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Reactions of liquid hydrogen sulfide on metals and oxides

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REACTIONS OF LIQUID HYDROGEN SULFIDE ON

METALS AND OXIDES

BY

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A Thesis Submitted to the Graduate Faculty

for the Degree of

DOCTOR OF PHILOSOPHY

Major subject - Inorganic Chemistry

Approved

In charge of Major Work.

Head of Major Department.

Dean of Graduate College.

Iowa State College

1928

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CONTENTS

I. REACTIONS OF LIQUID HYDROGEN SULFIDE

ON METALS AND OXIDES

Introduction

It is well known that gaseous hydrogen sulfide and aqueous hydrogen sulfide are very reactive in their reactions. Naturally scientific curiosity leads one to the inquiry into the reactivity of liquid hydrogen sulfide. Although some systematic work has been done on the reactions of other liquid hydrides like liquid water, liquid ammonia, and liquid halogen hydrides, no systematic work on the reactions of liquid hydrogen sulfide has been conducted except in this laboratory during the last few years.

The solvent action of liquid H_2S has been considerably investigated (1), (2), (3), (4), (5), (6), (7), (8). In general it has been found that liquid H_2S is an excellent solvent for organic substances, but is decidedly a very poor one for inorganic substances.

1. Skilling. Am. Chem. Jour., 26, 383 (1901)
2. McIntosh and Steel. Proc. Roy. Soc., 73, 450 (1904)
3. Archibald and McIntosh. Proc. Roy. Soc., 73, 454 (1904)
4. Walker, McIntosh and Archibald. Jour. Chem. Soc., 85, 1098 (1904)
5. Steel, McIntosh and Archibald. Phil. Trans. Roy. Soc., A. 205, 99 (1906)
6. Quam. Jour. Am. Chem. Soc., 47, 103 (1925)
7. Quam with Wilkinson. Jour. Am. Chem. Soc., 47, 989 (1925)
8. Ralston and Wilkinson. Jour. Am. Chem. Soc., 50, 258 (1928)

Until recently, only a few odd reactions have been reported (1), (9), (10).

Archibald and McIntosh (3), Walker, McIntosh and Archibald (4), and Steel, McIntosh and Archibald (5) report:

(a) that some inorganic substances dissolve in liquid H_2S with decomposition,

(b) that the variation in molecular conductivity of the electrolyte with dilution is probably complicated by the occurence of compounds which contain a different number of solvent molecules at different dilutions,

(c) that the want of agreement between conductivity and cryoscopic measurements is a necessary consequence of the occurence of polymers or compounds in solution, and may be taken as evidence of the existence of such compounds,

(d) that the conduction of organic substances when dissolved is best explained by the occurence of electrolytic compounds of organic substance with the solvent. Transport number measurements have shown that the organic substance is carried to the cathode as a component of the complex cation,

(e) that in every case where a conducting solution was formed, the dissolved substance was one containing an element

9. Moissan. Chem. Centralbl., 1, 296 (1902).
10. Baud. Compt. rend., 134, 1429 (1902).

the valence of which might be increased, thus dyad O or S becoming tetrad, or triad N becoming pentad.

Biltz (11) reports a number of thiohydrates with a number of inorganic halides.

Quam (6) reports a variety of reactions on organic substances, inorganic salts and some elements.

Ralston (8) (12) reports on thiohydrolysis, thiohydrates and a reaction on nitriles.

Fournier and Lang (13) report that iron, copper, and commercial aluminium did not react with liquid H_2S even though in contact for a period of over ten years.

Thus we see that there is yet a very wide field to investigate the properties and reactions of liquid hydrogen sulfide.

Purpose and Outline of the Investigation

The purpose of the present investigation is to observe, rather in a qualitative way, the reactions of liquid hydrogen on most of the metals and oxides.

The problem has been resolved into four phases, as follows:

11. Biltz. Zeit. anorg. allgem. Chem., 147, 171 (1925).
12. Ralston. Unpublished Ph.D. thesis, (1927) Iowa State College.
13. Fournier and Lang. Compt. rend., 184, 1174 (1927).

(I) As free energy decrease is one of the means of indicating the possibility of a reaction taking place, an attempt has been made to calculate a tentative value for the free energy of formation of liquid hydrogen sulfide.

(II) Actual qualitative observations of reactions of liquid hydrogen sulfide on most of the metals.

(III) As electrode potential is one of the means of indicating the possibility of a reaction taking place, an attempt has been made to measure tentative values for the single electrode potentials of a few metals in the saturated solutions of their chlorides in liquid hydrogen sulfide.

(IV) Actual qualitative observations of reactions of liquid hydrogen sulfide on most of the oxides.

Apparatus and Preparation of Liquid Hydrogen Sulfide

The apparatus used in the preparation of liquid hydrogen sulfide was a modification of that employed by Quam (6). The improved apparatus, as shown in Fig. i, and the details of manipulation and process of liquefaction will be fully described by Meints (14), a co-worker in the field.

14. Meints. A thesis to be submitted for M. S. degree. Iowa State College.(In preparation).

FIGURE 1.

APPARATUS FOR THE LIQUEFACTION OF HYDROGEN SULFIDE.
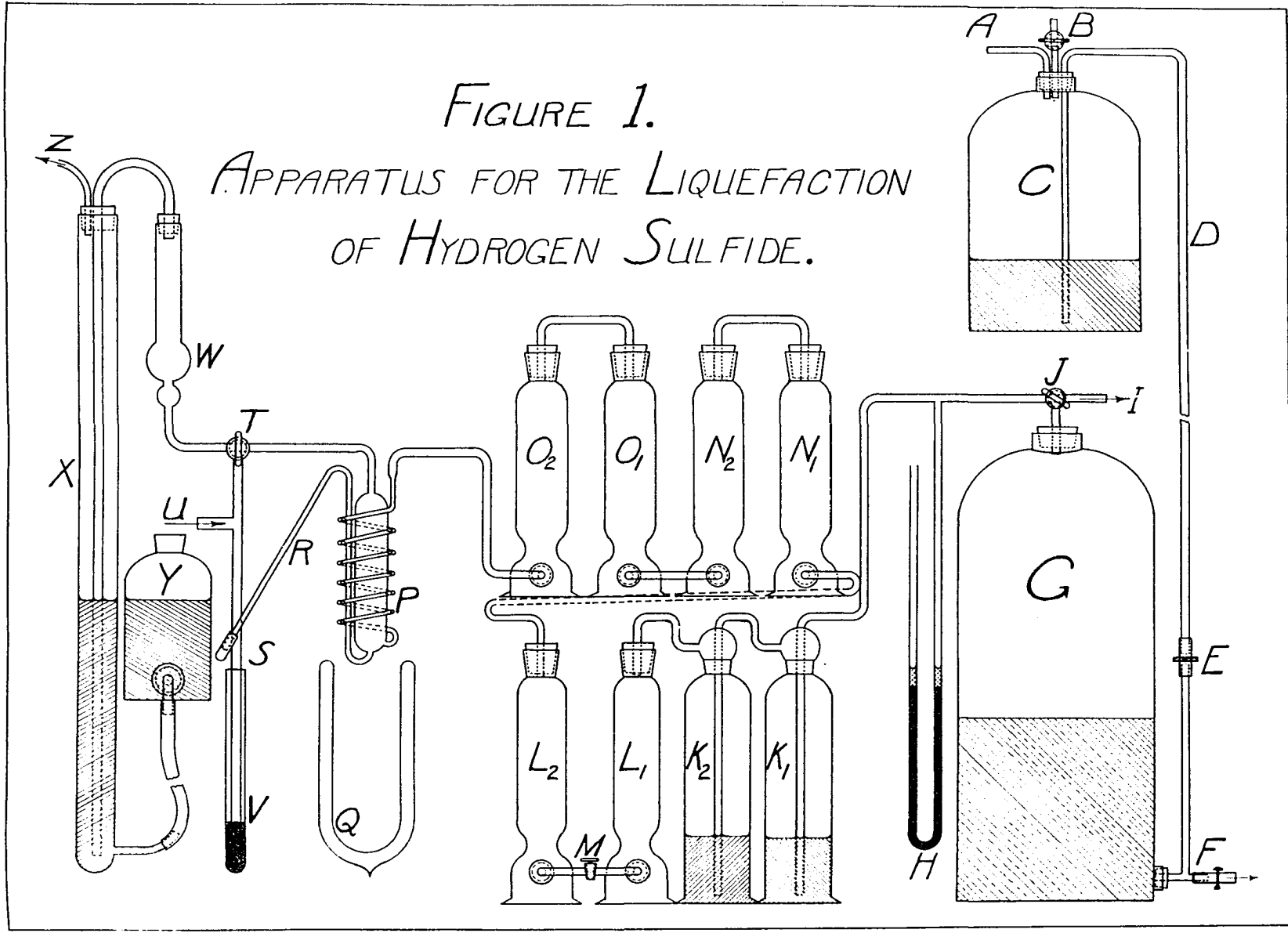
II. TENTATIVE VALUE FOR THE FREE ENERGY OF
FORMATION OF LIQUID HYDROGEN SULFIDE

Calculations

The free energy change (ΔF) for a system is a general criterion which shows whether the system is subject to spontaneous change. If we know the value of ΔF for any isothermal reaction, and if this value is positive, then we know that the reaction, in the direction indicated, is thermodynamically impossible. If, on the other hand, the value is negative the process is one which can occur in the direction indicated, although perhaps with no measurable speed. When the value is zero, the reaction has reached the state of equilibrium with respect to every possible change occuring at constant temperature and pressure. Such being the importance of free energy change, an attempt has been made here to calculate a tentative value for the free energy of formation of liquid hydrogen sulfide from the existing data, according to the free energy concepts and the required data from Lewis and Randall (15).

The free energy change in the vaporization of liquid hydrogen sulfide may be obtained from its vapor pressure. Ac-

15. Lewis and Randall. Thermodynamics, p.540. McGraw Hill Book Co., New York (1923).

cording to Regnault (16), the vapor pressure of liquid hydrogen sulfide at 25°C. is 21.05 atmospheres. Assuming that the vapor of liquid hydrogen sulfide at this temperature and pressure is sufficiently near to a perfect gas

$$H_2S(l) = H_2S(g)$$

$$\Delta F^0{}_{298} = -RT \ln p$$

$$= -1.9885 \times 298 \times 2.3026 \log 21.05$$

$$\Delta F^0{}_{298} = -1806 \text{ cal.}$$

Therefore, the free energy change in the condensation of gaseous hydrogen sulfide to liquid hydrogen sulfide at this pressure and temperature

$$H_2S(g) = H_2S(l); \quad \Delta F^0{}_{298} = 1806 \text{ cal.} \quad ----(a)$$

For the reaction,

$$H_2(g) + 1/2S_2(g) = H_2S(g); \quad \Delta F^0{}_{298} = -16980 \text{ cal.} \quad ----(b)$$

Combining (a) and (b), we get

$$H_2(g) + 1/2S_2(g) = H_2S(l); \quad \Delta F^0{}_{298} = -15174 \text{ cal.} \quad ----(c)$$
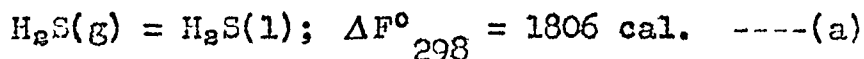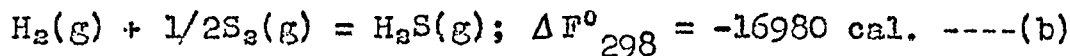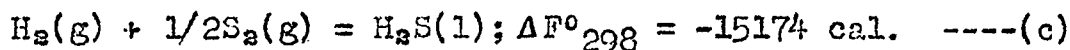
For the formation of diatomic sulfur from rhombic sulfur,

$$S(r) = 1/2S_2(g); \quad \Delta F^0{}_{298} = 9140 \text{ cal.} \quad ----(d)$$

Combining (c) and (d), we find

$$H_2(g) + S(r) = H_2S(l); \quad \Delta F^0{}_{298} = -6034 \text{ cal.} \quad ----(e)$$
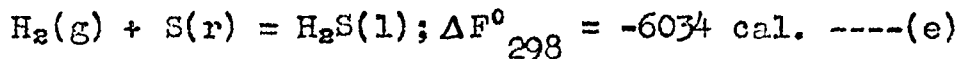
This value is the free energy of formation of liquid hydrogen sulfide at the temperature of 25°C. and at the pressure of 21.05 atmospheres from the composing elements, gaseous hy-

16. Regnault. Mem. acad. sci. inst. de France, 26, 612-618 (1862).

drogen and rhombic sulfur, in their standard states.

Discussion

The value found here is tentative because of the two assumptions made in the calculations, namely, that the heat capacity of the sulfur compounds is taken to be the same as that of the corresponding oxygen compounds, and that the hydrogen sulfide vapor at the temperature of $25^\circ C$. and at the pressure of 21.05 atmospheres behaves like an ideal gas. It is probable that further investigation will show that these assumptions give somewhat too low values for the sulfur compounds. But for the present, we use the value as it is, whenever required, until a more exact value is known.

The free energy of formation of liquid hydrogen sulfide could be used in determining whether a reaction is thermodynamically possible with liquid hydrogen sulfide. This can be predicted, if we know independently the values for the free energy of formation of every reacting substance and the products of the reaction. For instance in the reaction,

$$H_2S(l) + M(metal) = MS(s) + H_2(g)$$
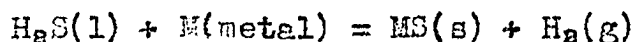
we have to know the free energy of $H_2S(l)$ and MS(s), before we can have some idea of the direction of the reaction in which it is possible for it to go. At the present time, the free energy for the metallic sulfides are not available except for

PbS and Ag_2S. Hudleston (17) calculated $\Delta F = -15200$ for

PbS(s) and $\Delta F = -2290$ for $Ag_2S(s)$. For the reaction

$$Pb + H_2S(l) = PbS(s) + H_2(g)$$
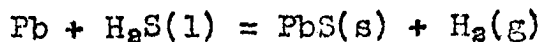
$$\Delta F^0_{298} = -15200 - (-6034) = -9166 \text{ cal.}$$

Since ΔF comes out to be negative, there is a considerable

tendency for the reaction to take place. That is, to say,

that Pb will react with liquid hydrogen sulfide under labora-

tory conditions. This is confirmed by experiment as shown

later on.

To consider one more reaction of a metal

$$2Ag + H_2S(l) = Ag_2S(s) + H_2(g)$$

for which

$$\Delta F^0_{298} = -2290 - (-6034) = 3744 \text{ cal.}$$

Here, since ΔF comes out to be positive, the tendency for

the reaction would be not to take place in the direction given,

but would possibly go in the reverse direction. It means that

Ag may not react with liquid hydrogen sulfide at $25^\circ C$. This

is contrary to Quam's (6) observation of a positive reaction

of liquid hydrogen sulfide on Ag.

Similar considerations hold in the reaction of liquid hy-

drogen sulfide on metallic oxides. To illustrate, for the re-

action

$$H_2S(l) + PbO(s) = PbS(s) + H_2O(l)$$
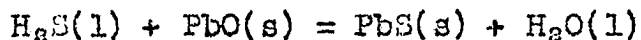
17. Hudleston. Chemical Affinity, p.130. Longmans Green and
Co. Ltd., New York (1928).

$$\Delta F^0_{298} = -15200 - 56560 - (-6034 - 45050) = -20676 \text{ cal.}$$

and for the reaction

$$H_2S(l) + Ag_2O(s) = Ag_2S(s) + H_2O(l)$$
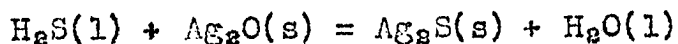
$$\Delta F^0_{298} = -2290 - 56560 - (-6034 - 2395) = -50421 \text{ cal.}$$

Since in both these reactions ΔF is negative, the reactions take place in the direction given. It means that PbO and Ag_2O react with liquid hydrogen sulfide at 25°C. The reaction in the case of PbO was confirmed by experiment as shown later on. We did not try the reaction with Ag_2O.

From the above four illustrations, it will be easily seen that $-\Delta F$ in the reactions of liquid hydrogen sulfide on oxides is far greater in magnitude compared to $-\Delta F$ for the reactions of liquid hydrogen sulfide on metals. In other words, liquid hydrogen sulfide reacts very readily on oxides to give sulfides and water, while it reacts rather very slowly, if at all, on metals to give hydrosulfides or sulfides and hydrogen gas. This general conclusion confirms pretty well the experimental observations for the reactions of liquid hydrogen sulfide on metals and oxides.

III. REACTIONS OF LIQUID HYDROGEN SULFIDE

ON METALS

Experimental Part

Materials:

All the metals used here were obtained mostly from the stock in the store-room. Their sources and make are indicated as follows:

Baker Chemical Co.: Fe (standard wire), Fe (purified by alcohol), and Al (powder).

Merck: K.

Kahlbaum: Cs and Si.

Baker's Analyzed: Zn (granular) and Sn (granular).

Wilkins Anderson Co.: Al (granular).

Mallinckrodt Chemical Works: Bi.

Sargent Co.: Cr and Mo (powder).

Ludlum Steel Co. (New York): V.

Dr. H. Gilman: Sr and Ba.

Mr. G. E. Irion: Mn, Ni, Co, Pt, Cd, Mg (crystals), Tl, Ta, U, Mo (wire), W and Be.

No specification: Pb (granular), Ca, Mg (ribbon), and Al (turnings).

The only special care taken regarding these metals excepting a few like K, Cs, Ca, Sr and Ba, was to keep off moisture from their surface by keeping them all the time over concentrated H_2SO_4 in a desiccator.

General Procedure:

All the reactions of the metals were carried out in the Franklin type or the Y shaped reaction tube made of specially thick lime-magnesia glass tubing.

The reaction tubes were cleaned by means of chromic acid solution and dried by alcohol and ether. The ether vapors in the tubes were finally removed by air dried over con. H_2SO_4 or P_2O_5.

About 2-3 cc. of liquid hydrogen sulfide from the storage tube were transferred, with all the necessary care and precautions, to one arm of the clean and dry reaction tube, which was previously kept in the cooling bath (-77^oC.) of ether and solid CO_2. Then a few drops of liquid hydrogen sulfide were allowed to go into and evaporate in the other arm of the tube, so that in the tube there was nothing else but liquid hydrogen sulfide in contact with its vapor.

A sample, about half to one gram, of the required metal was, whenever possible, burnished with a fine sand paper, or scraped with a steel knife to remove any oxidized film from the surface of the metal; wiped rapidly with a piece of cheese cloth or filter paper, as the case may be, to remove any foreign adhering particles from the surface of the metal. Then as quickly as possible this was put into the liquid hydrogen sulfide in the reaction tube kept at -77^oC. If the sample

was a powder, it was put into the reaction tube without any treatment as given above.

At -77°C. observations were taken on the sample in the reaction tube with respect to any noticeable change occurring therein, namely, change of color, evolution of gas, formation of a new solid etc., for from a half hour to three hours, before the tube was very carefully sealed, annealed, and kept aside in a special box for further observations at room temperature over a considerably long period of time (about two years) even though the reaction might have been completed long before.

When the reaction tube came to room temperature next day, observations were taken daily in the beginning, then weekly and afterwards monthly, depending upon the probable course of the reaction as indicated by the outside observations. Very great care and precaution have to be observed in handling these reaction tubes at the room temperature, as they develop about 20 atmospheres pressure inside which is likely to lead to a serious accident any time, if unheeded. The best way is to handle these tubes behind a thick glass screen, with tongs held in hand with strong leather gloves and one's eyes protected with goggles. Any possible change, as indicated before, occurring in the tube is noticed. When no more change of any kind could be noticed, the reaction was thought to have come to equilibrium, and hence, was completed under the

given conditions. After this the tube could be opened any time and the products of the reaction further examined. However, without opening the tube, the other arm of the tube was used to test whether any of the substances taking part in the reaction in the tube were soluble in the solvent liquid hydrogen sulfide. This is done as follows:

Transfer all of the liquid without any of the solid to one arm of the tube. Let the other arm with solid be at some little lower temperature than the one with liquid. The solvent will distill over to the cooler arm. If anything, solid or liquid, be left behind, it shows that something soluble in the solvent has been found there. What that is, has to be correctly determined by its chemical tests later on when the tube is opened.

When the reaction is completed, the tube is cooled to -77°C. and opened. All solid is transferred to one arm and all liquid to other arm which was kept in the cooling bath, and the excess liquid hydrogen sulfide is slowly allowed to evaporate as the cooling bath comes to room temperature to prevent the loss of liquid and hence of the solute by spurting.

Now some chemical tests are made on both the solid and the solute to determine the nature of the products.

In the reactions of metals, there was no solute left after the evaporation of the solvent. So, chemical tests were

run only on the solid to determine any positive indication of the presence of a sulfide. The usual method was to test the presence of gaseous hydrogen sulfide, by the blackening of lead acetate paper, which was evolved from the solid by the addition of some suitable acid; sometimes profuse sulfur separated on the addition of oxidizing acid; and in some cases the alkali solution of the solid turned lead acetate paper black. One of these methods was employed to show the presence or absence of chemically combined sulfur in the solid product. Whenever any positive test for combined sulfur was obtained, it was concluded that the metal under consideration had reacted with liquid hydrogen sulfide to give corresponding hydrosulfide, sulfide or polysulfide as the case might be. The particular composition and character of the product formed was not determined except in the case of potassium.

Observations:

Only reactions of a few metals, like potassium and caesium, which reacted rather rapidly with liquid hydrogen sulfide at -77°C. and which therefore could not be sealed in reaction tubes to observe the reaction over a longer period of time, will be described quite fully at first, and then will follow a summarized account of other reactions which took place at some higher temperature varying between -77°C. to room temperature and under pressure varying between 1 to 20

atmospheres, usually the higher in both cases.

Potassium: At -77°C., as soon as potassium came in contact with liquid hydrogen sulfide, it began to react giving off a slow but continuous stream of small gas bubbles and covering the surface of the metal with a white incrustation in a few minutes. The reaction thus continued even for 12 hours and the gas bubbles were still coming off, but quite slowly, as the incrustation had increased in thickness considerably. The metal with incrustation appeared like a swollen mass. When the reaction tube was exposed to room temperature, even for a short time, the reaction increased in intensity considerably.

After about 12 hours the solvent was slowly evaporated without leaving any residue behind, showing that neither metallic potassium nor the white product of the reaction was soluble in liquid hydrogen sulfide.

The white incrustation was scraped off very carefully from the surface of metallic potassium by means of a steel knife without removing any metallic particles as far as possible. The white scales were hygroscopic and would turn slightly yellow after some exposure to atmospheric conditions. A lead acetate paper was affected by vapors in the neighborhood of these scales, by vapors from their aqueous solution and by gas evolved on the addition of dilute HCl when some elementary sulfur was also set free. These reactions point

to the formation of some sulfide of potassium as one of the reaction products.

On analyzing the white scales, 0.03143 gm. of sulfur and 0.03505 gm. of potassium were obtained from the same sample. So, the atomic ratio of potassium to sulfur in the sample was found to be $\left(\frac{0.03505}{39.01}\right)/\left(\frac{0.03143}{32.06}\right) = 0.914$. The theoretical atomic ratio of K to S in K_2S and KSH is 2.0 and 1.0 respectively. Therefore the potassium sulfide formed during the reaction has the formula of KSH.

Caesium: A very vigorous reaction occurred as soon as caesium came in contact with liquid hydrogen sulfide at $-77^{\circ}C$. Gas bubbles were given off very rapidly, and a white solid of much larger volume than that of the metal was formed, which changed to yellow color in about two hours while still in the cooling bath.

None of the products were soluble in the solvent. The yellow solid gave all the indications, as in the case of potassium, of being a caesium sulfide.

In the following table No. I, the first column gives the name of a metal under consideration, the second column gives the probable time (in days) for completion of the reaction at room temperature, even though the observations continued for a considerably longer time, extending to about two years, and the third column contains the specific observations, namely, changes occurring in the physical appearance, particularly

the color of the solid, evolution of any gas like H_2, and
nature of a positive test for chemically combined sulfur,
usually the evolution of H_2S turning lead acetate paper
black. Inclusion of a positive test for hydrogen sulfide
means that the metal has reacted with liquid hydrogen sulfide
to form at least one of its sulfides under the laboratory con-
ditions.

It should be also noted that in the following cases, there
was no evidence of any reaction taking place at -77°C., that
none of the products of reaction that took place at room tem-
perature were soluble in the solvent, and that no evolution of
any gas could be noticed except in the case of barium.

Discussion

It has already been stated that the free energy change
in the reactions of liquid hydrogen sulfide on metal was us-
ually very small, and hence the speed of the reactions, when-
ever they occurred, would be rather slow, and their intensity
would be correspondingly low. This prediction was quite con-
firmed by the data presented above, from which we could easi-
ly see that the reactions were necessarily very, very slow
when compared to the corresponding reactions in aqueous medium.
For instance, the reaction of K with H_2O is so extremely vio-
lent and explosive that hydrogen set free catches fire. But
in the reaction of K with liquid hydrogen sulfide we can see
the slow evolution of gas for hours. One of the reasons for

TABLE I.

Reactions of Liquid Hydrogen Sulfide on Metals

Metal	Time of reaction (days)	Observations at room temperature and remarks
Calcium	15	Grayish white layer and powder. HCl(dil.) $\longrightarrow H_2S$ (very strong)
Strontium	15	Disintegrates to gray powder. HCl(dil.) $\longrightarrow H_2S$ (very strong)
Barium	15	Yellowish gray powder. Some gas evolved. HCl(dil.) $\longrightarrow H_2S$ (very strong)
Beryllium	indefinite	Surface probably little dull. HCl(dil.) $\longrightarrow H_2S$ (fairly strong)
Magnesium (crystal)	150	Faint yellowish tinge on surface and white powder. HCl(dil.) $\longrightarrow H_2S$ (fairly strong)
Zinc (granular)	90	Whitish layer sticking to glass. HCl(dil.) $\longrightarrow H_2S$ (fairly strong)
cadmium	90	Yellowish tinge on surface. HCl(con.) $\longrightarrow H_2S$ (strong)
Aluminum (granular)	indefinite	No change in color. HCl(dil.) $\longrightarrow H_2S$ (weak)
Thalium	indefinite	Bluish black surface. H_2SO_4(dil.) $\longrightarrow H_2S$ (strong)
Silicon	-	No reaction.
Tin (granular)	150	Yellowish layer sticking to glass. Solid dark brown or blackish. HCl(con.) $\longrightarrow H_2S$ (strong)
Lead (granular)	indefinite	No change in color. HNO_3(con.) $\longrightarrow$ free S (profuse)
Vanadium	60	Black powder. H_2SO_4(con.) $\longrightarrow$ free S.

TABLE I.

(continued)

Metal	Time of reaction: (days)	Observations at room temperature and remarks
Tantalum	-	No reaction
Bismuth	20	Black surface. HCl(con.) $\longrightarrow$ H_2S (weak)
Chromium	-	No reaction.
Molybdenum (wire)	300	Disintegrated to gray or black powder. KOH(con.) $\longrightarrow$ Pb(Ac)$_2$ paper slightly black.
Tungsten (wire)	indefi-nite	No change in appearance. KOH(con.) $\longrightarrow$ Pb(Ac)$_2$ paper black.
Uranium	indefi-nite	No change in color. HCl(con.) $\longrightarrow$ H_2S (weak)
Manganese (crystals)	500	Variety of colors but black or brown predominating. HCl(dil.) $\longrightarrow$ H_2S (strong)
Iron	10	Blackened, but wire not disintegrated. HCl(dil.) $\longrightarrow$ H_2S (strong)
Cobalt	indefi-nite	No change in appearance. HCl(con.) $\longrightarrow$ H_2S (weak)
Nickel	-	No reaction.
Platinum	-	No reaction

this difference in the speeds of the two similar reactions
is that the solid (KOH) formed during the reaction is soluble
in the solvent in one case and thus ever exposing a fresh
surface of the metal to the medium for further reaction,
while in the other case, the solid (KSH) formed, being insol-
uble in the solvent, forms a kind of hard incrustation on the
surface of the reacting metal, and so, prevents a fresh sur-
face of the metal from coming in contact with the reacting
medium.

Since the product of the reaction with K is KSH, the
mechanism of the reaction may be represented by the equation

$$2K(s) + 2H_2S(l) = 2KSH(s) + H_2(g)$$

which is similar to the chemical equation for the reaction of
K with H_2O

$$2K + 2H_2O = 2KOH + H_2,$$
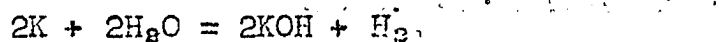
So, the gas given off during the reaction of K with liquid
hydrogen sulfide was hydrogen. We did not, however, chemical-
ly confirm the presence of hydrogen.

Now to compare the reactivity of the metals in the same
family of elements, let us consider the reactions of Na, K,
and Cs. Quam (6) reported that Na reacted rather slowly. We
saw above that K reacted fairly rapidly with some evolution
of gas, and that Cs reacted vigorously with rapid evolution
of gas. Also, the swelling of the solid product of reaction

was much more in the case of Cs than with K and Na. The change in the color of the solid product was more pronounced with Cs in a shorter time than in the case of K and Na.

A similar gradation in the reactivity will be found in the alkaline earth triad, Ca, Sr and Ba. Here the color of the solid product changes from grayish white in the case of Ca to yellowish gray with Ba. The solid product disintegrates to powder more rapidly as we go down from Ca to Ba. Some evolution of gas could be clearly observed in the reaction with Ba, but not so in the case of Ca and Sr.

Similar considerations regarding a gradation in the reactivity of elements in a family hold good in the case of any group in the periodic table arrangement of elements. Thus, we see that the reactivity of an element increases with the increase in atomic weight of an element in the same group. This is quite in agreement with the most general statement that the properties of the elements are a periodic function of the atomic weights.

Now, there is no doubt that evolution of hydrogen sulfide and separation of sulfur from a substance when treated with a proper chemical reagent is a positive sign which shows the presence of a sulfide in the substance. Where the evolution of hydrogen sulfide gas was pronounced, undoubtedly some reaction had taken place there. But when the indication for hydrogen sulfide gas was rather weak, as in the case of Al, Bi,

U and Co, a question might be raised as to whether any reaction had really taken place in these cases. Fournier and Lang (13) found that Fe, Cu and Al were not affected by liquid hydrogen sulfide. It is just possible that the coating of oxide which Al so readily forms on its surface was responsible for the reaction mentioned here. But we can not explain the reactions of Bi, U and Co by a similar assumption. The most probable thing seems to be that these reactions must be taking place only with imperceptible intensity. Moreover, Fournier and Lang's (13) observations have been contradicted by the work of Skilling (1) who reported a vigorous reaction with Fe wire, and of Quam (6) who found a positive reaction with Cu, and by the present investigation. It may be that Fournier and Lang observed their reactions with some other point in view. The main point in this investigation was to find any indication of a positive reaction of a metal with liquid hydrogen sulfide.

So, taking into consideration Quam's (8) work and the data presented above, it will be easily observed, in conclusion, that a surprisingly larger number of metals react with liquid hydrogen sulfide than that ordinarily expected, and that the reaction products are insoluble in the solvent. So, in general, it may be said that liquid hydrogen sulfide is a very good reacting medium at least for metals at room temperature and under a pressure of about 20 atmospheres.

IV. TENTATIVE VALUE FOR THE SINGLE ELECTRODE

POTENTIAL OF SOME METALS IN THE SATURATED SOLUTION

OF THEIR CHLORIDES IN LIQUID HYDROGEN SULFIDE

Experimental Part

Materials:

The sources of materials used are indicated as follows:

Mr. C. E. Irion, formerly a technician in the department, supplied in a most suitable form the wires or rods of Al, Zn, Sn and Sb in the purest form available on the market. They were always kept over concentrated H_2SO_4 in a desiccator to keep them dry.

Merck: Methyl alcohol, C.P. (free from acetone), and $SbCl_3$, C.P. crystals.

Dr. J. A. Wilkinson: $AlCl_3$ and $SnCl_4$.

No specification: $ZnCl_2$, calomel, KCl (twice recrystallized) and mercury (double distilled).

General Procedure:

A normal calomel electrode was prepared in the usual manner with all the necessary precautions, and its E.M.F. was assumed to be -0.28 volt. All the single potentials given below are calculated on this value of the normal electrode as a basis. An aqueous solution saturated with KCl, and a methyl alcohol solution saturated with KCl were prepared; and both of these saturated solutions were always in contact with excess of solid KCl to insure the saturation, and were pre-

served as stock solutions.

The vessel to hold the metal electrode was of H shaped type, made of two small test tubes connected together near the bottom by a small glass tube which served to prevent diffusion of liquids from one arm to the other.

On the day when the E.M.F. measurements were to be taken, a saturated solution of the metallic chloride in liquid hydrogen sulfide at -77°C. was made in the above previously cleaned and dried H shaped electrode tube, by adding excess of the chloride, until by raising the temperature of the solvent and cooling it again, some of the solute was precipitated from the solution.

The required metal wire or rod was scraped with a steel knife or burnished with a fine sand paper, wiped with a piece of cheese cloth or filter paper to remove foreign particles from the surface of the electrode, and then dipped into a solution in the arm of the electrode vessel through a small glass tubing.

The bridge connection between the two half cells was made by a methyl alcohol saturated solution of KCl filled in a long but narrow armed U tube with stopcock in the middle.

The general arrangement of the cell measured was as follows: The metal dipped into solution in one arm of the electrode vessel at -77°C. and into solution in the other arm was dipped   one end of the connecting bridge whose other end

was dipping into a saturated aqueous solution of KCl in a small beaker in which also was dipping the tip end of 1N calomel electrode. The skeleton of the cell looked like this:

Metal $\begin{array}{l} \text{:metal chloride:methyl alcohol:KCl} \qquad \text{:1N calomel} \\ \text{:(sat. liq.H}_2\text{S): (sat.KCl) :(sat. sol.):electrode} \end{array}$

The electromotive forces of the above combinations were measured, with all the due care and precaution, by means of the compensation method of Poggendorf, using Leeds and Northrup standard student potentiometer and D'Arsonval wall type galvanometer. In cases where the solutions offered very high resistance and so in consequence, were very poor conductors of electricity, a great degree of accuracy was not obtained. Two dry cells of 1.5 volts each were used as a source of electric current. A Weston element or cadmium standard cell, having an E.M.F. of 1.0189 volt was used to standardize the potentiometric set. The E.M.F. readings and corresponding time were recorded.

The E.M.F. measured values did not stay very constant, neither were they very reproduceable, although they were always of the same magnitude. It was thought that methyl alcohol gotten into the chloride solution might be the cause of these varying E.M.F. values. To determine the effect of methyl alcohol saturated with KCl on the E.M.F. measurements, a definite amount of it was added to the chloride solution in liquid hydrogen sulfide in one arm of the electrode vessel and the solutions well mixed. Then the electrode vessel was

set in its proper place in the cell arrangement, and the corresponding E.M.F. was read. Knowing the volume of methyl alcohol added, and the volume of the original chloride solution in the electrode vessel, and assuming that the volume of the mixture was equal to the total volume of the two liquids, the percentage of alcohol by volume in the mixture was calculated.

As the field around an electrode is made more uniform by rotation or stirring, the metal electrode was rotated by hand for a short time and then E.M.F. reading taken and the corresponding time noted.

Observations:

The first great difficulty to be noticed in the problem was to get a suitable liquid for bridge connections between liquid hydrogen sulfide solution at -77°C. and aqueous solution at room temperature. Such a liquid must satisfy the following conditions:

(a) It must stay in liquid condition over a wide range of temperature, from about -100°C. to 50°C.

(b) It must be soluble and non-reactive in both liquid hydrogen sulfide and water.

(c) It must be a fairly good conductor of electricity.

(d) It should dissolve KCl to a certain extent.

Because of the solvent power of liquid hydrogen sulfide, the choice of such a liquid was confined to a few organic liquids. After some experimentation, methyl alcohol saturat-

ed with KCl was selected as a suitable liquid for the bridge connections, as it gave the most sensitive values for E.M.F. under a given set of conditions when compared to other organic liquids, like ethyl alcohol and acetone.

The following E.M.F. values are for the whole cell, as set up above, in which a particular metal is in contact with a saturated solution of its chloride as indicated. In the tables for cells with or without alcohol, the column marked:

Cell No. indicates the number of the particular cell in the experiment.

% alcohol " the percentage of methyl alcohol sat-
(volume) urated with KCl in the whole mixture by volume in the electrode vessel.

E.M.F. " the first E.M.F. measurement on the
(starting) cell as assembled.

E.M.F. " the final or maximum E.M.F. reading
(final) in the experiment.

Time interval " the time in minutes from the first
(min.) reading to the final reading in the experiment.

Remarks " the nature of E.M.F. readings; and any other secondary observation special- ly noticed during the experiment.

The sign + before the E.M.F. reading shows that the val- ue was taken when the mercury in the

calomel cell was connected to the +

pole on the potentiometer circuit.

The sign - before the E.M.F. reading

shows that the value was taken when

the mercury in the calomel cell was

connected to the - pole on the po-

tentiometer circuit.

Treatment of Results and Discussion

It will be noticed, from measurements taken at time in-

tervals varying from 15 minutes to over two hours, that the

general tendency is for the potential either to decrease or

increase steadily. When the starting E.M.F. was lower than

the would be maximum, it generally increased to the maximum

and then decreased afterwards. But if the starting E.M.F. was

about the maximum, then it decreased later on. These vari-

ations may be due to many unknown causes, but the following

two appear to be more probable, namely, (a) the possibility

of a chemical reaction between the metal and the solvent, and

(b) a chemical reaction between the solute and the solvent in

the presence of a third solvent, like methyl alcohol from the

bridge connection. In considering these causes, we will take

into account the behavior of Sb in $SbCl_3$ cell.

(a) If a chemical reaction takes place between Sb and

liquid hydrogen sulfide, a sulfide film will be formed on Sb

electrode, as antimony sulfide is insoluble in the solvent,

TABLE II.

E.M.F. of Cell With Al in AlCl₃ Without Alcohol

No. (cell)	E.M.F. (start-ing)	E.M.F. (fin-al)	Time inter-val (min.)	Remarks
1	-0.100	-0.115	9	Not very sensitive; even on rotation decreased later on.
2	-0.160	-0.205	26	Increasing all time. Rotation has no effect. Some white colloidal precipitate formed in the arm in which bridge was introduced.
3	-0.210			Decreasing all time; rotation has no effect. The bridge from No.2 was used. No white precipitate formed.
4	-0.260			Do. Do. Do.
5	-0.255			Do. Do. Do.

TABLE III.

E.M.F. of Cell With Sb in SbCl$_3$ Without Alcohol

Number (cell)	E.M.F. (start-ing)	E.M.F. (fin-al)	Time inter-val (min.)		Remarks
1	-0.178	-0.252	50	Rest	) As soon as bridge was introduced in the arm, yellow precipitate was formed. Finally E.M.F. remained constant, but with different values for rotation & rest.
		-0.272	55	Rotation	
		-0.265	60	Rest	
2	-0.145	-0.176	6	Do.	Do. Do.
		-0.235	83		
		-0.232	92		
3	-0.164	-0.234	41		Continuously increasing; rotation has no effect. Yellow precipitate formed in the arm in which bridge was introduced.
4	-0.266	-0.257	6	Rest	) E.M.F. constant but with different values for rotation and rest. Bridge from No. 3 was used. No yellow precipitate formed in the arm.
		-0.265	7	Rotation	

TABLE IV

E.M.F. of Cell With Sn in SnCl$_4$ Without Alcohol

Number (cell)	E.M.F. (start-ing)	E.M.F. (fin-al)	Time inter-val (min.)	Remarks
1	-0.025	-0.035	7	Steadily decreased in spite of rotation; not very sensitive; little yellow ppt. was formed in the arm in which the bridge was introduced.
2	-0.030	-0.035	in-stant-ly	E.M.F. constant over 20 minutes. Bridge from No.1 was used. Very slight indication of very faint yellow ppt. in arm in which the bridge was introduced.

E.M.F. of Cell With Zn in ZnCl$_2$ Without Alcohol

Number (cell)	E.M.F. (start-ing)	E.M.F. (fin-al)	Time inter-val (min.)	Remarks
1	+0.5 to +0.6	+0.6 to +0.7	13	Not sensitive at all; rotation has no effect.
2	+0.6	+0.7	10	Do. Do. Do.

TABLE V

E.M.F. of Cell With Al in AlCl₃ With Alcohol

Cell Number	% Alcohol (volume)	E.M.F. (starting)	Remarks
3	0	-0.210	E.M.F. decreasing. No white ppt.
	1.04	+0.050	E.M.F. constant. White ppt. formed.
	3.06	+0.510	E.M.F. increasing. White ppt. dissolved.
	6.87	+0.620	E.M.F. increasing.
	13.18	+0.565	Do. Do.
4	0	-0.260	E.M.F. decreasing. No white ppt.
	1.05	+0.360	E.M.F. constant. White ppt.
	3.10	+0.560	E.M.F. increasing. White ppt. dissolved.
	6.94	+0.515	E.M.F. increasing.
	18.5	+0.595	Do. Do.
5	0	-0.255	E.M.F. decreasing. No white ppt.
	0.97	+0.110	E.M.F. decreasing. White ppt.
	3.01	+0.520	E.M.F. increasing. White ppt. dissolved.
	7.15	+0.520	E.M.F. increasing.
	28.82	+0.560	Do. Do.

TABLE VI.

E.M.F. of Cell With Zn in $ZnCl_2$ With Alcohol

Cell Number	Alcohol % (volume)	E.M.F. (starting)	Remarks
1	0	+0.60 to +0.70	Not sensitive.
	0.86	+0.70	Little more sensitive. E.M.F. decreasing.
	1.64	+0.71	Do.
	4.19	+0.751	Appreciably sensitive. E.M.F. decreasing.
	7.7	+0.715	Do.
	15.91	+0.720	Do.
2	0	+0.70	Not sensitive.
	0.94	+0.73	Little more sensitive. E.M.F. decreasing.
	1.96	+0.73	Do.
	4.84	+0.770	Appreciably sensitive. E.M.F. decreasing.
	8.86	+0.730	Do.
	17.32	+0.745	Do.

TABLE VII.

E.M.F. of Cell With Sn in SnCl₄ With Alcohol

Cell number	% Alcohol (volume)	E.M.F. (starting)	Remarks
2	0	-0.035	Not sensitive but constant. Very faint yellowish ppt.
	1.69	+0.205	E.M.F. decreasing. Little yellowish ppt.
	3.61	+0.500	E.M.F. decreasing. Yel. ppt. increasing.
	7.94	+0.520	Do.
	16.19	+0.525	E.M.F. increasing. Reddish brown ppt.
	27.4	+0.525	Do.

E.M.F. of Cell With Sb in SbCl₃ With Alcohol

Cell number	% Alcohol (volume)	E.M.F. (starting)	Remarks
4	0	-0.266	Constant with rotation. Yellow ppt.
	some alcohol	-0.090	E.M.F. increasing. Profuse yellow ppt.

and consequently as the surface condition of the electrode is changed, the corresponding E.M.F. will vary from time to time. If this adhering sulfide film be removed from the surface by rotating the electrode vigorously for some time, the surface could be restored to almost the original condition, and so the E.M.F. should also go back pretty near to the original value. But it was found that though rotation of the electrode showed some corresponding change in E.M.F., it did not affect the general tendency of the E.M.F. which might be either to increase or to decrease. It was possible that rotation did not altogether shake off all the film from the electrode and so, the electrode never came back to the original position, and so also the corresponding E.M.F. However, at the end of the experiment, when the electrode was taken out from the cell, and inspected for a sulfide layer on its surface, no film could be found. So, the possibility of a chemical reaction between metal and solvent is rather remote, but not impossible. As Quam (6) says that Sb reacts with liquid hydrogen sulfide at room temperatures, it may probably react at -77°C. even though imperceptibly.

Considering (b), it was clearly observed that as soon as the bridge liquid, methyl alcohol saturated with KCl, came in contact with the solution in the electrode vessel, a profuse yellow precipitate of antimony sulfide was formed. This precipitation changed the concentration of Sb in the

solution, and consequently there was a corresponding change
in the E.M.F. It was also found that if a bridge from one
cell be used without changing its contents in other cell,
the starting E.M.F. of the latter cell had almost the maxi-
mum value. No liquid diffused from or to this bridge in the
second cell, and so there was no change in concentration in
the electrode vessel, and hence the starting E.M.F. was max-
imum and constant at least for some time. This clearly
shows that the liquid diffusing from the bridge caused a
chemical reaction to take place between solute and solvent
which were inert otherwise, and hence, was a decided factor
to cause variations in the potential measurements. So, the
effect of addition of alcohol to the electrode solution was
studied.

It will be found that the addition of alcohol affected
the E.M.F. values of the cells considerably both in nature,
magnitude and sensitiveness. See Tables V-VIII. All cells
increased their E.M.F., the greatest increase being in the
case of Al, $AlCl_3$ cell and the least being with Zn, $ZnCl_2$
cell. All cells except Zn, $ZnCl_2$ cell changed the sign of
E.M.F. from - to +. In every case the E.M.F. after reach-
ing a maximum decreased very slowly or fluctuated between
certain limits.

The E.M.F. values gotten with the addition of methyl
alcohol are plotted as ordinate against the percentage vol-

TABLE VIII.

Effect of Alcohol on E.M.F.

Cell	No.	E.M.F. (starting)	E.M.F. (maximum)	% Alcohol	E.M.F. (increase)[*]
Al, $AlCl_3$	3	-0.210	+0.510 +0.620	3.06 6.87	0.73 0.83
	4	-0.260	+0.560 +0.515	3.10 6.94	0.82 0.76
	5	-0.255	+0.520 +0.520	3.01 7.15	0.77 0.77
Sn, $SnCl_4$	2	-0.035	+0.500 +0.520	3.61 7.94	0.53 0.54
Sb, $SbCl_3$	4	-0.266	-0.090	some alcohol	0.17
Zn, $ZnCl_2$	1	+0.70	+0.710 +0.751	1.64 4.19	0.01 0.05
	2	+0.70	+0.730 +0.770	1.96 4.84	0.03 0.07

[*] The last column in Table VIII gives the difference between the maximum and the starting E.M.F. in each case. This difference is the increase in E.M.F. over the starting E.M.F. of the cell.

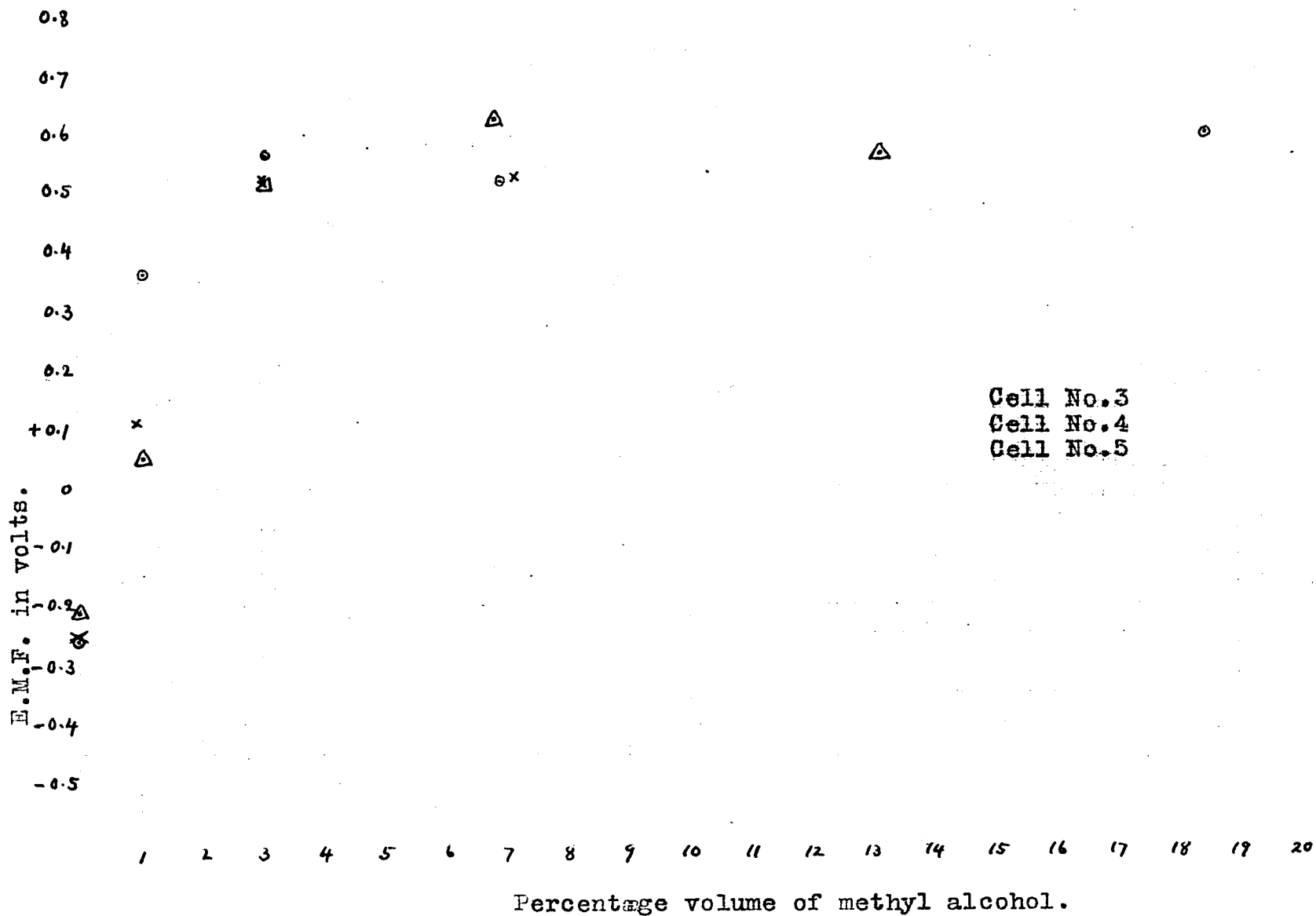Fig. 2. Effect of Alcohol on the E.M.F. of the Cell, Al in AlCl₃.

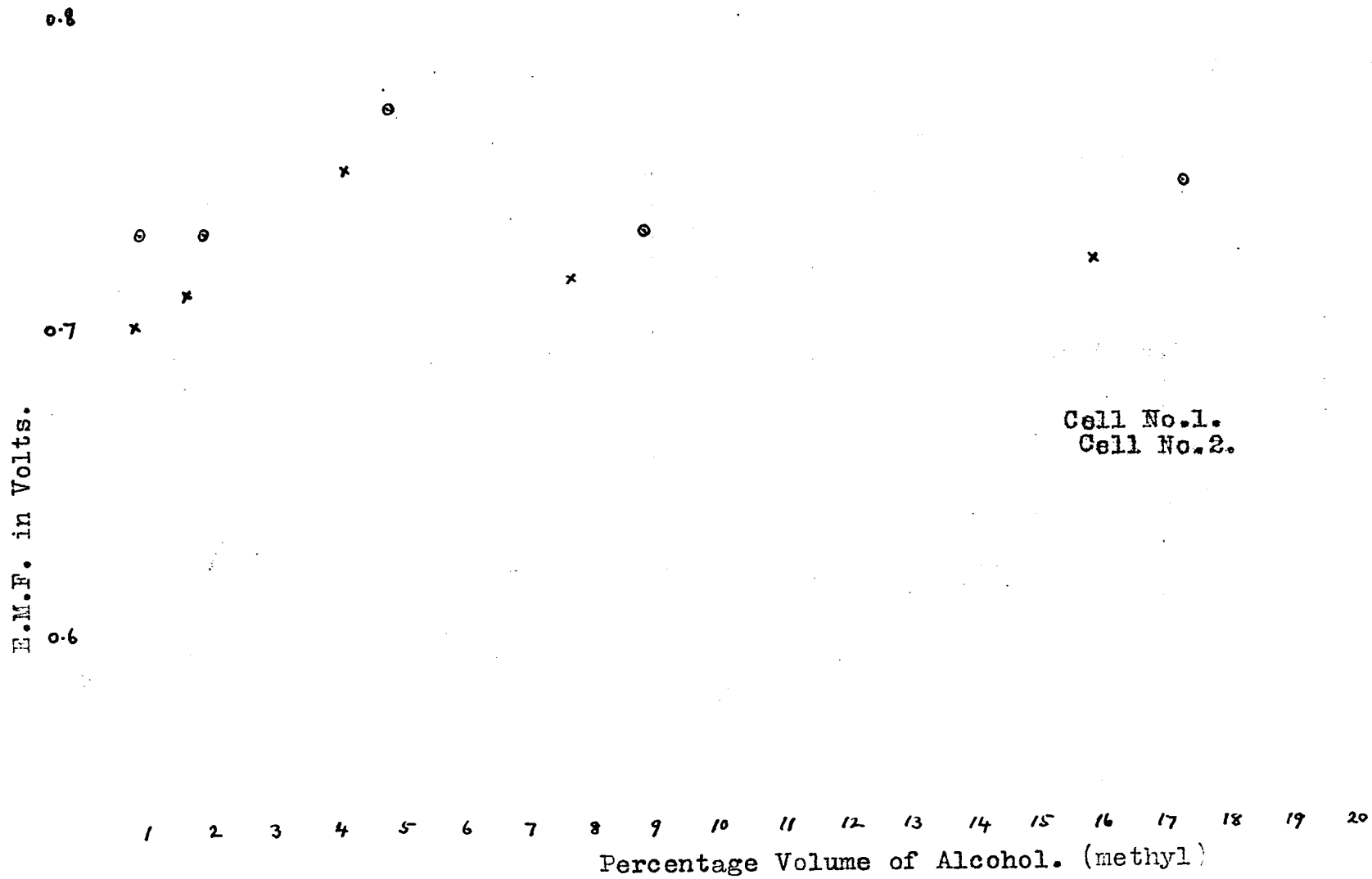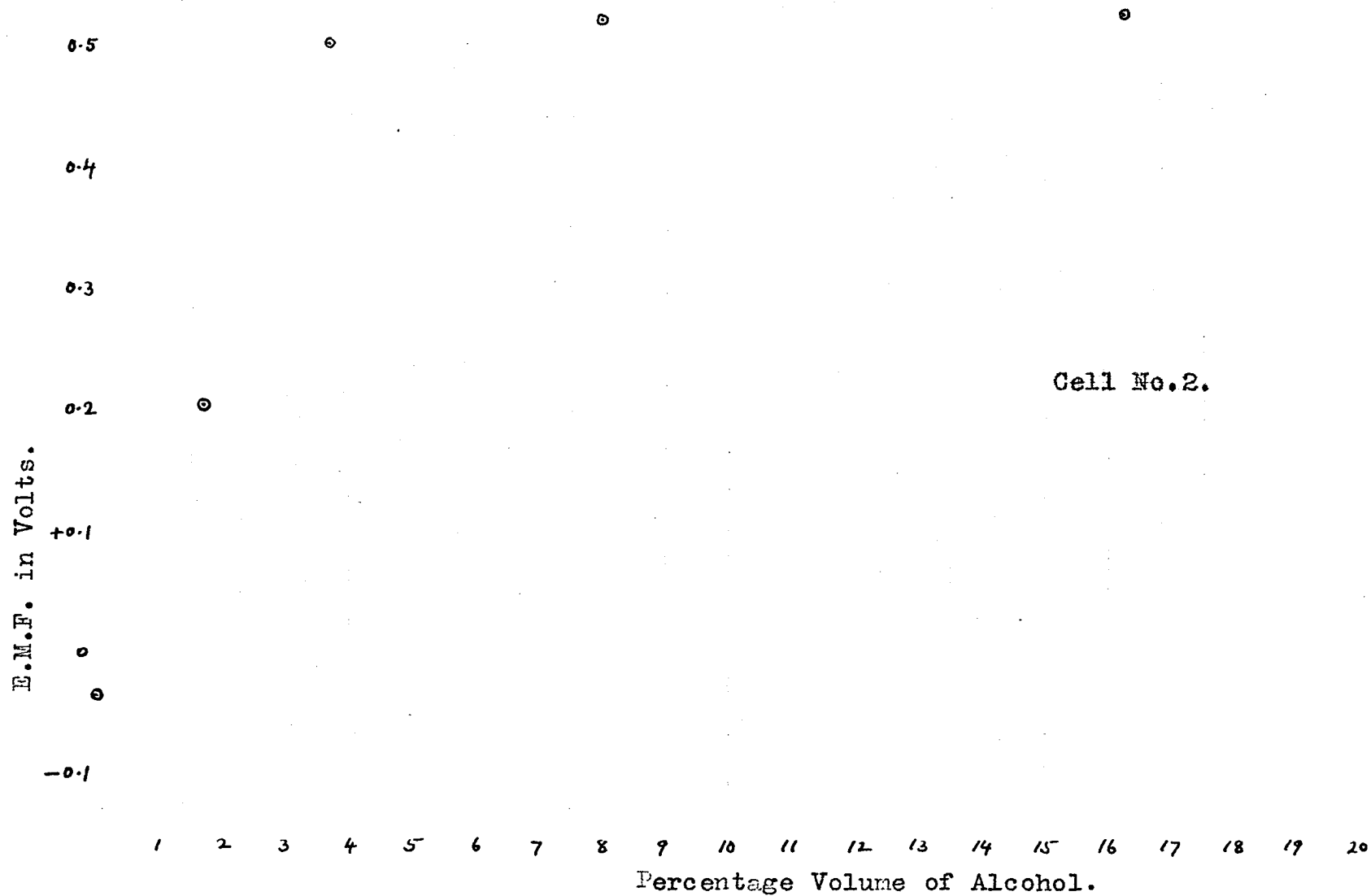Fig.3.. Effect of Alcohol on the E.M.F. of the Cell, Zn in $ZnCl_2$.

Cell No.1.
Cell No.2.

-44-

E.M.F. in Volts.

Percentage Volume of Alcohol. (methyl)

Fig. 4. Effect of Alcohol on the E.M.F. of the Cell, Sn in $SnCl_4$.

Cell No.2.

ume of methyl alcohol as abscissa to find any relation between the two. See Tables V-VII and Figures 2-4. The curve shows that the maximum E.M.F. in each case was reached very rapidly, and it occurred somewhere between 2 to 6% methyl alcohol.

If the curve be extrapolated back to zero percentage of alcohol to get the E.M.F. of the pure solution, it would give very different values for the same cell from curve to curve. But the extrapolated value for the mean curve falls pretty close to the E.M.F. at the start of each cell. So, the extrapolated values for the E.M.F. of the cell were not considered, but more reliance was placed on the starting E.M.F. or the maximum E.M.F. of the cell.

The average value of E.M.F. for each cell as assembled without alcohol is taken as the mean of the maximum values of E.M.F. in each experiment for that cell. The maximum value of E.M.F. in each experiment is taken as the true E.M.F. value for that cell because it stayed constant for some time, and because it approached almost the same value for the same cell for most of the time. Thus the average value of E.M.F. for each cell is given in Table IX.

The E.M.F. of the cells given above has been based on the assumption that the liquid potentials at the contact of various liquid junctions are pretty nearly negligible. If in aqueous solutions the magnitude of liquid potentials is

TABLE IX.

E.M.F. of Cell Without Alcohol

Cell	Number	E.M.F. (maximum)	E.M.F. (average)
Al, AlCl$_3$	3	-0.210	
	4	-0.260	-0.24
	5	-0.255	
Sb, SbCl$_3$	1	-0.272	
	2	-0.235	-0.25
	3	-0.234	
	4	-0.266	
Sn, SnCl$_4$	1	-0.035	
	2	-0.035	-0.035
Zn, ZnCl$_2$	1	+0.70	
	2	+0.70	+0.70

of the order of a few millivolts and very rarely a few hundredths of a volt, then the liquid potentials in a far less ionizing solvent like liquid hydrogen sulfide than water would be, most probably, still far less appreciable. So, they might be well neglected without affecting the results in the present investigation.

The single electrode potentials of metals are calculated from the formula,

$$E_{(cell)} = E_{(electrode)} - E_{(calomel)}$$

If normal calomel electrode be taken as zero, then E.M.F. of the cell corresponds to the single electrode potential. This is given in the second column in Table X. If the E.M.F. (-0.28 volt.) of normal calomel electrode against the normal hydrogen electrode be substituted in the above formula, then

$$E_{(electrode)} = E_{(cell)} - 0.28$$

For instance, for Sb, Sb^{+++}

$$E = -0.25 - 0.28 = -0.53$$

This E.M.F. of the electrode corresponds to normal hydrogen electrode as zero. These values are given in the third column of Table X.

. The order of the single electrode potentials in a saturated solution will be quite different from the one of the specific or normal electrode potentials which are represented by the usual electromotive force series of metals. So, the single electrode potentials obtained here do not

TABLE X.

Single Electrode Potentials of Metals in the Saturated Solution of their Chlorides

Electrode	Normal calomel electrode as zero	Normal hydrogen electrode as zero
Sb, Sb^{+++}	-0.25	-0.53
Al, Al^{+++}	-0.24	-0.52
Sn, Sn^{+++}	-0.035	-0.315
Zn, Zn^{++}	+0.70	+0.42

help us to arrange the metals to form a kind of electro-
motive force series of metals in liquid hydrogen sulfide.
But they show decidedly that there is a measurable poten-
tial difference between a metal and a solution of its salt
in liquid hydrogen sulfide.

It will be seen from the data and results presented
that the E.M.F. values are not very constant, neither very
reproduceable as they should be in a case of electromotive
force investigation. But taking into consideration the non-
solvent power of liquid hydrogen sulfide for inorganic salts,
its possible reactivity with the metal or metallic salt or
both, and the very high resistance or very low conductivity
offered by its solutions, it is easy to understand why the
E.M.F. is not constant. Moreover the same causes such as
polarization, surface films, dissolved gases, secondary re-
actions etc., that affect the variation of E.M.F. of aqueous
solutions may probably also affect in the same way the E.M.F.
of non-aqueous solutions. Therefore it is rather surprising
that the E.M.F. found in liquid hydrogen sulfide solutions
should be so nearly constant as it was under the given con-
ditions.

V. REACTIONS OF LIQUID HYDROGEN SULFIDE
ON OXIDES

Experimental Part

Materials:

The oxides used here were obtained mostly from the stock in the store-room. Their sources and make are indicated as follows:

Baker Chemical Co.: Fe_2O_3, CdO, Cu_2O, CuO (fine powder), CuO (wire), and NiO.

Merck: CaO, Sb_2O_3, PbO, NaOH, NiO_2, and BaO_2.

Kahlbaum: TiO_2.

Baker's Analyzed: SnO, Co_2O_3, MnO, PbO_2, MnO_2, $Ba(OH)_2$, and KOH (alcohol purified).

Wilkins Anderson Co.: ZnO, and Cr_2O_3.

Sargent Co.: HgO, and Sb_2O_5.

Ore Products Corporation (Denver): V_2O_5.

Dr. J. B. Quig: CrO_3.

Dr. A. W. Ralston: CaO, Al_2O_3, and SiO_2.

No specification: MgO, SnO_2, Pb_3O_4, and B_2O_3.

All the above oxides excepting a few like NaOH, KOH and BaO_2, were first dried in an electric oven at $110°C$. for a considerable time, and then were preserved dry by always keeping them over concentrated H_2SO_4 in a desiccator.

General Procedure:

The method of attacking the problem was exactly the same as described before in the reactions of liquid hydrogen sulfide on the metals.

Observations:

The observations on the reactions of liquid hydrogen sulfide on oxides are summarized in a tabular form in much the same way as in the case of metals. In Table XI, the first column gives the formula of the oxide under consideration, the second column contains the observations at $-77^\circ C.$, the third column shows the probable time for the completion of the reaction, and the last column gives the observations and a positive test for the presence of a sulfide in the reaction product at room temperature.

It should be also noted that in the following table, wherever any reaction had taken place, there was left some liquid but no solid residue after the evaporation of liquid hydrogen sulfide. The evidence of some liquid, although sometimes in traces, was an indication of formation of water as a product of the reaction; and the absence of residue showed that neither the oxide nor the sulfide formed in the reaction were soluble in the solvent liquid hydrogen sulfide.

TABLE XI.

Reactions of Liquid H_2S on Oxides

Oxide	Obser- vations at -77°C	Time of reaction (days)	Observations at room temperature and remarks
KOH	—	3	Solid unchanged. Liquid two layers - lower yellow and upper colorless. HCl (dil.) ⟶ H_2S (very strong).
CuO	?	Indef- inite	Black or rather blue colored. HNO_3 (con.) ⟶ free S.
Cu_2O	—	5	Black powder. HNO_3 (con.) ⟶ free S.
CaO	—	10	White ⟶ gray ⟶ flesh colored. Decomposing to yellowish gray and H_2S. HCl (dil.) ⟶ H_2S (very strong)
$Ba(OH)_2$	—	8	Yellow mass. HCl (dil.) ⟶ H_2S (very strong)
BaO_2	Flesh color	8	Yellowish gray powder. HCl (dil.) ⟶ H_2S (strong) + free S.
MgO	Yellow- ish	3	Yellow powder — colorless (later on). HCl (dil.) ⟶ H_2S (strong).
ZnO	—	8	Gray. HCl (dil.) ⟶ H_2S (strong)
CdO	—	2	Deep yellow. HCl (con.) ⟶ H_2S (very strong)
HgO	Yellow — brown — black	4	Reddish black. Dissolves in aqua regia.
B_2O_3	—	Indefi- nite	Apparently no change. H_2O ⟶ H_2S (strong)
Al_2O_3	—	15	Gray powder. HCl (dil.) ⟶ H_2S (fairly strong)
TiO_2	Gray	15	Greenish, bluish, yellowish gray, pre- dominating. Reaction ?
SiO_2	Gelati- nous mass	Indef- inite	White powder. HCl (dil.) ⟶ H_2S (fairly strong) Reaction ?

TABLE XI.

(continued)

Oxide	Observations at -77°C	Time of Reaction (days)	Observations at room temperature and remarks
SnO	—	15	Pronounced yellow color. HCl (con.) $\longrightarrow$ H_2S (strong)
SnO_2	—	5	Brown, reddish, yellowish brown. HCl (con.) $\longrightarrow$ H_2S (strong)
PbO	dark brown	3	Black. HCl (con.) $\longrightarrow$ H_2S (strong)
Pb_3O_4	brown	3	Black or blue gray. HCl (con.) $\longrightarrow$ H_2S (strong)
PbO_2	Explosion in gas phase; no change in solid.	2	Black or blue gray. HNO_3 $\longrightarrow$ free S (profuse)
V_2O_5	black	3	Black. KOH $\longrightarrow$ Pb(Ac)$_2$ paper black.
Sb_2O_3	yellowish	8	Yellow on exposure to orange, in air. HCl (con.) $\longrightarrow$ H_2S (strong)
Sb_2O_5	yellow	3	Dark red or orange. HCl (con.) $\longrightarrow$ H_2S (strong)
Cr_2O_3	—	—	—
CrO_3	—	indefinite	Blackish powder. Aqua regia $\longrightarrow$ free S.
MnO	Blackened	3	Black or dark brown. HCl (dil.) $\longrightarrow$ H_2S (strong)
MnO_2	—	15	Flesh color, brownish black. HCl (dil.) $\longrightarrow$ H_2S (strong) and free S.

TABLE XI.

(continued)

Oxide	Observations at -77°C	Time of Reaction (days)	Observations at room temperature and remarks
Fe_2O_3	blackened	2	Black. $HNO_3 \longrightarrow$ free S.
Co_2O_3	–	indefinite	Apparently no change in color. Aqua regia $\longrightarrow$ free S.
NiO	–	3	Black. HCl (con.) $\longrightarrow H_2S$ (fairly strong)
NiO_2	dark brown	3	Black. HCl (con.) $\longrightarrow H_2S$ (strong)
H_2O	white crystalline hydrate	15	White crystalline hydrate. Liquid two layers – lower H_2S in H_2O, upper H_2O in H_2S.

Discussion

From the data presented, it will be easily seen that most of the oxides excepting a few like TiO_2, SiO_2 and Cr_2O_3, have readily and definitely reacted with liquid hydrogen sulfide to form a corresponding sulfide. This rapidity and completeness of the reactions was naturally expected as the free energy change involved in the reaction of liquid hydrogen sulfide on an oxide to form a metallic sulfide and H_2O was comparatively very great. Another cause of the speediness of these reactions might possibly be that the water formed in the reactions would dissolve some of the reacting substances, liquid hydrogen sulfide and oxide, to form more of sulfide and water, as we know that aqueous solutions of hydrogen sulfide gas and oxide so react. The newly formed water would accelerate the reaction further in the same way, and so the longer the reaction goes, the faster it will go forward. Thus the reaction may be autocatalytic in character. But a limiting condition which stops the reaction going forward would soon be reached as the sulfide formed in the reaction, being mostly quite insoluble in the solvent, coats the exposed surface of the oxide particles with a rather hard insoluble incrustation, which in turn, as the action proceeds, prevents a further contact between the reacting substances; and so the reaction will come to a state of rest or equilibrium, as it were, after a time. Therefore in the above reactions, nei-

ther the oxide nor the metal did ever completely react, usually the reaction coming to an end, when the reacting substance was completely covered with an impervious coating of the insoluble product of the reaction.

There is the same gradation in reactivity of oxides of elements in a family in the periodic table of elements, as was seen in the case of metals. For instance, in the case of ZnO, CdO and HgO, ZnO and CdO do not react at $-77^{\circ}C.$, while HgO rapidly reacts as shown by changes in color from red $\longrightarrow$ yellow $\longrightarrow$ brown $\longrightarrow$ black. At room temperatures, all react but the rapidity of reaction probably increases from ZnO to HgO. So, the intensity of the reaction increases with the increase in molecular weight of normal oxides of elements in a group family in the periodic arrangement of elements.

It will also be observed that the higher oxides of an element are more reactive than the normal ones, as Sb_2O_5 reacts more rapidly than Sb_2O_3, and that the peroxides react vigorously compared to corresponding normal oxides, as BaO_2 reacted even $-77^{\circ}C.$ while $Ba(OH)_2$ reacts only at room temperature. A similar observation on peroxides is recorded by Vanino and Hauser (18).

18. Vanino and Hauser. Ber., 33, 625 (1900).

In conclusion, it may conveniently be said that a majority of oxides react appreciably rapidly with liquid hydrogen sulfide at -77°C., and much more so at room temperature.

VI. GENERAL SUMMARY AND CONCLUSIONS

The foregoing pages contain an account of the results of the present investigation. It has been shown:

(a) that, from the existing data and some necessary assumptions, the free energy of formation of liquid hydrogen sulfide was calculated to be

$$H_2\ (g) + S(r) = H_2S(l);\ \Delta F^o{}_{298} = -6034\ cal.$$
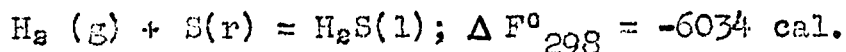
(b) that, the prediction that the reactions of liquid hydrogen sulfide on oxides would be much faster than on metals, from the free energy changes involved in the respective reactions, was justified by the laboratory experiments.

(c) that the majority of the metallic elements slowly reacted with liquid hydrogen sulfide at room temperature to form a hydrosulfide or a sulfide.

(d) that some of the oxides rapidly reacted with liquid hydrogen sulfide at $-77^o C.$, and most of them at room temperature, to form sulfides.

(e) that the peroxides reacted in a similar way to oxides, but probably with more vigor and with deposition of free sulfur in addition.

(f) that neither a metal nor an oxide nor a sulfide product of their reactions was soluble in the solvent liquid hydrogen sulfide.

(g) that there was exhibited a measurable E.M.F. between a metal and a saturated solution of its chloride in liquid hydrogen sulfide.

From the above observations, we may say, in conclusion, that liquid hydrogen sulfide is a very good reacting medium for inorganic substances, such as metals and oxides in particular, and is very rarely a solvent for them and their reaction products, such as hydrosulfides and sulfides.