of Sets I and II
minimum at 6.4 percent KBr and then rises to a maximum at approximately 30 percent KBr and slowly decreases again to its initial value as the concentration of KBr increases. The $S^+$ yield passes through a small maximum at 6.4 percent KBr followed by a slight maximum at 13.5 percent KBr and then increases to a limiting value at approximately 60 percent KBr. Reactions (68) and (69) appear to take place between 0 and 6.4 percent KBr with reaction (68) being faster. After 6.4 percent KBr there is some evidence that reaction (66) becomes important since the $S^+$ yield decreases. As the $S^0$ yield decreases the $S^-$ yield increases indicating that the predominant reaction is (67). At 13.5 percent KBr the $S^+$ yield begins to increase with the $S^0$ yield decreasing at about the same rate while the $S^-$ yield still increases, indicating that reactions (67) and (68) are competing for the $S^0$. Above approximately 25 percent KBr, the $S^-$ yield begins to decrease while the $S^0$ yield passes through a shallow minimum at approximately 50 percent KBr suggesting that now reactions (68) and (69) take place at about the same rate. There is no evidence for reaction (67) above about 25 percent KBr.

b) **Thermal annealing at 75°C**

(i) Yield vs. Composition, Annealed 3 Hours at 75°C

The data for these samples are shown in Table XXII and in Figure 37. In general the yield curves are the same as for the room temperature data indicating that the same processes occur at 3 hours of heating at 75°C as at room temperature. The yield of $S^+$ is higher than the $S^+$ yield at room temperature and the $S^0$ yield is lower than the $S^0$ yield at room temperature. The $S^-$ yield shows the same
TABLE XXII

Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed 3 Hours at 75.0 ± 0.5°C, Analysis by BaSO₄
Precipitation Method

Irradiated for 10 min at $1 \times 10^{12}$ neutrons/cm²/sec in ST-3C
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 3 hours at 75.0 ± 0.5°C
No light bleaching

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0 + S^-$</th>
<th>% $S^-$</th>
<th>% $S^0$</th>
<th>% $SO_3^- + SO_4^-$</th>
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Figure 37. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Watertown Irradiation, Annealed 3 Hours at 75.0 ± 0.5°C, Analysis by BaSO$_4$ Precipitation Method, No Light Bleaching
initial and final values as at room temperature, but the maximum is not as great. The important reactions are reactions (67) and (68) with a small contribution from reaction (69) only at 6.4 percent KBr. At compositions greater than 6.4 percent KBr, the relative importance of the reactions is the same as at room temperature.

(ii) Yield vs. Composition, Annealed 6 Hours at 75°C

The data are shown in Table XXIII and in Figure 38. The general shape of the yield curves is again the same as the data at room temperature and after 3 hours of heating at 75°C, indicating that the same processes are taking place. The $S^0$ and $S^-$ yields are slightly higher than for 3 hours of annealing and about the same as those for room temperature. The maximum in the $S^0$ yield and the minimum in the $S^-$ yield are more pronounced than at room temperature and at 3 hours of annealing. There is a minimum in the $S^0$ yield and a maximum in the yield of $S^+$ at approximately 50 percent KBr indicating that at this composition and later compositions, reaction (66) is important.

(iii) Yield vs. Composition, Annealed 12 Hours at 75°C

The data are shown in Table XXIV and in Figure 39. For these samples the initial values of all the yields are lower than for the previous annealing studies at 3 and 6 hours of heating. The same general shape of the yield curves indicates that the same reactions are taking place. The yield of $S^+$ increases very sharply after 6.4 percent KBr as the yield of $S^0$ decreases rapidly to a constant value at 30 percent KBr. The $S^-$ yield passes through a slight maximum at 13.5 percent KBr and then is independent of composition.
TABLE XIII

Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed for 6 Hours at 75.0 ± 0.5°C,
Analysis by BaSO₄ Precipitation Method

Irradiated for 10 min at $1 \times 10^{12}$ neutrons/cm²/sec in ST-3C
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 6 hours at 75.0 ± 0.5°C
No light bleaching

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Figure 38. Percent Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Watertown Irradiation, Annealed 6 Hours at 75.0 ± 0.5°C, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
TABLE XXIV

Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed for 12 Hours at 75.0 ± 0.5°C,
Analysis by BaSO₄ Precipitation Method

Irradiated for 10 min at $5 \times 10^{12}$ neutrons/cm²/sec in ST-3A
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 12 hours at 75.0 ± 0.5°C
No light bleaching

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<th>Mole % KBr</th>
<th>% $S^0 + S^-$</th>
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Figure 39. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Watertown Irradiation, Annealed 12 Hours at 75.0 ± 0.5°C, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
Some contribution from reaction (69) occurs at 6.4 percent KBr followed by a small effect from reaction (67) at 13.5 percent KBr. These reactions are complete at 20 percent KBr. The major reaction which occurs is reaction (68) and this is essentially complete above 30 percent KBr. The $S^-$ yield is greater than the $S^0$ yield above 13.5 percent KBr.

(iv) Yield vs. Composition, Annealed 24 Hours at 75°C

The data are shown in Table XXV and in Figure 40. Identical behavior to that for 12 hours of annealing is found for these samples. The same reactions take place and the values of the yields are not significantly different from those for 12 hours of annealing.

(v) Yield vs. Hours of Annealing at 75°C, Pure KCl

The data are taken from the yield vs. composition data for the various times of annealing and are shown in Figure 41. The yield of $S^+$ is fairly constant with a shallow minimum at 6 hours of heating after which the yield increases slowly and reaches a limiting value for 12 hours. The $S^0$ yield decreases slowly with increased time of heating and reaches a plateau value after 12 hours of annealing. The $S^-$ yield is constant until 3 hours of annealing then increases and passes through a maximum at 6 hours of heating, decreasing to a limiting value after 12 hours. Between 0 and 3 hours of annealing reaction (68) occurs to a small extent while between 3 and 6 hours of heating reactions (67) and (68) are important. After 6 hours of annealing there is no contribution from reaction (67) while reaction (69) contributes to the $S^0$ yield up until 12 hours of annealing at which time this reaction is complete. Reaction (68) also occurs between 6 and 12 hours of annealing and is complete after 12 hours.
TABLE XXV

Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed for 24 Hours at 75.0 ± 0.5°C,
Analysis by BaSO$_4$ Precipitation Method

Irradiated for 10 min at $5 \times 10^{12}$ neutrons/cm$^2$/sec in ST-3A
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 24 hours at 75.0 ± 0.5°C
No light bleaching

<table>
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<th>Mole % KBr</th>
<th>% S$^0$+S$^-$</th>
<th>% S$^-$</th>
<th>% S$^0$</th>
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Figure 40. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Watertown Irradiation, Annealed 24 Hours at 75.0 ± 0.5°C, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
Figure 41. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C, for Pure KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching.
(vi) Yield vs. Hours of Annealing at 75°C, 6.4 percent KBr

Data are taken from the yield vs. composition curves after the various times of annealing and are shown in Figure 42. The yield curves show the same trends as that for the pure KCl samples. The maxima and the minima in the $S^+$ and $S^0$ yields are more pronounced than those in the pure KCl and the maximum in the $S^-$ yield is absent. The $S^-$ yield increases only rather slowly to a slightly higher value after 24 hours of annealing. From 0 to 3 hours of heating reaction (68) occurs while from 3 to 6 hours of heating reaction (66) occurs. After 6 hours of heating the only reaction that takes place is reaction (68). The limiting values reached for all the yields after 24 hours of heating are the same as for the pure KCl annealed samples.

(vii) Yield vs. Hours of Annealing at 75°C, 13.5 percent KBr

Data are taken from the yield vs. composition curves at the various times of annealing and are shown in Figure 43. The curves are of the same shape as those for the preceding composition. Again the maxima and the minima in the $S^+$ and $S^0$ yields are more pronounced than the preceding composition. This indicates that between 0 and 3 hours of heating reaction (66) occurs to a greater extent than before and that between 0 and 6 hours of heating reaction (68) plays a more important role. After 6 hours of heating the $S^0$ yield decreases faster than for 6.4 percent KBr while the $S^+$ yield increases faster than for 6.4 percent KBr. The $S^-$ yield shows a slight maximum between 3 and 12 hours of heating, falling to a constant value after 12 hours of heating. Reaction (68) becomes the only important reaction at 6 hours of heating and is complete by
Figure 42. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 6.4 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching.
Figure 43. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at $75.0 \pm 0.5^\circ C$ for 13.5 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO$_4$ Precipitation Method, No Light Bleaching.
12 hours of annealing.

(viii) Yield vs. Hours of Annealing at 75°C, 21.4 percent KBr

Data are taken from the yield vs. composition curves for the various times of annealing and are shown in Figure 44. The data resemble the data for the preceding compositions and indicate that the same processes are taking place. The initial yields are lower by about 10% than the preceding data for 13.5 percent KBr. This occurs up to 12 hours of heating at which time the yields again are equal. Again the maxima and minima occur in the $S^0$ and $S^+$ yields; at this composition the same behavior is found for the $S^-$ yield. From 0 to 3 hours of heating reactions (69) and (68) take place. Reactions (66) and (67) occur between 3 and 6 hours of heating, with reaction (66) occurring to a greater extent than (67). Between 6 and 12 hours of annealing reaction (68) again occurs to a considerable degree but is complete after 12 hours of annealing. Reaction (69) begins to occur at 6 hours of heating and is complete by 12 hours of annealing. After 12 hours of annealing the $S^-$ yield is lower than the $S^0$ yield.

(ix) Yield vs. Hours of Annealing at 75°C, 38.6 percent KBr

The data are taken from the yield vs. composition data for the various times of annealing and are shown in Figure 45. The curves are of the same general shape as those for 21.4 percent KBr. The maxima and minima are not as pronounced as before indicating less competition between reactions (66) and (69) in the 0 to 6 hour heating range. The yields are lower than for the 21.4 percent KBr data for the lower oxidation states, but after 12 hours of heating
Figure 44. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 21.4 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
Figure 45. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 38.6 Mole Percent KBr in KC1, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
they are identical with those for 21.4 percent KBr. The same processes occur as those discussed for 21.4 percent KBr. The $S^-$ yield becomes greater than the $S^0$ yield after 4 hours of heating.

(x) **Yield vs. Hours of Annealing at 75°C, 59.0 percent KBr**

The data are taken from the yield vs. composition data for the various times of annealing and are shown in Figure 46. The data show the same general features as that for the preceding composition indicating that the same processes are taking place. The $S^0$ and $S^-$ yields are lower than those for 38.6 percent KBr.

(xi) **Yield vs. Hours of Annealing at 75°C, 85.0 percent KBr**

The data are taken from the yield vs. composition data for the various times of annealing and are shown in Figure 47. The data show that the same processes are taking place as in the previous composition. The maxima and minima in the various yields are more pronounced than in the preceding composition indicating greater contribution from these reactions. The yields are higher in the 0 to 12 hour region than for the 59.0 percent composition, but the same plateau values are reached after 12 hours of annealing.

c) **Thermal annealing at 215°C**

(i) **Yield vs. Composition, Annealed 3 Hours at 215°C**

The data are shown in Table XXVI and in Figure 48. The yield of $S^+$ goes through a maximum at 6.4 percent KBr, decreases to a minimum at 13.5 percent KBr, and then
Figure 46. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 59.0 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
Figure 47. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 75.0 ± 0.5°C for 85.0 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
TABLE XXVI
Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed for 3 Hours at 215 ± 2°C,
Analysis by the BaSO₄ Precipitation Method

Irradiated for 10 min at 1 x 10^{12} neutrons/cm²/sec in ST-3C
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 3 hours at 215 ± 2°C
No light bleaching

<table>
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<th>Sample</th>
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</table>
Figure 48. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Annealed 3 Hours at 215 ± 2°C, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
increases slowly with increasing composition. The yield of $S^+$ reaches a higher plateau value than at 75°C. This behavior is quite different than at 75°C. The $S^-$ yield is constant until 13.5 percent KBr, passes through a maximum at 21.4 percent KBr, and then decreases with increasing concentration of KBr. The $S^-$ yields at 215°C are about twice as high as 215°C as at 75°C for all compositions. The $S^0$ yield goes through a minimum at 6.4 percent KBr, passes through a maximum at 13.5 percent KBr, and then decreases rapidly to a constant value after 21.4 percent KBr. This behavior of $S^0$ was not observed at 75°C. Since the $S^-$ yield is constant up until 13.5 percent KBr, reaction (68) is important between 0 and 6.4 percent KBr, reaction (66) between 6.4 and 13.5 percent KBr, and reactions (67) and (68) from 13.4 to 21.4 percent KBr. At 21.4 percent KBr and at higher KBr concentrations, reaction (69) occurs with all the $S^0$ produced undergoing reaction (68) to yield $S^+$. 

(ii) Yield vs. Composition, Annealed 6 Hours at 215°C

The data are shown in Table XXVII and in Figure 49. The yield of $S^+$ behaves as after 3 hours of annealing, going through a maximum at 6.4 percent KBr, decreasing to a minimum at 13.5 percent KBr, and then slowly increasing to a limiting value at about 60 percent KBr. The $S^0$ yield is initially much lower than at 3 hours of heating and decreases to a minimum at 6.4 and 13.5 percent KBr, rising through a small maximum and then decreasing to a plateau value at about 60 percent KBr. The $S^-$ yield is initially higher than at 3 hours of heating, passes through a minimum at 6.4 percent KBr, then increases and passes through at maximum at 13.5 percent KBr, and then decreases
TABLE XXVII

Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed for 6 Hours at 215 ± 2°C,
Analysis by BaSO₄ Precipitation Method

Irradiated for 10 min at $1 \times 10^{12}$ neutrons/cm²/sec in ST-3C
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 6 hours at 215 ± 2°C
No light bleaching

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^0 + S^\equiv$</th>
<th>% $S^\equiv$</th>
<th>% $S^0$</th>
<th>% $SO_3^\equiv + SO_4^\equiv$</th>
</tr>
</thead>
<tbody>
<tr>
<td>144-8</td>
<td>0</td>
<td>64.0</td>
<td>47.9</td>
<td>16.1</td>
<td>36.0</td>
</tr>
<tr>
<td>145-8</td>
<td>6.4</td>
<td>46.0</td>
<td>42.6</td>
<td>3.4</td>
<td>54.0</td>
</tr>
<tr>
<td>146-8</td>
<td>13.5</td>
<td>51.3</td>
<td>47.9</td>
<td>3.4</td>
<td>48.7</td>
</tr>
<tr>
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<td>21.4</td>
<td>49.8</td>
<td>39.0</td>
<td>10.8</td>
<td>50.2</td>
</tr>
<tr>
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<td>38.6</td>
<td>29.9</td>
<td>29.0</td>
<td>10.9</td>
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</tr>
<tr>
<td>131-8</td>
<td>59.0</td>
<td>19.2</td>
<td>17.3</td>
<td>1.9</td>
<td>80.8</td>
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<tr>
<td>133-8</td>
<td>85.0</td>
<td>23.8</td>
<td>20.0</td>
<td>3.8</td>
<td>76.2</td>
</tr>
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</table>
Figure 49. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Annealed of 6 Hours at 215 ± 2°C, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
to a limiting value at about 60 percent KBr. From 0 to 6.4 percent KBr reaction (69) occurs to a small extent with reaction (68) predominating. Between 6.4 and 13.5 percent KBr, reactions (66) and (67) occur slowly increasing the S⁻ yield. From 13.5 to 21.4 percent KBr reaction (69) and reaction (68) occur in a manner such that the yield of S⁺ increases faster than the yield of S⁰. These reactions occur up to about 60 percent KBr at which time all reactions appear to have gone to completion. The reactions here are very similar to the ones that took place at 75°C except that the yield of S⁻ is much greater than the yield of S⁰. At 215°C the S⁺ yield increases mostly at the expense of the yield of S⁻ while at 75°C the S⁺ yield increases mostly at the expense of the S⁰ yield.

(iii) Yield vs. Composition, Annealed 12 Hours at 215°C

Data are shown in Table XXVIII and in Figure 50. Here the maxima and minima in the yield curves are absent in the KBr-rich region. The yields are initially lower than the corresponding yields at 75°C, but reach the same limiting values at about 60 percent KBr. The only reactions which are evident are reactions (68) and (69) with very little reaction occurring after 60 percent KBr.

(iv) Yield vs. Composition, Annealed 24 Hours at 215°C

Data are shown in Table XXIX and in Figure 51. The data looks very peculiar because of the reappearance of the maxima and minima in the yields in the 0 to 13.5 percent KBr region. A possible reason for this peculiarity may be that the irradiation conditions for the samples were varied as the composition changed. The samples from 0 to 21.4 per-
TABLE XXVIII

Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed for 12 Hours at 215 ± 2°C,
Analysis by the BaSO₄ Precipitation Method

Irradiated for 10 min at 5 x 10¹² neutrons/cm²/sec in ST-3A
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 12 hours at 215 ± 2°C
No light bleaching

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>% KBr</th>
<th>% S₀+S⁻</th>
<th>% S⁻</th>
<th>% S₀</th>
<th>% SO₃⁻+SO₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>144-9</td>
<td>0</td>
<td>42.3</td>
<td>29.0</td>
<td>13.3</td>
<td>57.7</td>
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<tr>
<td>145-9</td>
<td>6.4</td>
<td>37.6</td>
<td>27.3</td>
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<tr>
<td>146-9</td>
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<td>24.5</td>
<td>4.0</td>
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<td>127-9</td>
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<td>21.3</td>
<td>18.7</td>
<td>2.6</td>
<td>78.7</td>
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<tr>
<td>129-9</td>
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<td>15.7</td>
<td>15.5</td>
<td>0.2</td>
<td>84.3</td>
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<td>59.0</td>
<td>11.6</td>
<td>9.7</td>
<td>1.9</td>
<td>88.4</td>
<td></td>
</tr>
<tr>
<td>133-9</td>
<td>85.0</td>
<td>8.1</td>
<td>7.9</td>
<td>0.2</td>
<td>91.9</td>
<td></td>
</tr>
</tbody>
</table>
Figure 50. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Annealed 12 Hours at 215 ± 2°C, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
TABLE XXIX

Series III, Mixed KCl-KBr, Watertown (AMRA) Irradiation,
Annealed for 24 Hours at 215 ± 2°C,
Analysis by the BaSO₄ Precipitation Method

Irradiated for 10 min in ST-3C (1 x 10¹² neutrons/cm²/sec)ᵃ
and in ST-3A (5 x 10¹² neutrons/cm²/sec)ᵇ
Samples in evacuated quartz vials wrapped in aluminum foil
Thermally annealed for 24 hours at 215 ± 2°C
No light bleaching

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % KBr</th>
<th>% $S^{0}+S^{=}</th>
<th>% S^{=}</th>
<th>% S^{0}</th>
<th>% $SO_{3}^{=}+SO_{4}^{=}</th>
</tr>
</thead>
<tbody>
<tr>
<td>144-10ᵃ</td>
<td>0</td>
<td>44.2</td>
<td>38.2</td>
<td>6.0</td>
<td>55.8</td>
</tr>
<tr>
<td>145-10ᵃ</td>
<td>6.4</td>
<td>58.1</td>
<td>28.3</td>
<td>29.8</td>
<td>41.9</td>
</tr>
<tr>
<td>146-10ᵃ</td>
<td>13.5</td>
<td>47.8</td>
<td>44.6</td>
<td>3.2</td>
<td>52.2</td>
</tr>
<tr>
<td>127-10ᵃ</td>
<td>21.4</td>
<td>49.2</td>
<td>44.1</td>
<td>5.1</td>
<td>50.8</td>
</tr>
<tr>
<td>129-10ᵇ</td>
<td>38.6</td>
<td>12.3</td>
<td>11.5</td>
<td>0.8</td>
<td>87.7</td>
</tr>
<tr>
<td>131-10ᵇ</td>
<td>59.0</td>
<td>8.5</td>
<td>8.9</td>
<td>-</td>
<td>91.5</td>
</tr>
<tr>
<td>133-10ᵇ</td>
<td>85.0</td>
<td>7.2</td>
<td>7.1</td>
<td>0.1</td>
<td>92.8</td>
</tr>
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</table>
Figure 51. Percent Yield of Radiosulfur in Various Oxidation States vs. Composition of Mixed KCl-KBr, Annealed for 24 Hours at 215 ± 2°C, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
cent KBr were irradiated at one flux while the samples from 38.6 to 85.0 percent were irradiated at a different flux. Other than this difference, there is no reason to expect that the data should behave as shown in Figure 51. But because the curves are significantly different from other comparable curves, the data are not considered reliable.

(v) Yield vs. Hours of Annealing at 215°C, Pure KCl

The data are taken from the yield vs. composition data for various times of annealing and are shown in Figure 52. The general shapes of the yield curves are identical to those for the annealing of pure KCl at 75°C. The yield of $S^+$ increases slightly faster at 215°C than at 75°C, but the yield of $S^0$ decreases much more rapidly at 215°C than at 75°C. The yield of $S^-$ shows the same maximum after 6 hours of heating, but at 215°C the yield of $S^-$ becomes much higher than at 75°C. The main reactions occurring during annealing at 215°C are reactions (67) and (68) with reaction (67) being faster than (68). After 6 hours of annealing there is evidence for reaction (69) occurring, but this reaction goes to completion after 12 hours of annealing at 215°C.

(vi) Yield vs. Hours of Annealing at 215°C, 6.4 percent KBr

Data are compiled from the yield vs. composition data for various times of annealing and are shown in Figure 53. The general shapes of the curves are similar to those for the pure KCl mentioned above, except that from 12 to 24 hours of annealing the yield of $S^+$ decreases rather sharply while the yield of $S^0$ increases. This may be due to the peculiarity of the 24 hour annealing data mentioned in section (iv). Ignoring this 24 hour annealing data the
Figure 52. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 100 Percent KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
Figure 53. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 6.4 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
same general reactions are indicated as in pure KCl. The yield of $S^+$ slowly increases with annealing. The yield of $S^0$ decreases rapidly as the yield of $S^-$ increases and remains greater than the $S^0$ yield for the rest of the time of annealing.

(vii) Yield vs. Hours of Annealing at 215°C, 13.5 percent KBr

The data are taken from the yield vs. composition data at various times of annealing and are shown in Figure 54. The yield curves show the same behavior as in the previous composition and the 24 hour annealing data is again somewhat questionable. The curves indicate that the same processes occur as in pure KCl or in the 6.4 percent KBr solutions. The yield of $S^-$ again increases while the $S^0$ yield decreases with the $S^-$ yield remaining higher than the $S^0$ yield with heating.

(viii) Yield vs. Hours of Annealing at 215°C, 21.4 percent KBr

The data are taken from the yield vs. composition data for various times of annealing and are shown in Figure 55. The general shapes of the yield curves are the same as those in the preceding compositions except that the $S^-$ maximum and the $S^0$ minimum occur after 3 hours of heating. Again the yields after 24 hours of heating look peculiar. The same reactions appear to take place as in the previous compositions.

(ix) Yield vs. Hours of Annealing at 215°C, 38.6 percent KBr

Data are taken from the yield vs. composition data for the various times of annealing and are shown in Figure 56. The $S^+$ yield is constant up to 6 hours of heating
Figure 54. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 13.5 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
Figure 55. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 21.4 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO$_4$ Precipitation Method, No Light Bleaching
Figure 56. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 38.6 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
at which time it increases to a constant value at 12 hours of heating. The $S^-$ yield goes through a maximum after 3 hours of heating and then slowly decreases to a limiting value after 12 hours of annealing. The $S^0$ yield initially decreases and passes through a maximum at 6 hours of heating then decreases to a constant value after 12 hours. From 0 to 3 hours of heating reaction (67) is the only reaction occurring. Between 3 and 6 hours of annealing, only reaction (69) occurs. After 6 hours of heating, reaction (69) is complete; reaction (68) occurs and is complete after 12 hours. The yield of $S^+$ is higher than in the preceding compositions and the yield of $S^-$ is lower.

(x) Yield vs. Hours of Annealing at 215°C, 59.0 percent KBr

Data are taken from the yield vs. composition data for the various times of annealing and are shown in Figure 57. The curves of the yields are identical to those for the preceding compositions except that the yield of $S^+$ slowly increases initially instead of remaining constant. The $S^0$ and $S^-$ yields are initially lower than for the 38.6 percent KBr samples, but attain the same limiting values after 12 hours of annealing. The annealing reactions again appear to be complete after about 10 hours of heating. Also the yield of $S^0$ is practically zero after 6 hours of annealing.

(xi) Yield vs. Hours of Annealing at 215°C, 85.0 percent KBr

The data are taken from the yield vs. composition data for various hours of heating and are shown in Figure 58. The data are essentially the same as that for the preceding composition with the exception that the yield
Figure 57. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 \pm 2^\circ C for 59.0 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO$_4$ Precipitation Method, No Light Bleaching
Figure 58. Percent Yield of Radiosulfur in Various Oxidation States vs. Hours of Annealing at 215 ± 2°C for 85.0 Mole Percent KBr in KCl, Watertown Irradiation, Analysis by BaSO₄ Precipitation Method, No Light Bleaching
of S<sup>−</sup> reaches a maximum at 3 hours of annealing. The dis-
cussion for the 50-9 percent KBr samples applies for these
samples.

E. Discussion

This discussion will concentrate on the results for
the BaSO<sub>4</sub> precipitation method since the method is more
precise than the electrophoretic separations and the condi-
tions of irradiation and analysis are known. However,
mention will be made of results and conclusions that are
common to all sets of the samples regardless of the analysis
or irradiation conditions.

On the basis of the analysis of the results as given
in the foregoing section, the data can be explained fairly
well by the proposed hot-zone model on page 14. It should be
pointed out that reactions between the recoil species and
the more complex color centers such as R- and M-centers have
not been included in the model because the existence, struc-
ture, and behavior of these complex centers have not been
well established.

Damn and Tompkins<sup>90</sup> have studied the kinetics of the
thermal bleaching of V- and F-centers in X-irradiated KCl at
25°C. They concluded that the F-centers give up their trapped
electrons during optical and thermal bleaching and that the
electrons are captured by the V<sub>2</sub>-centers. From these studies
they suggested that optical and thermal bleaching occur by
the same mechanisms.

Kobayshi<sup>89</sup> found very little change in the concentra-
tion of F- and V-centers thermally annealed at 100°C. How-
ever, between 100°C and 200°C the F- and V-center optical
bands decrease with increasing temperature. At 225°C and
higher there was no evidence of any color centers. Harrison
found that F-centers can be destroyed by the application of
light of the F-band wavelength, liberating the trapped
electron. V-centers can also be destroyed by the applica-
tion of light of the V-band wavelength. Thus, it can be seen that the application of heat and light can destroy the F- and V-centers, liberating electrons and holes, respectively.

Looking now at the thermal annealing curves at 75°C and at 215°C for all the samples, it is seen that as the temperature is increased from 75°C to 215°C, the yield of $S^+$ increases, the yield of $S^0$ decreases, and the yield of $S^-$ increases. This is consistent with the above observations that as the temperature of annealing is increased the color centers are destroyed, thereby liberating holes and electrons which act as oxidizing and reducing agents. Thus, as the temperature is raised one can see that reactions (67) and (68) can take place. It is not known whether the recoil species reacts directly with the color centers or with the products of the destruction of the color centers.

\begin{align*}
S^0 + [F\text{-red}] & \rightarrow S^- \quad (67) \\
S^0 + [V\text{-oxd}] & \rightarrow S^+ \quad (68)
\end{align*}

It is difficult to ascertain from these data the actual effect of light exposure on the yield, since the conditions of the light exposure are not accurately known and since a complete series of light bleaching experiments was not carried out. Also, the data were taken with light exposure followed by thermal annealing and the two effects cannot be easily separated. Cifka\textsuperscript{14} has reported some interesting data concerning the light bleaching of $^{32}\text{P}$ recoils in KCl. For $P^{5+}$, $P^{3+}$, and $P^{1+}$, the quantity $[R_t - R_{oo}]/[R_o - R_{oo}]$ decreased with increasing time of photo annealing in the same manner that the concentration of F-centers decreases with increased time of light bleaching.
In the above expression, $R_t$ is the retention at time $t$, $R_0$ is the initial value of the retention, and $R_{\infty}$ is the retention at infinite time or at the limiting value of the annealing curve. The above ratio is the ratio of the amount of un-annealed species at time $t$ to the total amount of annealed material. This supports the idea that the $^{32}$P recoils in KCl react with the products of the destruction of the F-centers during the photo annealing.

Campbell and Butterworth\(^{17}\) have shown a direct relationship between the change of retention of $^{32}$P in the lower valance states in neutron irradiated KCl as a function of temperature and the change in the density of F-centers in proton irradiated KCl as a function of temperature. Their data, shown in Figure 59, suggest a distinct inverse correlation between $\Delta R$, the change in retention, and the effectiveness of F-center destruction at different temperatures, which is indirect evidence for the role of F-centers as the reducing agents of the $^{32}$P recoils.

It would be expected that such reactions would take place more easily by movement of the products of the destruction of the color centers, i.e., electrons and holes, to the recoil species where reaction would occur since the electrons and holes could more easily diffuse through the crystals than the recoil atoms or ions.

In all the samples the annealing reactions for the various oxidation states are almost nearly complete after 12 hours of annealing at both 75°C and 215°C. Also the extent of thermal annealing in the samples containing 38.5 percent KBr or greater is about the same at both 75°C and 215°C. That is, the values reached at the plateaus are the same at both temperatures and hence, one can say that annealing takes place faster in the KBr-rich solutions.
Figure 59. Change in Retention of $^{32}$P vs. Temperature of Annealing and the Change in Density of F-Centers in Proton Irradiated NaCl as a Function of Annealing Temperature.
The thermal annealing curves for the samples that were light bleached are very similar to the curves of the normal thermal annealing data shown in Figure 2. From this it would seem that the thermal annealing studies reported here fit the simple model of the recombination of initially correlated pairs.\textsuperscript{70,77,78} This simple model might be modified to include the fact that one of the members of this initially correlated pair is now a color center or the product of the destruction of a color center, and that this center is an unstable state. Thus, the activation energy necessary for the recombination may now be lower since one member of the pair is in a somewhat excited state or in an energy level in the crystal quite different from that of a normal lattice atom.

The thermal annealing curves for the samples that were not light bleached were markedly different from those for the light bleached samples. It may be that the light bleaching promoted recombination of the holes and electrons thereby decreasing the number of defects and reactive species which may undergo reaction upon thermal annealing. The effect of light then may have been to remove any unusual structure or defect configurations that would exist in a sample which was not light bleached. The maxima and minima in the annealing curves for the samples which were not light bleached reflect the various oxidation and reduction reactions taking place in the early stages of the annealing.

The maxima and minima in the $S^+$ yield are present at 75°C, but are largely absent from the data at 215°C. This behavior is not entirely new. Campbell and Butterworth\textsuperscript{17} noted similar oxidation followed by reduction in the lower valance states of $^{32}P$ in neutron irradiated KCl upon thermal
annealing. They found these processes to be present even at 263°C, but absent at 300°C. Cifka found similar results for the $^{32}$P recoils distribution in neutron irradiated KCl doped with 0.06 percent Ca$^{2+}$. Cifka proposed that the Ca$^{2+}$ induced more defects in the KCl and that these defects changed the behavior of the annealing of the recoil species in the samples. His data is shown in Figure 60. The data indicate that at some temperature between 210°C and 290°C the annealing curves do not show the oxidation and reduction behavior found at the lower temperatures.

The most intriguing results of these experiments are the behavior of the yields as a function of the composition of the mixed KCl-KBr at the various times of annealing. The $S^+$ yield at room temperature for the 10-40 minutes of light bleaching and for the no light bleaching data passes through a maximum at 6.4 percent KBr, a minimum at 13.5 percent KBr, and increases slowly to a plateau value. This unusual behavior is also evident from the thermal annealing curves. For the thermal annealing data at 75°C and at 215°C, the yield of $S^+$ goes through a minimum in the 6.4-13.5 percent KBr region.

The $S^-$ yields show a trend almost the opposite from that of the $S^0$ yield at room temperature for both the bleached and non-bleached samples. The samples light bleached for 10-40 minutes show maxima in the $S^-$ yield at 6.4 percent KBr followed by a general decrease to a constant value for annealing at both temperatures. The maximum at 13.5 percent KBr found at room temperature is absent for the annealed samples. The $S^-$ yields for the non-bleached samples exhibit behavior similar to the room temperature samples when the temperature is raised.
Figure 60. Thermal Annealing in KCl Doped with 0.06 Mole Percent Ca$^{2+}$ Data from (14)
The yield of $S^0$ as a function of composition generally passes through a maximum between 6.4 and 13.5 percent KBr regardless of the treatment. However, for all the samples annealed at 215°C the yield of $S^0$ is nearly constant for 12 and 24 hours of annealing.

At first this behavior seemed puzzling as it was initially expected that the curves would be smooth functions of the composition. However, a survey of the literature revealed that discrepancies have been noted in other properties of the mixed KCl-KBr in the 0 to 20 percent KBr region.

Kondo and Matsumoto\textsuperscript{108} studied the color centers in KCl-KBr mixed crystals in the visible region and found that a plot of the position of the F-band as a function of composition showed a maximum at 11.0 percent KBr. They concluded that the Br$^-$ ions were apt to locate around the cations surrounding the negative vacancy owing to the weaker binding force of Br$^-$ for the potassium ions than of chloride ions; so that small quantities of Br$^-$ ions may almost flock together around the vacancies and push the cations toward the vacancy site. They surmised that this may result in a decrease of the radii of the single negative vacancies in spite of the increase in the mean ionic distances, and that this may lead to the observed shift in wavelength of the F-band. This is suggesting that there appears to be a different type of defect of the F-center variety at this composition as compared to those of the pure KCl and other mixed crystals with higher KBr content.

Wallace and Flinn\textsuperscript{109}, and Wollam and Wallace\textsuperscript{110} have compared the X-ray densities and the pynometric densities of the KCl-KBr and the NaCl-NaBr solid solutions. In the KCl-KBr system a density difference of 1.2 percent was found for
30 percent KBr and a 1.9 percent density difference at 20 percent KBr. Similar data were also found for the NaCl-NaBr system with the density difference occurring in the 30-40 percent KBr region. The density difference was interpreted as due to an increased number of Schottky defects. They postulated that strains arising from the distribution of components of unequal size over a given set of lattice sites could be relieved if an occasional lattice site were left vacant. They concluded then that strains and defect concentrations would be greatest where larger ions attempt to fit themselves into a smaller lattice. Pauling\textsuperscript{110} gives the crystal radii of chloride and bromide ions as 1.81 and 1.95 Å respectively. Thus forcing a larger bromide ion into a potassium chloride lattice leads to a distortion of the lattice, introducing a larger number of defects in the process.

The fact that there may be more defects present in the mixed crystal than in the pure components prior to irradiation may lead to either an increased number of color centers produced upon irradiation or a new type of defect or color center produced at a particular composition upon irradiation.

Recently Wakita and Hiari\textsuperscript{111} have studied the intrinsic luminescence induced by X-rays in the KCl-KBr crystals at liquid helium temperature. They observed a band at 3420 Å which occurred in the composition range of 0 to 60 percent KBr with a maximum at 15 percent KBr. The luminescence intensity of the band is shown plotted against the mole percent of KBr in the sample in Figure 61. They postulated that this band in the luminescence spectra was due to a $V_K^-$-center which they suggest is a ClBr$^-$ complex.
Figure 61. Luminescence Intensity of $V_k$ Band in Mixed KCl-KBr vs. Mole Percent of KBr. Data from (11)
Thus, there is evidence to suggest that between 0 and 20 percent KBr in mixed KCl-KBr crystals, there are some peculiarities in the structure, number and type of defects produced in these crystals prior to and after irradiation. There are either a greater number of defects produced in this region or else there is a particular type of defect peculiar to this composition. It is quite possible that the effect of composition on the yields can be explained by these peculiarities. Assuming that the number of defects is greater and there are a larger number of V-centers such as ClBr\(^-\) at this composition; the results can be explained by the greater number of oxidizing defects in this region. Hence, in the region of 0 to 6.4 percent KBr reactions (66) and (69) are important. At 6.4 percent KBr reactions (67) and (68) are the only important reactions with possibly some contribution from reaction (66) in some cases. After 13.5 percent KBr reactions (69) and (68) are the reactions which take place. In the majority of the yield vs. composition curves there is very little change occurring after 40 percent KBr, indicating that these series of oxidations and reductions are peculiar to the sample in the low KBr region.

One effect which has not been investigated and could possibly influence the data is the possibility that as the KBr concentration is increased more isotopes of bromine will be produced in the samples. The bromine isotopes emit several gamma rays with energies between 0.2 and 0.8 Mev. It is possible that the gamma rays from the bromine isotopes could cause some radiation annealing. At present there seems to be no way in which to check if this is influencing the data. This effect may also depend upon how long the sample were stored before analysis and thus the extent of any possible radiation annealing would also be related to
this. The samples were analyzed in sets but the order of the sets was random as was the order of analysis of individual samples in the sets. The samples with the largest KBr content would receive the greatest amount of internal radiation.

The exact nature of the stabilized recoil $^{35}\text{S}$ species in the crystal is not known. If the $^{35}\text{Cl}$ ion underwent the $(n,p)$ reaction without perturbation of its orbital electrons, then the $^{35}\text{S}$ would be expected to appear as a $^{35}\text{S}^-$ ion. However, ionization due to the emission of the proton and the reorganization energy of the orbital electrons may occur. This may then raise the $^{35}\text{S}$ to the $^{35}\text{S}^-$, $^{35}\text{S}^0$, and possibly even higher oxidation states. Studies by Wexler$^{113}$ and Thompson and Miller$^{114}$ have shown that ionization can occur with proton and alpha particle emission. Thus, it might be expected that the $^{35}\text{S}$ atoms are present in the irradiated crystal initially in the oxidation states $^{35}\text{S}^0$ and $^{35}\text{S}^-$ with possibly some $^{35}\text{S}^+$. However, the actual stabilization of the $^{35}\text{S}$ occurs only when the recoil atom has lost the greatest part of its energy and this stabilization is then dependent upon the environment of the recoil atom as it dissipates its excess energy seems to be the predominating factor.

The experiments recorded here seem to support Maddock$^{12}$ and Willard$^{11}$ suggestion that the stabilized recoil species exist as $^{35}\text{S}^0$, $^{35}\text{S}^-$, and $^{35}\text{S}^+$. The $^{35}\text{S}^0$ is atomic sulfur and is assumed to be the precursor of the $^{35}\text{S}^0$ fraction. The $^{35}\text{S}^-$ species is considered to be the precursor of the $^{35}\text{S}^-$ fraction. This assignment leaves $^{35}\text{S}^+$ as the precursor of $^{35}\text{SO}_3^-$ and $^{35}\text{SO}_4^-$. Maddock$^{12}$ has pointed out that $^{35}\text{S}^-$ or $^{35}\text{S}^-$ can occupy only anionic sites in the lattice; interstitial sites are improbable because of the size of these ions. $^{35}\text{S}^0$ could probably occupy cationic, anionic, or interstitial sites,
while $S^+$ would be restricted to cationic and possibly interstitial sites. Maddock\textsuperscript{115} has indicated that since $S^+$ can be in cationic or intersitial sites, the precursor of $SO_3^{=}$ and $SO_4^{=} \text{may in actuality be } S^+ \text{ located in two different S-Cl}_x \text{ defects in the crystals (x being variable). Upon dissolution these two species react to give the } SO_3^{=} \text{ and } SO_4^{=}.$

\textbf{F. Suggestions for Future Work}

There is a large amount of work that could be undertaken to determine the types, structures, composition, and behavior of the various defects in KCl and KBr and their mixed crystals. Very little is known concerning the nature of the V-centers and their properties. Much of this type of data would have to depend upon the proper theoretical calculations before any valid conclusions could be made. Such data might include the kinetics of formation and of light and thermal bleaching, spectra, and accurate density measurements of the mixed crystals.

Thermo-luminescence studies on the mixed crystals might reveal additional information concerning the nature of the defects in the low KBr region of the mixed crystals. From the thermo luminescence data, the thermal activation energy for emission of the glow peak is found to be equivalent to the energy needed to release carriers from the trapping levels. Thus, this data would indicate the possible defects and at what temperature they would be available for reaction. This would be helpful in conjunction with neutron irradiations at lower temperature.

Low temperature neutron irradiations would be of interest since various defects are stable only at lower temperatures. Thus, one might find entirely different dis-
tributions of the recoil species if the samples were irradiated at liquid nitrogen or liquid helium temperatures. From the thermal annealing data for such irradiations the $\Delta R$ as a function of $1/T$ data could be investigated and this might say something about the activation energies for the annealing reactions.

A complete study of light bleaching should be undertaken. This would involve irradiation of the crystals with light of certain wavelengths for times from minutes to days. Samples could also be light bleached for days and then thermal bleaching experiments could be carried out. This would better establish the separate effects of thermal and light bleaching and the result could then be tied in with the work reported here.
SUMMARY

These experiments have shown that the composition of mixed crystals has a definite influence on the stabilization of the recoil species in mixed KCl-KBr. The suggestion that the defects which affect this stabilization are the F- and V-centers in the irradiated crystals is consistent with the results.

It has been found that the yield vs. composition data can be explained on the basis of the following reactions

\[ S^+ + [\text{F-red}] \rightarrow S^0 \] (1)

\[ S^0 + [\text{F-red}] \rightarrow S^- \] (2)

\[ S^0 + [\text{V-oxd}] \rightarrow S^+ \] (3)

\[ S^- + [\text{V-oxd}] \rightarrow S^0 \] (4)

Thermal annealing studies have shown that very little annealing takes place at 75°C except for the samples with low KBr content, i.e., for, 0-20 percent KBr. Increasing the annealing temperature to 215°C promoted reactions (2) and (3), increasing the \( S^+ \) and \( S^- \) yield and decreasing the \( S^0 \) yield. These observations are consistent with the known behavior of defects in alkali halides upon thermal annealing.

These data are also in agreement with the assignment of \( S^+ \), \( S^0 \), and \( S^- \) as the stabilized species and the precursors of the observed products. The exact distribution of these species in the crystal is not known. \( S^0 \) is believed to be the precursors of \( S^0 \), \( S^- \) the precursor of \( S^= \), and \( S^+ \) is left as the precursor of \( SO_3^- \) and \( SO_4^- \). The results indicate that
the distribution of $^{35}\text{S}$ among these oxidation states is influenced by the composition of the mixed KCl-KBr.

The data is not sufficient to determine whether or not the hot zone model applies to this system. The number of color centers is much greater than the number of hot atoms. Thus, a particular hot-zone may contain many color centers, but the distribution in the hot zone is not known. The color centers may be mobile enough to participate in chemical reactions even though they are outside of the hot zone.
LIST OF REFERENCES


