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TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM**

II. CHEMICAL PROPERTIES

By **JOY BEAR** and **F. K. McTAGGART**

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Summary

Reactions of the main phases (AX_n where $n \geq 1$) occurring in the 12 systems comprising the sulphides, selenides, and tellurides of Ti, Zr, Hf, and Th are discussed. These reactions include those with oxygen, chlorine, alkali metals, sulphur, and selenium, acids, alkalis, oxidizing agents, alcohols, hydrogen, and thermal degradation in a vacuum. A number of heats of formation are given.

I. INTRODUCTION

Recently a re-examination of the systems Ti-S, Ti-Se, Ti-Te, and Zr-S was made by McTaggart and Wadsley (1958), who also investigated the previously undescribed systems Zr-Se, † Zr-Te, † Hf-S, Hf-Se, Hf-Te. In addition, McTaggart (unpublished data) has re-examined the systems Th-S, Th-Se, Th-Te, and it is believed that between the limits $AX_{1.0} - AX_{\max}$ the main phases occurring in the 12 chalcogenide systems have now been identified.

Previous workers concerned themselves almost entirely with the phases present, and only to a limited extent with problems such as the extent of phase regions, variations in molecular volumes, and crystal structures. In a few cases data were given on the reactions of the compounds with certain acids (usually HCl, H_2SO_4 , and HNO_3), alkalis, H_2O_2 , and bromine water, but this was scarcely more than a side issue. In addition to this, over the past few years there have been isolated reports on certain reactions of several sulphides, mainly of titanium, such as the reduction with alkali and alkali earth metals of TiS_2 to titanium metal, the reaction of TiS_2 with alcohol, and the reaction of TiS_2 with BaS, etc. to form compounds of the sulphospinel type, e.g. $BaTiS_3$. There have also been reports on the reduction of the sulphides of titanium and thorium by means of hydrogen.

However, in all, the chemical reactions of this large group of compounds were almost unknown. Using the materials synthesized for the studies on the 12 systems described by McTaggart and Wadsley, an effort has been made to elucidate some of the chemical behaviour of these chalcogenides and to place their

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† During the writing of this paper two notes by Hahn and Ness (1957a, 1957b) appeared on the Zr-Se and Zr-Te systems. Their data are in agreement with ours so far as the phases present are concerned.

chemistry on a more systematic basis. The work of the above authors should be referred to for descriptions of the preparation of the compounds, the structures of the phases present, and the appearance and density of each phase.

In the present paper some results obtained are at variance with previously reported reactions. These differences may be ascribed, firstly, to the fact that earlier workers frequently used materials containing relatively large amounts of impurities; secondly, to their failure to realize that surface oxidation of the chalcogenides is often rapid and in such cases protective layers are formed; and thirdly, to their failure to identify accurately the products of reaction, for example, a residue of tellurium was often assumed to be unattacked chalcogenide.

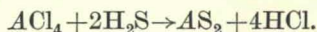
With the object of avoiding these possible sources of error, all our chalcogenides were prepared from highly pure materials and they were all stored and manipulated in an atmosphere of dry argon.

II. METHODS OF PREPARATION

It may not be out of place at this point to mention methods that have been proposed for the preparation of these chalcogenides, other than direct synthesis from the elements. This becomes a discussion of methods for sulphides only as there are no data in the literature on the preparation of selenides and tellurides other than by direct reactions.

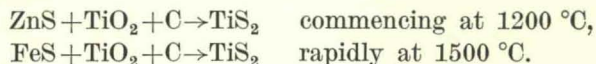
Montigne (1947) claimed that Th_3Te was formed by reducing $\text{ThTeO}_4 \cdot 8\text{H}_2\text{O}$ with hydrogen at 400°C , but we have not been concerned with phases lower than AX.

(i) Disulphides may be synthesized by reacting the anhydrous metal chlorides with H_2S at a red heat



This method is satisfactory and is capable of producing disulphides of high purity provided precautions are taken to remove or prevent contamination due to chlorides. It would probably be the most favourable method for production of large quantities.

(ii) Oxides will react under some conditions to yield sulphides. Thus Schwartz and Koster (1956) produced a titanium sulphide containing 46 to 48 per cent. Ti and 52 to 54 per cent. S (a mixture of Ti_2S_3 and TiS_2 phases) from TiO_2 , H_2S , and CS_2 at 900 to 1000°C . Eastman *et al.* (1950) formed ThS_2 from ThO_2 , H_2S , and C. Instead of H_2S , solid sulphides such as ZnS and FeS have been used (Kleffner 1934), thus:



(iii) Instead of reacting metals with sulphur, metal hydrides may be used. Also, metals or metal hydrides may be reacted with H_2S instead of sulphur, for example, Eastman *et al.* (1950) found that the reaction between ThH_4 and H_2S could be controlled to yield any desired sulphide.

(iv) Having obtained disulphides, higher sulphides such as the AS_3 type may be formed by heating the former with sulphur in evacuated vessels. Some

lower sulphides may be formed by degradation ; others by reacting the disulphides with metal.

Of the above methods, (iv) applies equally well to selenides and tellurides and it is likely that (iii) does also.

However, it has been concluded that for the preparation of chalcogenides of high purity for research purposes the direct synthesis from the elements is to be preferred.

III. HEATS OF FORMATION

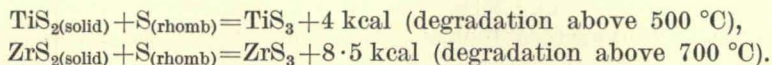
Very few data are available on the heats of formation of these chalcogenide compounds. Eastman *et al.* (1950) quoted a value of 131 kcal for Th_2S_3 , the result of direct measurement ; but their other values for their thorium sulphides were calculated. The difficulties encountered in determining heats of combustion of this class of compound in a bomb calorimeter are considerable. It is often impossible to burn all the sample even in the presence of combustible material, and some of the higher compounds, especially tellurides, lose chalcogen by degradation and volatilization during burning, the latter subliming onto the walls of the bomb. In the cases of sulphur and sulphides the formation of SO_3 as well as SO_2 and the formation of sulphuric acid, if any moisture is present, can lead to large errors. These effects are well recognized (see, for example, Hubbard, Katz, and Waddington 1954). It was apparent from our work that similar problems are encountered with selenium and tellurium and their compounds.

Sulphur itself, under the conditions obtaining in the bomb as a result of the systematized procedure of drying, sweeping with oxygen, pressure adjustment, etc. yielded a consistent heat of combustion of 74.5 kcal. This may be compared to $\Delta H_f^0 = 69.3$ (g) and 75.2 (liq.) accepted in the literature (for example, Handbook of Chemistry and Physics 1954-55) as the heats of formation of SO_2 . Similarly, selenium and tellurium when ignited with sulphur as the combustion aid, consistently yielded 70 and 108 kcal respectively (compare $\Delta H_f^0 = 56.4$ and 78.3 kcal found in the literature). The values found by experiment were used in our calculations. Indeed, the use of the quoted value for TeO_2 led to the improbable result of a negative heat of formation for all the tellurides. The following heats of formation (kcal/g-mol) were also used in our calculations: TiO_2 226 (Humphrey 1951), ZrO_2 261.5 (Humphrey 1954), HfO_2 266 (Humphrey 1953), and ThO_2 293 (Huber, Holley, and Meierkord 1952).

After a number of determinations involving most of the compounds at our disposal we derived only two series of values which are sufficiently accurate and reproducible to warrant discussion. These were obtained using sulphur as a combustion aid, and are listed in Table 1.

The diminution in affinity between the metals and the chalcogens as one proceeds from sulphur to tellurium is evident. As the $\text{ThX}_{1.5}$ compounds all have greater heats of formation than the TiX_2 compounds, in spite of their lower chalcogen content, it is evident also that there is an increase in affinity between metal and a given chalcogen as one goes from titanium to thorium. This may be compared to the increasing values shown in the series of dioxides.

We were unable to distinguish between the heats of formation of the pairs of compounds TiS_3 and TiS_2 , $\text{ThS}_{2.5}$ and ThS_2 , these being the only pairs that behaved satisfactorily in the bomb. This is in agreement with Biltz and Ehrlich (1937) and Strotzer, Biltz, and Meisel (1939), who calculated from vapour pressure data that there could be only small differences in the heats of formation of the tri- and disulphides of titanium and zirconium.



Similar considerations should apply to all the tri- (or $\text{AX}_{2.5}$) compounds of this group as they all degrade readily on heating in vacuum. Degradation is discussed in Section IV.

TABLE I
HEATS OF FORMATION OF CHALCOGENIDES

Compound	TiS_2	$\text{ThS}_{1.5}$	TiSe_2	$\text{ThSe}_{1.5}$	TiTe_2	$\text{ThTe}_{1.5}$
Heats of formation (kcal/g-mol)	102	119	97	112	55	75

IV. THERMAL STABILITY

Normally when AX_{max} compounds are synthesized by direct reaction of the elements, they are freed from excess chalcogen by heating the chalcogenide end of the synthesis tube to 350°C in the case of sulphides, 450°C for selenides, and 550°C for tellurides, with the other end at or below room temperature. Under these conditions excess chalcogen sublimes off. The AX_{max} compounds so obtained are listed in Table 2, the second column of which gives the n values to the nearest 0.05 as determined by analysis. The manner in which the various compounds degrade when heated in vacuum is shown by reference to the third column, in which formulae are given of the chalcogenides resulting from heating to approximately 950°C in the manner described above. It will be seen that dichalcogenide phases result in every case from the degradation of the tri-, or $n=2.5$ compounds. The diselenide and ditelluride of titanium degrade without change of phase, as for these compounds the region $\text{TiX}_{1.0}$ to $\text{TiX}_{2.0}$ may be regarded as a single phase.

Two tendencies are evident:

- (i) The stability of the compounds increased from titanium, through zirconium and hafnium, which are closely similar, to thorium.
- (ii) The stability decreases, for each Group IV metal, as one goes from sulphide, through selenide, to telluride.

Both these trends are in keeping with other known properties of the metals and the chalcogens and confirm the increasingly saltlike character of the compounds of thorium, compared with the preceding Group IV elements on the one hand, and the more metallic nature of tellurium, which tends to form alloylike compounds, on the other.

Temperatures higher than those indicated in Table 2 were not used. Eastman *et al.* (1950) have claimed that ThS_2 is stable to its melting point (about 1900 °C) but loses some sulphur above this temperature. D'Eye, Sellman, and Murray (1952) stated that $\text{ThSe}_{2.0}$ degrades to $\text{ThSe}_{1.7}$ above 1000 °C. We were, however, unable to confirm the statement of D'Eye and Sellmann (1954) that ThTe_2 (and indeed all lower thorium tellurides also) decompose above 500 °C, eventually forming the elements. Our ThTe_2 and $\text{ThTe}_{1.0}$ were stable at 950 °C. It is likely that the high oxygen content of D'Eye's materials, which gave rise to oxy compounds such as ThOTe , was the cause of the decomposition. The reaction $2\text{ThOTe} \rightarrow \text{ThO}_2 + 2\text{Te} + \text{Th}$ proceeds readily, and if the tellurium is sublimed off, as is the case in the type of degradation under discussion, the ThO_2 would react with the telluride present, thus eventually causing complete decomposition.

TABLE 2
THERMAL STABILITY AND HYDROGEN REDUCTION DATA FOR CHALCOGENIDES

Compound	Formula after Removal of Excess Chalcogen	Degraded at °C in a Vacuum	Dichalcogenide after Hydrogen Reduction at 950 °C
TiS_3	$\text{TiS}_{2.95}$	900° $\text{TiS}_{1.65}$	$\text{TiS}_{1.25}$
TiSe_2	$\text{TiSe}_{2.0}$	950° $\text{TiSe}_{1.7}$	$\text{TiSe}_{1.4}$
TiTe_2	$\text{TiTe}_{2.0}$	950° $\text{TiTe}_{1.55}$	$\text{TiTe}_{1.45}$
ZrS_3	$\text{ZrS}_{2.95}$	950° $\text{ZrS}_{1.9}$	$\text{ZrS}_{1.4}$
ZrSe_2	$\text{ZrSe}_{2.05}$	950° $\text{ZrSe}_{1.9}$	$\text{ZrSe}_{1.7}$
ZrTe_3	$\text{ZrTe}_{2.9}$	950° $\text{ZrTe}_{1.7}$	$\text{ZrTe}_{1.7}$
HfS_3	$\text{HfS}_{3.0}$	940° $\text{HfS}_{1.95}$	$\text{HfS}_{1.5}$
HfSe_3	$\text{HfSe}_{2.9}$	940° $\text{HfSe}_{1.85}$	$\text{HfSe}_{1.75}$
HfTe_3	$\text{HfTe}_{1.5}$	940° $\text{HfTe}_{1.2}$	$\text{HfTe}_{1.1}$
$\text{ThS}_{2.5}$	$\text{ThS}_{2.5}$	950° $\text{ThS}_{2.0}$	$\text{ThS}_{2.0}$
$\text{ThSe}_{2.5}$	$\text{ThSe}_{2.5}$	950° $\text{ThSe}_{2.0}$	$\text{ThSe}_{2.0}$
$\text{ThTe}_{2.5}$	$\text{ThTe}_{2.5}^*$	950° $\text{ThTe}_{1.95}$	$\text{ThTe}_{1.9}$

* Removal of excess Te in this case required special care (McTaggart, unpublished data).

The fact that all the higher chalcogenides (i.e. AX_3 and $\text{AX}_{2.5}$ types) lose part of their sulphur, selenium, or tellurium, when heated in a vacuum has been used by several of the earlier workers to determine the compositional upper limits of certain phases, notably the dichalcogenide phases. This so-called "tension analysis" depends on the fact that for a given chalcogenide at a given temperature there is a certain vapour pressure of chalcogen above the compound. This chalcogen is gradually condensed off and a series of vapour pressure values is obtained corresponding to different compositions of the solid chalcogenide. Curves, one for each temperature, may be drawn by plotting vapour pressures against n values in the chalcogenide formula AX_n . Each curve will intersect the composition axis when the vapour pressure value is zero. Such curves are useful for determining the minimum temperature necessary to bring about degradation of a compound and may give information on the extent of a phase

region. However, with the advent of better X-ray techniques and an improvement in the interpretation of X-ray patterns, this rather laborious technique has been found to be less useful for this group of compounds than was first thought. Further use may be found for the technique in the elucidation of the nature of the bonding present in certain chalcogenides which take up large excesses (50 per cent. upwards) of chalcogen without significant change in their general appearance and without the formation of another phase. Such "excess" chalcogen may be sublimed off fairly readily but requires a higher temperature to produce a given vapour pressure than is necessary for free chalcogen. The Th-Te system provides an example of this and it is hoped to report in more detail on this and other similar systems in a subsequent paper.

V. HYDROGEN REDUCTION

All the dichalcogenides were reduced in highly purified hydrogen for 3 hr at 950 °C. The compositions of the resulting materials are given in column four of Table 2. It will be seen that once again there is a marked difference in the stabilities, the titanium compounds being again the least stable and the thorium compounds the most stable. TiS_2 , for example, reduces to $TiS_{1.25}$, while ThS_2 is not reduced at all. Between these two extremes, zirconium and hafnium compounds exhibit intermediate stability and resemble one another closely, except for hafnium telluride, which is exceptional throughout. Under the conditions of hydrogen reduction the tellurides are more stable than the corresponding selenides, and selenides are more stable than sulphides. None of the thorium compounds appears to undergo appreciable reduction.

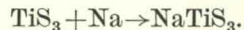
Schwartz and Koster (1956) have shown that, at 1100 °C, hydrogen reduces TiS_2 to $TiS_{1.0}$. This is in agreement with our findings. No evidence could be obtained to suggest that hydrogen entered the chalcogenide lattice during reduction. Analysis of the compounds for hydrogen before and after the reductions yielded results that did not differ significantly.

VI. REDUCTION WITH METALS

(a) *Alkali and Alkaline Earth Metals*

The alkali metals reduce all the sulphides, selenides, and tellurides, regardless of composition, to the Group IV metal. This fact has been used as a basis for the analyses of this class of compound as described previously.

If less than the theoretical amount of Na or K is used, compounds may be formed by reactions typified by the following:



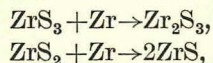
Schwartz and Koster (1956) found that Al, Ca, and CaH_2 all reduced titanium sulphides to the metal, while Mg in argon at 1000 °C produced 98–99 per cent. of titanium metal.

Hahn and Harder (1956) have prepared $CuTi_2S_4$, which has a spinel structure, from Cu_2S , TiS_2 , and S, and Hahn and Mutschke (1956) have prepared thioperovskites such as $SrTiS_3$, $BaTiS_3$, and $BaZrS_3$ from TiS_2 (or ZrS_2) and the appropriate alkaline earth sulphide. The properties of these latter compounds are stated to

be akin to those of the alkaline earth sulphides themselves. It appears likely that a wide range of compounds may be produced by this type of reaction forming a series analogous to the titanates.

(b) *Reaction with Other Subgroup IV Metals*

The technique of forming a lower chalcogenide by heating together a higher one and the metal in the correct proportions, for example,



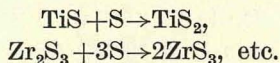
was used to some extent by earlier workers. These reactions are quite general and form a useful basis for the preparation of compounds of a wide range of composition when the necessary higher chalcogenide has been prepared.

As the thorium compounds are more stable than those of the other elements it was of interest to determine to what extent thorium would reduce compounds of the other elements and vice versa. The sulphides ThS_2 and TiS_2 were chosen for experiments. ThS_2 was intimately mixed with titanium powder and TiS_2 with thorium powder. The mixtures were sealed under vacuum in silica tubes and heated to 800 °C for several days.

X-Ray analysis then showed that for $\text{ThS}_2 + \text{Ti}$ the ThS_2 had been reduced to approximately $\text{ThS}_{1.5}$ and that there was still a trace of free titanium metal. However, in the reaction between TiS_2 and Th the product consisted mainly of a thorium sulphide of composition about $\text{ThS}_{1.5}$ and a subsulphide of titanium ($\text{TiS}_{<1.0}$) of undetermined composition. These results are in keeping with the stabilities of the Ti-S and Th-S systems and confirm that thorium exerts a greater affinity towards sulphur than does titanium.

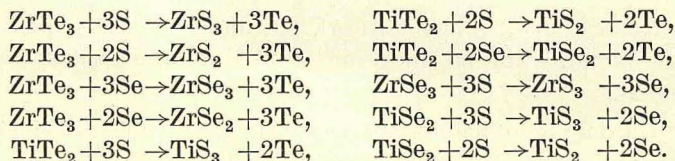
VII. REACTIONS WITH SULPHUR AND SELENIUM

It has been established that a higher chalcogenide may be formed from a lower compound by the direct reaction of the lower compound with the appropriate chalcogen, for example,



These reactions are generally applicable and have been used at times in the synthesis of certain phases.

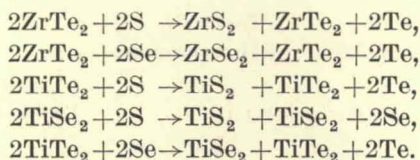
Our experimental work has shown that sulphur will displace both selenium and tellurium quantitatively from selenides and tellurides, and that selenium will displace tellurium from tellurides. The following are a few examples of what also appears to be a general type of reaction :



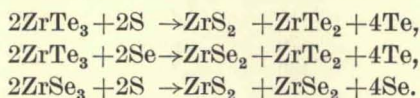
These reactions may be carried out by sealing the chalcogenide and chalcogen in a silica tube, after evacuation, and heating homogeneously to 600–700 °C

for some time. At the completion of the reaction the free chalcogen is sublimed off to the other end of the tube under the appropriate conditions as discussed under the synthesis of chalcogenides. An exception to the above temperature range must be made if TiS_3 is the desired product, as TiS_3 will not be formed if the temperature exceeds about 550°C .

If less than the stoichiometric quantities of chalcogen are used, a part of the chalcogenide will be completely reacted and the remainder may be left unchanged. Thus if one-half of the theoretical quantity is used, the following type of reaction results :



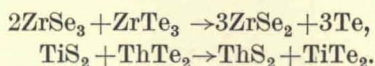
However, if the initial chalcogenide itself suffers degradation at the reaction temperature the following type of reaction will occur :



There is no evidence to suggest the formation of mixed chalcogenides containing two chalcogens : ASSe , ASTe , etc.

VIII. REACTIONS BETWEEN CHALCOGENIDES

It may be inferred from the above reactions that many interactions between the chalcogenides are possible. This has been found to be so. Two examples show the type of reaction that may be expected :



IX. OXIDATION

It has already been noted that many of the chalcogenides undergo oxidation in the air. This varies from slight surface oxidation to inflammability and it was because of these effects that it became our practice to open, store, and manipulate all samples in dry argon. Even the compounds that show no visible change were found to undergo slow oxidation. For example, TiS_3 , which when freshly prepared had a sulphur content of 66.3 per cent., after storage in air for some months was found to contain 65.4 per cent. sulphur, and on chlorination left a small residue of TiO_2 , whereas TiS_3 stored in argon neither changed its sulphur content nor left any visible residue of TiO_2 on chlorination. ZrS_2 absorbed oxygen rapidly, as described by McTaggart (1958), the quantity amounting to 0.25 per cent. after a few days. In this case, a protective layer apparently formed so that the rate of absorption slowed to almost zero. Several of the compounds and notably the monotellurides of titanium and zirconium, were spontaneously inflammable when opened in air (compare Zr powder), but when first opened in argon and subsequently allowed slow access to air they oxidized only slowly and to a limited extent.

An attempt was made to measure and compare rates of oxidation for a number of the chalcogenides of titanium and zirconium at 150 and 300 °C in air. This was not very successful, probably due to the samples having different particle size, crystal structure, etc. However, it appeared that tellurides tend to be more resistant to oxidation than selenides and sulphides (see Table 3), although this is not always so at the lower temperature. The higher chalcogenides tend to be slightly more resistant than the lower ones (see the right-hand section of Table 3), although there are apparent exceptions to this.

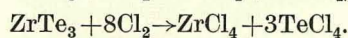
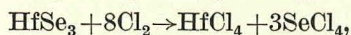
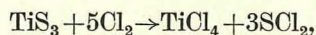
TABLE 3
OXIDATION OF CHALCOGENIDES IN AIR

Compound	Percentage Sample Oxidized at :			Compound	Percentage Sample Oxidized at :		
	150 °C for 10 Days	300 °C for 1 Day	300 °C for 3 Days		150 °C for 10 Days	300 °C for 1 Day	300 °C for 3 Days
TiTe ₂	3	8	15	ZrSe ₃	20	35	70
TiSe ₂	15	—	70	ZrSe ₂	25	25	70
TiS ₂	35	87	100	ZrSe _{1.0}	25	100	100
ZrTe ₃	—	25	37	ZrTe ₃	—	25	37
ZrSe ₃	20	35	70	ZrTe ₂	33	38	45
ZrS ₃	3	40	100	ZrTe _{1.0}	40	45	63
ZrTe ₂	7	38	45				
ZrSe ₂	25	25	70				
ZrS ₂	4	53	60				

All the chalcogenides, when heated in air or oxygen, ultimately yield the metal oxide and the oxide of the chalcogen associated with them, namely, SO₂, SeO₂, or TeO₂. The protective layer of oxide which forms on the surface of the compounds of zirconium, hafnium, and thorium undoubtedly slows the rate of oxidation and frequently makes it appear that oxidation has ceased at between 40 and 60 per cent. Also, the formation of TeO₂ may provide some protection for the tellurides. The presence of an oxide film has probably been responsible for a number of incorrect properties being attributed to those compounds that have been investigated previously.

X. REACTIONS WITH CHLORINE

The chalcogenides all react readily with chlorine below 300 °C, the reaction in some cases commencing at room temperature. The products consist of the tetrachloride of the Group IV metal together with the chloride of the chalcogen. The following are typical reactions :



These reactions all proceed to completion on moderate heating. In many of them the products may be separated by a simple type of fractional condensation, but $\text{SCl}_2 + \text{TiCl}_4$, for example, form an addition compound—a yellow solid.

If the sample of chalcogenide has undergone partial oxidation some metal oxide remains.

XI. REACTIONS WITH ACIDS, ALKALIS, ETC.

In the discussion of these reactions the compounds $\text{ThX}_{2.5}$ are treated as if they were AX_3 compounds. It may also be remarked that difficulties due to the formation of protective layers of insoluble materials on the surfaces of the chalcogenides sometimes arose and attempts were made to overcome these by vigorous stirring and breaking up of the samples and by allowing ample time for observations on the reactions. If the results were ambiguous, both quantitative and qualitative analyses were done on solutions and solid materials in order to determine what change had occurred.

(a) Water

None of the compounds appeared to react with water, either at room temperature or at the boiling point, although on boiling, most of the sulphides and selenides gave traces of H_2S or H_2Se and the tellurides often imparted to the water a pale mauve colour. However, as certain AX_3 and AX_2 compounds react with alcohols to form esters (see below), in these circumstances the esters being soluble in the alcohols, it must be assumed that reaction with water does occur, at least with the same compounds, but that insoluble hydroxide products are formed which protect the chalcogenides from further attack.

(b) Oxidizing Agents

(i) *Concentrated HNO_3* .—Cold concentrated HNO_3 reacts without exception with the compounds. The reaction is vigorous for the AX_3 and AX_2 chalcogenides and usually explosive and accompanied by flashes of light with the A_2X_3 and lower types. Brown fumes are evolved and some white to grey residue, an oxide material, is left in a yellow to green solution. The bulk of the metal is found in the acid solution, together with the chalcogens, although SO_2 , SeO_2 , etc. may be evolved during the action.

(ii) *50 Volume H_2O_2* .—All AS_3 , AS_2 , ASe_3 , and ASe_2 compounds, except those of thorium, react at room temperature to yield white insoluble residues. Boiling the peroxide causes accelerated action and the thorium compounds ($\text{ThS}_{2.5}$, $\text{ThSe}_{2.5}$, and $\text{ThTe}_{2.5}$ and the di-compounds) also react. All these reactions go to completion on boiling. Most of the lower chalcogenides do not react at room temperature, and only slowly and partially at the boiling point. However, $\text{TiS}_{1.5}$, $\text{TiS}_{1.0}$, $\text{TiSe}_{1.0}$, $\text{ZrSe}_{1.5}$, $\text{ZrSe}_{1.0}$, $\text{ZrTe}_{1.0}$, and $\text{HfS}_{1.5}$ react completely on boiling. For all types of sulphides and selenides the stability increases from titanium to thorium. The higher tellurides are markedly more stable than the corresponding sulphides and selenides, for example, TiTe_3 and ZrTe_3 do not react under any conditions, but the lower tellurides of all four elements react slowly at the boiling point and there is little sign of increased stability here as one goes from titanium to thorium.

(c) Concentrated H_2SO_4

Cold concentrated sulphuric acid reacts completely with ZrS_2 , HfS_2 , and ThS_2 giving H_2S and depositing a thick white precipitate. $ZrS_{1.5}$, $ZrS_{1.0}$, $HfS_{1.5}$, and $HfS_{1.0}$ react in a similar manner but to a limited extent. None of the other compounds is attacked. On boiling, however, all the chalcogenides are attacked. With the sulphides there is a brisk effervescence of SO_2 , some sulphur usually separates, a whitish residue containing metal oxide or sulphate remains and part of the metal is found in solution. With the selenides there is also a brisk effervescence as SeO_2 is evolved; black globules of selenium form and the solution usually clears, but there may be some white or grey flocculent residue. The metals are found to be almost wholly in the acid solution. From the tellurides there is also vigorous effervescence and a strong smell resembling SO_2 . A deep purple colouration develops, then fades, but the solution usually remains milky. On cooling, masses of fine crystals of tellurium separate and the metals are found to be almost wholly in solution.

(d) Concentrated HCl

At room temperature the only chalcogenides found to react are the thorium tellurides, all of which give a steady effervescence; tellurium separates and the thorium is found in the solution. Some of the sulphides, namely, ZrS_2 , HfS_2 , $ThS_{1.5}$, and $ThS_{1.0}$, yield some H_2S but the reactions do not proceed far. Some of the selenides behave similarly.

On boiling, the following sulphides appear to be non-reactive: TiS_3 , TiS_2 , ZrS_3 , HfS_3 , and $ThS_{2.5}$. However, ZrS_2 , HfS_2 , and ThS_2 dissolve completely with the evolution of H_2S , the metals going into solution. The remaining lower sulphides suffer only partial attack ranging from negligible for those of titanium to almost complete for those of thorium.

The selenides are, in general, more reactive than the sulphides. Thus the higher compounds, unlike the corresponding sulphides, suffer slight attack and $TiSe_2$ dissolves completely. However, the other diselenides are not attacked to any great extent.

The tellurides all react completely, usually with no evolution of gas. Metallic tellurium is precipitated and this is often difficult to distinguish in appearance from the original chalcogenide. Probably for this reason earlier workers reported that there was no reaction between $TiTe_2$ and $TiTe_{1.0}$ and boiling HCl.

(e) 2N H_2SO_4

This acid may be taken as representing dilute mineral acids in its action on the chalcogenides.

In the cold, slow steady reactions with effervescence of H_2S are found for ZrS_2 , HfS_2 , ThS_2 , and $ThS_{1.5}$ but not for TiS_2 . The AS_3 type of sulphides does not react at all and the other lower sulphides yield some H_2S while being slowly attacked. The selenides are non-reactive except for the $ASe_{1.5}$ and ASe compounds of Hf and Th which evolve some H_2Se . These show decreasing stability from titanium to thorium, the $ThSe_{1.5}$ and $ThSe_{1.0}$ compounds reacting almost completely. Except for $TiTe_2$, the tellurides all react slowly.

On boiling, the AS_3 compounds are still found to be stable. The AS_2 compounds range from TiS_2 , which is the most stable and gives only a slow incomplete reaction, to ThS_2 which dissolves rapidly and completely with evolution of H_2S and precipitation of white, hydrated thorium sulphate. The lower sulphides are more reactive than the AS_2 type and the same trend is found from titanium to thorium.

The selenides behave similarly to the sulphides throughout, the diselenides being somewhat less reactive than the disulphides.

With regard to the tellurides, there is no action for $TiTe_2$ and only a very slow one for $ZrTe_3$. All the others go to completion, the reactions being more vigorous as the tellurium content decreases and also as one goes from titanium to thorium.

(f) 5N NaOH Solution

The AS_3 and AS_2 compounds of titanium, zirconium, and hafnium react readily and to completion in boiling NaOH to yield white flocculent residues and bright yellow solutions. The lower sulphides of these three metals react slowly and partially, becoming somewhat flocculent, but otherwise not changing in appearance. The two higher sulphides of thorium do not react, nor do the lower ones. Although these become flocculent, no chemical evidence for reaction is found.

The selenides all react to give dark red to red-brown solutions and white residues. On cooling, selenium separates as a layer of crystals on top of the solution.

The tellurides react even more readily than the selenides, yielding darker residues and crystalline masses of tellurium on cooling.

(g) Discussion of Wet-Way Reactions

Except for TiS_2 , the disulphides show noticeable saltlike characteristics in that they react readily with strong or dilute mineral acids to form H_2S . TiS_2 , which does not behave in this manner, is more typical of the semimetallic sulphides. This is in keeping with the tendency found within the group for the basicity to increase up to thorium. As thorium is approached there is a greater likelihood of the metal exerting the normal valency of four and this causes increased stability towards some reagents, e.g. NaOH and H_2O_2 .

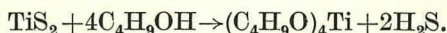
The higher sulphides, AS_3 and $AS_{2.5}$ types, behave like polysulphides and tend to resist attack by acids but not by oxidizing agents, while the lower ones are more metallic. The tellurides are more akin to alloys and the action of certain of the reagents suggests this. In general, the stability of the tellurides decreases towards thorium. The selenides fall between the sulphides and the tellurides, usually resembling the former but sometimes being more like the latter.

XII. REACTIONS WITH ALCOHOLS

It has been stated by Boyd (1951) that TiS_2 reacts with alcohols and phenols, under anhydrous conditions, to form esters of orthotitanic acid, and with amines to form amides of the acid. In our work use was made of *n*-butyl alcohol to test

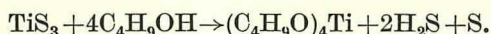
the reactivity of certain chalcogenides. The butyl alcohol was carefully dried and samples were refluxed with it, under anhydrous conditions, for periods of several days. The evolution of H_2S and H_2Se was detected by lead acetate papers placed at the top of the drying tube on the reflux condenser, and the residues were analysed both chemically and by X-ray diffraction.

(i) Sulphides : TiS_2 reacted readily with the evolution of H_2S :



ZrS_2 reacted less rapidly and HfS_2 gave a small amount of H_2S initially, but the reaction did not proceed. ThS_2 did not react at all.

The trisulphides TiS_3 and ZrS_3 also reacted, the latter only slowly to deposit sulphur :



(ii) Selenides : TiSe_2 reacted readily, yielding H_2Se , and depositing some selenium.

(iii) Tellurides : TiTe_2 reacted readily and completely, depositing metallic tellurium. ZrTe_3 also reacted fairly readily. ThTe_2 appeared to react to a very limited extent only.

In general, it may be said that the chalcogenides of the lower members of the group react readily to yield esters. Those of the higher members less readily, and for thorium there is little tendency for this type of reaction to occur. The tellurides appear to react faster than the sulphides.

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