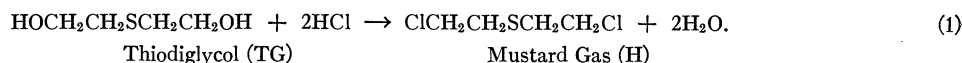


The Polysulfides in Levinstein Process Mustard Gas

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IN WORLD WAR I THE GERMANS HAD THE facilities and materials available to prepare mustard gas by a relatively simple process from thiodiglycol and hydrochloric acid:



The product of this reaction is referred to in this country as TGH, the symbol H representing mustard gas, bis(β -chloroethyl)sulfide. The materials for this process were not available to the Allies in World War I, but by brilliant teamwork the British and Americans rapidly developed the so-called Levinstein process (named after the British drug manufacturer), the product of which is known as Levinstein H. The method consists in reacting ethylene and sulfur monochloride; the stoichiometry of the reaction is usually written as follows:



When the reaction is allowed to run at about 60°, most of the excess sulfur indicated by this equation precipitates rapidly. If the reaction temperature is held to 35–38°, however, the “excess” sulfur atom does not begin to precipitate until the product has been stored for at least a few weeks. These processes for making TGH and Levinstein H have been reviewed by Sartori (11).

The mechanism of the Levinstein process was well understood by Conant (see Sartori, p. 218), but a more complete explanation has recently been found by a research group working at the University of Illinois under Fuson (6).

The behavior of the extra sulfur atom in Levinstein H was somewhat of a mystery from World War I to World War II. For a long time it was supposed that the “excess” sulfur was in colloidal suspension, because, as it precipitated, there was very little change in freezing point. Somewhat fanciful suggestions were sometimes offered as to the nature of this colloidal system. The literature, however, does contain suggestions to the effect that the sulfur atom is in chemical combination. For example, Conant, *et al.* (3) proposed that part of the sulfur is in the free state, probably colloidal, and the rest in combination as a pentasulfide ($\text{ClCH}_2\text{CH}_2\text{S}_5$). This suggestion of the presence of a pentasulfide was based on the analysis of

the residue from distillation of a sample of Levinstein H. Bennett (2) prepared the disulfide ($\text{ClCH}_2\text{CH}_2\text{S}_2$), and Mann, Pope, and Vernon (9) isolated a trisulfide ($\text{ClCH}_2\text{CH}_2\text{S}_3$). (The polysulfides will be referred to in

this paper as HS_2 for the disulfide, HS_3 for the trisulfide, etc.)

It is the purpose of this paper to review briefly the part played by Edgewood Arsenal personnel in the elucidation of the mystery of Levinstein H. In order to assist in the interpretation of this work, data are shown

TABLE 1
REPRESENTATIVE ANALYSES OF LEVINSTEIN H SAMPLES

	New sample	Aged sample
Acidity (as HCl), %.....	0.16	0.38
Iron (as FeCl_2), %.....	0.22	0.41
Melting point, °C.....	7.7	7.6
Density at 20°C., grams/cc.....	1.351	1.340
Sulfur, %.....	33.46	30.70
Chlorine, %.....	36.35	38.42
Distillation analysis:		
Distillate, %.....	78.3	76.2
Residue, %.....	20.7	22.1
Loss, %.....	1.0	1.7
M.P. of distillate, °C.....	10.2	12.1
Purity of distillate*, %.....	88.5	93.8
Mustard content, %.....	69.3	71.5

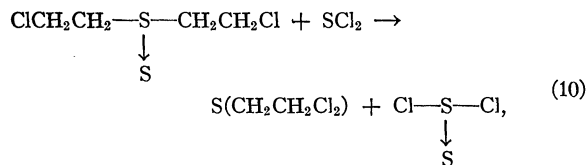
* Calculated from melting point, assuming that pure H melts at 14.4° C.

(Table 1) which illustrate the nature of Levinstein H as manufactured in steel reactors on a large scale. The composition of a sample is generally determined by distillation under certain specified conditions, with the still-pot at 150° C. under a pressure of about 5 mm. Samples stored in steel containers increase in iron content at a more or less rapid rate.

Contribution of Jarman and Morrison (7): The pure H content of newly made Levinstein H lies in the range of 68–73 per cent by weight. The residue remaining after the distillation of a sample of Levinstein H was fractionally distilled in a 12-plate column; it yielded a fraction of pure H, a quantity of HS_2 , and some p-dithiane, which condensed in the column. The presence of p-dithiane is probably due to decomposition in the still-pot of sul-

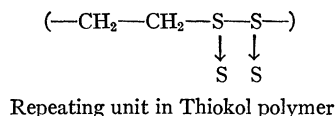
be formed and there would be more sulfur given off than could be taken up by the disulfide $\text{ClCH}_2\text{CH}_2\text{S}-\text{SCH}_2\text{CH}_2\text{Cl}$. The excess of sulfur would probably precipitate out, as in the 60° process.

If SCl_2 can be added so that it takes the extra sulfur from the reaction product of Equation 6 in this manner,



the absorption of ethylene can continue without the formation of much of the disulfide $\text{ClCH}_2\text{CH}_2\text{S}-\text{SCH}_2\text{CH}_2\text{Cl}$, which takes up sulfur to give the pentasulfide. All of the polysulfides above the disulfide are to be considered as "statistical" compounds. The composition of a given product may correspond to R_2S_3 , R_2S_4 , or R_2S_5 , but it may be a mixture of all of these, with some disulfide and some free sulfur.

This theory, proposed by Dr. Reid in the fall of 1942, contained the first plausible mechanism for the Levinstein process. Admittedly, it was an armchair theory based on a number of assumptions rather than on laboratory experience, but it served as a useful guide to later work (see reference to Fuson's theory, below, based on a study of the reactions of HS_2). The relation between the Reid theory and the composition of Thiokol is obvious:

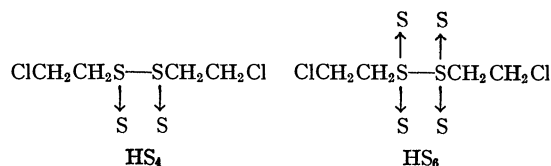


The dative-bonded sulfur atoms in Thiokol are easily removed by treatment with alkali or sodium sulfide and are easily replaced by milling with sulfur at about 70° C. Of considerable interest, also, is the recent work on the structure of ethylene polysulfides reported by personnel of the Mellon Institute (13), who presented experimental evidence for similar structures containing labile sulfur.

Contribution of Macy (8): This consisted of a study of the probable products of the reaction between ethylene and sulfur monochloride in the light of available data at Edgewood Arsenal with respect to the S and Cl contents of Levinstein H, its freezing point, and its average molecular weight. The structures of the polysulfides arrived at were influenced to a large degree by the Reid theory just described.

The pure H content of Levinstein H lies in the narrow range of about 68–73 per cent by weight, as already stated. The remainder consists of polysulfides. The analysis of the plant product (Table 1) gives close to 33.5 per cent S and 37.1 per cent Cl, in agreement with the stoichiometry expressed by Equation 2.

If all the "excess" sulfur indicated by Equation 2 were to precipitate, it would amount to 16.8 per cent of the total. After Levinstein H has been in storage a few weeks the deposition of sulfur usually starts, and in the course of a few months or a few years the deposit amounts to about 5–8 per cent of the weight of the initial sample. A large volume of data available, however, shows that the deposition does not proceed any further, even under treatment with chemical agents such as ammonia. For example, a sample of Levinstein H, after storage for 25 years in a steel 1-ton container, gave the following analysis: H content by distillation, 76.7 per cent; sulfur (total), 26.8 per cent; chlorine (total), 40.5 per cent. This indicated a deposit of about 6.7 per cent of sulfur in the container. It will be observed that the purity of the sample, with respect to H content, increased as the sulfur precipitated, which is to be expected (also see Table 1). In an effort to explain the composition of the resulting liquid phase, based on this analysis, it was postulated that it consisted of H and a polysulfide of the composition HS_4 , the final degradation product of a polysulfide HS_6 .



On the basis of the H content in the above analysis, and assuming HS_4 as the principal impurity, the calculated sulfur content is 27.0 per cent, in close agreement with the experimental value. Separation of sulfur from the higher polysulfides to form the lower polysulfides would not affect the freezing point. *Constancy of freezing point was one factor which led to the original belief that the sulfur is present in colloid form.*

These considerations led to the postulate that freshly prepared Levinstein H, which contains about 70 per cent by weight of H, will also contain 30 per cent of polysulfides represented by HS_6 , and that the polysulfides lose S slowly to the HS_4 level. It was also postulated that polysulfides higher than HS_6 may exist, the additional S atoms being extended as side chains on those already present in HS_6 .

Support for the proposal that the polysulfides in Levinstein H are at least HS_6 was obtained by a study of available freezing point data such as are shown in Table 2. Column III gives the H content of the sample as determined by the usual distillation analysis illustrated in Table 1. In order to determine the H content more rapidly, it was at one time the practice to determine the freezing point and apply Raoult's law, $\Delta t = K N$, where Δt is the depression in freezing point; N, the mole fraction of impurity; and K, the constant for pure H (the value of which is 36.4). For a long time it was

thought that the principal impurity in Levinstein H was chloroethyl chlorovinyl sulfide, the molecular weight of which is 157. The data obtained, assuming the impurity to have a molecular weight of 157, are considerably at variance with the H contents determined by distillation. In column IV the data obtained, assuming the impurity to have a molecular weight of 319 (that is, HS_6), are in quite good agreement with distillation data. The agreement of H content by distillation, and H content by

TABLE 2
FREEZING POINT AND H CONTENT OF LEVINSTEIN H

I No. of runs	II Average F.P.* (°C.)	III Net H by distillation	IV Net H by F.P.†
Edgewood Arsenal Manufacture, 1918			
1	4.0	67.3	55.3
17	7.16	71.1	66.6
1	7.8	72.4	69.0
10	8.09	71.2	70.2
7	8.67	72.4	72.5
1	10.0	73.6	78.1
Edgewood Arsenal Manufacture, 1937			
1	4.25	58.7	56.2
5	6.30	65.8	63.4
9	6.76	66.9	65.1
3	7.16	67.5	66.6
1	7.82	65.3	69.0
2	8.27	67.8	70.9

* Averages of data with maximum spread of 0.5° C.

† Calculated from Raoult's law, assuming impurity with M.W. = 319.

freezing point, assuming the polysulfide impurity to average HS_6 , is shown graphically by curve AA in Fig. 1.

It can be calculated from Raoult's law that a Levinstein H sample with an H content of 72.5 per cent and a freezing point of 9.05° (Fig. 1) contains an impurity with an average molecular weight of 351, which corresponds to HS_7 .

The line BB of Fig. 1 is of interest in that it shows how the H content of plant samples can be determined to within a few per cent by means of the freezing point after the data have been obtained for a comparatively few samples. The lower portion of the line gives data obtained in certain tests to determine storage stability of Levinstein H in steel munitions under tropical conditions. Levinstein H decomposes fairly rapidly under these conditions, but in the first stages of the decomposition there is a rapid decrease in freezing point with relatively small decrease in H content. This indicates that the polysulfides decompose first by disproportionation. The data for the plant samples obtained in 1937 apparently fall on a line parallel to BB but displaced slightly to the left of it.

The decomposition of Levinstein H in small steel containers is remarkably rapid under tropical conditions

(100–150° F.), probably due to the oxidizing nature of the sulfur in the polysulfides, $\text{Fe} + \ddot{\text{S}}: \rightarrow \text{Fe}^{++} : \ddot{\text{S}}:-$, and subsequent reaction with ionic species in mustard similar to those indicated by Equation 3 and postulated by Bell, Bennett, and Hock (1). On the other hand,

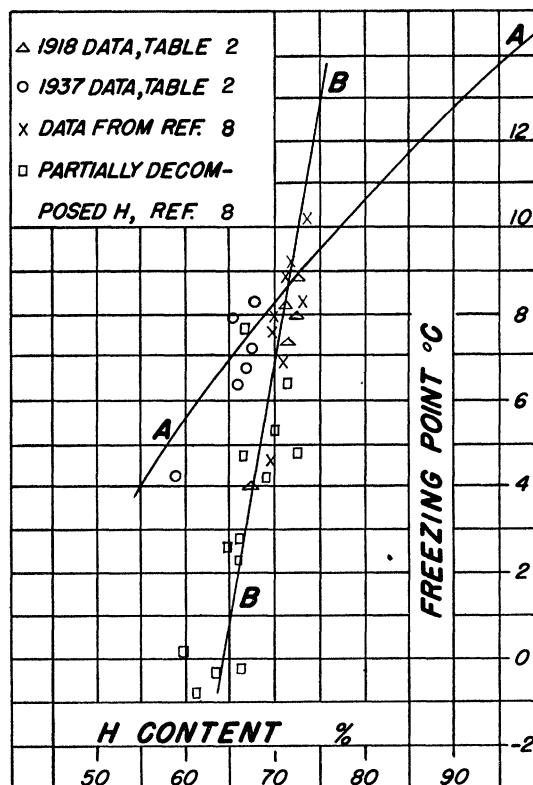
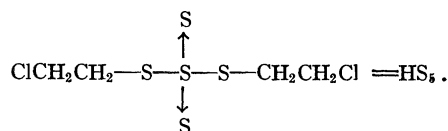


FIG. 1. Curve AA—Relation between freezing point and H content of Levinstein H according to Raoult's law for impurity with molecular weight of 319. Line BB—Freezing point and H content of plant runs of Levinstein H.

Levinstein H is quite stable toward aluminum, the tight aluminum sulfide coat formed by oxidation with the polysulfides apparently giving the same sort of protection that is afforded by aluminum oxide.

A result which at first appeared to be quite startling was the fact that, when samples of Levinstein H have decomposed in steel containers to the extent that very little pure H can be found by distillation, the material is even more vesicant than the original samples. It was suggested to Dr. Fuson at the University of Illinois, through OSRD channels, that the tarry decomposition products may contain higher homologs of mustard, which are known to be more vesicant and that the products obtained by heating mustard would be worthy of study. The result of this work was reported recently by Fuson (6), who found such homologs and points out that the mechanism of such decomposition by mustard had been thought out nearly 20 years ago by Bell, Bennett, and Hock (1).

Current status due to Fuson, et al. (6): The Edgewood Arsenal postulates were summarized (8, 10) in June 1943. Intensive work on the isolation and properties of the polysulfides in Levinstein H was undertaken not only by Fuson's group at the University of Illinois but also by British investigators. Both sets of investigators reached the conclusion that HS₂ does not sulfurize readily (the basis of the Edgewood theory) but that HS₃ does add sulfur easily and is the structurally important unit among the polysulfides:



Fuson (and British workers) assume that the —S—S—S— unit in HS₃ adds more sulfur at the central atom. The polysulfide generally present in highest concentration in Levinstein H newly made is HS₇, but all these higher polysulfides lose sulfur readily down to the stable HS₃ level with is illustrated here. This new conception is quite different from the well-known Thiokol two-in-line structure described earlier in this article.

The Edgewood theory assumed that polysulfides of H are built up on the HS₂ unit. Fuson, in experiments designed to find out how HS₂ disappears in the Levinstein process, discovered that it reacts with sulfur

monochloride to yield S₃Cl₂ as a most important product. This reacts with ethylene in the Levinstein process



and the HS₃ is sulfurized by the S₂Cl₂ present to higher polysulfides. For further details on a brilliant piece of work the reader is referred to the papers by Fuson and his associates (6).

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Starring in *American Men of Science*

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IN 1903 J. MCKEEN CATTELL, THEN PROFESSOR of psychology at Columbia University and editor of *Science*, undertook to prepare a list of the 1,000 most significant living American scientists. The methods which he used were, in brief, as follows:

Ten outstanding leaders in each of 12 sciences were asked to list in order of merit the leading research scientists in their science. These 120 judges were well distributed geographically, represented several different educational institutions, and were considered to have good judgment. From their lists, Cattell worked out the average rank of each of the scientists voted upon. The number selected in each science to make up the 1,000 was approximately one-fourth of the number of such scientists then productive in America. Biographical sketches were obtained of all the scientists of 1903 judged worthy of sketching in a biographical directory. When the first *American men of science* was published in 1906, asterisks were inserted to indicate the 1,000 leaders.

The directory proved so widely useful that later editions were issued in 1910, 1921, 1928, 1933, 1938, and 1944. These successive editions contained an increasing number of sketches—approximately 4,000, 5,500, 9,500, 13,500, 22,000, and 34,000, respectively.

For the second edition, voting on starring was done by all living starred scientists who would cooperate. For subsequent editions, all those nominated by a number of persons as meriting starring also were asked to vote.

The decision as to which fields of work were to be recognized by the starring of leaders was made personally by Cattell. He chose anatomy, anthropology, astronomy, botany, chemistry, geology, mathematics, pathology, physics, physiology, psychology, and zoology. Thus, even the most eminent workers in other fields were not eligible for a star. Moreover, a man who worked between well-recognized fields—in biochemistry, geophysics, or astrophysics, for example—or whose work overlapped two or more sciences, as does that of many ecologists and biologists, was rarely starred unless highly distinguished.