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CHEMICAL EFFECTS FOLLOWING THE  $S^{34}(n, \gamma)S^{35}$  REACTION IN GASEOUS SULFUR COMPOUNDS

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Berkeley, California

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Berkeley, California  
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IN GASEOUS SULFUR COMPOUNDS

Monte Lee Hyder  
(Ph.D. Thesis)

July 11, 1962

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Contents

Abstract . . . . .	v
I. Introduction	
A. General Considerations . . . . .	1
B. Molecular Breakup . . . . .	3
C. Types of Chemical Reaction . . . . .	9
II. Experimental Procedure	
A. Sample Containment and Irradiation . . . . .	12
B. Monitoring the Neutron Flux . . . . .	13
C. Radiation Damage . . . . .	15
D. Chemical Preparations . . . . .	15
E. Chemical Separations . . . . .	16
F. Counting Techniques . . . . .	19
III. Results	
A. Errors . . . . .	25
B. Experimental Data . . . . .	26
C. $H_2S$ . . . . .	26
D. $SO_2$ . . . . .	43
E. $SF_6$ . . . . .	44
F. $CH_3SH$ . . . . .	45
G. $C_4H_4S$ (Thiophene) . . . . .	45
IV. Discussion	
A. Breakup . . . . .	46
B. Products of Breakup . . . . .	47
C. Epithermal Reactions . . . . .	48
D. Reactions in $H_2S$ . . . . .	49
E. Reactions in $SO_2$ . . . . .	51
F. Reactions in $SF_6$ . . . . .	53

G. Reactions in Organic Molecules . . . . .	54
H. Summary . . . . .	55
Acknowledgments . . . . .	56
Footnotes and References . . . . .	57

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ABSTRACT

The chemical behavior of  $S^{35}$  formed by  $S^{34}(n,\gamma)$  has been studied in gaseous  $H_2S$ ,  $SO_2$ ,  $SF_6$ ,  $CH_3SH$ , and thiophene. The reaction was carried out by sealing the gases in quartz ampules and irradiating them with thermal neutrons in the LPTR reactor. Among the effects studied were those of pressure, surface area, and additive gases including argon, nitric oxide, oxygen, and hydrogen.  $S^{35}$  was recovered both in gaseous compounds and in deposits on the walls of the ampules; the chemical compositions of both portions of activity were determined by carrier techniques and aqueous chemistry. The results support a model in which the original molecule is broken up in the recoil process and the resulting fragments containing  $S^{35}$  react with the surroundings only after they have slowed to thermal energies; in general the final chemical form of the  $S^{35}$  is determined by the chemical environment in which the  $S^{35}$  is produced rather than by its original oxidation state or chemical form. An exception to this was the results obtained with added nitric oxide, which suggest that the original molecule may not be completely broken up in all cases.



Also, in solid and liquid systems great complications are introduced into these chemical reactions because the energy of the original recoiling species is quickly distributed to its nearest neighbors by collision. These neighbors in turn restrict the recoil to a region near its origin, so that it becomes one of a closely associated group of atoms or radicals that may then proceed to react with one another. The resulting very complex reaction systems have been widely studied.<sup>4</sup> In order to study the reactions of the "hot" species with thermal surroundings, it is necessary to work in the gaseous phase, in which the mean free path is large--at least of the order of thousands of angstroms--so that collisions are widely separated.

A wide variety of reactions of this type has been studied in the gas phase. These studies have generally involved the reactions of the recoil species with organic compounds of various types. In general some incorporation of the recoil into the organic system is observed, but the complexity of the products increases rapidly with the complexity of the system, and it is often impossible to arrive at a specific mechanism for a reaction. Among the isotopes used in these reactions are  $C^{11}$  (Ref. 5) and  $N^{13}$  (Ref. 6) produced in high-energy nuclear reactions;  $C^{14}$  formed by  $N^{14}(n,p)C^{14}$ ;<sup>7</sup> halogen activities formed by neutron capture;<sup>8</sup> and tritium, usually formed by  $He^3(n,p)T$ .<sup>9</sup> The last two cases have been particularly well studied, and have led to the characterization of reactions resulting from the high kinetic energy of the recoil<sup>10</sup> or from its ionization.<sup>11</sup>

The results obtained from relatively simple systems such as halogens or tritium suggested the extension of studies of this type to an isotope which forms more complex molecules, in which there are several bonds to be broken and in which several stable oxidation states exist. Sulfur is virtually the only element with these properties that is contained in a variety of compounds which are gaseous at ordinary temperatures.

The most convenient radioactive isotope of sulfur,  $S^{35}$ , may be formed by thermal neutron capture in  $S^{34}$ . The latter isotope is 4.2% abundant in natural sulfur,<sup>12</sup> and has a capture cross section of 0.26

barn.<sup>13</sup>  $S^{35}$  decays by emitting  $\beta^-$  particles with maximum energy 0.167 MeV; the half life is 87 days. No gamma radiation accompanies decay.<sup>12</sup>

The reactions of  $S^{35}$  produced by  $Cl^{35}(n,p)$  have been reviewed by Herber.<sup>14</sup> These have generally been carried out in solid or liquid systems. In crystalline systems it has been demonstrated that the preparation and condition of the crystal are very important, as the sulfur is easily oxidized in these trace amounts. The experiments of Herber have been interpreted as showing that ionization or other immediate effects of the nuclear reaction are not important in determining the final oxidation state of the  $S^{35}$ , but that this is dependent on the nature of the material in which it is formed.<sup>14</sup> A single experiment using the  $S^{34}(n,\gamma)$  reaction in gaseous  $H_2S$  was carried out by Willard et al.<sup>15</sup>

In this study the reactions of  $S^{35}$  produced by thermal neutrons with natural sulfur were investigated by using  $H_2S$ ,  $SO_2$ ,  $SF_6$ ,  $CH_3SH$ , and thiophene as sources of sulfur. These materials furnish the sulfur in all its oxidation states and in a series of molecules of varying complexity. Attempts were made to answer the following questions:

What is the extent of molecular breakup, and how is it affected by the complexity of the original molecule?

What kinds of reaction take place following breakup, and are the reactions dependent on the kinetic energy of the recoil?

When does oxidation or reduction take place?

#### B. Molecular Breakup

The amount of breakup of the original molecule following a nuclear reaction has been the subject of discussion and experiment since the early attempt of Suess to determine this quantity.<sup>16</sup> Various investigators have studied break-up following beta decay<sup>17</sup> and isomeric transition,<sup>18</sup> as well as neutron capture.<sup>19</sup> Although the energy of recoil from nuclear de-excitation by a single  $\gamma$  ray following neutron capture would be many times chemical bond energies, several factors increase the probability that the atom receiving the impulse will not

break all its bonds. First, there is the tendency, at energies not greatly above bond energy, for the molecule to recoil as a whole rather than dissociate. Second, the de-excitation of the nucleus generally takes place through a cascade of  $\gamma$  rays. Since, by Eq. (1), the energy of the recoil is proportional to  $E_{\gamma}^2$ , this lowers the total momentum given to the nucleus, and the emission of radiation in opposing directions may further lower the resultant momentum. Finally, in complex molecules, the energy may be distributed among the bonds in such a way that only some of them are broken.

The first two points have been treated experimentally and theoretically by other authors, and their findings are applied to the  $S^{35}$  case in the following pages. The third is an unsolved problem, difficult to calculate; it was hoped that this work would shed light on it.

The problem of the tendency of the molecule to recoil as a whole was first considered by Suess,<sup>16</sup> who estimated that the fraction  $S$  of the recoil energy available for bond breakage was given by

$$S = M_2 / (M_1 + M_2) \quad (2)$$

for a diatomic molecule, where  $M_1$  is the mass of the atom undergoing nuclear reaction, and  $M_2$  is the mass of the substituent atom bonded to it. Hsiung and Gordus have attempted to calculate this quantity more exactly, by the use of approximate interatomic potentials.<sup>17</sup> These authors determine explicitly the contribution to the vibrational and rotational energy of the molecules resulting from an impulse given to one atom. Unfortunately they have worked this out in detail for only that case in which the atom given the impulse is singly bonded to the remainder of the molecule, though in Hsiung's thesis<sup>20</sup>  $CO_2$  is considered. The calculations by these authors, like those by Suess, suggest that an increase in the mass of the substituent group increases the probability of breakup; their  $S$  values are in the range of 10 to 40% lower than those given by the Suess formula. It should be noted that the  $S$  factor for hydrogen is much lower than for other covalently

bonding substituents; for a S-H bond it is 0.028, from Eq. (2).

The problem of calculating the cancellation of momenta due to the emission of multiple  $\gamma$  radiation demands a very detailed knowledge of the decay scheme of the excited state formed by neutron capture. One must know what levels are populated, and in what ratio; what the lifetimes for the various transitions are; and what angular correlation exists among the various radiations. This large amount of information is not generally available for cases of neutron capture; for  $S^{34}(n,\gamma)$  the only information available is the total energy of the  $\gamma$  rays, which is 6.98 MeV.<sup>21</sup> This is because the radiation from  $S^{32}(n,\gamma)$  greatly predominates when the radiations from sulfur in its natural isotopic ratio are studied.<sup>22</sup>

It may be demonstrated, however, that it is improbable that a molecule containing  $S^{34}$  will remain intact following neutron capture. The following calculation, although based on a hypothetical decay scheme, considers each of the factors involved and shows its effect on the dissociation of the molecule.

The most reasonable assumption it is possible to make about the  $\gamma$  rays emitted by  $S^{35*}$  formed by  $S^{34}(n,\gamma)$  is that they are similar to those from  $S^{32}(n,\gamma)$ , as shown in Fig. 1. Both nuclei have the same spin both before neutron capture (spin 0) and after (spin 3/2); the only difference is a pair of added neutrons in  $S^{34}$ .<sup>12</sup> In each case the excited state formed by neutron capture must have spin 1/2.

The following assumptions are derived from this analogy:

(a) Most of the nuclei decay by the emission of one or more  $\gamma$  rays of several MeV, such as the 5.46-MeV  $\gamma$  ray that occurs in 84% of the cases in  $S^{32}(n,\gamma)S^{33}$ .

(b) The  $\gamma$  rays emitted are predominantly of low multipolarity. This appears likely, since the total spin change between the uppermost state and the ground state is small, and this type of de-excitation proceeds very rapidly if allowed at all.

The second assumption is important in that for the momenta from several  $\gamma$  rays to counteract one another, they must be emitted in a time that is short compared with molecular vibrations. For the molecules of interest here this implies that the interval between radiations

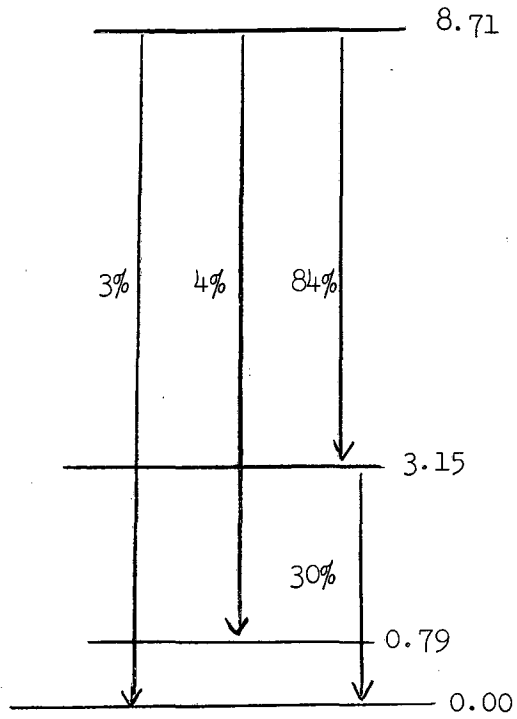


Fig. 1. Decay scheme for radiations from  $S^{32}(n,\gamma)S^{33}$  (Ref.22).

Gamma rays of  $E < 2.5$  MeV were not resolved. Other  $\gamma$  rays were observed but not assigned.

should not be greater than about  $10^{-14}$  sec; this will be the case for E1 radiations with energy greater than about 400 keV.<sup>23</sup>

It should also be noted that in the likely decay schemes of this type, the theoretical, maximum anisotropy between two successive  $\gamma$  rays may be determined from published tables as 20% (for spins 1/2, 3/2, 3/2 in the states connected by the transitions).<sup>24</sup> This anisotropy is neglected here.

It may be readily determined from Eq. (1) that if there is one  $\gamma$  ray emitted in the de-excitation process which has an energy of the order of half the total energy of the excited state, it cannot be effectively counterbalanced by multiple gamma emissions. This is due to the  $E_{\gamma}^2$  term in the energy expression. To counteract one large  $\gamma$  ray, another of comparable magnitude is required. The case of this type which would be expected to give a maximum amount of cancellation of momentum is that of two equally energetic  $\gamma$  rays in succession, as represented in Fig. 2. Dissociation resulting from this artificial case, constructed to minimize dissociation, can be calculated as follows for the H-S bond in  $H_2S$ , which has the highest Suess factor and is therefore the least likely to dissociate:

The HS-H bond energy is 4.13 eV,<sup>25</sup> and the Suess factor is 0.028 (neglecting the second H), so that by Suess' assumption 149 eV is required to break a bond. Each of the two  $\gamma$  rays imparts an energy of 188 eV to the nucleus. Campbell has given formulas based on random-walk theory for determining what percentage of the time a series of randomly oriented impulses will sum below a certain value;<sup>26</sup> from his equations the fraction of the time that the two 188-eV impulses sum to less than 149 eV can be calculated as

$$\frac{1}{4} \frac{(149)^2}{(188)^2} = 0.16,$$

so that even here 84% of the molecules will break up. Since this is an artificial case constructed to minimize dissociation, and since

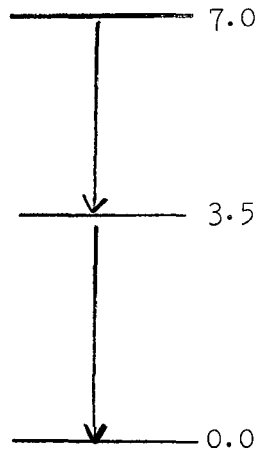


Fig. 2. Hypothetical decay scheme for the  $\gamma$  radiation from  $S^{34}(n,\gamma)S^{35}$ . (Constructed to minimize molecular dissociation.)

the Suess factor in other molecules is an order of magnitude higher, it is clear that dissociation is generally to be expected.

The extension of these considerations to more complex molecules is complicated by two factors. It has been suggested that energy could be distributed through a complex molecule by vibration, so that part of the energy goes into bonds that do not involve the atom receiving the impulse.<sup>19</sup> This would lower the energy available to bonds that do involve the latter atom. It also seems possible that, when an atom bonded to several substituents is given an impulse, some of the substituents would receive excess kinetic energy on dissociating. Thus less energy would be available to break the remaining bonds. Both these processes would tend to reduce the amount of total breakup; how important their effects may be is not yet clear. Gordus and Hsiung, in studies of organic halides, attributed deviations between their calculated breakup values and their experimental data to the first factor;<sup>19</sup> the second has been little studied. The assumption by Hsiung that one bond of two equivalent bonds receives  $3/4$  of the energy on the average<sup>20</sup> would seem to need further confirmation.

It should be noted that there is an important problem in correlating experimental results with calculations of this type. Experiments can be expected to show more dissociation than is suggested by above considerations, since molecules that are not excited sufficiently to dissociate at once may still be highly reactive owing to vibrational or kinetic energy given to them by the recoil process. For this reason calculations of the type given above can only suggest an upper limit for the chances of survival of the original molecule.

### C. Types of Chemical Reaction

It would be very desirable, for the purpose of interpreting experiments, to know the nature of the primary products of molecular breakup, but unfortunately they can at present only be inferred. Since the energetic requirements for bond breakage are generally much less than those of ionization in the  $S^{35}$  systems, and the process of breakup



is relatively slow compared with electron motion, one would expect the dissociation products to be atoms or radicals. Ionization, if it occurred, would be chiefly due to internal conversion of the  $\gamma$  rays emitted. Snell and Pleasanton have shown that this process, and the Auger processes associated with it, can produce highly charged ions with great efficiency.<sup>18</sup> However, if the de-excitation takes place through  $\gamma$  rays of low multipolarity, as expected (IB), the fraction of events converted should be negligible.

The recoil energy alone would not be expected to produce ionization of the recoil sulfur after dissociation. According to the theory of Bohr,<sup>27</sup> ionization of recoiling atom by its passage through matter becomes probable only when the recoil velocity approaches that of the most loosely bound electron. For a sulfur atom this is 664 keV.<sup>28</sup>

If the reaction is one involving radicals, it is possible to influence the reaction by the addition of a radical scavenger. These substances are themselves generally radicals, which react with and remove from the system whatever radicals are produced. The further course of the reaction then depends on the behavior of the resulting compounds. In this work nitric oxide, NO, was added to the systems in which the effect of a radical scavenger was of interest.

If ionization should occur, then ion-molecule reactions would become possible. These reactions have been observed to have high cross sections,<sup>29</sup> and have been postulated to explain a wide variety of radiation-induced reactions.<sup>30</sup>

Ion-molecule reactions are difficult to identify as such from chemical evidence. The usual technique consists of adding to the system a substance that is nonreactive but has an ionization potential near that of the suspected ion. The charge exchange that results neutralizes the ions before they can react chemically. No special studies of this type were made in this work, but whenever it was possible to draw inferences concerning such reactions it was done.

It has been postulated that some reactions of recoil atoms can take place before they have been slowed to thermal energies by collision. These reactions can be distinguished, according to Estrup and Wolfgang,<sup>10a</sup> by the addition of an inert gas, with which the

recoil atom collides and thus is slowed without reacting. These reactions are postulated as occurring for recoil energies of 2 to 20 eV. Thus the yield of these "hot" or "epithermal" reactions decreases as the fraction of inert gas increases. These reactions can, of course, be distinguished only when they do not occur in the thermalized system. Several such cases have been reported.<sup>10</sup>

A search was made for this type of reaction in the  $H_2S$  and  $SO_2$  systems, with argon as a moderator.

If reactions in the gas phase do not proceed rapidly, the dissociation products may diffuse to the walls and react with materials adsorbed there. The amount of oxygen or water that can be adsorbed on the wall of a quartz tube is considerably greater than the amount of material that actually undergoes nuclear reaction, so that reactions of this type may be very important.<sup>31</sup> Also, reactions that are unlikely in the gas phase because they require the presence of a third body take place readily at the walls. This type of reaction is believed to be important in some of the systems studied in this work. Such reactions have also been reported for recoil carbon atoms.<sup>32</sup>

A method used in this work for studying surface effects was to pack some of the sample tubes that were to be irradiated with quartz wool. It was estimated, from measurements of the diameters of the quartz fibers and of the total weight of quartz wool used, that this increased the total amount of surface within the tube by a factor of ten, as well as greatly decreasing the average time required for a molecule to diffuse to a surface.

## II. EXPERIMENTAL PROCEDURE

### A. Sample Containment and Irradiation

All irradiations were carried out in cylindrical quartz tubes approximately 7 cm long and from 8 to 18 mm in diameter. The tubes were filled through a small tube (2 to 3 mm o.d.) on one end which could then be sealed with a torch and could readily be broken open after irradiation. The tubes were cleaned by repeated washing with distilled water before they were sealed by deKhotinsky cement to the vacuum line. They were then further treated by heating to a red heat with a torch while under vacuum, in the hope of removing as much water and other materials as possible from the walls. Gases were added through the vacuum line, and were frozen in the bottom of the tube with liquid nitrogen to protect them from the heat while the seal was being made. The volumes of the tubes were determined before use by weighing them empty and filled with water.

Protective shields shaped from foils of 7- or 10-mil aluminum were taped around the break-off capillary before the samples were sent to the reactor for irradiation.

All irradiations were carried out at the chemistry thermal facility of the Lawrence Radiation Laboratory LPTR (Livermore Pool Type Reactor) at Livermore, California. Access to this facility is possible only when the reactor is not operating, and only 16-hour irradiations could be carried out. The thermal neutron flux available ranged from  $10^{11}$  to  $10^{12}$  neutrons per  $\text{cm}^2$  per sec. The high cross section for the production of  $\text{P}^{32}$  by the reaction  $\text{S}^{32}(\text{n},\text{p})$  with neutrons of energy greater than 1 MeV made it necessary to exclude fast neutrons. The fast-neutron flux was monitored by determining the amount of  $\text{P}^{32}$  produced, as described below.  $\text{P}^{32}$  and traces of  $\text{P}^{33}$  were the only contaminating activities expected or found in the course of this work.

The work described here was all done by irradiating at neutron fluxes in the range 1 to  $5 \times 10^{11}$   $\text{n}/\text{cm}^2/\text{sec}$  for bombardment times of approximately 16 hours. Convenient temperature control of the sample was not possible, but the facility is water-cooled, and the temperature during irradiation was estimated to be 35 to  $40^\circ \text{C}$ .<sup>32</sup>

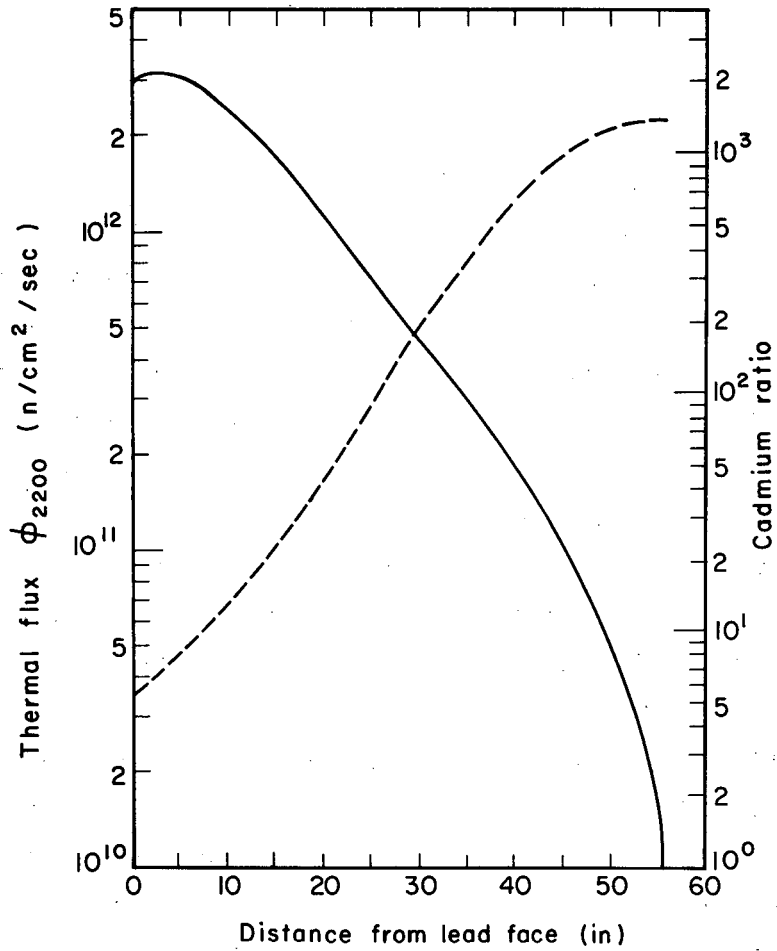
Ordinarily 10 to 20 tubes were irradiated simultaneously and stored for approximately 1 week before any handling, because of the high radiation level from the tubes and their shielding. Each was then placed in the vacuum line, opened with a magnetic plunger, and analyzed. To complete the analysis of a large number of samples required several months, but no effects dependent on the time interval between irradiation and analysis were noted.

#### B. Monitoring the Neutron Flux

Although most of the data reported are based only on the activity actually recovered in a given sample, experiments were carried out to determine the neutron flux and amount of activity induced in the samples.

The principal problem involved is indicated in Fig. 3, which shows the neutron flux as a function of position in the LPTR thermal facility. The large changes in flux over a distance of a few centimeters introduce considerable error in monitoring.

Monitoring was carried out as follows: gold foils of about 1/2 mg weight were weighed on a microbalance to  $\pm 5 \mu\text{g}$ . These were taped to the sample tubes before irradiation, and also to small tubes containing  $(\text{NH}_4)_2\text{SO}_4$  which were included in the irradiation. After irradiation the  $\text{Au}^{198}$  activity induced in each of the foils by the reaction  $\text{Au}^{197}(n,\gamma)$  was determined by counting them on a calibrated end-window beta proportional counter. The ammonium sulfate tubes were broken open in an alkaline  $\text{H}_2\text{O}_2$  solution, so that all  $\text{S}^{35}$  would be converted to  $\text{SO}_4^{=}$ . The  $\text{S}^{35}$  activity was then precipitated as  $\text{BaSO}_4$ , and converted to  $\text{SO}_2$  for counting as described below. The fast-neutron flux was also determined by adding carrier  $\text{PO}_4^{=}$  to this solution, and precipitating  $\text{Mg}(\text{NH}_4)\text{PO}_4$  for counting. The  $\text{Au}^{198}$  activity was used to determine the flux received by the tubes relative to the  $(\text{NH}_4)_2\text{SO}_4$  standard. In some cases absolute measurements of the  $\text{Au}^{198}$  activity were made by  $4\pi$  beta counting, and satisfactory agreements with the published relative cross sections were obtained.<sup>13</sup>



MU-27349

Fig. 3. Neutron characteristics as a function of position, west thermal column, LPTR reactor. (Prepared by LPTR Reactor Group)

———— Thermal flux  
----- Cadmium ratio

The variations in flux observed between individual foils in a particular irradiation amounted to as much as a factor of three in some cases. Foils placed on the same sample tube a few centimeters apart often differed by 30 to 50%. For this reason it was difficult to assign the flux to a tube. Results of attempts to calculate the activity expected in a sample from the neutron flux are recorded in Tables I through XVI as the ratio of activity recovered to activity calculated, R/C.

The  $P^{32}$  activity was found to be 2% or less of the  $S^{35}$  activity in all irradiations. Thus the fast-neutron flux was shown to be low, and contamination by this activity not important.

#### C. Radiation Damage

The gross radiation level in the region of irradiation was estimated by the reactor physicists as about  $5 \times 10^5$  roentgens per hour. This would result in radiation damage to the sample considerably less than 1%.<sup>33</sup> Observation that recovery of the original chemical form of the sample was always essentially complete and that there were no perceptible amounts of volatile products ( $O_2$ ,  $H_2$  etc.) indicates that no gross radiation damage occurred. Trace amounts of radiation-produced species might, however, be very important in the reactions of the  $S^{35}$ , which is itself present in very small amounts.

#### D. Chemical Preparations

Most of the gases used were Matheson cp grade, and were used without further purification. It was, however, necessary to purify Matheson nitric oxide from other nitrogen oxides by distilling it from a bulb immersed in a  $CO_2$ -trichloroethylene bath. Methyl mercaptan was obtained from the American Oil Co. Chemical Division, Lamarque, Texas, and was used without further purification, as was thiophene obtained from Eastman Organic Chemicals Division.  $H_2S$  enriched in

deuterium was prepared by reaction of  $\text{Al}_2\text{S}_3$  with 99+%  $\text{D}_2\text{O}$  obtained from the Stuart Oxygen Co. Unfortunately it was later found by mass spectrometric analysis that this " $\text{D}_2\text{S}$ " had been contaminated with normal hydrogen during preparation or handling and contained only 45% deuterium during irradiation.<sup>34</sup>

#### E. Chemical Separations

The activity was recovered in two fractions: gaseous activity, and activity recovered from the wall of the sample tube. All chemical separations were carried out in aqueous solution. Carriers were added to the samples as early as possible to avoid loss of trace amounts of species containing activity. The small amount of material that could be accommodated in the counter and the desire to maintain high specific activities limited the amounts of carriers used to those which would give 5 to 50 mg of precipitate.

Most of the separations involved only  $\text{S}^-$ ,  $\text{SO}_3^-$ , and  $\text{SO}_4^-$ . It is known that at room temperature the exchange rate in solution is negligible for these species.<sup>35</sup> Elemental sulfur in trace amounts exchanges with and appears as  $\text{S}^-$ ; <sup>35</sup> this fact was made use in analysis. Mercaptan was the only other material analyzed, as described below. Other compounds appear as their hydrolysis products or as materials with which they exchange; thus  $\text{SF}_4$  hydrolyzes to  $\text{SO}_3^-$ ,<sup>36</sup> and  $\text{H}_2\text{S}_2$  appears in the  $\text{S}^-$  fraction.

#### General Separation Procedure

When  $\text{S}^-$ ,  $\text{SO}_3^-$ , and  $\text{SO}_4^-$  were all to be determined in the same sample, sample and carriers were introduced into a de-aerated alkaline solution connected in a gas train with absorbing vessels.  $\text{CuCl}_2$  solution was added to precipitate  $\text{CuS}$ . The solution was then acidified with  $\text{HCl}$ , and argon gas was bubbled through to carry the  $\text{SO}_2$  evolved into an absorbing vessel containing alkaline  $\text{H}_2\text{O}_2$ , where it was absorbed and oxidized to  $\text{SO}_4^-$ .  $\text{CuS}$  was filtered off,

and the  $\text{SO}_4^{=}$  solutions were precipitated as  $\text{BaSO}_4$ . In many cases it was necessary only to analyze for two of the components, and the process was simplified accordingly.

#### Analysis of Activities from the Tube Walls

The sample tube was removed from the breaking vessel and crushed with a mortar and pestle under a solution containing  $\text{S}^{=}$ ,  $\text{SO}_4^{=}$ , and sometimes  $\text{SO}_3^{=}$  carriers. The pieces of tube were allowed to remain in contact with the solution for approximately 15 min before they were filtered off; the analysis was then made as described above. Where  $\text{SO}_3^{=}$  was to be determined it was necessary to carry out all operations in a glove box containing a nitrogen atmosphere to avoid oxidation of this carrier. When only the total amount of activity on the tube walls was to be determined, the tube was broken with sulfate carrier under an alkaline solution of  $\text{H}_2\text{O}_2$ .

Active sulfur on the walls was recovered as sulfide by the exchange with carrier sulfide mentioned. Some attempts were made to recover sulfur directly for counting or ignition by extracting it with benzene and evaporating the benzene. These were unsuccessful, as the low surface tension of the benzene caused it to spread during volatilization and to disperse the sulfur carrier, so that the latter could be counted or recovered only with great difficulty.

It was not possible to determine by direct counting if any activity remained on the walls after washing, as activated trace impurities in the quartz caused too high a background. Studies of the activity removed by successive washings and comparison of results from sample tubes washed by different solutions indicated that the techniques used removed this activity essentially completely.

#### Analysis of Gaseous Samples

Gaseous samples were recovered from the methane counting gas by passing the mixture through a U-tube trap packed with quartz wool and cooled by liquid nitrogen. They were put into solution either by bubbling with argon carrier gas into alkaline solution or by freezing



with liquid nitrogen into a vessel containing a frozen solution, which was then allowed to thaw. Mercaptans were determined by addition of the sample to a saturated  $\text{HgCl}_2$  solution, to form the precipitate  $\text{Hg}(\text{CH}_3\text{S})\text{Cl}$ , after removing  $\text{H}_2\text{S}$  by exposing the sample to a  $\text{CuCl}_2$  solution.<sup>37</sup> It is probable that trace amounts of other mercaptan activities coprecipitate with the methyl mercaptan salt.

The determination of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  activities in the same sample was complicated by the reaction of the two compounds with each other, producing water and sulfur. This was found to be catalyzed by the walls of the vacuum line when the two gases were frozen together. The analyses were therefore carried out by adding the two materials to solution with as little intermediate handling as possible. This was at least partially successful in that activity could be recovered in both fractions in many cases; but one could never be sure that some of the activity that was originally present in trace amounts was not lost in handling before the addition of carrier.

In some of the gaseous samples a check on the identification of the gaseous activity was possible by determining the specific activity of the gas before and after chemical separations. This technique was used to show that the gaseous fraction of the activity from irradiated  $\text{SO}_2$  was entirely  $\text{SO}_2$  and that most of the activity from irradiated  $\text{H}_2\text{S}$  was carried by  $\text{H}_2\text{S}$ . In the more complex organic systems, it was not possible to account for all the activity in this manner.

The  $\text{BaSO}_4$  and  $\text{CuS}$  precipitates were converted to  $\text{SO}_2$  for counting by ignition with red phosphorous in an oxygen atmosphere, as described by Merritt and Hawkings.<sup>38</sup>

Standardized carriers were used throughout this work. Where measurable amounts of  $\text{SO}_3^-$  were oxidized to  $\text{SO}_4^-$ , this was corrected for on the basis of the known specific activity of  $\text{SO}_3^-$  and the weights of precipitates recovered. Loss of material for any other reasons, such as incomplete precipitation or by sulfite-sulfide reaction, was similarly corrected for. Once routine techniques were developed, these corrections were usually no more than 10%.

#### F. Counting Techniques

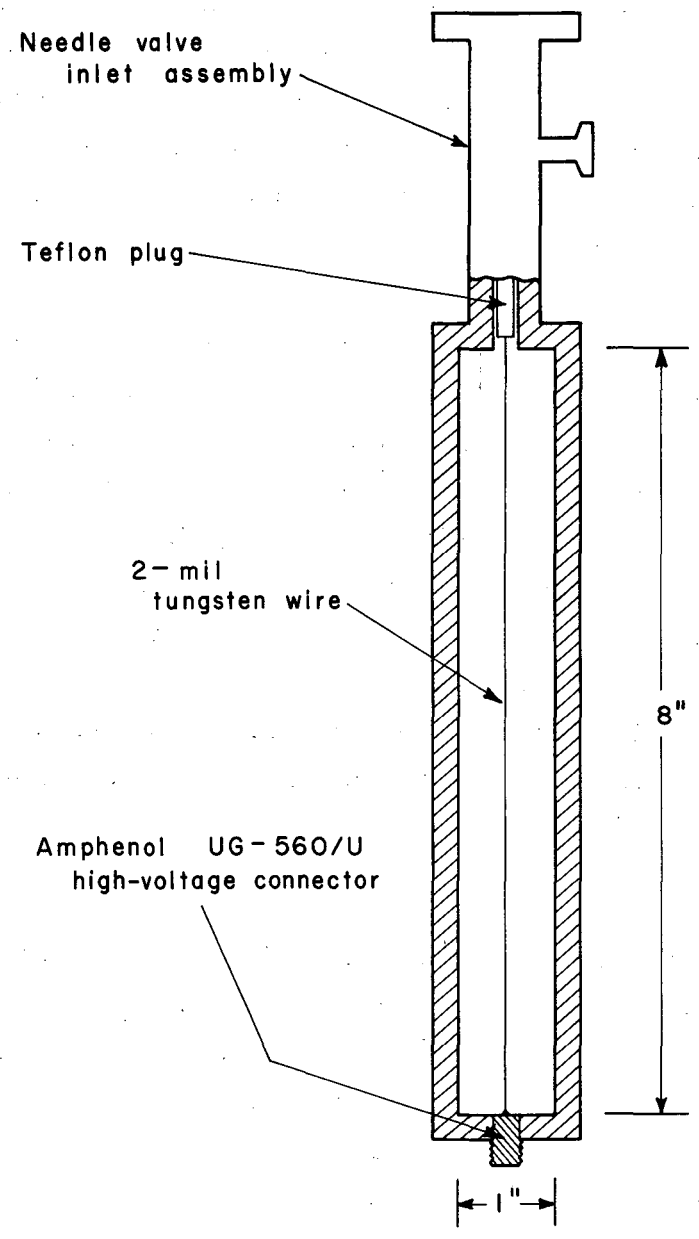
Because the maximum energy of  $S^{35}$   $\beta$  particles is only 168 keV,<sup>12</sup> counting of solid samples involves large corrections for self-absorption and counting rates that may be inconveniently low because of low counting efficiency. Uncertainty in the corrections may cause considerable error in the assay. In order to increase counter efficiency and eliminate absorption corrections, techniques were developed and used in this work for counting  $S^{35}$  as  $SO_2$ ,  $H_2S$ ,  $CH_3SH$ , thiophene, and  $SF_6$  internally in a gas proportional counter.

The counting tube used is shown in Fig. 4; it is based on a design by Wolfgang and McKay.<sup>39</sup> The body of the counter was machined from brass, and a thin layer of chromium was electroplated on the inside to minimize any retention of activity on the counter wall. A 2-mil tungsten wire formed the center electrode, and Teflon gaskets were used throughout. The threaded joints allowed easy disassembly for cleaning. The tube was connected to a conventional proportional-counter amplifier and scaler.

The counting characteristics of the counter were determined, by using an external radiation source, for pure methane and for a 90% argon-10% methane mixture as counting gases. As shown in Figs. 5 and 6, the pure methane gives a longer, flatter plateau, and was therefore used in all experiments.

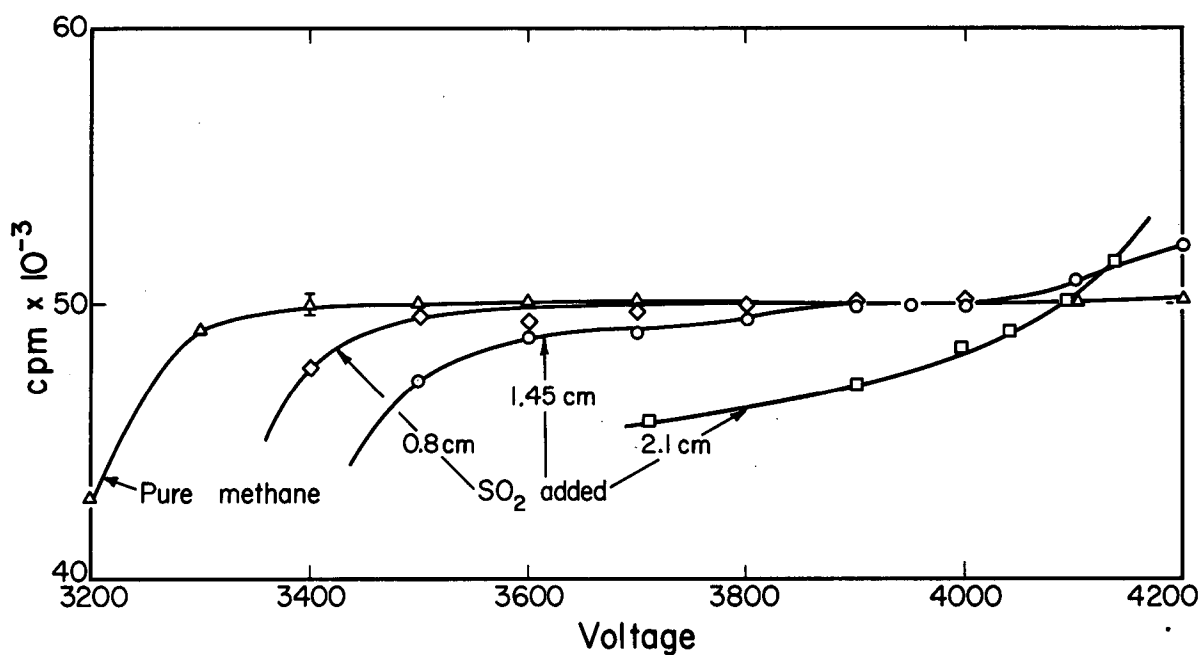
#### $SO_2$

The effect of diluting  $SO_2$  into methane for proportional counting has been described by Merritt and Hawkings in a work published after this work was carried out.<sup>40</sup> The plateau curves found in this work, as shown in Fig. 5, agree closely with the published curves. It is seen that small amounts of added  $SO_2$  may be satisfactorily counted without loss of efficiency, but that 3% or more of  $SO_2$  in 1 atm of methane destroys the plateau. Similar results were obtained when  $SO_2$  was added to the argon-methane mixture. (Fig. 6). This result limited the amount of  $SO_2$  gas that could be placed in the counter, and experimental work was carried out with concentrations of  $SO_2$  well below those that destroy the plateau. Plateaus and efficiencies were periodically checked with a  $Co^{60}$  external standard. No difference was observed between these



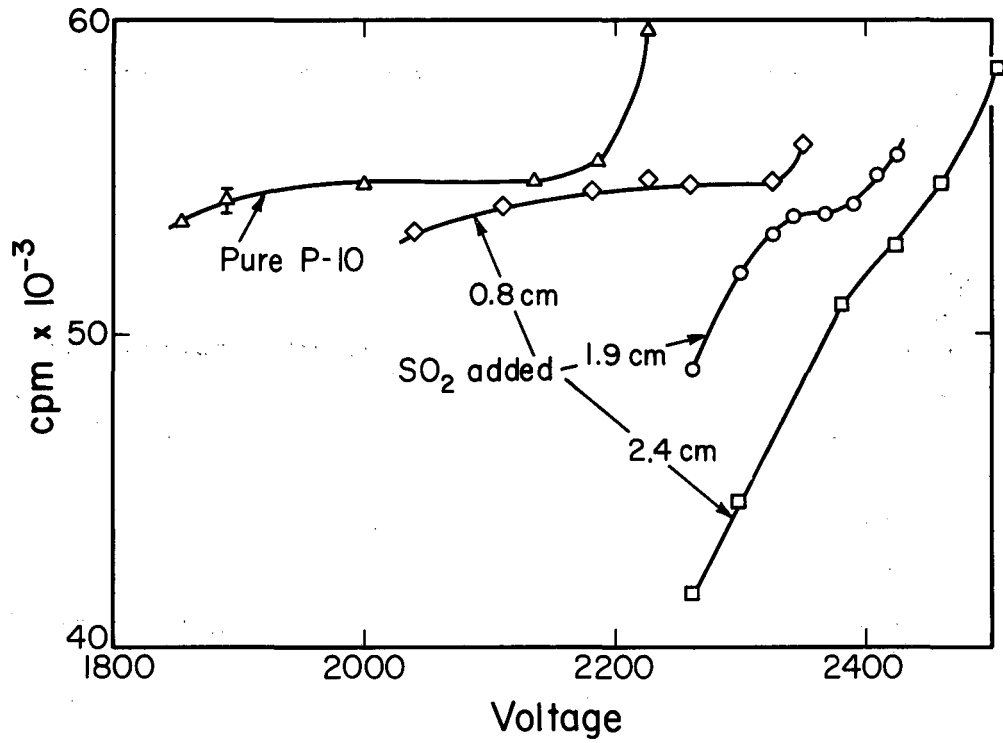
MU-27350

Fig. 4. Schematic diagram of proportional counting tube.



MU - 19549

Fig. 5. Counter plateaus for methane gas plus various pressures of SO<sub>2</sub>. The source is Co<sup>60</sup> external to the counter.



MU - 19550

Fig. 6. Counter plateaus for P-10 gas (90% Argon + 10% Methane) plus various pressures of SO<sub>2</sub>. The source is Co<sup>60</sup> external to the counter.

plateaus and those determined from internal  $S^{35}$  radiations.

The absolute efficiency of the counter for countings  $S^{35}$  as  $SO_2$  in methane was determined to be  $90 \pm 2\%$  by counting  $SO_2$  prepared from standard  $H_2S^{35}O_4$  furnished by the Nuclear-Chicago Co. The standardization furnished was checked by  $4\pi\beta$  counting. Since all counts were either made with or referred to the same counter, this factor was not critical.

### $H_2S$ and Organic Gases

Brief experiments showed that low concentrations of  $H_2S$  may be added to the methane counting gas, without lowering the efficiency of the counter as measured by the external standard. The plateau curves obtained from  $H_2S$ -methane mixtures resemble those from  $SO_2$ -methane mixtures. The plateau appears to break down in the same region of approximately 3% additive. Methyl-mercaptan and thiophene were found to be usable in higher proportion, but no thorough study was carried out.

### $SF_6$

This is a very efficient counter poison, as it tends to attach electrons.  $SF_6$  could be counted at only dilutions of about 0.3% or less, and the efficiency for each mixture had to be determined from the external standard; it was generally 20 to 30%. These counting rates are known to be quite inaccurate compared with the others, because of the small amount of sample used and uncertainty in the efficiency correction. In some samples as much as 35% more activity was recovered from the sample as  $SO_2$  than was calculated from the gross gas count.

### Other Counting Techniques

In several cases the half life of the activity found in the experiments was checked by sealing samples in silver-walled glass proportional counters similar to those described by Rowland et al.<sup>40</sup> and counting occasionally over a period of several months. The resulting decay always followed the 87-day  $S^{35}$  half life.

It was sometimes convenient to count solid samples of  $\text{BaSO}_4$  or  $\text{Hg}(\text{CH}_3\text{S})\text{Cl}$ , when great accuracy was not necessary. This was done with an end-window proportional counter, which was calibrated against the gas counter by counting some samples on both counters. The absorption corrections used were obtained from Herber.<sup>41</sup>

### III. RESULTS

#### A. Errors

The two basic sources of error in the data are:

- (a) error in measuring the sizes of the samples and the aliquots taken for counting; and
- (b) the statistical counting error.

In general the total size of the sample was known from pressure and volume measurements to  $\pm 1\%$ . In the very smallest samples this increased to  $\pm 5\%$ , but this was compensated for to some extent in that it was not necessary to take aliquots for counting. Aliquots were measured manometrically in a calibrated volume; the error here was generally  $\pm 2\%$ , except in the very small  $\text{SF}_6$  samples, in which it was in the range of  $\pm 5$  to  $10\%$ . The error in carrier standardization and delivery was about  $\pm 2\%$ .

Whenever possible the samples were counted for a length of time sufficient to hold the statistical counting error to  $\pm 1\%$ . The background of the counting tube, which was frequently checked, was in the range of 60 to 150 counts per min during these experiments. Portions of the sample that gave counting rates of this order could not be so accurately determined, and in some cases the error went as high as  $\pm 10\%$ . This was not an important problem, since it was not generally necessary to determine the activity in these relatively inactive fractions to a high degree of accuracy.

In counting of solid precipitates (all mercaptan samples and all precipitates recovered from Run # 12), an error in reproducibility was found which was in the range of  $\pm 10\%$  and which was probably due to inhomogeneities in the sample.

From summation of the individual errors the cumulative error is seen to be  $\pm 4\%$  in most cases; in the special cases mentioned it may be higher. Many of the data, such as those obtained from  $\text{H}_2\text{S}$ , were reproducible to within this range. Variations in excess of this,-- e.g., those obtained in the results with  $\text{SO}_2$ -- are believed due to experimental conditions such as differences in the condition of the walls of the capsule.



Some experimental problems could not be readily corrected. Very small samples which underwent phosphorus ignition were diluted to an appreciable extent with  $\text{CO}_2$  from impurities in the phosphorus: this inactive material could not be distinguished from  $\text{SO}_2$  in handling. In these cases the activity reported for certain fractions is a lower limit and is noted as such. Cases in which the  $\text{H}_2\text{S}-\text{SO}_2$  reaction appears to have affected the results are also noted.

#### B. Experimental Data

Tables I through XVI show the distribution of  $\text{S}^{35}$  activity among the various chemical forms as found for the systems studied. The percentages reported in the columns are percentages of the total activity actually recovered for that particular sample. In cases in which a portion of the activity was not recovered, this is indicated by NR. The column headed "total gaseous" is obtained from a gross count of gaseous products, unless otherwise noted. The column R/C indicates the ratio of the activity recovered to that calculated by the monitoring technique described in Section II B.

#### C. $\text{H}_2\text{S}$

The chemical form of the activity recovered from irradiated  $\text{H}_2\text{S}$  was as follows:

Pure  $\text{H}_2\text{S}$  (Table I). The principle radioactive product at all pressures was  $\text{H}_2\text{S}$ , or perhaps hydrogen polysulfides which would follow  $\text{H}_2\text{S}$  chemistry. Minor products (less than about 20% total) are S and  $\text{SO}_3$  from the tube walls, which are recovered as  $\text{S}^-$  and  $\text{SO}_4^-$  in washings, and gaseous  $\text{SO}_2$ . The fraction of activity found on the walls decreases greatly with increasing  $\text{H}_2\text{S}$  pressure; the yield of  $\text{SO}_2$  is variable.

Pure  $\text{H}_2\text{S}$ , in tubes packed with quartz wool (Table II). The results resemble those obtained without quartz wool.

Table I. Percentages of activity recovered by chemical form in irradiations of H<sub>2</sub>S.

Irradiation No.	P H <sub>2</sub> S (cm Hg)	Gaseous fraction			Wall fraction			R/C
		H <sub>2</sub> S	SO <sub>2</sub>	total gaseous	S	SO <sub>3(a)</sub>	total wall	
8	1.65		11	81	4	15	19	1.59
8	9.6		6	92	3	5	8	1.56
8	9.6			94			6	1.56
11	10.7			91			9	0.93
11	10.8	79	5	84	5	12	17	1.25
4	25.0			94	3	3	6	
4	25.6			96	2	2	4	
8	47.3		13	98	<1	2	2	≈ 1
8	47.3			97	2	2	3	0.90

(a) Absorbed SO<sub>2</sub> < 1% in all cases.

Table II. Percentages of activity recovered by chemical form in irradiations of tubes packed with quartz wool.

Irradiation No.	P H <sub>2</sub> S (cm Hg)	Gaseous fraction			Wall fraction			R/C
		H <sub>2</sub> S	SO <sub>2</sub>	total gaseous	S	SO <sub>3</sub>	total wall	
8	9.7			97	1	2	3	1.22
8	49.0			99			1	1.43
8	48.2		1	99			1	1.34

Table III. Percentages of activity recovered by chemical form in irradiations of H<sub>2</sub>S-Ar mixtures.

Irradiation No.	P H <sub>2</sub> S (cm Hg)	P Ar (cm Hg)	Gaseous fraction			Wall fraction			R/C
			H <sub>2</sub> S	SO <sub>2</sub>	total gaseous	S	oxides	total wall	
4	5.8	48.7			93			7	
8	9.55	61.0			97	2	1	3	0.76
11	10.5	53.0	80	7	87	5	9	14	0.78

Table IV. Percentages of activity recovered by chemical form in irradiations of H<sub>2</sub>S-NO mixtures.

Irradiation No.	P H <sub>2</sub> S (cm Hg)	P NO (cm Hg)	Gaseous fraction			Wall fraction			R/C
			"H <sub>2</sub> S"	SO <sub>2</sub>	total gaseous	S	oxides	total wall	
10	7.2	1.8	40	1	82	8	9	17	1.04
12(a)	8.4	7.7	-	-	NR (b)			10	
12(a)	8.5	8.35	39	1	NR(c)	5	5	10	

(a) Percentages based on calculated activity due to loss of activity while handling; see Sect. IIIC.

(b) High, but lost through reaction with counter walls.

(c) Sample placed directly in solution without first counting.

Table V. Percentages of activity recovered by chemical form in irradiations of H<sub>2</sub>S-O<sub>2</sub> mixtures.

Irradiation No.	P H <sub>2</sub> S (cm Hg)	P O <sub>2</sub> (cm Hg)	Gaseous fraction			Wall fraction			R/C
			H <sub>2</sub> S	SO <sub>2</sub> (a)	total gaseous	S	oxides	total wall	
8	9.55	1.6	3	39	78	10	13	23	0.76
8	9.55	1.65			71			29	0.84
8	9.55	10.6		70	80	5	14	19	0.74
8	9.50	10.25	≈ 3	36	78	6	17	23	0.93
11	10.1	10.45	16	40	NR <sub>(b)</sub>	15	29	44	0.77

(a) Represents lower limit because of possible loss by reaction with H<sub>2</sub>S.

(b) Sample put directly into solution without first counting as gas.

Table VI. Percentages of activity recovered by chemical form in irradiations of  $H_2S$  45% enriched in deuterium.

Irradiation No.	P $H_2S$ (cm Hg)	Gaseous fraction			Wall fraction			R/C
		$H_2S$	$SO_2$	total gaseous	S	oxides	total wall	
10	7.0	82	1	83	6	11	17	1.10
10	6.75			79	14	7	21	1.22
10	8.1			88			12	
10	30.1			92	4	4	8	0.83
10	28.5			94	3	3	6	

Table VII. Percentages of activity recovered by chemical form in irradiations of SO<sub>2</sub>.

Irradiation		Gaseous fraction	Wall fraction					R/C
No.	(cm Hg)		SO <sub>2</sub> <sup>(a)</sup>	S	"SO <sub>2</sub> "	SO <sub>3</sub>	total wall	
5	0.85	25	14	23	39	75	48	
5	0.90	14	30	24	31	86	38	
6	1.45	25 <sup>(b)</sup>	NR	25 <sup>(b)</sup>	50 <sup>(b)</sup>	75 <sup>(b)</sup>	50 <sup>(b)</sup>	
5	8.0	30	19	12	38	70	42	
5	8.05	42	19	10	30	58	52	
6	8.0	42	17	14	27	58	56	
7	10.2	42	27	13	19	58	55	
11	10.45	31	43	total oxides = 26		69		0.81
11	10.6	44	47	" "	= 18	56		0.55
11	55.6	93	5	" "	= 2	7		0.51
5	64.3	54	8	25	14	46	79	
6	67.9	79	9	6	7	21	85	

(a) The gaseous fraction was found by constant specific activity measurements in numerous samples to contain only SO<sub>2</sub>.

(b) Based on total activity recovered; S fraction lost.



Table VIII. Percentages of activity recovered by chemical form in irradiations of  $\text{SO}_2$  in tubes packed with quartz wool.

Irradiation No.	P $\text{SO}_2$ (cm Hg)	Gaseous fraction			wall fraction		
		$\text{SO}_2$	S	" $\text{SO}_2$ "	$\text{SO}_3$	total wall	total " $\text{SO}_2$ "
5	8.1	55	18	9	17	45	62
5	8.1	31	27	4	39	70	35
7	10.35	58	16	9	17	42	67
5	70.1	58	18	6	20	43	64
5	70.1	70	13	6	12	31	76

Table IX. Percentages of activity recovered by chemical form in irradiations of SO<sub>2</sub>-Ar mixtures.

Irradiation No.	P SO <sub>2</sub> (cm Hg)	P Ar (cm Hg)	<u>Gaseous fraction</u> SO <sub>2</sub>	<u>Wall fraction</u>				
				S	"SO <sub>2</sub> "	SO <sub>3</sub>	total wall	total "SO <sub>2</sub> "
5	8.0	64.4	47	18	11	24	53	58
6	8.4	60.3	68	12	8	13	32	76
6	8.5	62.1	49	11	13	25	51	62

Table X. Percentages of activity recovered by chemical form in irradiations of SO<sub>2</sub>-NO mixtures.

Irradiation No.	P SO <sub>2</sub> (cm Hg)	P NO (cm Hg)	Gaseous fraction <sup>(a)</sup>			Wall fraction				R/c	
			"SO <sub>2</sub> "	"S"	total gaseous	S	"SO <sub>2</sub> "	SO <sub>3</sub>	total wall		
6	18.7	1.2			88	3	4	4	12		
6	20.1	10.6			96	1	1	2	4		
6	20.0	10.0			93 <sup>(b)</sup>	NR	1 <sup>(b)</sup>	6 <sup>(b)</sup>	7 <sup>(b)</sup>		
12	10.75	9.1	76	11	NR <sup>(c)</sup>	6 Total oxides = 6			13	1.25	
12	10.2	10.05	72	24	NR <sup>(c)</sup>	3	"	"	= 3	5	1.1

(a) See text, Sect. III D, for explanation.

(b) Based on total recovered activity, but S fraction lost.

(c) Sample added directly to solution without first counting as gas.

Table XI. Percentages of activity recovered by chemical form in irradiation of SO<sub>2</sub>-O<sub>2</sub> mixtures.

Irradiation No.	P SO <sub>2</sub> (cm Hg)	P O <sub>2</sub> (cm Hg)	Gaseous fraction		Wall fraction		
			SO <sub>2</sub>	S	"SO <sub>2</sub> "	SO <sub>3</sub>	total wall
7	10.25	1.3	55	8	2	36	45
7	10.2	1.4	60	3	1	36	40
7	10.6	11.0	56	1	1	41	44
7	10.4	9.85	61				39
7(a)	10.0	11.4	59				41
7(a)	10.35	10.8	63	2	1	34	37
7	10.25	60.1	83	3	6	8	17
7	10.2	59.4	75	8	2	14	25

(a) Tube packed with quartz wool.

Table XII. Percentages of activity recovered by chemical form in irradiations of  $\text{SO}_2\text{-CH}_4$  and  $\text{SO}_2\text{-H}_2$  mixtures.

Irradiation No.	P $\text{SO}_2$ (cm Hg)	P $\text{CH}_4$ (cm Hg)	Gaseous fraction			Wall fraction			R/C	
			mercaptans	$\text{H}_2\text{S}$	$\text{SO}_2$	total	S	oxides		total wall
9	10.10	1.4	0.3			48	25	27	52	1.45
9	10.1	1.0				NR <sup>(a)</sup>	35	65		
9	10.1	11.4	2			44	30	26	56	1.36
9	10.2	11.6				NR <sup>(a)</sup>	59	41		
		P $\text{H}_2$ (cm Hg)	$\text{H}_2\text{S}$	$\text{SO}_2$		total				
11	10.3	10.7	5	15		22	56	22	78	0.76
11	11.7	9.4	3	27		NR <sup>(b)</sup>	55	16	70	1.19

(a) Gaseous fraction lost.

(b) Sample put in solution immediately without first counting.

Table XIII. Percentages of activity recovered by chemical form in irradiations of SF<sub>6</sub>.

Irradiation No.	P SF <sub>6</sub> (cm Hg)	Gaseous fraction		Wall fraction			R/C
		"SO <sub>2</sub> "	total	S	oxides	total wall	
9	4.95	23	(a)	46	31	77	0.19
12	11.1	10	19	25	48	73	1.16
12	11.1	8	NR	38	54	92	1.03

(a) Gas count less than count of SO<sub>2</sub>. See Sect. II F for comments on counting.

Table XIV. Percentages of activity recovered by chemical form in irradiations of SF<sub>6</sub>-O<sub>2</sub> and SF<sub>6</sub>-NO mixtures.

Irradiation No.	P SF <sub>6</sub> (cm Hg)	P NO (cm Hg)	P O <sub>2</sub> (cm Hg)	Gaseous fraction			Wall fraction			R/C
				"SO <sub>2</sub> "	"S <sup>=</sup> "	total gaseous	S	oxides	total wall	
9	4.95	--	5.1	37	--	71	<2	29	29	0.58
9	5.1	--	5.1	57	--	68	4	28	32	1.20
10	11.3	2.5	--	82	NR	(a)	4	14	18	1.59
10	11.1	2.9	--	93	NR	(a)	3	4	7	1.32
12	11.7	9.0	--	65	26	NR(b)	5	4	9	0.87
12	12.1	10.2	--	78	16	NR(b)	2	4	6	1.16

(a) Gas count less than SO<sub>2</sub> activity. See Sect. II F for comments on counting.

(b) Sample put in solution immediately without first counting.

Table XV. Percentages of activity recovered by chemical form in irradiations of  $\text{CH}_3\text{SH}$ ,  $\text{CH}_3\text{SH-O}_2$  mixtures, and  $\text{CH}_3\text{SH-NO}$  mixtures.

Irradiation No.	P $\text{CH}_3\text{SH}$ (cm Hg)	P $\text{O}_2$ (cm Hg)	P NO (cm Hg)	Gaseous fraction				Wall fraction			R/C
				$\text{SO}_2$	$\text{H}_2\text{S}$	mercap.	total gaseous	S	oxides	total wall	
10	24.35	--	--	7	34	7	98	2	1	2	1.49
10	23.6	--	--	NR	35 <sup>(a)</sup>	NR	94			6	1.54
10	24.2	--	--	2	50 <sup>(a)</sup>	NR	97			3	1.09
10	16.9	--	--	NR	58	4	94			6	1.14
10	17.6	12.0	--	57	--	10 <sup>(b)</sup>	94	6	NR <sup>(c)</sup>	6	
10	18.4	12.0	--	46	39	NR	85	7	8	15	
10	17.6	--	10.1	12	47	8	86	7	7	14	0.53

(a) Part of this may have been lost by reaction with carrier  $\text{SO}_2$ ; represents lower limit.

(b) Probably includes some  $\text{H}_2\text{S}$ .

(c) This portion lost.



Table XVI. Percentages of activity recovered by chemical from in irradiations of thiophene and thiophene-O<sub>2</sub> mixtures.

Irradiation No.	P C <sub>4</sub> H <sub>4</sub> S (cm Hg)	P O <sub>2</sub> (cm Hg)	Gaseous fraction				Wall fraction			R/C
			mercap.	H <sub>2</sub> S	SO <sub>2</sub>	gaseous	S	oxides	total wall	
11	6.0	--	NR	NR	NR	64	21	15	36	1.31
11	6.0	--	4	24	NR	63	21	16	37	1.02
11	6.9	--	12	33	17	NR(a)	22	17	39	1.75
11	6.1	6.8	2	NR	41	73	14	12	26	0.72

(a) Sample added directly to solution without first counting.

H<sub>2</sub>S + Ar (Table III). The results resemble those obtained in the absence of argon.

H<sub>2</sub>S + NO (Table IV). The activity appeared mainly as a substance that hydrolyzes to S<sup>=</sup>. However, in the handling of this material, it reacted differently from H<sub>2</sub>S; in particular, it deposited quantitatively on the inside of the counter without the H<sub>2</sub>S itself being affected. Only 1% or less of the activity gave SO<sub>3</sub><sup>=</sup> or SO<sub>4</sub><sup>=</sup> on hydrolysis.

H<sub>2</sub>S + O<sub>2</sub> (Table V). The greater part of the activity appears as oxides, in the approximate ratio of 80% SO<sub>2</sub> to 20% SO<sub>3</sub>. H<sub>2</sub>S activity was recovered only to the extent of about 3%.

H<sub>2</sub>S 45% enriched in deuterium (Table VI). The results resemble those obtained for natural H<sub>2</sub>S.

#### D. SO<sub>2</sub>

The chemical form of the activity recovered from irradiated SO<sub>2</sub> was as follows:

Pure SO<sub>2</sub> (Table VII). The radioactive products include gaseous SO<sub>2</sub>, and fractions washed from the walls which follow the chemistry of S<sup>=</sup>, SO<sub>3</sub><sup>=</sup>, and SO<sub>4</sub><sup>=</sup>. These will be referred to as S, "adsorbed SO<sub>2</sub>" , and SO<sub>3</sub>, respectively. There is considerable scatter in these data, which is at least partly due to varying amounts of adsorbed SO<sub>2</sub>. The total SO<sub>2</sub> yield increases at pressures higher than 10 cm Hg, from about 50% at this pressure to about 85% at pressures near 1 atm.

Pure SO<sub>2</sub>, in tubes packed with quartz wool (Table VIII). The results at lower pressures are similar to those found in the absence of quartz wool, but at higher pressures the increase of the SO<sub>2</sub> yield is not so marked.

SO<sub>2</sub> + Ar (Table IX). No perceptible differences are observed between these samples and those not containing argon.

SO<sub>2</sub> + NO (Table X). Almost all the activity appears in the gas phase.

A small part (about 15%) of this hydrolyzes to give S<sup>=</sup>; the remainder yields SO<sub>3</sub><sup>=</sup> or SO<sub>4</sub><sup>=</sup>.

SO<sub>2</sub> + O<sub>2</sub> (Table XI). SO<sub>2</sub> and SO<sub>3</sub> are the only major products; the SO<sub>2</sub> yield increases from about 60% at 10 mole % of O<sub>2</sub> to 80% at 80 mole % of O<sub>2</sub>.

SO<sub>2</sub> + CH<sub>4</sub> (Table XII). Yields resemble those obtained in the absence of CH<sub>4</sub>. Only small amounts of H<sub>2</sub>S or mercaptan activity are found, although the H<sub>2</sub>S activity may have been lost by the H<sub>2</sub>S-SO<sub>2</sub> reaction in these samples.

SO<sub>2</sub> + H<sub>2</sub> (Table XII). About 55% of activity is recovered as S, considerably higher than in any other system. A few per cent of H<sub>2</sub>S is also found. The remaining activity is about evenly divided between SO<sub>2</sub> and SO<sub>3</sub>.

#### E. SF<sub>6</sub>

The chemical form of the activity recovered from irradiated SF<sub>6</sub> was as follows:

Pure SF<sub>6</sub> (Table XIII). A maximum of a few per cent of activity appears as SF<sub>6</sub>; about 4/5 is found on the walls, as S or as oxides, and the remainder is recovered as SO<sub>2</sub>.

SF<sub>6</sub> + O<sub>2</sub> (Table XIV). 95% of the activity is recovered as SO<sub>2</sub> or as SO<sub>3</sub>, in a ratio of about 3:1.

SF<sub>6</sub> + NO (Table XIV). Roughly 90% of the activity appears in the gas phase, and is mainly recoverable as SO<sub>3</sub><sup>=</sup> or SO<sub>4</sub><sup>=</sup>; however, about 20% of the gaseous S<sup>35</sup> hydrolyzes to S<sup>=</sup>.

F. CH<sub>3</sub>SH

Table XV shows the chemical form of the activity recovered from irradiated CH<sub>3</sub>SH. When pure CH<sub>3</sub>SH was irradiated, about 50% of the activity appeared as H<sub>2</sub>S following hydrolysis; less than 10% of the activity was recovered as mercaptans. In irradiations of CH<sub>3</sub>SH-O<sub>2</sub> mixtures, only about 50% of the activity was recovered as SO<sub>2</sub> when O<sub>2</sub> was present to the extent of about 40 mole %. About 10% was recovered as SO<sub>3</sub>; the remainder was mostly H<sub>2</sub>S. The gaseous activity produced in CH<sub>3</sub>SH-No mixtures constituted about 85% of the total and hydrolyzed mainly to S<sup>=</sup>.

G. C<sub>4</sub>H<sub>4</sub>S (Thiophene)

Table XVI shows the chemical form of the activity recovered from irradiated thiophene. H<sub>2</sub>S contains about 30% of the activity, and most of the remainder is found as S or as oxides. A few per cent was recovered as mercaptans. The irradiation of a thiophene-O<sub>2</sub> mixture led to 53% of the activity as oxides, 12% S, and 2% mercaptans; the remainder was gaseous but not identified.

#### IV. DISCUSSION

##### A. Breakup

The percentage of activity recovered in the original compound represents the fraction of molecules that remain intact following the nuclear process only if it is made impossible for this compound to be re-formed by subsequent reaction. This would be the case if the parent compound were greatly diluted in a gas that would react with the fragments resulting from breakup to form other compounds. In many of these experiments this was the case, and the minimum amounts of activity recovered in the various original compounds are as follows:

$H_2S$  (+ $O_2$ ) (Table V), 3%;

$SO_2$  (+ $H_2$ ) (Table XII), 15%;

$SF_6$  (All experiments, Tables XIII-XIV),  
less than about 5%;

$CH_3SH$  (Table XV), Less than 5%.

These percentages represent upper limits, since the experiments were not carried to limiting values by adding increasingly greater ratios of additive to parent compound. Since, however, the Suess factor for an H-S bond is higher by an order of magnitude than that for other bonds, it is expected that the  $H_2S$  molecule is least likely to break up. If breakup occurs in 97% of  $H_2S$  molecules irradiated, it should occur in > 99% in other compounds, from the considerations outlined in Sect. I B. Thus the retention of activity observed in the original compounds would appear to be the result of synthesis from the fragments produced by breakup.

There remains the possibility that not all the bonds will be broken in a given molecule. Evidence for this is presented in the following section.

### B. Products of Breakup

The data obtained from the hydrolysis of samples irradiated in the presence of NO give evidence that there are at least two different types of primary  $S^{35}$ -containing species formed, and that these are related to the nature of the parent compound. In irradiated mixtures of  $H_2S$  and NO, the bulk of the activity appears as a species that is distinct from  $H_2S$  but which yields only  $S^-$  on hydrolysis. Similar results were obtained in the  $CH_3SH$ -NO mixture studied. In  $SF_6$ , where most of the activity normally accumulates on the walls, addition of NO causes the activity to be produced primarily as gaseous compounds. These hydrolyze predominantly to  $SO_3^-$  or  $SO_4^-$ ,<sup>42</sup> but also produce some  $S^-$ . It would appear that the primary fragments formed in breakup react with NO to give intermediate compounds which form these hydrolysis products.  $SO_2$ -NO mixtures also yield gaseous activities which give both  $S^-$  and  $SO_3^-$  or  $SO_4^-$  on hydrolysis. Thus it appears that there are at least two types of intermediate compounds produced by reaction of fragments with NO, and the extent to which each is formed depends upon the parent molecule.

There are two possible explanations for these results. The first is based on the assumption that the product of breakup is identical in all cases: atomic S. This implies that the final chemical form is the result of the reaction of the parent gas and NO with the S atoms. The different reactions of the various parent gases would account for the differences in the intermediate compounds observed. This hypothesis can in principle explain all the results, if one makes enough assumptions about these reactions. The most difficult point is the apparent production of two types of intermediate compounds in the presence of the relatively inert parent gas  $SF_6$ .

An alternative explanation is that the nature of the primary  $S^{35}$ -containing species left from breakup varies with the parent compound. It is conceivable that in an important number of cases the original molecule is not entirely dissociated, so that one deals here with the reactions of various molecular fragments, such as  $SF_2$ , HS, etc.

This would require that most of the original impulse energy be lost in the kinetic energy given those atoms which are broken away. Whether this is likely is uncertain. Another possibility is that the products in all cases are S atoms, but that the S atoms from some compounds may be formed in excited states, which would react with NO in a manner different from that of ground-state S atoms. Such a difference in reaction mechanisms has been observed in the reactions of oxygen atoms in different electronic states.<sup>43</sup>

These explanations are not mutually exclusive, as even if various primary species are produced, it does not follow that the subsequent reaction necessarily involves only the primary species and NO. Further experimentation will be necessary to resolve the nature of the reactants and reactions in this system.

### C. Epithermal Reactions

Tests for reactions proceeding by "hot" or "epithermal" mechanisms were made in SO<sub>2</sub> and in H<sub>2</sub>S by adding argon to the sample irradiated (Tables III and IX). Such reactions, which involve reactions of recoil atoms a few eV or tens of eV in energy, were first described and characterized in reactions of recoil tritium with methane, in a paper by Estrup and Wolfgang.<sup>10a</sup> In the experiments with S<sup>35</sup> in this work, no deviation from the yields of activity obtained in the absence of argon was observed, although the mole fraction of argon was typically in the range 80 to 90%.

According to the theory developed by Estrup and Wolfgang, the sensitivity of these reactions to the effect of moderator is governed by the mass ratio of the inert gas to the recoil, the cross section for the hot reaction, and the range of energy in which the reaction is possible. Ar<sup>40</sup> is a better moderator for S<sup>35</sup> than He<sup>4</sup> is for T, and it seems unlikely from mechanistic considerations that any reaction involving a "hot" S<sup>35</sup> would proceed with greater efficiency or over a wider range than the tritium-methane reaction, so that such reactions of S<sup>35</sup> should be at least as sensitive to moderation as that of tritium

with methane. However, in the latter reaction as well as in others of this type that have been reported,<sup>10</sup> the addition of so much moderator was sufficient to reduce the yield of "hot" products to the order of 30% or less of that obtained in unmoderated systems. For this reason it is felt that the reactions of  $S^{35}$  in  $SO_2$  and  $H_2S$  are those of thermal species.

#### D. Reactions in $H_2S$

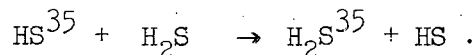
As shown in Tables I, II III, and VI, >80% of the  $S^{35}$  from irradiated  $H_2S$  appears in the gas phase and follows the chemistry of  $H_2S$ , and this result is not greatly affected by the addition of argon, by packing the tubes with quartz wool, or by deuterium enrichment. (The activity observed may not be entirely  $H_2S$ , but may include  $H_2S_2$ , which would follow the  $H_2S$  chemistry.) This contrasts with the work of Willard et al.,<sup>15</sup> who found that molecular sulfur was the principal product, but differences in irradiation conditions and analytical technique make it difficult to compare their work with this.

From the considerations on breakup and on argon moderation previously mentioned, it appears that the incorporation of the activity into the gas phase is due to thermal reactions of  $S$  or  $SH$ , the primary products of breakup.

The reactions responsible for producing the  $H_2S$  activity very likely take place in the gas phase, rather than on the walls. It is known from experiments with  $SF_6$  (to be described later) that when the gas phase is inert and the fragments can reach the walls by diffusion the result is that most of the activity is deposited on the walls as  $S$  or as oxides. In accordance with this hypothesis, the proportion of  $S$  and  $SO_3$  found on the walls decreases with increasing pressure. However, the data taken with quartz wool in the tubes do not greatly differ from those found without it. A possible explanation for this behavior is that the reaction which incorporates the  $S^{35}$  into the gaseous form is of order greater than 1 in  $H_2S$ , and that this is competing with a reaction which is responsible for the activity found on the walls.

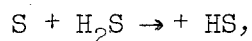


If a major part of the activity is left in the form HS by the breakage of only one H-S bond, it should be possible for it to form H<sub>2</sub>S readily by exchange at thermal energies, thus:



Lability of the hydrogens of H<sub>2</sub>S that would permit such an exchange may be expected from the known exchange of these hydrogens with water, and from the other evidence for hydrogen bond formation by H<sub>2</sub>S.<sup>44</sup>

The formation of an HS intermediate from S atoms in H<sub>2</sub>S is more difficult. The abstraction of an H from H<sub>2</sub>S,



is very endothermic and would not be expected for S atoms at thermal energies.<sup>45</sup> It is more likely that the S atom will add to H<sub>2</sub>S to form a H<sub>2</sub>S<sub>2</sub> complex, which would then yield H<sub>2</sub>S or stable H<sub>2</sub>S<sub>2</sub> by subsequent reaction. Either of these would appear in the H<sub>2</sub>S fraction in the analysis used.

It should be noted that in this system, even if S<sup>+</sup> ions were formed in the nuclear process, charge-exchange reactions would be expected to inhibit ion-molecule reactions. This is because (as mentioned earlier) the charge-exchange cross section is highest when the ionization potentials of the species involved are close together. The relevant ionization potentials are: H<sub>2</sub>S, 10.4 eV;<sup>46</sup> HS, about 11 eV;<sup>47</sup> S, 10.4 eV.<sup>48</sup>

Oxidation of either S or SH to SO<sub>2</sub> and SO<sub>3</sub> by added oxygen would be expected, in view of other radiation chemical studies on oxidation.<sup>49</sup> This is in accordance with the data obtained from irradiations of H<sub>2</sub>S-O<sub>2</sub> mixtures (Table V).

### E. Reactions in SO<sub>2</sub>

From the data obtained from irradiating SO<sub>2</sub>-NO mixtures, described in Sect. IV. B, it appears that more than one chemical species results from the nuclear transformation in SO<sub>2</sub>. From the data in Tables VII and VIII, it is clear that the final chemical fate of the activity produced varies considerably from sample to sample, so that factors which are difficult to control are determining the final chemical yields. From the following analysis of the data, it appears that the chief factor is the condition of the tube walls.

The following points stand out in the data:

(1) As noted, argon addition has no discernible effect on the reaction, so it is likely that the reactions occurring are those of thermalized species (Table IX).

(2) At low SO<sub>2</sub> pressures the yield is independent of the presence of quartz wool in the tube (Tables VII, VIII).

(3) The yield of SO<sub>2</sub> activity increases with increasing pressure of SO<sub>2</sub> gas at pressures above approximately 10 cm Hg. There is less increase in tubes containing quartz wool (Tables VII, VIII).

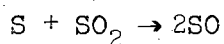
(4) A considerable, but variable, amount of SO<sub>2</sub> activity is found adsorbed on the wall of the tube (Tables VII, VIII).

It is clear that the "SO<sub>2</sub>" activity found on the wall must have been formed there, since the amount of "adsorbed SO<sub>2</sub>" relative to that of the gaseous SO<sub>2</sub> is quite small. SO<sub>3</sub> must also be formed at the wall, since any mechanism involving gaseous SO<sub>2</sub> would not give high specific activity of SO<sub>3</sub>; and the reaction with trace oxygen,  $SO + O_2 \rightarrow SO_3$ , which requires a third body, would not be expected to compete with the reaction  $SO + O_2 \rightarrow SO_2 + O$  in the gas phase. The first reaction could take place more readily with oxygen adsorbed on the walls, however.

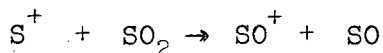
Because the presence of quartz wool has no effect at the lower pressures of SO<sub>2</sub> studied, it can be inferred that wall reactions predominate in determining the final chemical form of the activity at these pressures; that is, that the reaction of the S<sup>35</sup>-containing fragment is unlikely except at the wall (or the quartz wool surface).

If this is the case, then it is clear that variations in the amount and nature of impurity gases adsorbed on the walls can greatly influence the final chemical form of the  $S^{35}$  and account for the scatter in the data. At the higher pressures of  $SO_2$ , however, an increase is found in the yield of  $SO_2$  activity, which is not so marked when quartz wool is present. This can be explained by the competition of a gas-phase reaction with the wall reactions.

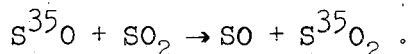
It is rather difficult for a gas-phase reaction to produce  $SO_2$  unless  $SO$  can first be formed. The reactions



and



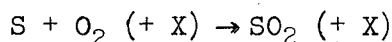
are both quite endothermic.<sup>50</sup> Once  $S^{35}O$  is present, however, it is possible that  $S^{35}O_2$  may be formed by the exchange of oxygen:



How fast this reaction would take place is quite uncertain, however; it would surely be much slower than the exchange of hydrogen in  $H_2S$ . It may be that the gas-phase reaction is merely the oxidation of  $S$  (or  $SO$ ) by trace oxygen, which is favored at higher pressures because of the longer interval between collisions of  $SO$  with the walls.  $SO$  might be present from partial breakup of the  $SO_2$ , or, more likely, from partial oxidation at the walls.

(Very little is known of the chemistry and behavior of  $SO$ , but it is known to be oxidized readily to  $SO_2$  by  $O_2$ .<sup>51</sup> The metastable species, to which the formula  $SO$  is assigned in many texts, has been shown by Meschi and Myers to have the composition  $S_2O$ .<sup>52</sup>)

The effect of other additives is consistent with these mechanisms. The  $\text{SO}_3$  yield decreases upon the addition of oxygen (Table XI), and  $\text{SO}_2$  becomes the principal product. This is consistent with the idea expressed earlier that  $\text{SO}_3$  is formed mainly by reactions with impurities at the walls, rather than in the gas phase. With large amounts of gaseous oxygen present such a gas-phase reaction as



can take place more readily than reactions at the wall, and it is certain that  $\text{SO}$  formed by any process will be quickly oxidized to  $\text{SO}_2$  by oxygen, as is known to happen in the gas phase.<sup>51</sup>

The large yield of  $\text{S}$  on the walls when mixtures of  $\text{S}$  and  $\text{H}_2$  are irradiated (Table XII) may be due to reaction of the  $\text{H}_2$  with the impurities at the walls which cause oxidation there. As is noted, the reaction(s) to produce  $\text{H}_2\text{S}$  are of lesser importance.

For comparison with the above, it is interesting to note the results of MacKay, Pandow, Polak, and Wolfgang, who studied the reactions of  $\text{C}^{11}$  recoils.  $\text{CO}$  was found in general to be a major product, even when the only source of oxygen was trace impurities in the gases used or on the walls of the brass reaction vessel.<sup>5</sup>

#### F. Reactions in $\text{SF}_6$

The great chemical inertness of  $\text{SF}_6$  makes it very unlikely that it undergoes any thermal reaction with the  $\text{S}^{35}$  species produced by breakup. Indeed, the main forms in which the activity is found are those expected from reactions with impurities in the gas or on the walls, as discussed in the preceding section (Table XIII). These forms include  $\text{S}$ ,  $\text{SO}_2$ , and  $\text{SO}_3$ . It is however, possible that some of the activity actually remains in the form of fluorides, which give the same hydrolysis products as the compounds listed.  $\text{SF}_4$ , for example, is fairly stable in the gas phase and hydrolyzes to  $\text{SO}_3$ . Other lower fluorides would be expected to attack the walls and leave oxides or sulfur.<sup>36</sup>

As in other systems,  $\text{SO}_2$  predominates on the addition of oxygen (Table XIV). Since, however, not all the gaseous activity could be accounted for as  $\text{SO}_2$ , it is possible that oxyfluorides are also formed. This point requires better analytical methods for determination.

The  $\text{SF}_6$  experiments confirm that the kinds of wall and impurity reactions postulated to explain the  $\text{SO}_2$  results do take place. Another important result is that  $\text{SO}_2$  is a principal product arising from irradiations with oxygen present, though the sulfur was originally in the +6 state. Thus here the chemical environment, rather than the original oxidation state of the sulfur, determines the final result.

#### G. Reactions in Organic Molecules

The high recovery of the activity in the form of  $\text{H}_2\text{S}$  (Table XV) from irradiations of  $\text{CH}_3\text{SH}$  can be explained by reactions of the same type as those postulated for the  $\text{H}_2\text{S}$  system. Thus, for example, an S atom may attack the SH group in  $\text{CH}_3\text{SH}$  and form a disulfide link, which gives eventually  $\text{S}^-$  on hydrolysis. It may also be that HS is produced directly from the recoil process in an important fraction of cases here, since the difference in Sues factors between the C-S and the H-S bonds might cause a large part of the recoil energy to go to the C-S bond. An HS radical, once formed, could acquire a second hydrogen by exchange in a manner similar to that postulated in  $\text{H}_2\text{S}$ . At any rate, in view of the results from thiophene described below, it would seem that there are numerous possibilities in a system so rich in hydrogens.

$\text{H}_2\text{S}$  is an important product from thiophene irradiations (Table XVI), where the only mechanisms available for its production are abstraction of an H from a C-H bond or by reactions with radiation-produced species. The C-H abstraction would require a "hot" reaction. Here, however, the yield of  $\text{H}_2\text{S}$  is lower than in  $\text{CH}_3\text{SH}$ , and a large part of the activity is found on the walls.

As shown in Tables XV and XVI, the addition of oxygen to these two systems during irradiation results in the production of oxides to the extent of only about 60%, compared with 90% in other systems studied. It would seem that these systems, and the reactions that take place in them, are quite complex. More efficient analytical techniques, such as gas chromatographic methods, will be needed to resolve these complexities.

#### H. Summary

Breakup of the original compounds has been shown to be general following  $S^{34}(n,r)S^{35}$ , but there remains a possibility that not all the bonds of a given molecule may be broken, particularly in view of the results from NO addition.

No epithermal reactions have been identified for  $S^{35}$ ; they have probably been ruled out in the  $SO_2$  and  $H_2S$  systems.

Interesting results were obtained from irradiations of various gases mixed with NO. The  $S^{35}$  was recovered in gaseous compounds which could not be definitely identified. However, the study of the hydrolysis products of these compounds suggests that the chemical form of the  $S^{35}$  following the breakup process may vary, depending on the nature of the original compound. This point seems worthy of further investigation.

Except for these results of NO addition, it would appear that oxidation or reduction of the sulfur activity is primarily dependent on its surroundings--walls, reactive gases, etc.--rather than on the oxidation state or the nature of the original molecule.

$H_2S^{35}$  has been found, within the limitations of the analytical techniques used, as a major product in irradiations of  $H_2S$ ,  $CH_3SH$ , and thiophene. In irradiations of  $SO_2$  the results are complex, and much reaction appears to take place on the walls. In particular, oxidation on the walls seems to be quite general when gas-phase reactions do not compete; this is not unexpected in view of oxidation phenomena observed for  $C^{11}$  recoils<sup>5</sup> and for  $S^{35}$  formed in crystals.<sup>14</sup>

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