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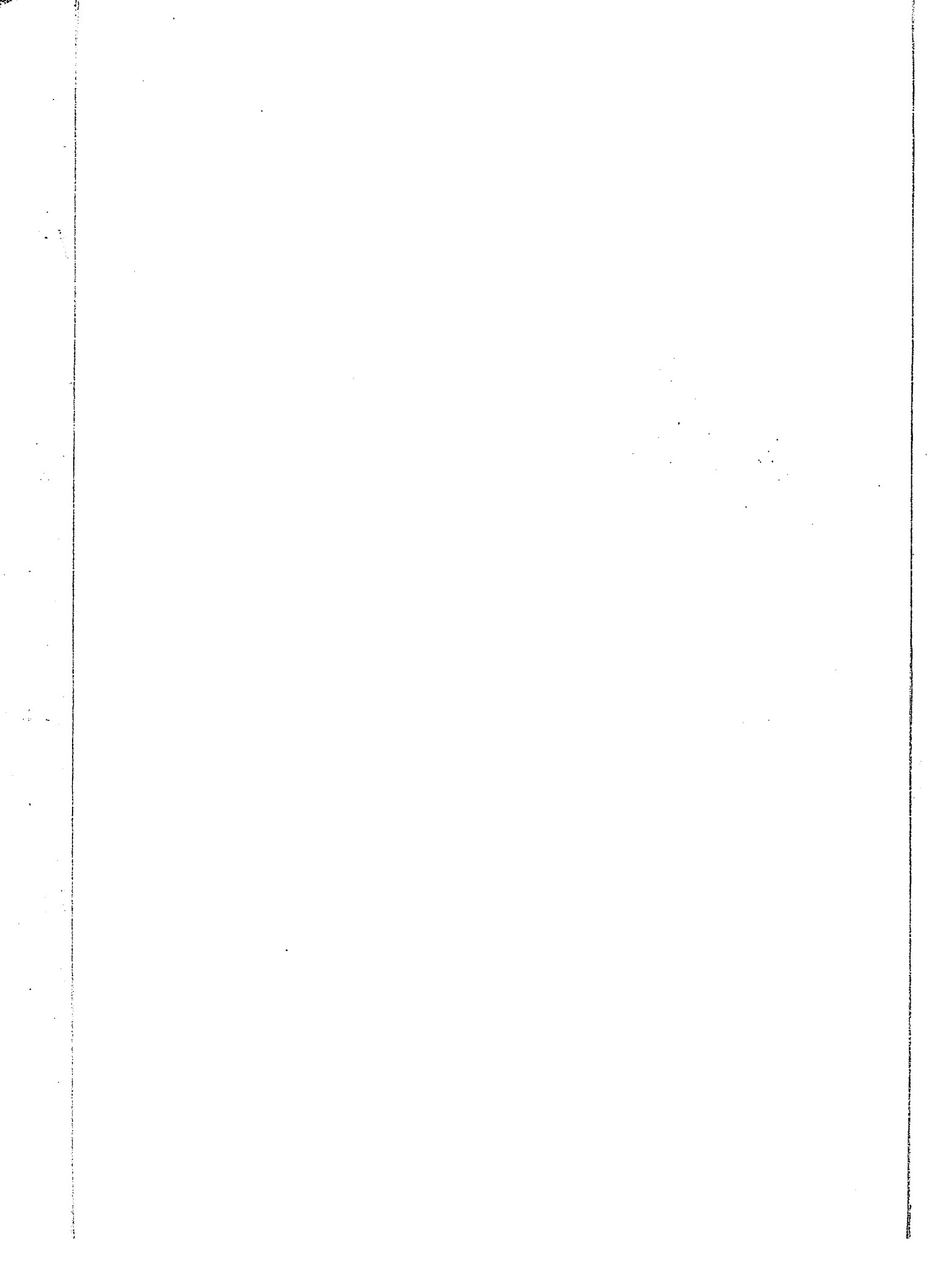
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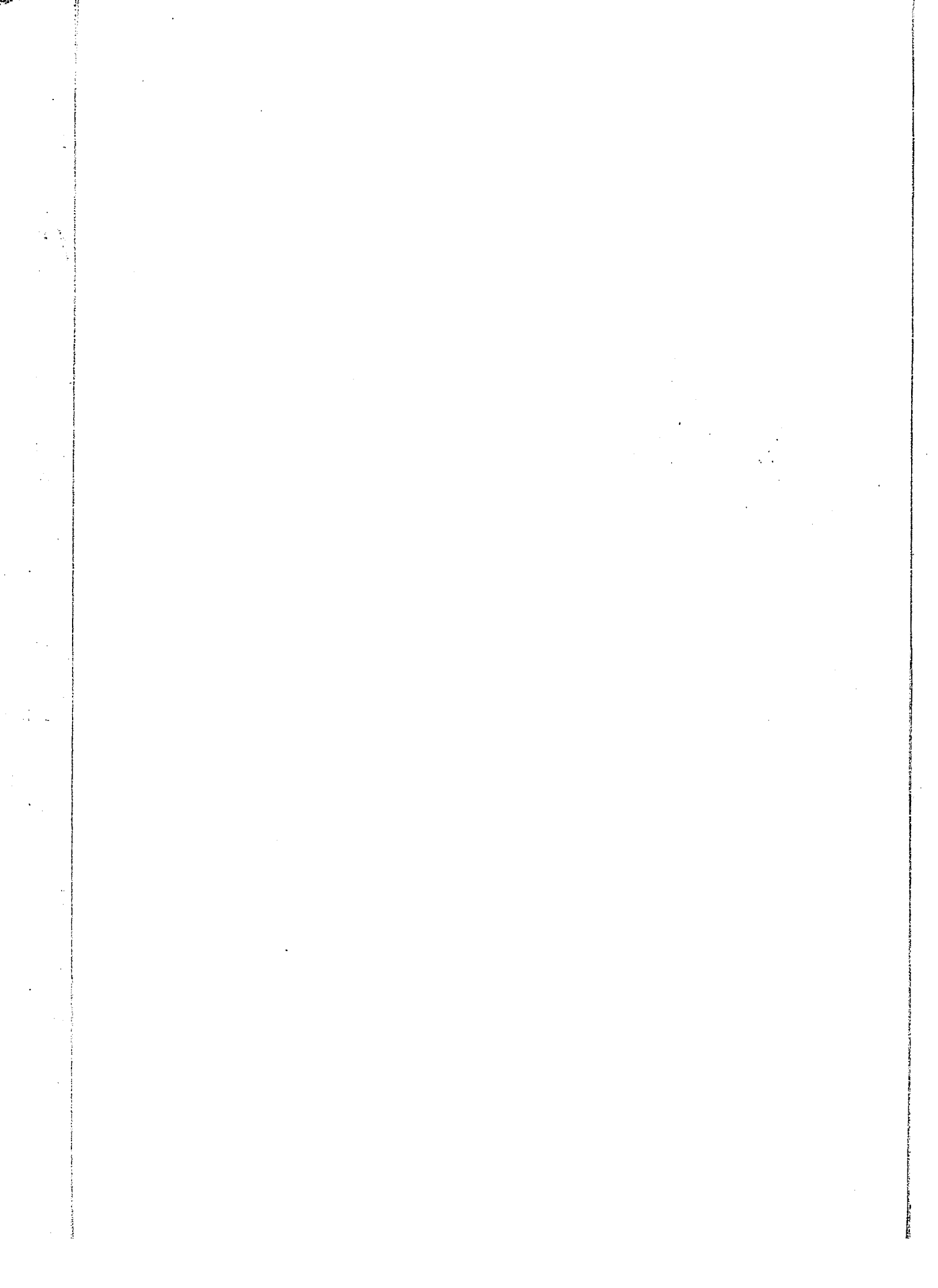
A STUDY OF REACTIONS IN LIQUID HYDROGEN SULPHIDE

by

George Norman Quam

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject -- Inorganic Chemistry

Approved

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Signature was redacted for privacy.

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Signature was redacted for privacy.

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1924

ACKNOWLEDGEMENT

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A STUDY OF REACTIONS IN LIQUID HYDROGEN SULPHIDE

I. Introduction

A. Purpose.

A study of the solvent action of liquid hydrogen sulphide has been made by several investigators[1,2,3,4,5,6] but it is apparent that in every case the observations were made over a very limited period of time and only at low temperatures. Likewise, reactions[2,3,4] and conductivity measurements[1,2,3,5] in liquid hydrogen sulphide have been observed under similar conditions of time and temperature. In the investigation conducted in this laboratory the attempt was made to make observations over a long period of time, thus lending greater assurance of reaching equilibrium, and over a comparatively wide range of temperature. Observations were extended to a large number of additional products, more especially to the inorganic class of compounds. Preliminary observations in this laboratory showed that a more extended study of solubilities, reactions and conductivity measurements in liquid hydrogen sulphide would tend

1. McIntosh and Steel, Proc. Roy. Soc., 73, 450 (1904).
2. Walker, McIntosh and Archibald, J.Chem.Soc.,85,1098 (1904).
3. Antony and Magri, Gazz. Chim. ital., 35, 206 (1905).
4. Magri, Atti. R. accad. Lincei., V, 16, 171 (1907).
5. Archibald and McIntosh, Proc. Roy. Soc. 73, 454 (1904).
6. Skilling, A.C.J., 26, 383 (1901).

to clarify the chemistry of liquid hydrogen sulphide and show relationships that would enhance, or at least verify, our knowledge of the present systems of classification of elements and compounds. With the above possibilities in view the investigation was undertaken.

B. Hydrogen Sulphide and Related Hydrides.

The hydrides of the right-hand families of groups five, six and seven of the periodic table show concordant relationships but the gradation of physical and chemical properties are not always what one would expect from the periodic arrangement of the elements. From a comparison of properties of the hydrides of oxygen, sulphur, selenium, and tellurium Forcrand, Fonzes and Diacon[1] pointed out that the first and last differ markedly from the second and third, and that the two median members, hydrogen sulphide and hydrogen selenide, show striking similarities in both physical and chemical properties. Altho this cannot be considered the rule we do note many instances of marked dissimilarity between the first and second members of a group. The hydride of oxygen holds a very unique position in that it is the only liquid hydride, at room temperature, of the right-hand families of the fifth,

1. Forcrand, Fonzes and Diacon, Compt. rend., 134, 281 (1902).

sixth and seventh groups; its heat of formation is the highest; parallel with this it is the most difficult to dissociate by heat; it is a neutral product; and shows the tendency to polymerize[1,2].

If the differences of boiling points and melting points of these hydrides are calculated the following relationships are shown:

TABLE I

Differences of Boiling Points and Melting Points
(Degrees Centigrade)

NH_3	39	H_2O	100	HF	101.7
PH_3	48.5	H_2S	23.6	HCl	29.4
AsH_3	58.7	H_2Se	22	HBr	17.4
SbH_3	73.5	H_2Te	57	HI	15.7

The fifth and seventh groups of the periodic table show a reversal while the sixth shows outstanding irregularity. Further the lack of uniformity between the first and second members of the sixth and seventh groups is prominent.

The data in Table II are gathered from the Smithsonian Tables except where otherwise indicated. It is to be noted that the dielectric constant, the viscosity,

1. Sutherland, Phil. Mag., V, 50, 460 (1900).
2. Tamman, Z. physik. Chem. 72, 609 (1910).

TABLE II

Physical Constants

	H_2O	H_2S	NH_3
Melting point	0	-83.2_1*	-77.34
Boiling point	100	-60.2_1*	-38.5
Crit. Temp.	374	100.4_1	130.0
Crit. Pres.	217.5	89.05_1	115.0
Density	1	$0.95(-60°C.)$*	0.6234
Ht. of Vap. (small cal. per gm.)	538.7	131.98_2*	321.3_2
Surf. Tension	75.6(0°C.)	$25.434(-60°C.)_3$	23.34(11.1°C)
Viscosity (x 10^{-3})	10.63(18°C)	$4.17(-60°C.)_3$	2.558(-38.5°C.)
Dielect. Const.	80	10.2_3	22
Temp. of rapid decomp.	2000°C.	400-600°C.	1300°C.
Heat of form.	684	47	118.9

*Melting points have been determined by others to be:
-83.6_4 and -83_3. Other boiling points reported are: -60.1_5,
-60.0_4, and -62.0_3. The density has also been given as:
0.964_5. Mol. heats of vaporization have been reported as:
4683_6, 4494.8_2, and 4659.4_4 calories.

and the surface tension are all very much lower for hydrogen

sulphide than for water.

1. Cardoso and Arni, J. chim. phys., 10, 504 (1912).
2. Estreicher and Schnerr, Zentr. Blatt, IV, 1737 (1910).
3. Magri, Atti. R. accad. Lincei, V, 16, 518 (1907).
4. Maas and McIntosh, Trans. Roy. Soc. Canada 8, 65 (1914).
5. McIntosh and Steel, Proc. Roy. Soc., 73, 450 (1904).
6. Elliott and McIntosh, J. Phys. Chem., 12, 163 (1908).

A comparison of physical constants does not indicate a very close relationship of hydrides of oxygen and sulphur. With this in view we have no reason to suppose that the chemistry of liquid hydrogen sulphide should show very close resemblance to that of liquid water. The conduct of hydrogen sulphide in water should not be confused with the chemistry of pure liquid hydrogen sulphide as discussed in the following pages.

II. Historical

A. Introduction.

The first allusion to the existence of hydrogen sulphide is probably the description in Papyrus of Leyden[1] in which Zosimus speaks of the unpleasant smell produced from a solution of polysulphides of calcium, which was then known as "divine water".

The first attempt to liquefy hydrogen sulphide was made by Foncroy and Vanquelin[2] but without success as the lowest temperature reached was -40° C.

In his memorable experiments on liquefaction of gases Faraday[3] succeeded in preparing liquid hydrogen sulphide by allowing pure ferrous sulphide and sulphuric acid to act in a strong bent tube. By introducing a small gauge into the tube he found the pressure to be 17 atmo. at 50° F.

In the investigations discussed below hydrogen sulphide was liquefied either by compression[4] or by lowering the temperature[5].

B. Physical Constants.

The physical constants for liquid hydrogen sulphide have already been enumerated in Table II.

1. Roscoe and Schorlemmer, Treatise on Chemistry I, 4 (1920 Ed.).
2. Foncroy and Vanquelin, Ann. chim. 29, 287.
3. Faraday, Phil. Trans., 113, 189 (1823).
4. Skilling, A.C.J., 26, 383 (1901).
5. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).

The accepted M.P., B.P., T_c and P_c recorded in Table II are those of Cardosi and Arni[1]. For these measurements the gas was prepared from purified ferrous sulphide and hydrochloric acid, then it was dried and fractionated fourteen times before being finally liquefied for use. The hydrogen sulphide used in the determination of density, dielectric constant, surface tension, viscosity and conductivity measurements by Magri[2] was prepared from ferrous sulphide and sulphuric acid. The elaborate scheme for purification which was resorted to will be discussed under "Preparation of Pure Liquid Hydrogen Sulphide".

The latent heat of vaporization was calculated by Maas and McIntosh[3] from dp/dt values by means of Clausius Equation. Elliott and McIntosh[4] found the calculated values to be 19.3×10^{10} ergs and the mean experimental value to be 19.6×10^{10} ergs. The measurements were made in a modified Marshall-Ramsay apparatus[5].

C. Solvent Action and Reactivity of Liquid Hydrogen Sulphide.

Skilling[6] attempted a study of the solvent action of liquid hydrogen sulphide by placing a crystal of potassium chloride in liquid hydrogen sulphide prepared in a Pictet compressor. He reported that the potassium chloride dissolv-

1. Cardoso and Arni, J. chim. phys., 10, 504 (1912).
2. Magri, Atti. R. accad. Lincei, V, 16, 518 (1907).
3. Maas and McIntosh, Trans. Roy. Soc. Canada 8, 65 (1914).
4. Elliott and McIntosh, J. Phys. Chem. 12, 163 (1908).
5. Franklin and Kraus, J. Phys. Chem., 11, 553 (1907).
6. Skilling, A.C.J. 26, 383 (1901).

ed readily. Antony and Magri[1], however, found that inorganic salts are invariably insoluble and non-reactive, even the oxidizing agents such as chromates and permanganates indicated no action. Non-metallic compounds dissolved slightly and a large number of organic compounds dissolved to a marked degree. With the exception of the halogens the elements studied were found to be insoluble and non-reactive.

Archibald and McIntosh[2] reported observations which confirm those above. McIntosh and Steele[3] found that hydrogen chloride and hydrogen bromide were the only inorganic substances which would readily dissolve and the organic ammonium salts were readily soluble. It must be borne in mind that all these observations were made at temperatures below the boiling point of liquid hydrogen sulphide over a very short period of time and, further, that the classes of compounds observed were very limited and in most cases only a few products were studied. The conclusions in many respects should necessarily be considered tentatively until more complete data can be gathered and better methods of observation perfected.

D. Electrical Conductivity in Liquid Hydrogen Sulphide.

In the observation on potassium chloride Skilling[4]

1. Antony and Magri, Gazz. chim. ital., 35, 306 (1905).
2. Archibald and McIntosh, Proc. Roy. Soc., 73, 454 (1904).
3. McIntosh and Steel, Proc. Roy. Soc., 73, 450 (1904).
4. Skilling, A.C.J., 26, 383 (1901).

found that a solution of potassium chloride in hydrogen
sulphide would not conduct the electric current.

McIntosh and Steel[1] reported that no solutions
of inorganic products in hydrogen sulphide would conduct
and that solutions of organic ammonium salts did conduct
the electric current to a fair degree.   In the same year
Archibald and McIntosh[2] found the values for solutions of
triethyl ammonium chloride to be:

Mol. Conc.	Cond. (recip. ohms X 10^{-6})
0.014	117.0
0.401	1580.0

In a large number of cases the temperature coefficients
were found to be positive over a small range of tempera-
ture at normal pressure.   They arrived at the general
conclusion that in all cases the organic solute seemed to
be the carrier and not the hydride, hydrogen sulphide.
This idea was reiterated in a paper by Walker, McIntosh,
and Archibald[3] in which they stated that ionization occurs,
if at all, in only such substances as seem to combine.   In
their extensive study of the liquid hydrides of the halogen
family they included some observations on liquid hydrogen
sulphide.   The comparative study was made by placing 4 c.c.
of the solvent in a conductivity cell and adding four drops,

1. McIntosh and Steel, Proc. Roy. Soc., 73, 450 (1904).
2. Archibald and McIntosh, Proc. Roy. Soc., 73, 454 (1904).
3. Walker, McIntosh and Archibald, J.Chem.Soc.,85, 1098 (1904).

or a few crystals, of the product and the results tabulated in a way that showed the approximate relative conductance values. The result was that only solutions of pyridene, piperidene, nicotine, and quinoline showed appreciable conductivities and only a few scattered organic compounds showed fair or poor conductance values. Over ninty per-cent of the solutions were indicated as non-conductors.

In a more specialized piece of work Antony and Magri[1] made conductance measurements in a number of solutions of inorganic products, as well as organic. They reported that iodine, sulphur monochloride, phosphorus trichloride, bismuth trichloride, phosphorus triodide, and phosphorus tribromide were the only solutions of inorganic products which would conduct. The work on solutions of iodine was continued and compared to solutions of sulphur monoiodide by Magri[2]. A 1.1% solution of iodine had a conductance value of 1.34×10^{-5} recip. ohms ($-60°$ C.) and a 1.2% solution of sulphur monoiodide had a value of 5.8×10^{-6} recip. ohms, which is much less than that for iodine. His conclusion was that the difference must be due to the dissociation of iodine molecules according to Walden's[3] idea of abnormal electrolytes.

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).
2. Magri, Atti. R. accad. Lincei, V, 16, 518 (1907).
3. Walden, Z. physik. Chem., 43, 385 (1903).

Thus: $I_2 = I^- + I^+$

or, $2I_2 = 3I^- + I^{+++}$
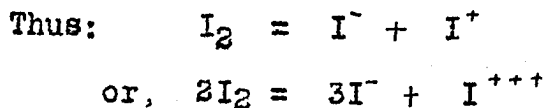
E. Summary.

The study of the solvent action of liquid hydrogen sulphide has been limited almost wholly to that of organic products and these did not include any of the sulphur derivatives such as sulphides and mercaptans. In the inorganic field little has been done aside from a study of a few metallic elements, the halogens, several salts, and a few oxidizing agents. In general, the investigators have come to the conclusion that liquid hydrogen sulphide conducts itself much like an organic solvent.

The conductivity measurements recorded are few and all have been taken at low temperatures. Here again the work has been limited largely to the organic class of compounds.

The studies of reactions in pure H_2S are all subject to the same criticism. The periods of observation were very short and the experiments were carried on at temperatures below the boiling points of liquid hydrogen sulphide. It is reasonable to suppose that equilibrium conditions were not observed in most cases.

III. Preparation of Pure Hydrogen Sulphide

A. Historical.

The method of liquifying hydrogen sulphide adopted in this laboratory was a combination of lowering the temperature and slightly increasing the pressure. The design of the apparatus was a modification of that used by Antony and Magri[1] and therefore a brief description of their apparatus is deemed necessary at this point.

Antony and Magri prepared hydrogen sulphide by allowing sulphuric acid to act upon ferrous sulphide. The acid spray was caught in a large trap and the arsine, which was found present, was held back in a tower filled with layers of pumice and iodine. The gas was then washed in distilled water in a series of wash towers and then cooled by passing thru a lead coil. It was then dried by passing thru a series of towers filled with anhydrous calcium chloride, thru a tower filled with glass wool, thru a series of towers containing phosphoric acid anhydride, and finally thru a tall tower containing layers of pumice and pieces of metallic sodium. The sodium was used as a means to take up the last traces of water. The hydrogen sulphide, then considered pure and dry, was liquefied by passing thru glass coils immersed in a cooling mixture of methyl alcohol and solid carbon dioxide. These coils were

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).

made a fixed part of the Dewar's vacuum tube by passing the outlet tube thru the bottoms.

B. Materials Used.

FERROUS SULPHIDE: The stick ferrous sulphide supplied by J. T. Baker Chem. Co. was used in the hydrogen sulphide generator.

HYDROCHLORIC ACID: Baker's analyzed product, J. T. Baker Chem. Co.

POTASSIUM SULPHIDE: Fused, granulated potassium sulphide supplied by Eimer and Amend.

IODINE: Baker and Adamson's resublimed iodine.

SODIUM: Metallic sodium from J. T. Baker Chem. Co.

PHOSPHORIC ACID ANHYDRIDE: Mallinkrodt's anhydrous phosphoric acid.

ALUMINUM SULPHIDE: This product was prepared in this laboratory by direct union of powdered aluminum and flowers of sulphur in the proportion of 1:2. The method of Stein[1] was modified to the extent that the process was made continuous.

A large sand crucible C (Fig. 1) was covered by a second inverted crucible B with a hole in its bottom. After the process was started additional charges were in-

1. Gmelin-Kraut-Handbuk der Anorg. Chem., II$_2$, 605.

troduced thru the quartz tube A leading into the hole of
the upper crucible.   The process was started by placing a
small charge in the lower crucible and heating with a Meker

Fig. 1.
Apparatus
for the preparation of Al₂S₃
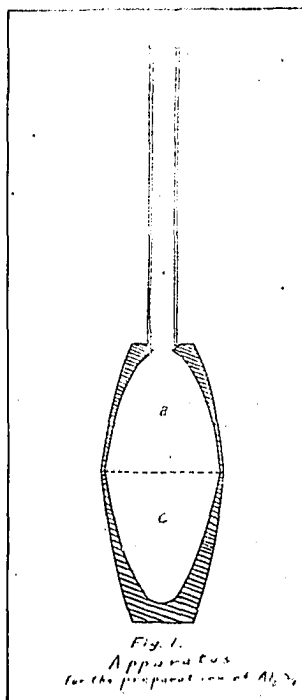
burner up to about 100° C.   The charge was then ignited
by means of a hand torch.   By careful control each success-
ive charge added thru the quartz tube A would ignite when
it struck the hot mass of sulphide already formed.   The
process could thus be continued until the lower crucible
was practically filled with aluminum sulphide.   The crucible
was then broken away from the mass and a new crucible in-
stalled for the next run.

The product contained tiny globules of pure Al scattered thruout the mass but the analysis of the pure yellow-gray product satisfied the formula Al_2S_3.

CARBON DIOXIDE AND ETHER: Solid carbon dioxide was used to lower the temperature of the ether-carbon dioxide bath and was also used free in cooling the tubes in which liquid hydrogen sulphide was sealed.

C. Apparatus.

The apparatus, Fig. 2, was designed in such a way that all parts that are not standard could be made in this laboratory and serve the purpose desired to bhe best advantage. All the glass used was a soft lime-glass so that all tubes could be readily sealed together. All parts beyond the drying chain and to the calcium chloride tube W are sealed together so that the hydrogen sulphide vapor and liquid were exposed to no other material than the glass surfaces.

The generator consisted of bottles G and B and flask A, so arranged that the pressure built up was equal to the hydrostatic pressure. Funnel C was included for the purpose of replenishing the acid conveniently during the operation by forcing the acid into bottle B with compressed air, being careful not to introduce any air. Stop-cook D made it possible to drain G thru E while B and A were filled. The lower part of G was packed with layers

APPARATUS FOR LIQUEFACTION OF HYDROGEN SULPH...
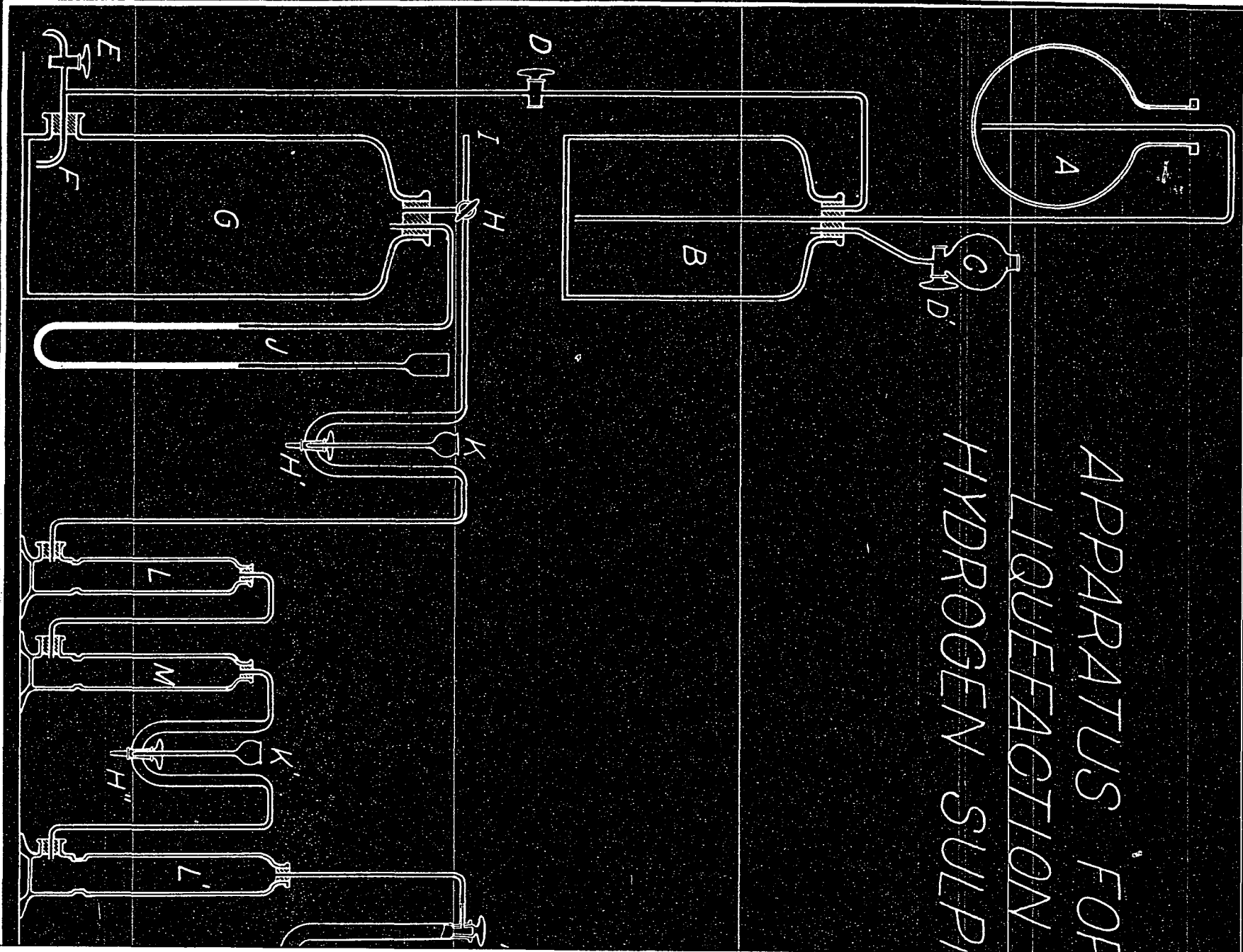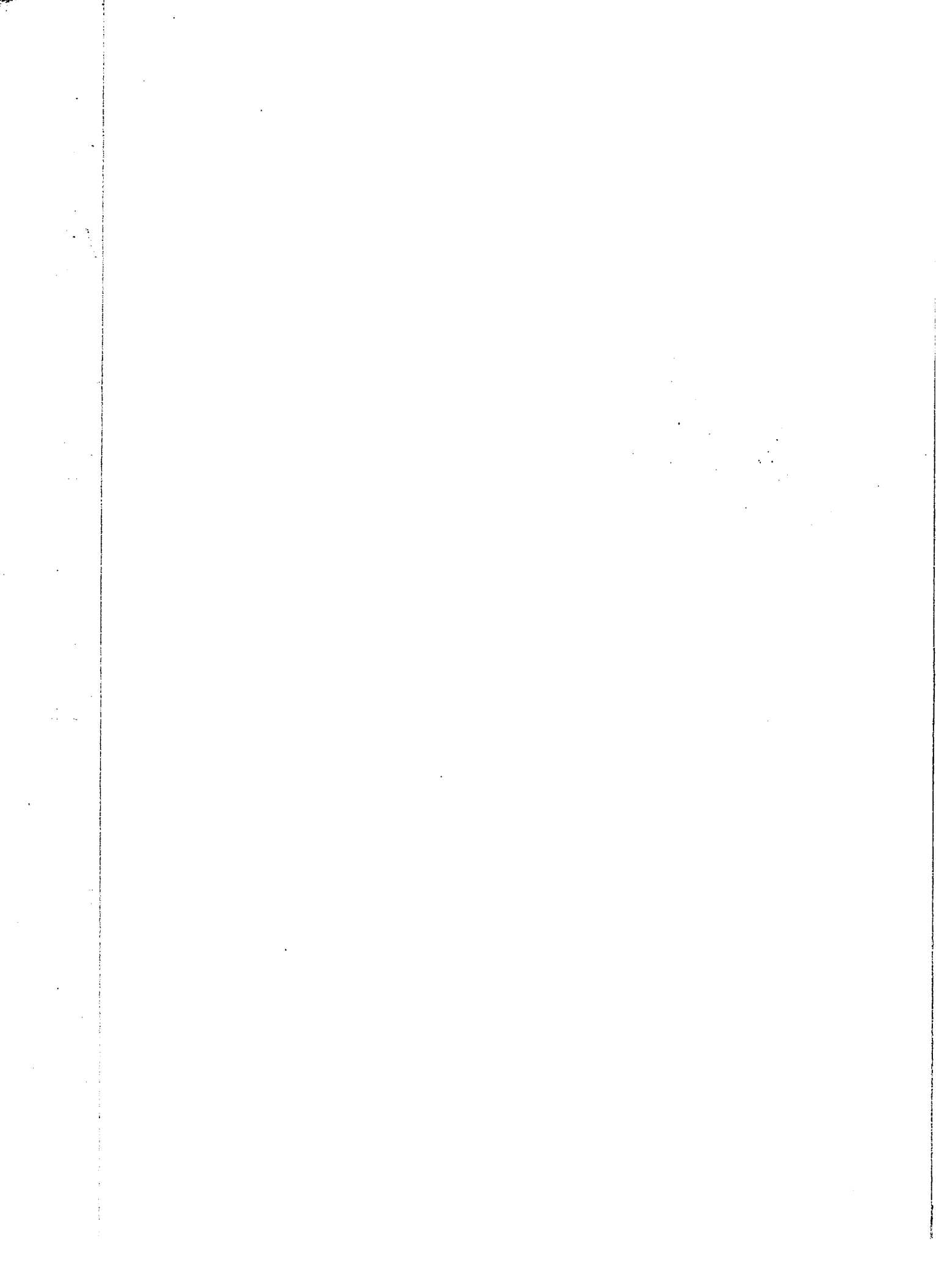
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LIQUEFACTION OF
HYDROGEN SULPHIDE
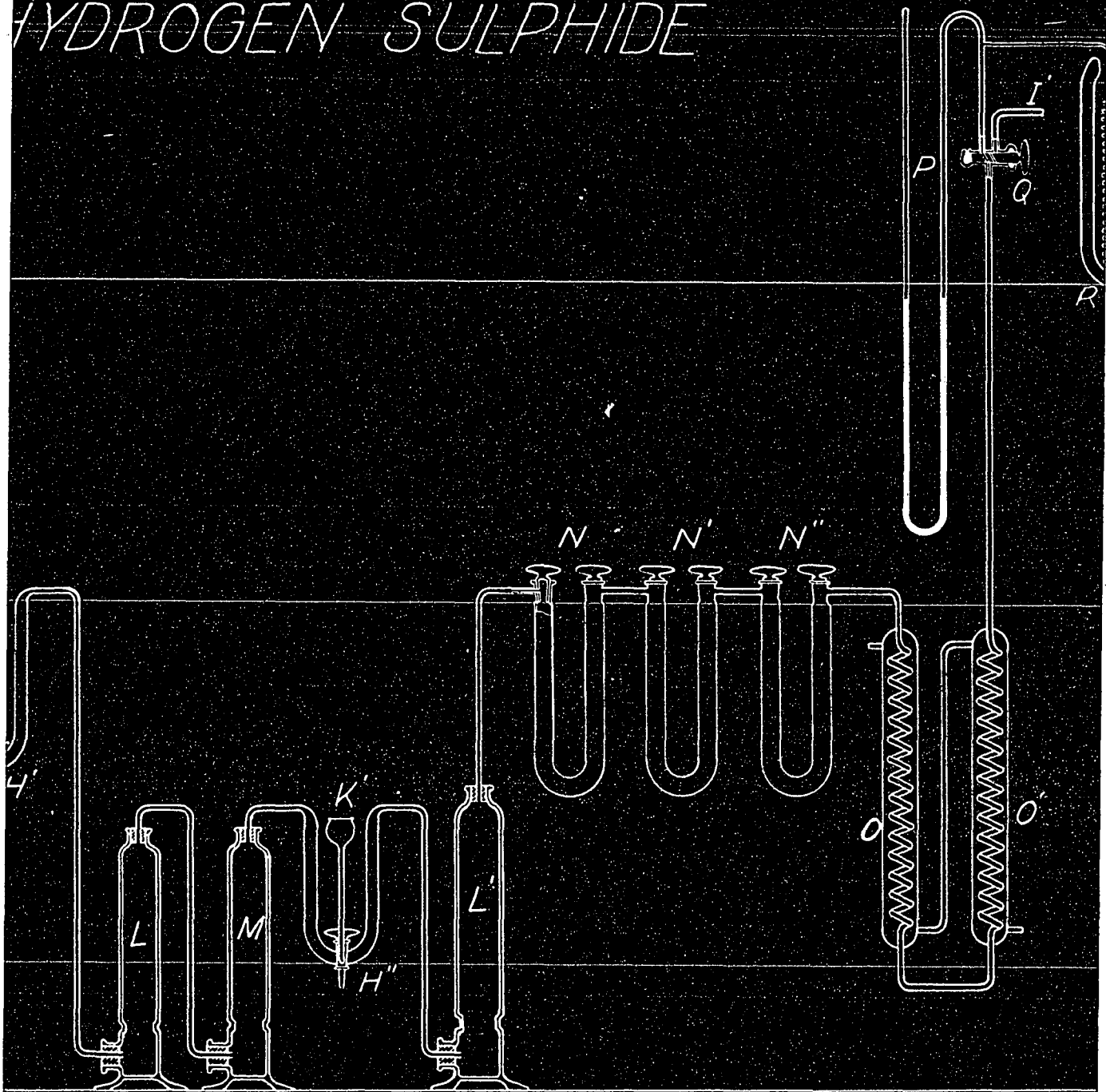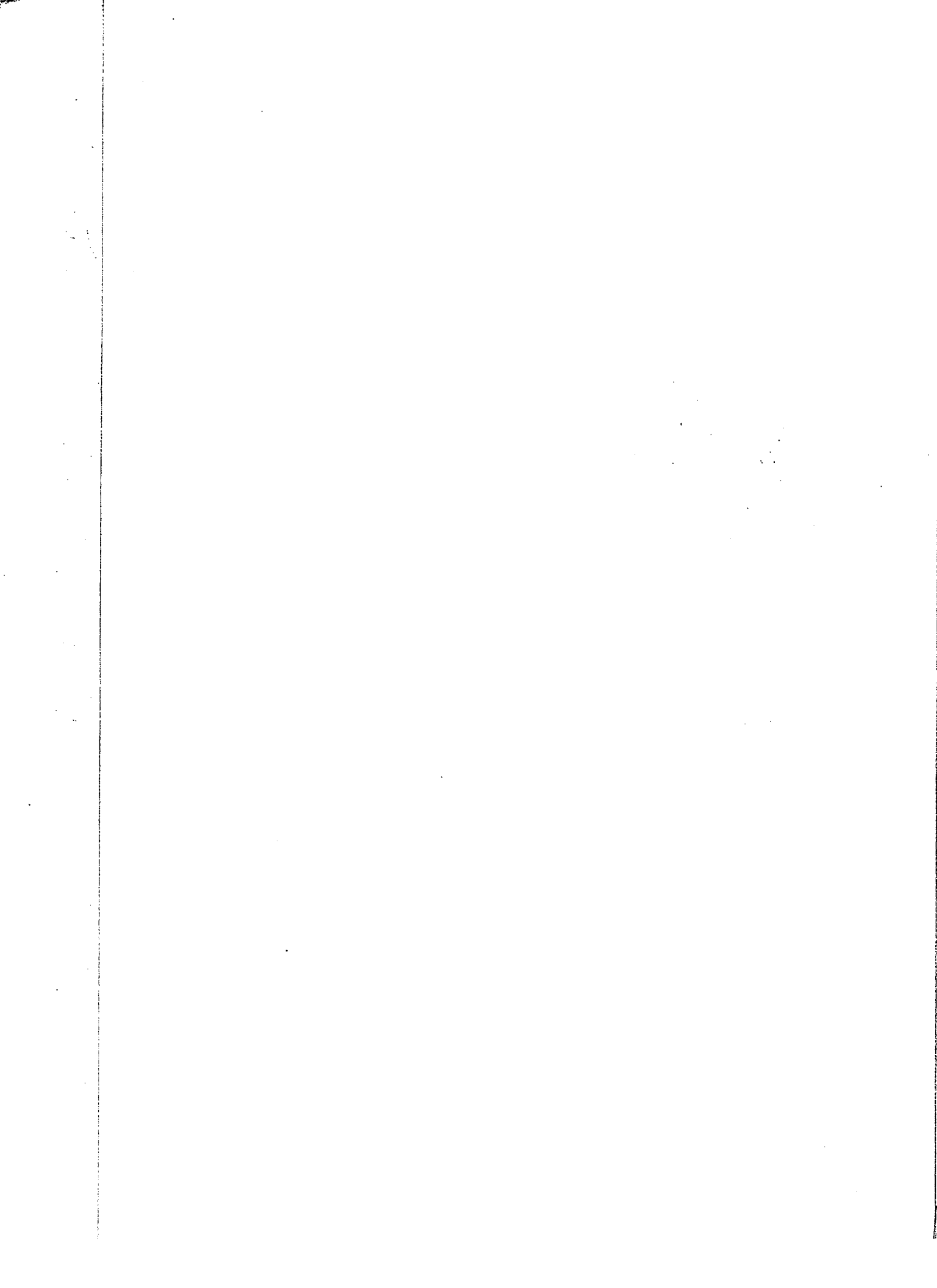
of pumice to prevent clogging at F and also to provide
additional space for acid. The mercury gauge J served
only as a safety valve. The three-way stop-cock H made
it possible to relieve the system thru I or receive hydro-
gen sulphide gas from a reserve Kipp generator by way of I
at any time. U-tubes K and K' were equipped with three-
way stop-cocks H' and H'' so that the potassium sulphide
solution could be replenished without breaking the chain.
Towers L and L' were filled with crushed aluminum sul-
phide and M contained pumice and iodine placed in layers.
N, N' and N'' were filled with phosphoric acid anhydride
and N''' (not shown) was filled with metallic sodium and
pumice. The latter, however, was not kept in the chain
for reasons discussed below. Coil condensers O and O' were
water cooled. Three-way stop-cock Q made it possible to
draw off dry hydrogen sulphide gas or pass it on to the
liquefaction coils R and R'. Coils R and R' and reservoir
T were immersed in the carbon dioxide-ether mixtures kept
in Dewar vacuum tubes. The coil about reservoir T mini-
mized the loss in transfer from R' to T. The asbestos cov-
ering S, S', and S'' was placed around the glass tubes to
prevent vaporization of the liquid hydrogen sulphide in its
course from one bath to the next and also out thru the out-
let tube V by way of stop-cock Q'. The asbestos at S, S'
and S'' was prepared in the form of a paste with ether, ap-

plied at once, and wrapped with cloth tape. Thus baking
was avoided and a good insulating cover was afforded. By
closing stop-cock Q" the liquid hydrogen sulphide in T
could be more readily forced thru outlet tube V into the
charging tubes. Calcium chloride tower W was inserted to
prevent back diffusion of water vapor from the back-pres-
sure column X. The water level in X could be controlled
by the reservoir Y, thus creating a back pressure on the
gas in the coils approximately to the extent of the hydro-
static pressure in X. The excess gas passed into Z and
was washed into the sewer by flowing water.

D. Process.

MANIPULATION: The apparatus, Fig. 2, proved to
be very effective and no difficulties were experienced in
manipulation. The simplicity of operation made it possible
for one to conduct the process, while charging reaction
tubes and making conductivity measurements.

The generator was charged by filling A and B with
dilute hydrochloric acid (1:1) and partially filling G with
stick ferrous sulphide. The siphons were started by clos-
ing valve D and blowing air in at C until the acid from B
started to flow into A. By closing D' and opening D the
acid started to flow into G. Stop-cock H was set to allow
the gas to flow thru the drying chain. In K the acid spray

was held back by a saturated solution of potassium sulphide;
the gas was then dried by aluminum sulphide in L, with sub-
sequent evolution of more hydrogen sulphide, and passed over
iodine in M to remove possible traces of arsine. Any hydro-
gen iodide that might be set free was held back in the sat-
urated potassium sulphide solution in K'. Again the gas was
dried by passing over layers of aluminum sulphide in L'.
The final drying was accomplished by allowing the gas to
pass over phosphoric acid anhydride in N, N' and N".

Before the refrigerating process was started the
gas was allowed to flow thru the system until all air had
been swept out and the inner surfaces were dry. (All parts
had been cleaned with chromic acid before the apparatus was
assembled.)

The water condensers O and O' were started and the
liquefaction was completed by allowing the pure dry hydrogen
sulphide to flow thru the coils, in R and R', which were
kept at -83° C. (Toluol Thermometer) in a bath of solid car-
bon dioxide and ether. The liquid hydrogen sulphide was
collected in the reservoir T in a third Dewar vacuum tube
containing the same refrigerating mixture. The free gas was
allowed to flow out by way of Q over calcium chloride in W
and into the back-pressure column X. The water level in X
was raised as high as the action of the generator would per-
mit.

The liquid hydrogen sulphide was removed from the reservoir T by closing stop-cock Q" and opening Q', allowing it to flow out at V. A rubber cap was slipped over the end of V to prevent condensation on the inner wall after the liquid had been removed.

Samples of dry gas were drawn off at I by setting stop-cock Q. No impurities were found by repeated tests but the iodine tower was kept in the chain as a precaution.

DISCUSSION: As has been previously mentioned, a fourth U-tube N''' containing metallic sodium and pumice, not shown in Fig. 2, was used at first. Antony and Magri[1] had used metallic sodium as a final drying agent. It was discovered that after a time the sodium lost its metallic luster and changed to a yellow color. Preliminary observations showed that sodium (in kerosene) and liquid hydrogen sulphide would react slowly to form the sulphide. The sodium product in tube N''' was removed, after it had changed to orange-yellow, and was analyzed. The smaller particles, when placed in water, gave no evolution of gas. The analysis of three representative samples for sulphur as copper sulphide and sodium as sodium chloride are shown in Table III. The results

TABLE III

Analysis of Sodium Product

Percent of	I	II	III	Theory (for Na_2S)
Na	60.76	62.34	61.32	58.98
S	35.83	37.11	37.90	41.02

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).

did not show any advantage in continuing the use of metallic sodium as a drying agent.

In the process hydrochloric acid was used instead of sulphuric, as recommended by Angony and Magri[1]. The presence of sulphuric acid would no doubt result in the formation of sulphur dioxide and thus cause distress in manipulation and make the process a questionable one.

The use of potassium sulphide had the advantage of not only neutralizing the acid spray but also of furnishing hydrogen sulphide in doing so.

Likewise, aluminum sulphide not only served as a drying agent but also as a producer of more hydrogen sulphide when either water or acid came in contact with it.

Preliminary observations showed that the activity of hydrogen sulphide was such that no metallic substances or rubber should come in contact with the pure gas or liquid during the process. In their apparatus Antony and Magri[1] freely used lead coils and caps, mercury seals and rubber connections. Paraffine, altho slightly soluble, is not altered chemically by the pure gas or liquid. Wherever it was necessary to use rubber stoppers and connections all exposed surfaces were coated heavily with paraffine. Fig. 2 indicates the extent of the all-glass section of the apparatus used in this laboratory.

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).

IV. A Study of Solubilities and Reactions

A. Apparatus.

The study of reactions in liquid hydrogen sulphide, at low temperatures (below -60° C.) and at normal pressure, over an extended period of time, would be prohibitive because of the cost of chemicals for the cooling mixtures necessary to maintain such low temperatures. In order to make such observations possible the mixture of the liquid and the product was sealed in strong glass tubes which would withstand the vapor pressure of the solutions within at room temperature. The tubes, Fig. 3, I and II, were made to withstand approximately one-hundred atmospheres pressure (Tested by a Cailletet pressure pump) under favorable conditions.
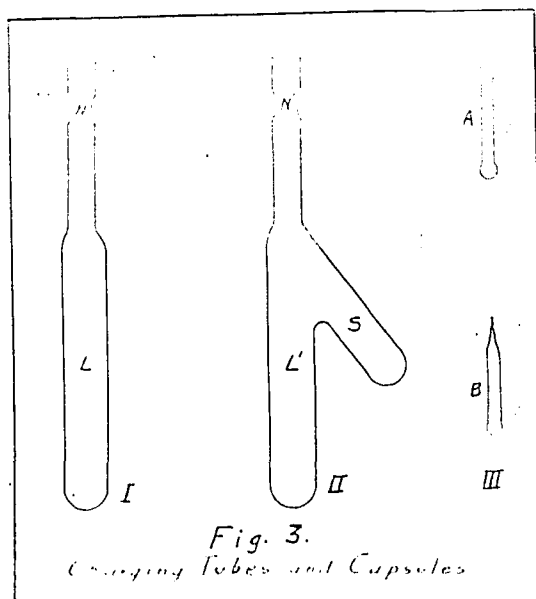
Fig. 3.
Charging Tubes and Capsules

The tube with the side arm, Fig. 3, II, was used when it was found that more than one liquid layer formed and thus a better separation was possible. The tubes of the type illustrated by Fig. 3, I, were 15 cm. long and made of glass tubes of 8 mm. and 12 mm. in diameter. Those illustrated by Fig. 3, II, were made of tubes of 8, 16, and 12 mm. diameter, the side-arm S being 12 mm. in diameter. The constrictions N and N' facilitated sealing off after the tubes were charged with liquid hydrogen sulphide.

The capsules, Fig. 3, III, were of thin-walled, soft glass tubes, 4mm. in diameter. The bottoms were blown very thin and after the liquid or solid was introduced the tube was drawn down and sealed, as illustrated by B, as near the product as possible without causing decomposition.

B. Manipulation.

In preparing to store away reaction tubes for extended observations the capsules were charged with the products that were to be placed in contact with liquid hydrogen sulphide. They were let down into the heavy glass tubes, Fig. 3, I and II, and placed in a desiccator ready for use. When ready to fill with liquid hydrogen sulphide the tube was capped with a drying tube and packed·in solid carbon dioxide. After the temperature of the tube had reached that of the carbon dioxide it was slipped over the outlet tube V of the liquefaction apparatus (refer to Fig. 2) as shown in

Fig. 4.

Fig. 4.
Charging Apparatus
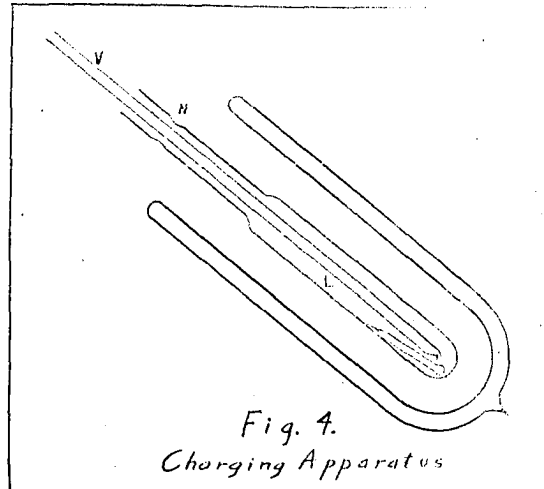
The liquid that first came into tube V was vaporized and
this displaced the air in tube L with hydrogen sulphide gas.
When the required amount of liquid hydrogen sulphide had
been introduced the tube L was sealed off at N.   At this
stage in the operation the charged tube was put to the sev-
erest test.   While the lower end was at the temperature of
solid carbon dioxide the point of sealing, 4 cm. or less
above, was at the temperature of melting glass.   Lack of
sufficient care at this stage was probably responsible for
a large part of the losses by explosions, which on some oc-
casions reached thirty per-cent.   After the seal had reached

room temperature the tube was removed from the Dewar vacuum
tube and suspended in a lead pipe for twenty minutes. It
was then placed in a tank of water for several hours. The
tubes were then taken out and the capsules rattled until
the thin end was shattered, permitting the liquid hydrogen
sulphide to come in contact with the solute. Observations
were made from time to time over a period of several months.
In some cases the temperature was lowered again in order to
observe separations. A reasonable length of time, after no
further visible change seemed to be taking place, was allowed
before opening the tubes for analysis.

The solid materials were washed into one end of
the tube and the other end, containing the solution or liquid
layers, was covered with solid carbon dioxide. When the tube
had cooled sufficiently it was cut off just below the collec-
tion of solids and each part treated separately.

The outstanding advantage of this method was that a
reaction could be studied over an extended period of time
until equilibrium conditions were reached. Observations could
be made at the start at room temperature or at low temperature
at will. A large number of reaction tubes could be stored
and observations made at any time until the tubes were opened
for analysis.

C. Observations (Inorganic Products).

PURE LIQUID H_2S (alone): It was found that pure

liquid hydrogen sulphide suffered slight decomposition upon standing in light. To determine this rate of decomposition equivalent quantities of the liquid were sealed in glass tubes of the same size and quality of glass and at the end of given periods the tubes were opened. After evaporation of the liquid hydrogen sulphide the sulphur deposited was determined. The results were:

Days exposure	0	15.	30
Aver. per-cent of S (by wt.)	0.092	0.1135	0.1132

ELEMENTS: With the exception of carbon all the products were placed in capsules and exposed to liquid hydrogen sulphide at room temperature. About 0.05 grams of the element was added to 2 to 3 c.c. of the liquid.

Sodium slowly changed to Na_2S. Silver and copper showed sulphide formation at once and by disintegration of the sulphide formed all the metal was finally converted to the sulphide. Gold was unaltered. Mercury darkened slowly and even after two months there was still a small particle of the unchanged element. The sulphide film seemed to hold intact until disturbed. Carbon was unaltered. Red phosphorus was not changed but arsenic and antimony were slowly changed to yellow and orange sulphides. Evidence of reaction with antimony was not shown until the second day and with arsenic the action was still slower. Sulphur was sol-

uble in hydrogen sulphide to the extent of 0.57 per-cent.
Selenium was slightly soluble and there was evidence of a
replacement reaction as well formed rhombic sulphur crystals
separated out during the second month. The solution gave a
definite test for selenium. Tellurium was not altered or
dissolved. Chlorine and bromine caused the separation of
free sulphur and the solutions turned to a light color while
iodine formed a violet brown solution and indicated no de-
composition. When the tubes containing bromine and chlorine
were opened excess pressure was evidenced by evolution of
hydrogen bromide and hydrogen chloride gas.

From the above it is apparent that the highly
positive elements tend to form stable sulphides in liquid
hydrogen sulphide while the highly negative tend to oxidize
the sulphur. The excess chlorine partially unites with the
liberated sulphur to form sulphur chloride. The border line
of reactivity is quite evident with the fifth group elements
of the periodic table studied. Altho selenium is less nega-
tive than sulphur it apparently is not negative enough to
form seleno-sulphide but still negative enough to replace
sulphur in establishing the equilibrium:

$$H_2S + Se = H_2Se + S$$
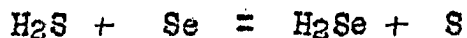
OXIDES AND PEROXIDES: Much free sulphur separated
out when sodium peroxide and barium peroxide were allowed to
come in contact with liquid hydrogen sulphide and sulphides

of sodium and barium were formed.

Carbon dioxide was soluble in liquid hydrogen sulphide. This is in accord with the observations of Thiel and Schulte[1].

Phosphorus pentoxide was very slightly soluble and arsenous oxide slowly reacted to form the sulphide.

Dry sulphur dioxide reacts vigorously with liquid hydrogen sulphide at room temperature with the separation of free sulphur. Antony and Magri[2] reported that a mixture of sulphur dioxide and liquid hydrogen sulphide was nonreactive but it was found in this laboratory that the reaction did take place slowly even at low temperatures.

Selenium dioxide reacts slowly to form free sulphur, free selenium, and water. The reaction

$$2 \ H_2S \ + \ SeO_2 \ = \ 3 \ S \ + \ Se \ + \ 2 \ H_2O$$
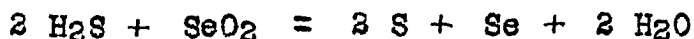
goes to completion.

Liquid hydrogen sulphide and liquid water formed a white crystalline hydrate. The composition was found to be $H_2S \cdot 5.7H_2O$. de Forcrand[3] found the hydrate to be of the composition $H_2S \cdot 6H_2O$ after a series of investigations in which the number of mols of H_2O reported varied from 15 to 5. Scheffer[4] gave the formula $H_2S \cdot 5H_2O$, but in 1919 Schef-

1. Thiel and Schulte, Z. physik. Chem., 96, 312 (1920).
2. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).
3. de Forcrand, Compt. rend., 135, 959 (1902).
4. Scheffer, Proc. Sci. K. Akad. Wet. Amsterdam, 14, 195 (1911).

for and Meijer[1] by indirect analysis by thermodynamic means determined the formula to be $H_2S \cdot 6H_2O$.

SULPHIDES and sulphydrates: The sulphides studied were: K_2S, CuS, HgS (red and black), PbS, Al_2S_3, P_2S_5, As_2S_3, Sb_2S_3, and FeS. Of all these sulphides only those of phosphorus, arsenic and antimony indicated solubility. More of the arsenous sulphide separated upon evaporation of the solution than of antimony sulphide, and phosphorus pentasulphide showed very slight solubility.

POTASSIUM SULPHYDRATE was insoluble but ammonium sulphydrate was slightly soluble. The degree of solubility was not determined because of the instability of the product. When the solution was cooled to -83° C. a large mass of light yellow crystals separated out and upon evaporation gave tests for the sulphide and ammonium radicals.

ACIDS: Meta-phosphoric and ortho-boric acids were insoluble.

Pyrosulphuric acid reacted vigorously with liquid hydrogen sulphide forming a yellow oil and much free sulphur. The solid finally all precipitated and two liquid layers were formed. The lower layer was a water solution of sulphuric acid while the upper contained free sulphur in what was apparently a mixture of persulphides. The latter gave sulphide tests and its conduct toward organic solvents and

1. Scheffer and Meijer, Verk. K. Akad. Wet., Amsterdam, 27, 1104 (1919).

alkalies indicated that a mixture of H_2S_2 and H_2S_3 was no doubt present.

Hydrogen chloride and hydrogen bromide are both soluble in hydrogen sulphide to a marked degree. The gases dried by sulphuric acid were passed into hydrogen sulphide for a long period of time. In the case of hydrogen chloride this was done until no further change in conductivity could be noticed. The maximum solubility of hydrogen chloride at the temperature of the solid carbon dioxide was 43.2 mol. per-cent.

HALIDES: The chlorides of ammonium, potassium, barium, and aluminum showed no change when in contact with liquid hydrogen sulphide. Lead chloride slowly changed to the lead sulphide. Anhydrous cuprous chloride and cobaltous chloride darkened at once in liquid hydrogen sulphide and after a long period the former had all changed to the sulphide and hydrochloric acid. With cobaltous chloride an equilibrium condition was reached and CoS, $CoCl_2$ and HCl were all found present. Mercuric chloride changed first to the black sulphide and then to the red variety in which form it remained stable in contact with liquid hydrogen sulphide. Zinc chloride was slightly soluble. Stannous chloride goes into solution and separates out as the sulphide while stannic chloride remains in solution and only upon evaporation

1. Sabatier, Compt. rend., 100, 1346 (1885).

is the yellow sulphide, SnS_2, thrown down. It is apparent that the higher concentration of hydrogen chloride in the latter tended to hold the sulphide in solution.

The trichloride and pentachloride of phosphorus are both soluble in liquid hydrogen sulphide. Slow decomposition took place with the separation of the respective sulphides. The separation, however, was more pronounced with the phosphorus compound. In both cases excess pressure in the tubes was due to the presence of hydrogen chloride. With arsenous chloride the formation of solution and decomposition was almost simultaneous. Antimony trichloride on the contrary was readily soluble and remained as a clear solution. Upon evaporation or cooling, however, a yellow solid separated from the solution which gave qualitative tests for antimony, sulphur and chlorine. Quantitative determinations of different samples did not give the same ratios. The results, however, always indicated a mixture of $SbSCl$ and Sb_2S_3. Ouvrard[1] has reported the formation of SbS_2Cl by the action of hydrogen sulphide gas on molten antimony trisulphide. Bismuth trichloride reacted in a manner similar to antimony trichloride but decomposition took place more readily. The red-orange solid separated out completely and the analysis consistently satisfied the formula $BiSCl$. Muir-Eagles[2] prepared $BiSCl$ by passing

1. Ouvrard, Compt. rend. 116, 1516 (1893).
2. Muir and Eagles, J.C.S., 67, 90 (1895).

hydrogen sulphide gas over bismuth trichloride at dull red-
ness.

The above four chlorides of the fifth group of
the periodic table were consistent in that the phosphorus
and arsenic chlorides formed the sulphides, the arsenous
sulphide being the most insoluble; antimony trichloride ap-
parently made a departure in that the product is more soluble
and is a mixture of sulphide and a sulpho-chloride; while
bismuth trichloride showed the change completely toward the
insoluble sulpho compound. In this group we do see some
analogy to the chemistry of water. In the place of hydroly-
sis we have the analogous phenomena which may well be called
thiohydrolysis, since the only difference is the replacement
of oxygen by sulphur. To illustrate we have:

Hydrolysis $BiCl_3 + H_2O = BiOCl + 2 HCl$

Thiohydrolysis $BiCl_3 + H_2S = BiSCl + 2 HCl$
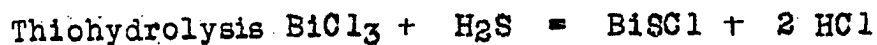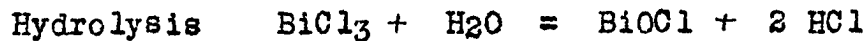
Sulphur monochloride formed a clear solution with
liquid hydrogen sulphide which soon became colloidal. On the
fifth day yellow solid had separated and a yellow liquid
formed. The solid was free sulphur and the yellow liquid
was sulphur monochloride with sulphur in solution. Appar-
ently the equilibrium, illustrated by the equation

$$S_2Cl_2 + H_2S = 2 HCl + 3 S,$$
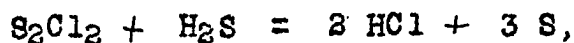
was reached. Selenium tetrachloride reacted vigorously with
hydrogen sulphide to form a colloidal solution. On the

fifth day the liquid was clear and the selenium and sulphur had precipitated. Excessive pressure due to hydrogen chloride was evidenced when the tubes were opened. The reaction may be expressed thus:

$$SeCl_4 + 2 H_2S = 4 HCl + Se + 2 S$$

Tellurium chloride reacted in a similar way but equilibrium was reached more quickly.

Iodine trichloride reacted more vigorously than any of the chlorides discussed above. Considerable pressure due to hydrogen chloride was created. Rhombic tablets of sulphur monoiodide formed. The probable reaction may be stated thus:

$$2 ICl_3 + 3 H_2S = 6 HCl + S_2I_2 + S$$

Of the several attempts with this product all but one sample were lost by explosions of the tubes.

From a comparison of the halides discussed we can conclude that as the basicity of the positive radical decreases the solubility increases and for any one group a given type reaction has the greater tendency to go to completion the lower the atomic weight.

The results with phosphorus tribromide were analogous to those with the trichloride. Reactivity with the bromide seemed more pronounced than with the chloride.

The bromide and iodide of mercury were both soluble and both formed the red sulphide as the end product. With the mercury halides as with those of phosphorus the reactiv-

ity increased with atomic weight of the halide.

Cadmium iodide and potassium iodide showed no tendency to dissolve in or react with liquid hydrogen sulphide.

OXYHALIDES: Only the oxyhalides of phosphorus, sulphur and selenium were studied.

The mixture of phosphorus oxychloride and liquid hydrogen sulphide formed a clear solution. Very slow decomposition took place with the formation of a sulphide of phosphorus. An intermediate product$_1$ may have been formed but no attempt was made to verify that supposition.

With thionyl chloride the reaction was rapid with the formation of a colloidal solution. In a few days much sulphur had separated and two liquid layers formed. Excessive pressure in the tubes was due to the pressure of hydrogen chloride. The liquids consisted of hydrochloric acid and a small quantity of sulphur chloride, mainly. With the data at hand it is quite impossible to hazard a guess as to just what specific reactions did take place.

With selenium oxychloride a similar reaction was observed. The speed of reaction or reaction was much greater and in addition to the above decomposition products free selenium separated out. The oxychloride reacts in much the same way in liquid hydrogen disulphide.

1. Besson, Compt. rend. 124, 151 (1897).
2. Lenher, J. Am. Chem. Soc. 44, 1664 (1922).

Sulphuryl chloride was miscible with liquid hydrogen sulphide at first but within an hour a white suspension had formed and yellow droplets separated out. Analysis of the decomposition products indicated the presence of free sulphur, sulphur dioxide in water, hydrogen chloride, and sulphur monochloride. The standard reactions would account for the results given but no proof for such a conclusion was obtained.

The study of the oxychlorides presents a series of complex reactions which upon further study may reveal further analogy between the chemistry of hydrogen sulphide and water. With liquid H_2O we have the reaction:

$$SOCl_2 + 2 H_2O = H_2O + SO_2 + 2 HCl$$
$$(H_2SO_3 = H_2O + SO_2)$$
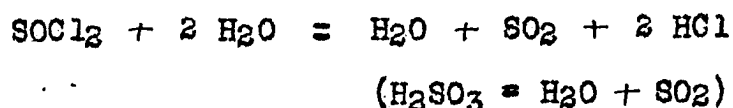
With liquid H_2S we may have:

$$SOCl_2 + 2 H_2S = H_2O + 3 S + 2 HCl$$
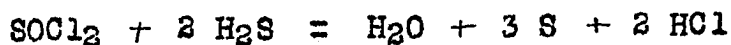
SALTS: The salts, other than halides, studied were few in number. The selection was guided by the purity of the products obtainable and also by the classes of salts to be studied.

The salts that showed no change were: ammonium acetate, ammonium cyanate, zinc sulphate, di-sodium phosphate, barium sulphate, boron nitride and barium thiocarbonate.

Silver nitrate and bismuth nitrate slowly changed to the black sulphides. In both cases much free sulphur was

present also. Ammonium nitrate was slowly changed to a yellow solid which gave the sulphide test with lead acetate. The water solution formed was yellow and indicated the presence of sulphides of ammonium.

Of the distinctive oxidizing agents the following were studied: potassium permanganate, potassium chromate and dichromate, sodium bromate, ammonium persulphate, and potassium ferricyanide. All caused the separation of much free sulphur in liquid hydrogen sulphide and indicated decomposition to lower states of oxidation. Potassium permanganate passed thru the color changes: violet--green--dark brown--reddish brown. The chromate and dichromate showed but slight color change. The ferricyanide changed to a dark green.

Potassium carbonate partially changed to a light yellow product. The water solution gave a sulphide reaction. Anhydrous copper sulphate changed to black at once and in the course of a short time all was converted to the sulphide. The presence of sulphuric acid was verified.

Sodium nitro prusside changed from the red to a greenish blue solid and with water a prussian blue solution was formed. Apparently the product had partially changed to the ferrous compound which is yellow. Ferric citrate also indicated partial reduction.

PRODUCTS DISSOLVED IN PYRIDINE: Samples of anhydrous cobaltous chloride, mercuric iodide and mercuric chlor-

ide were dissolved in pyridine and added to liquid hydrogen
sulphide. In each case the reaction was very rapid. The
black sulphide appeared at once. With mercury salts, how-
ever, the black sulphide changed to the red variety in the
course of a half minute. It is interesting to note from the
discussion under "Halides" that these mercury salts alone
react in a similar manner in pure liquid hydrogen sulphide
but at a very much slower rate. Analysis in each case
verified the composition of the sulphides formed. The liq-
uid layer in the case of the iodide was colored yellow while
in both chlorides it was colorless.

These observations are in harmony with the work of
Schroeder[1] who passed dry hydrogen sulphide gas into the
solution of mercuric iodide and chloride in pyridine.

The yellow solution in the case of the iodide was
due to the mercuric iodide which was in equilibrium.

$$HgI_2 + H_2S = HgS + 2 HI$$

The solution was yellow because of the transition of the red
mercuric iodide to the yellow variety. Kastle and Reed[2] had
found this to be the case with such solvents as acetone,
ethyl bromide, etc.

DISCUSSION: From the observations recorded above
it is apparent that the activity of inorganic products in
liquid hydrogen sulphide is relatively low and one would not
accredit an analogy between H_2O and H_2S at first thot. Yet

1. Schroeder, Z...... anorg. Chem., 44, 16 (1905).
2. Kastle and Reed, A.C.J., 27, 209 (1902).

we do have some similarities in reactivity. With the strong-
ly positive elements there is the tendency to form the sul-
phides instead of the oxides and with the strongly negative
elements free sulphur, instead of oxygen, is displaced. With
the data at hand it is difficult to account for the observa-
tions with the sulphides and sulphohydrates. Here it appears
that reactivity is almost nil within the inorganic field of
products--the highly acid sulphides being the only ones to
show any change. The more negative halides and oxyhalides
show striking similarities to the chemistry of water. The
speeds of reactions are comparatively lower but the order is
consistent.

The observations of reactions when pyridine was
present was interesting in that the reactions were the same
as when there was no pyridine but the rates were markedly
different. Hydrogen sulphide must be ionized in both cases
but more ions were present when pyridine was used. Work of
Kahlenberg and others has shown that pyridine is a very good
ionizing medium.

The observations described below will bring out
further relationships.

D. Observations (Organic Products).

HYDROCARBONS: Of the aliphatic series, gasoline,
kerosene and vaseline were studied. The first two were sol-
uble but vaseline was only slightly soluble.

Benzene, toluene and xylene were soluble in all proportions. Diphenyl, naphthalene, and anthracene all went into solution at once.

None of the hydrocarbons showed any indications of reaction.

HALOGEN DERIVATIVES: Chloroform, bromoform, iodoform, carbon tetrachloride, and normal amyl bromide were soluble and non-reactive in liquid hydrogen sulphide.

SULPHUR DERIVATIVES: Ethyl di-sulphide, normal butyl sulphide, normal butyl mercaptan, thiophenol, thio-naphthol, and thiocresol formed solutions but showed no indication of reaction.

Thiophene was soluble and non-reactive.

Cystine was insoluble.

Thiourea was insoluble but thiocarbanilide was very soluble. No reaction was observed in either case. The addition of the two phenyl groups is apparently responsible for the change in solubility. We shall note further examples of this general nature. Thiobarbituric acid was insoluble. Normal butyl sulphonal was soluble but there was no indication of reaction. Congo red and methyl orange showed no indication of forming solutions but after standing in contact with liquid hydrogen sulphide for two weeks methyl orange had changed to a blue-green residue and the liquid had taken on a slightly yellow color.

Thioacetic acid went into solution at once in liquid hydrogen sulphide and in the course of two weeks lemon-yellow crystals appeared. These crystals were quite stable in air and were apparently insoluble in thioacetic acid. Analysis for total sulphur gave results which would indicate that one mol of hydrogen sulphide was attached to one mol of thioacetic acid. We can either assume the formula $CH_3COSH \cdot H_2S$ or $CH_3C(OH)(SH)_2$. The latter, ortho di-thio acetic acid, is more likely the true formula of the new product.

OXYGEN DERIVATIVES: The alcohols and phenols studied were: isobutyl alcohol, glycerol, phenol, resorcine, and pyrogallol. All were soluble and none were reactive in liquid hydrogen sulphide.

Ethyl ether and acetone were both soluble and non-reactive.

The acids which were found soluble and indicated no reaction were: acetic, trichloracetic, stearic, palmitic, benzoic, salicylic, and cinnamic. Phthalic acid was very slightly soluble. Tartaric and citric were both insoluble. The higher aliphatic acids separated out when the temperature was lowered.

The three aldehydes: benzaldehyde, nitrobenzaldehyde, and furfural, all dissolved readily and reacted with liquid hydrogen sulphide. The benzaldehyde solution showed a slight precipitate after two months. The yellow

solution, left after evaporation of the hydrogen sulphide, had a distinct mercaptan odor. Nitrobenzaldehyde was soluble and gave a white precipitate also but no mercaptan odor was evident. Furfural was soluble and after a few days a dark brown floculent precipitate separated out. Upon evaporation of the liquid hydrogen sulphide the precipitate was found to be a sticky rubber-like mass and had the odor of an organic sulphide body. When exposed to bromine vapors a blue-violet color appeared.

The sugars studied were: raffinose, sucrose, maltose, lactose, mannose, glucose, arabinose. All appeared to be insoluble and non-reactive since no sugar could be found upon evaporation of the liquid phase. The glucose and lactose mixtures, however, gave unusually high per cent of sulphur deposits when the liquid phase was evaporated. There is reason to believe that the presence of the aldehyde group may cause reactions resulting in the high per cent of sulphur. The mechanism is no doubt unusual and deserving of study.

NITROGEN DERIVATIVES: Pyridine dissolved in liquid hydrogen sulphide and after two months a yellow coloration appeared. When cooled a yellow solid separated. Walker and others[1] reported a similar observation and stated that an addition product had formed. Observations with pip-

1. Walker, McIntosh and Archibald, J. Chem. Soc.,85,1098 (1904).

eridine and quinoline in liquid hydrogen sulphide were also in agreement with those reported by Walker and others.

Azobenzene and dimethyl amido azobenzene went into solution in liquid hydrogen sulphide at once and colored the solutions yellow. Reaction was indicated by the fact that when the liquid hydrogen sulphide was evaporated, the former solution left a light yellow deposit while in the latter case a black deposit remained. The nature of the residue was not investigated.

Di-nitrobenzene and picric acid were both soluble in liquid hydrogen sulphide and in both cases much free sulphur was left upon evaporation of the solution. The hydrogen sulphide had been oxidized with subsequent reduction of the organic nitro compound.

Aniline was very soluble in liquid hydrogen sulphide and an addition product formed as reported by Walker and others[1].

Acetamide was soluble but amino acetic acid indicated no solubility.

Hydrazine hydrochloride was insoluble but phenyl hydrazine hydrochloride and hydroxylamine hydrochloride were soluble.

Pyrolle was soluble in liquid hydrogen sulphide.

MISCELLANEOUS: Some of the hydrocarbon derivatives in bituminous coal were soluble in liquid hydrogen

1. Walker, McIntosh and Archibald, J.Chem.Soc. 85, 1098 (1904).

sulphide. The solution became colored and a tarry residue remained upon evaporation of the solution.

Phenolphthalein was insoluble.

Litmus cubes showed no change in liquid hydrogen sulphide until about the seventh week when the solid showed a change in color to a blue-green.

Calcium carbide did not appear to go into solution but a color change of the solid from gray to light yellow took place during a period of about 30 days. The residue which remained after evaporation of hydrogen sulphide did not yield acetylene with water and had the odor of a mercaptan or organic sulphide. The observations indicate the possibility of the formation of a thio-acetaldehyde as described in Richter's organic chemistry I, 302.

The action of liquid hydrogen sulphide on several kinds of rubber was also made the subject of a short study. The samples of plantation, para, smoked and vulcanized rubber were obtained from Dr. C. E. Frick, Van Cleef Bros., Chicago. The other samples were pieces of red rubber tubing and black rubber stoppers.

The sample of plantation rubber went into solution completely, forming a thick syrup. The para and smoked rubber were very soluble also but the solution did not become viscous. The latter was the more soluble. The vulcanized rubber was not very soluble and the sample, unlike the above, retained its original shape.

.The samples of the red tubing and of the black stopper were old and therefore were not a good comparison with the above sample of vulcanized rubber. The solution of the red rubber became red from free antimony sulphide and that of the black rubber became black from the carbon filling.

The data below in Table IV indicates the amount in per-cent by weight of the solid left after evaporation of the solution, also the time for solution to form.

TABLE IV
Solubility of Rubber

	Para	Smoked	Vulcanized
Per-cent by Wt.	0.9955	1.235	0.3043
Time for Equilibrium	1 mo.	1 mo.	1 mo.

The red and black samples gave values of 5.145 and 1.35 per-cent by weight respectively. The high values are no doubt due in part to the antimony sulphide and carbon held in suspension when the solutions were transferred.

DISCUSSION: With organic products liquid hydrogen sulphide acts very much like an organic solvent. It appears to show a closer relationship to such solvents than to water. Reactions with the solute seem to occur best when a double bonded oxygen or a tri-valent nitrogen are present. This would lead one to believe that reactions result in addition

products. Apparently such is the case with thioacetic acid, for example.

The activity in the case of glucose and lactose is most prominent, among the sugars studied, and if the above supposition is correct these sugars should show the tendency to combine with liquid hydrogen sulphide.

From the number of cases of simple solubility we are almost justified in saying that hydrocarbons, alcohols, mercaptans, normal aliphatic acids, and aliphatic halogen substitution products are soluble in liquid hydrogen sulphide. We might safely extend the list to include ethers and ketones.

E. General Summary.

. The discussions following the data concerning observations on inorganic and organic products need not be repeated here.

A review of all the individual observations made shows that nearly fifty per-cent of the organic products studied were cases of simple solubility while with inorganic products over fifty per-cent showed indications of reaction (Refer Table V).

Reactions in liquid hydrogen sulphide, in general, take place very slowly even at room temperature. The reason that Antony and Magri[1] observed neither solubility nor re-

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).

action in the case of the oxidizing agents, of sulphuric acid, and other products shown to be soluble or reactive, was probably because they made all their observations at low temperatures and for a relatively short period of time.

At the outset of this investigation it was presupposed that inorganic sulphohydrates and sulphides should show solubility relationships similar to those in water but only the sulphides of the highly negative elements were found to dissolve and those only slightly.

The chemistry of liquid hydrogen sulphide in general is so different from the chemistry of liquid water that one cannot safely hazard a guess, by analogy, as to solubilities and reactions.

The table below summarizes the observations made under the four heads and the inorganic and organic products are enumerated in the order considered above.

TABLE V

Summary of Chemical Activities

Soluble and non-reactive	Soluble and reactive	Apparently insoluble and reactive	Insoluble and non-reactive
(Inorganic)	(Inorganic)	(Inorganic)	(Inorganic)
Sulphur	Selenium	Sodium	Carbon
Iodine	Chlorine	Silver	Gold
Carbon dioxide	Bromine	Copper	Phosphorus (red)
Phosphorus pentasul-phide	Phosphorus pentoxide	Mercury	Tellurium
Arsenic trisulphide	Sulphur dioxide	Arsenic	Lead sulphide
Antimony	Pyrosulphuric acid	Antimony	Aluminum sulphide
Ammonium sulphohydrate	Stannous chloride	Sodium peroxide	Ferrous sulphide
Hydrogen chloride	Stannic chloride	Barium peroxide	Potassium sulpho-hydrate
Hydrogen bromide	Phosphorus trichloride	Arsenic trioxide	Phosphorous acid
Zinc chloride	Phosphorus pentachloride	Selenium dioxide	Meta boric acid
-------------	Arsenic trichloride	Water	Potassium chloride
(Organic)	Antimony trichloride	Lead Chloride	Ammonium chloride
	Bismuth trichloride	Cuprous chloride	Barium chloride
	Sulphur monochloride	Cobaltous chloride	Aluminum chloride
Gasoline	Iodine trichloride	Mercuric chloride	Cadmium iodide
Kerosene	Mercuric iodide	Selenium tetrachloride	Potassium iodide
Vaseline	Mercuric bromide	Tellurium tetrachloride	Ammonium acetate
Benzene	Phosphorus oxychloride	Silver nitrate	Ammonium thio-cyanate
Toluene	Thionyl chloride	Bismuth nitrate	Zinc sulphate
Diphenyl	Selenium oxychloride	Ammonium nitrate	Di-sodium phos-phate
Naphthalene	Sulphuryl chloride	Potassium permanganate	
Anthracene	-------------	Potassium chromate	Barium sulphate
Chloroform	(Organic)	Potassium dichromate	Boron nitride
Bromoform		Sodium bromate	Barium thiocar-bonate
Iodoform	Thioacetic acid	Ammonium persulphate	-------------
Carbon tetrachloride	Benzaldehyde	Potassium ferri-cyanide	
n-amyl bromide	Nitro benzaldehyde	Potassium carbonate	(Organic)
Ethyl di-sulphide	Furfural	Copper sulphate	
n-butyl sulphide	Pyridine	Sodium nitroprusside	
n-butyl mercaptan	Piperidine	Ferric citrate	Cystine
Thiophenol	Quinoline	-------------	Thiourea

Chloroform
Bromoform
Iodoform
Carbon tetrachloride
n-amyl bromide
Ethyl di-sulphide
n-butyl sulphide
n-butyl mercaptan
Thiophenol
Thiocresol

Thiophene
Thiocarbanilide
n-butyl sulphonal
Iso butyl alcohol
Glycerol
Phenol
Resorcine
Pyrogallol
Ethyl ether
Acetone
Trichloracetic acid
Stearic acid
Palmitic acid
Salicylic acid
Cinnamic acid
Phthalic acid
Acetamide
Phenylhydrazine hydrochloride
Hydroxylamine hydrochloride
Pyrolle
Plantation rubber
Para rubber
Smoked rubber
Vulcanized rubber

(Organic)

Thioacetic acid
Benzaldehyde
Nitro benzaldehyde
Furfural
Pyridine
Piperidine
Quinoline
Azo benzene

Di methyl amido azo-
   benzene
Di nitro benzene
Picric acid
Aniline

Potassium dichromate
Sodium bromate
Ammonium persulphate
Potassium ferri-cyanide
Potassium carbonate
Copper sulphate
Sodium nitroprusside
Ferric citrate

(Organic)

Methyl orange
Glucose (?)
Lactose (?)
Coal, bituminous
Litmus
Calcium carbide

Barium sulphate
Boron nitride
Barium thiocar-
   bonate

(Organic)

Cystine
Thiourea

Thio barbituric
   acid
Congo red
Tartaric acid
Citric acid
Raffinose
Sucrose
Maltose
Lactose
Mannose
Glucose
Arabinose
Amino acetic acid
Phenolphthalein

V. Conductivity Measurements in Liquid Hydrogen Sulphide

A. Apparatus.

DESIGN OF CONDUCTIVITY CELLS: The conductivity cells had to be designed to determine very low conductance values and to use relatively small amounts of the solutions. The cells were all made of the same kind of thick-wall, soft, glass tubing so as to have uniform expansion and contraction for all the cells used. Two types were made so that measurements could be obtained at low temperatures and ordinary pressure or at ordinary temperature and high pressure. The general design was the same but the cell for high pressure was equipped with a long neck that could be sealed off at the constriction N, Fig. 5, B. The total length was 24 cm. The cell of the open type, Fig. 5, C, was 14 mm. in diameter and 15 cm. long. The platinum electrodes were about 18 mm. square and were held about 2 mm. apart. The entire cell was made sturdy and the electrodes were held rigidly in place, as shown in Fig. 5, A, in order to maintain a constant value for the cells under the experimental conditions.

Electrode, d, was sealed in place first and then electrode, f, which had tiny glass rods, g, wrapped onto it, was drawn in. In order to hold the two electrodes in place and as close together as the rods, f, would permit, a short glass tube, c, was pushed in before closing off the base of the cell. The side-arm, b, was constricted near the bend

at, a, so as to make it more easy to determine volumes of
solution.   Side-arm, b, was filled with mercury and was
long enough so that the wire lead would not be exposed to

Fig. 5. Conductivity Cells
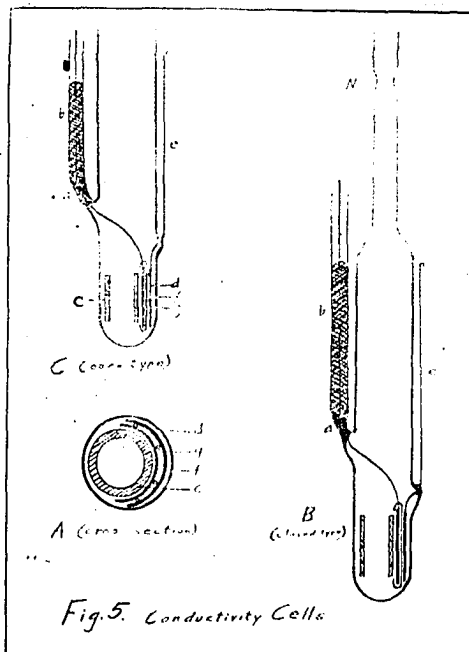
the cooling mixture as in the case of, e.   The purpose
here was to avoid any possibility of a potential being set
up outside of the cell.

The cell constants were determined at 25° C. and
the determinations of specific conductance values of liquid
hydrogen sulphide solutions were made at temperatures vary-
ing from -80° C. to room temperature.   The contraction and

expansion of the cells were not corrected for in any of the determinations but it is quite possible that all values reported are subject to slight errors due to such changes.

All the data presented is comparable, nevertheless, for care was taken to make all the cells used from glass tubing which was made from the same batch of glass. Cell constants were frequently determined and it was found that no difference could be noted, due to passing the cell thru wide temperature changes.

VOLUME DETERMINATION: The cell was calibrated by passing in water from a calibrated burette and determining the volume in cubic centimeters in terms of the height of the column in millimeters from the base of the cell to the bottom of the meniscus. Thus when the cell was charged with liquid hydrogen sulphide solution it was taken out of the cooling bath, the height of the liquid column quickly measured, and the equivalent number of cubic centimeters recorded.

CONDUCTIVITY SET-UP: The Wheatstone bridge arrangement, with induction coil and telephone receiver, was used in determining conductivity values. One plug-resistance box (111 ohms) and a dial resistance box (9990 ohms) were used for high conductivities and five resistance coils of 10000 ohms resistance each were thrown into the circuit for measurements in solutions having low conductivity values.

Heavy copper wire leads were used thruout and contacts with
the terminate at the cell were made by means of clamps.
When open cells were used the solution was kept at the temp-
erature of solid carbon dioxide. When conductance measure-
ments were made on solutions up to room temperature an ether-
carbon dioxide bath was used and the temperature readings
taken with a toluol thermometer.

CONDUCTIVITY MEASUREMENTS WITH THE DIRECT CURRENT:
In order to compare results with the data of Antony and
Magri[1] conductivity measurements were made using the 110
volt D.C. circuit. A milliammeter, reading in units, was
used in determining the conductivity values in milliamperes
for a number of saturated solutions.

With the same circuit, a wall-type D'Arsonval gal-
vanometer was used in detecting extremely low conductivity
values or proving the absence of conductance.

B. Conduction of Pure Liquid Hydrogen Sulphide.

Magri[2] reported no definite value for the specific
conductivity of pure liquid hydrogen sulphide that simply
stated that it was less than 4×10^{-7} reciprocal ohms. In
this laboratory no indication of conduction was evident
either with the high frequency current of the conductivity
set-up or with the 110 volt direct current. The wall-type

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).
2. Magri, Atti. R. accad. Lincei, V, 16, 518 (1907).

D'Arsonval galvanometer was not deflected at all when the
110 volt D.C. circuit was closed.

The conclusion reached in this laboratory, there-
fore, is that liquid hydrogen sulphide does not show any
indications of conducting the electric current. At any
rate, the conductivity of pure liquid hydrogen sulphide was
so low that it was not measurable with the apparatus at hand.

In all cases thruout the work on conductivity mea-
surements in this laboratory, the functioning of the cells
was checked, before declaring no conduction for a solution,
by adding a product which was known to cause conduction of
the electric current in liquid hydrogen sulphide.

C. Observations of Conductivity Values for Saturated Solu-
tions.

Preliminary observations of conductivity values
of liquid hydrogen sulphide solutions were made almost en-
tirely with the open type cells, at low temperatures. The
solutions were saturated with the solute in almost every
case. Only about three hours were allowed for such satura-
tion to be reached. The exceptions were those cases where
the solute was apparently miscible in liquid hydrogen sul-
phide in all proportions and then the concentration was grad-
ually brot up to approximately 15 per-cent by volume. When
observations were made at higher temperatures (up to room
temperature) the solutions were sealed in the cells and the

temperature of the solution allowed to rise to about 20° C.

The specific conductivity of a number of saturated solutions was determined and the results obtained are recorded in Table VI.

TABLE VI

Specific Conductance of Saturated Solutions

Solute	Spec. Cond. (recip. ohms)	
	At low Temp.	At room Temp.
Potassium Sulphydrate	nil	nil
Ammonium Sulphydrate	"	"
Thionaphthol	"	
p-Thio cresol	"	
n-Butyl mercaptan	"	
n-Butyl sulphide	"	
Thiophenol	"	
Hydrate of hydrogen sulphide	"	
Chloroform	"	
Bromoform	"	
Iodoform	"	
Dinitrobenzene	"	
Stearic Acid	"	
Palmitic Acid	"	
Benzoic Acid	"	
Phenolphthalein	"	
Congo Red	"	
Carbon disulphide	"	
Hydrogen chloride	9.813×10^{-7} ←	
Chlorine	1.787×10^{-7}	
Bromine	1.614×10^{-7}	
Iodine	1.36×10^{-5}	
Iodine trichloride	1.348×10^{-6}	
Sulphur monochloride	1.034×10^{-6}	
Phosphorus trichloride	4.254×10^{-8}	
Phosphorus tribromide	5.269×10^{-8}	
Arsenic trichloride	1.151×10^{-6}	
Antimony trichloride	4.244×10^{-4}	
Bismuth trichloride	Nil	
Stannic chloride	1.68×10^{-7}	
*Isoamyl bromide	2.25×10^{-7}	
Thiocarbanilide	9.61×10^{-7}	

Solute	: At Low Temp.:	At Room Temp.
*Acetic Acid	nil	6.32×10^{-8}
Acetic acid anhydride	4.126×10^{-6}	
Thioacetic acid	2.96×10^{-7}	
Acetyl chloride	1.88×10^{-6}	
Trichlor acetic acid	nil	
Acetamide	1.68×10^{-7}	
Amino acetic acid	nil	

*Isoamyl bromide was not observed for more than two hours. The concentration of acetic acid was 0.1 mols.

The chloroform solution did not conduct altho Antony and Magri[1] reported a value of 3 milliamperes.

The saturated solution of hydrogen chloride contained 43.2 mol per-cent of the acid. McIntosh and Steele[2] pronounced such a solution a non-conductor.

Chlorine and bromine both reached a maximum conductance value and then a lowering of conductivity, which seemed to be parallel to the oxidation of the sulphur of hydrogen sulphide, followed. The value for iodine compared very well with that of Magri[3] who found it to be 1.34×10^{-5} reciprocal ohms.

The fifth group halides presented an interesting gradation. The solutions of the chloride and bromide of phosphorus reached a maximum, antimony trichloride solutions gave a very high value, comparatively while those of

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).
2. McIntosh and Steele, Proc. Roy. Soc., 73, 450 (1904).
3. Magri, Atti. R. accad. Lincei, V, 16, 518 (1907).

bismuth trichloride were non-conductors. Antony and Magri[1], however, reported a conductance value of 3 milliamperes for a saturated solution of bismuth trichloride.

Acetic acid and its derivatives will be discussed at length in the pages that follow.

Solutions of pyridine and piperidine conducted very well and both indicated gradual increase of conductivity with increase of concentration. The addition of two drops of pyridine to 3.5 c.c. liquid hydrogen sulphide gave a specific conductance value of 2.19×10^{-6} reciprocal ohms, and by continued addition, until sixty drops had been added, and conductivity increased to 1.07×10^{-4} reciprocal ohms. Pyridine itself has a conductance value of 7.6×10^{-7} reciprocal ohms[2], and therefore the conductivity of a liquid hydrogen sulphide solution would likely continue to increase with concentration until finally it would be a case of determining the conductivity of a solution of hydrogen sulphide in pyridine. This observation confirmed that made by Walker and others[3].

SUMMARY: From the preliminary observations recorded above, it is evident that solutions in which liquid hydrogen sulphide serves as the solvent do conduct the electric

1. Antony and Magri, Gazz. chim. ital., 35, 206 (1905).
2. Lincoln, J. Phy. Chem. 3, 457 (1899).
3. Walker, McIntosh and Archibald, J. Chem. Soc., 85, 1098 (1904).

current to a considerable extent. In many instances conductivity might have resulted at higher temperatures, as in the case of acetic acid, the other fatty acids studied might have given conductance values if the determinations had been made at room temperature instead of at the temperature of solid carbon dioxide. In an extensive study of that nature, considerable time would be required as each determination would be for but one concentration and the cell would have to be cooled down before opening, each time.

The outstanding contradictions with work of earlier investigators are those of the hydrogen chloride, chloroform and bismuth trichloride values as noted above.

At first thot, one might be led to believe that the conductivities of the fifth group halides were due to the liberation of the halogen acids. That, however, is probably not the case since the values vary greatly from that for hydrogen chloride and, further, antimony trichloride gave conductivity values much higher than that for the saturated solution of hydrogen chloride. It is difficult to account for the lack of conductivity in the solution of bismuth trichloride unless we grant that the BiSCl formed is insoluble and further that the HCl thus formed is a part of the BiSCl molecule in the form of an addition as, $BiSCl \cdot 3HCl$ or that the product is of the type $BiCl_3 \cdot H_2S$.

Further summary and postulations will be made at the close of the next section.

D. Electrolysis of Iodine Solutions.

It is difficult to account for the conductivity of solutions of halogens in liquid hydrogen sulphide unless

we assume that the halogen furnishes the cation as well as the anion, as postulated by Walden[1]. Since an iodine solution gave the highest conductance value it was chosen as the subject for study.

By passing a direct current thru a solution of iodine in liquid hydrogen sulphide for a long time a separation of ions should occur. The iodine acts only as an anion; the intensity of iodine color should increase at the anode and diminish at the cathode while if it served both as cation and anion there would be no change of intensity. There are several intermediate possibilities such as addition products forming or breaking up of iodine molecules into positive and negative particles with differences of mass.

In order to make this study an apparatus, Fig. 6, was constructed so that the liquid after electrolysis could be

Fig. 6 Electrolysis Apparatus
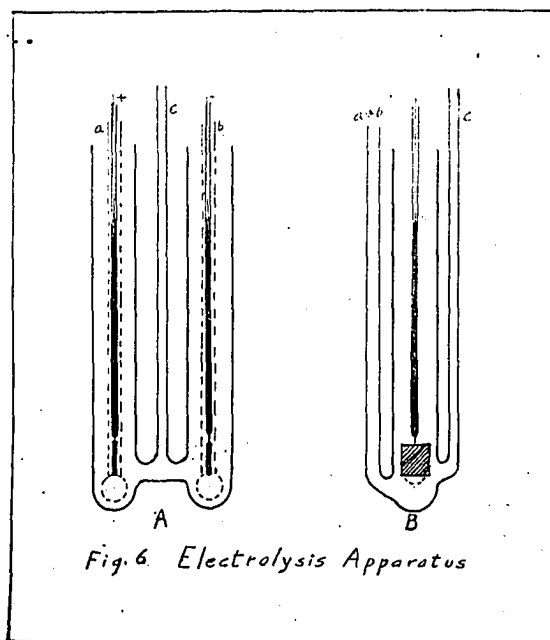
1. Walden, Z. physik. Chem., 43, 385 (1903).

removed thru tube a and b for analysis. Tube c was present
to break the liquid line and permit free flow out thru a and

b. About 3 c.c. of iodine solution was placed in the cell
equipped with platinum electrodes, 10 mm. square and 20 mm.
apart, and subjected to electrolysis (110 v. D.C.) for ten
hours. No change in color in the two compartments could be
notices and the percentage of iodine showed no appreciable
difference. From these results it has been concluded, tenta-
tively, in this laboratory that the carriers, both cations and
anions, consisted of iodine, either free or combined.

E. Observations of Conductivity Values of Solutions at Various
Concentrations.

Mention of conductivity values has already been made
above for the solutions to be considered here but the purpose
in this section is to summarize a few of the groups of related
compounds showing conductivity values over a series of concen-
trations. In all cases the cells were kept imbedded in solid
carbon dioxide thruout the operations.

SOLUTIONS OF HALIDES OF THE FIFTH GROUP: Table VII
shows conductivity values from solutions of 0.1 to 0.2155 mol
concentration. With the same halogen conductivity increases
with the increase of molecular weight of the positive radical.
It is also apparent that there is an increase in conductance
with increase of atomic weight of the halogen, keeping the
positive radical the same. PCl_3 and PBr_3 both indicate de-

composition, however, above 0.1 mol concentration with sub-
sequent lowering of specific conductance.

TABLE VII

Specific Conductance of Some Fifth Group Halides in
Liquid H_2S (sp. cond. X 10^{-6})

Mol. Conc.	PCl_3	PBr_3	$AsCl_3$	$SbCl_3$	$BiCl_3$
0.01	----	----	0.03703	4.967	nil
0.05	----	----	----	87.54	"
0.0538	----	0.1072	----	----	"
0.069	0.04254	----	----	----	"
0.1	----	----	0.4916	424.45	"
0.1076	nil	.1179	----	----	"
0.163	"	.08165	----	----	----
0.2	----	----	1.151	----	----
0.2155	----	.05369	----	----	----

SOLUTIONS OF ACETIC ACID AND ITS DERIVATIVES: Acetic
acid did not conduct at low temperatures but the data secured
at high temperatures are given in Table VIII below. Acetic
acid anhydride solution does not compare directly with the oth-
er solutions but was studied in connection with glacial acetic
acid. If addition products form, as with CH_3 COSH then the
greater possibility of adding an H_2S group to the anhydride
acid may be said to account for its higher conductance value.

TABLE VIII

Specific Conductance of Acetic Acid Derivatives in Liquid H$_2$S (sp. cond. X 10^{-6})

Mol. Conc.	CH$_3$COOH	CH$_3$CO O CH$_3$CO	CH$_3$COSH	CH$_3$COCl	CH$_3$CONH$_2$	CCl$_3$COOH	CH$_2$NH$_2$COOH
0.05	----	1.5	0.086	0.1134		----	----
0.10	0.0541	3.519	0.205	0.2964		nil	nil
0.15	----	4.126	0.2432	0.6258		"	"
0.20	----	----	0.2562	1.15		"	"
0.25	----	----	0.296	1.188		"	"

Concentration less than 0.01 mol since not all would go into solution when 0.01 mol is added. At close of two hours the specific conductance was constant at 0.168 X 10^{-6} recip. ohms.

Here again we note that conductance increases with concentration. Considering only a 0.1 mol concentration the conductance of the solutions was increased when the solute contained an NH_2, SH, or Cl group in place of the OH of the acetic acid molecule. But if an H of the CH_3 group was replaced by NH_2 or all three by Cl groups the conductance was lowered to zero. These considerations are more fully developed in the summary below.

SOLUTIONS OF NH_4Cl AND ITS DERIVATIVES: Ammonium chloride solution did not conduct at all but compounds having the hydrogen of the ammonium radicals replaced by alkyl radicals furnished solutions having appreciable conductance values. The conductivity increased with the number of alkyl radicals present and also with increase of concentration.

TABLE IX.

Specific Conductance of Ammonium Chloride Derivatives in Liquid H_2S. (sp. cond. X 10^{-6})

Mol. Conc.	NH_4Cl	CH_3NH_3Cl	$(CH_3)_2NH_2Cl$	$(C_2H_5)_3NHCl$
0.0104	nil	---	---	15.94
0.0113	"	---	7.345	---
0.0133	"	0.2836	---	---
0.014	"	---	---	117.0
0.034	"	---	518.7	---
0.0448	"	---	---	1935.0
0.0468	---	3.671	---	---
0.0508	---	---	---	3353.0
0.0544	---	7.313	---	---

The values in Table IX verify the above statement and show marked influence of the increase of alkyl groups attached to the nitrogen nucleus. It is a known fact that such a change causes an increase in the positive value of the ammonium radical.

SUMMARY: A study of conductance values of solutions of related organic compounds and halogen containing compounds reveals some striking relationships.

In general it appears that the more distinctly positive radicals are and the more distinctly negative the negative radicals are, for the electrolyte, the higher the conductance value. Considering first the solutions of NH_4Cl and its derivatives we note that the NH_4 radical is positive. The NH_4Cl solution did not conduct. If a CH_3 group replaces one of the hydrogens the NH_4 group becomes more positive; add another CH_3 group and it becomes still more positive. With each such successive replacement there was found a corresponding increase in the conductivity. To illustrate we may note the gradation of conductance values of solutions of approximately .04 mols from Table IX.

Chloroform solutions did not conduct. Here we have a carbon with but one hydrogen attached and therefore its positive value is very low. Attach a number of methyl groups to the single carbon, as in the case of iso-amyl bromide, and we have an alkyl radical of much higher positive value. Iso-amyl bromide solutions did conduct to a fair degree.

Acetic acid solutions conducted the current but if the hydrogens of the alkyl group were all replaced by Cl, as in CCl_3COOH, no conductance was evident. Likewise, if NH_2 had replaced one of the hydrogens as in CH_2NH_2COOH the solution was a non-conductor. Here we have cases where the positivity of the alkyl group has been lowered by adding negative groups with subsequent lowering of conductance values. Passing to the other substitution products of acetic acid studied we note replacement of the OH of the carboxyl group by other negative groups such as SH, Cl and NH_2. By reason of the foregoing statements the relative difference between the positive value of the positive group and the negative value of the negative group could be increased by increasing the negative value of the negative group, instead of increasing the positive value of the positive group as shown above. This is virtually what happens when the OH of the carboxyl group is replaced by SH, Cl or NH_2 groups and conductance value in Table VIII shows this to be the case.

Apparently the same reasoning holds true for inorganic products. In Table VII the solutions of chlorides of phosphorus, arsenic, and antimony show increase of conductivity with increase of atomic weight of the positive radical. We know that the positivity of elements in a given group increases with increase of atomic weight. Bismuth trichloride is not concerned in this comparison for reasons of chemical activity discussed above.

VI. Conductance as a Function of Temperature and Pressure.

When a cell containing a solution of an electrolyte in liquid hydrogen sulphide is sealed and the temperature permitted to rise the pressure, due to the vapor pressure of the solution, becomes an influencing factor. The influence of temperature and pressure upon conductivity has been the subject of many investigations.

With non-aqueous solvents of low dielectric constant the temperature coefficient is generally positive for all concentrations[1] and decreases as temperature rises, reaching a maximum. For high concentrations (0.1 to 0.3 mol) the maximum is reached at lower temperatures and at higher temperatures the coefficient may even become negative. As the pressure increases the resistance of the electrolyte decreases initially and as the temperature rises the value of the decrease diminishes[2]. At sufficiently high temperatures the isotherm minimum may disappear entirely.

EXPERIMENTATION: A 0.1 mol solution of acetic acid in liquid hydrogen sulphide was used in making a study of temperature-pressure effects on conductivity. The cell of type B, Fig. 5, was used. No conductance was observed at first, as previously stated, but as the temperature approached that of room temperature conductance was evident. The solution was then cooled to $-70°$ C., by adding solid carbon
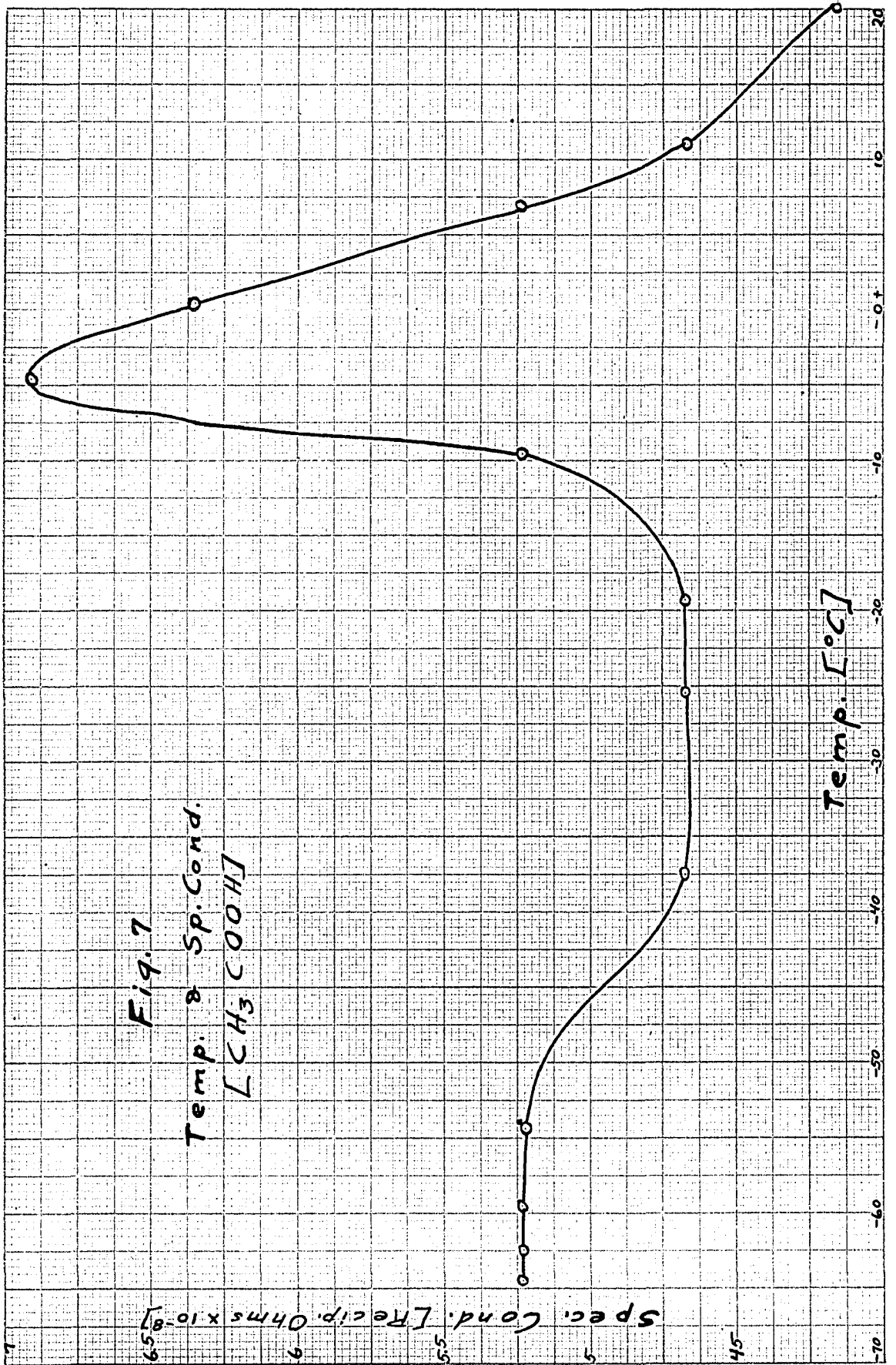
1. Kraus, Properties of Electrically Conducting Systems, pg. 160.
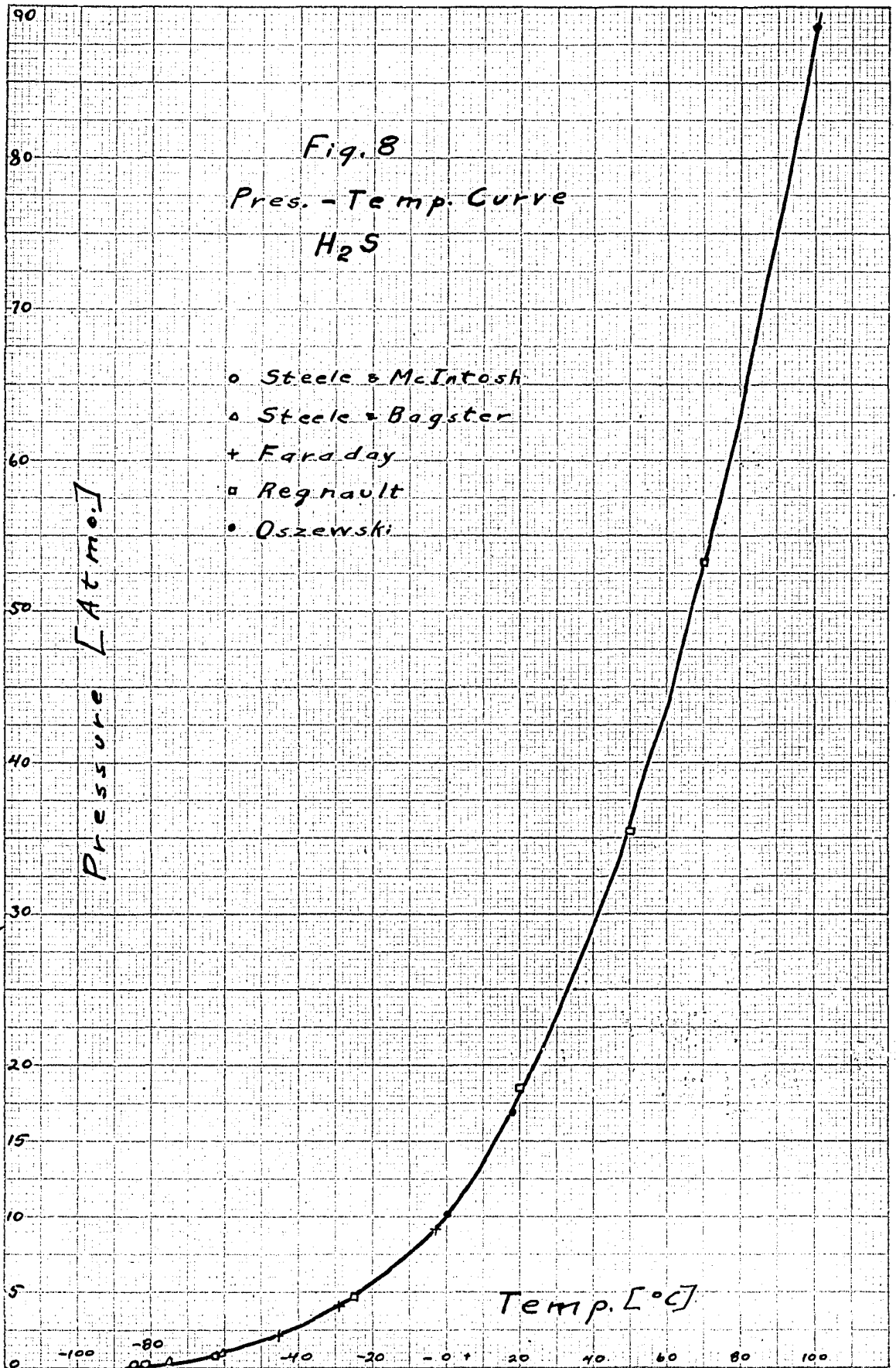2. Ibid., pg. 129.

dioxide to ether, with the result that the solution conducted
the current at the low temperature. Apparently the acetic
acid did not form a solution until higher temperatures were
reached and when once formed the temperature could be lowered
without any separation taking place. The conductance values
obtained as the temperature was allowed to rise to 21° C.
were used in plotting the curve, Fig. 7, and are those re-
corded in Table IX.

TABLE IX

Temperature-Conductivity Data for
Acetic Acid in Liquid Hydrogen Sulphide

Temp. °C.	Specific Conduct. recip. ohms X 10⁻⁸
- 65	5.215
- 63	5.215
- 60	5.215
- 55	5.215
- 38	4.668
- 26	4.668
- 20	4.668
- 10	5.215
- 5	6.888
0	6.324
6.5	5.215
10.5	4.668
21	4.128

Form E-4

Fig. 7

Temp. & Sp. Cond.
[CH₃ COOH]

Spec. Cond. [Recip. Ohms × 10⁻⁸]

Temp. [°C]

Fig. 8
Pres. - Temp. Curve
H₂S

o Steele & McIntosh
△ Steele & Bagster
+ Faraday
□ Regnault
● Oszewski

In order to show the approximate pressure conditions a temperature-pressure curve, Fig. 8, for pure liquid hydrogen sulphide was constructed from data collected from sources as indicated. Altho these values are not those for the solution under consideration the data is sufficiently accurate to show the general rise in pressure with temperature.

The interpretation of the curve, Fig. 7, is difficult since we have the influence of both pressure and temperature to consider. From -5° to 20° C. the rapid increase of pressure apparently caused an increase of viscosity sufficient to overcome the influence of temperature. From -38° to -5° C. the reverse condition seemed to be evident. The change in conductivity with temperature from -65° to -38° is negative. Apparently the influence of pressure on viscosity predominates in that region.

VII. BIBLIOGRAPHY

1. McIntosh and Steels, Proc. Roy. Soc. 73, 450 (1904).

2. Walker, McIntosh and Archibald, J. Chem. Soc. 85, 1098 (1904).

3. Archibald and McIntosh, Proc. Roy. Soc. 73, 454 (1904).

4. Antony and Magri, Gazz. chim. Ital. 35, 206 (1905).

5. Magri, Atti. accad. Lincei V, 16, 171 (1907).

6. Magri, Atti. accad. Lincei V, 16, 518 (1907).

7. Cardoso and Arni, J. chim. phys. 10, 504 (1912).

8. Maas and McIntosh, Trans. Roy. Soc. Canada III, 8, 65 (1914).

9. Elliot and McIntosh, J. Phys. Chem. 12, 163 (1908).

10. Estreicher and Schuerr, Chem. Zentr. IV, 1737 (1910).

11. Skilling, Am. Chem. J. 26, 383 (1901).

12. Gmelin-Kraut, Handbuch der Anorg. Chem. II₂, 605.

13. Fororand, Fonzes and Diacon, Compt. rend. 134, 281 (1902).

14. Sutherland, Phil. Mag. V, 50, 460 (1900).

15. Tammon, Z. physik. Chem. 72, 609 (1910).

16. Roscoe and Schorlemmer, Treatise on Chemistry I, 4 (1920 Ed.).

17. Foucroy and Vanquelin, Ann. chim. 29, 287.

18. Franklin and Kraus, J. Phys. Chem. 11, 553 (1907).

19. Walden, Z. physik. Chem. 43, 385 (1903).

20. Lincoln, J. Phys. Chem. 3, 457 (1899).

21. Thiel and Schulte, Z. physik. Chem. 96, 312 (1920).

22. Forcrand, Compt. rend. 135, 959 (1902).

23. Scheffer, Proc. Sci . K. Akad. Wet. Amsterdam 13, 829 (1911).

24. Scheffer, Proc. Sci. K. Akad. Wet. Amsterdam 14, 195 (1911).

25. Scheffer and Meijer, Verslag. Akad. Wetenschapper, Amsterdam 27, 1104 (1919).

26. Sabatier, Compt. rend. 100, 1346 (1885).

27. Ouvrard, Compt. rend. 116, 1516 (1893).

28. Muir and Eagles, J. Chem. Soc. 67, 90 (1695).

29. Besson, Compt. rend. 124, 151 (1897).

30. Schroeder, Z. anorg. Chem. 44, 16 (1905).

31. Kastle and Reed, Am. Chem. J. 27, 209 (1902).

32. Lenher, J. Am. Chem. Soc. 44, 1664 (1922).

33. Kraus, Properties of Electrically Conducting Systems, pg. 160.

34. Kraus, Properties of Electrically Conducting Systems, pg. 129.