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Reactivity of Sulphides

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The characteristic features of the interaction of metal sulphides in sintering, fusion, and coprecipitation from their solutions are discussed in this review. It is shown that the formation of solid substitutional solutions at elevated temperatures is due to the similarity of the effective radii of the metals, determined taking into account the degree of covalence of the M-S bond. It has been found that, as the composition of the reacting sulphides becomes more complicated, their miscibility increases and that the greater the similarity of the ionic radii of the metals the easier the formation of solid solutions of the sulphides when the latter are coprecipitated from solution. The bibliography incorporates 213 references.

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I. INTRODUCTION

Sulphides have been attracting the attention of inorganic and analytical chemists for a long time because their low solubility and in most cases a characteristic colour make them suitable for qualitative and quantitative analyses. However, more thorough investigation of the conditions for their isolation from complex solutions and also of the properties of the pure sulphides synthesised showed that changes in the acidity of the solution, which is the decisive factor in their precipitation, is insufficient for quantitative separation. The attempts to prevent coprecipitation by adding to the solution before precipitation various organic and inorganic complex-forming agents were unsuccessful in most cases. The interest in sulphides in the last decade is due to the fact that they, and chalcogenides in general, have semiconductor properties[1-5] and, since their melting points are high, they can be successfully employed up to 800–900°C. Their high stability to thermal dissociation at elevated temperatures in the absence of oxidising agents makes it possible to employ sulphides as constructional materials in the preparation of pure substances.

The vigorous development of the rare-metals industry, which is based mainly on the processing of polymetallic sulphide ores, also requires a more complete study of the chemical behaviour of sulphides.

The reason for the high reactivity of sulphides probably consists in the fact that for most sulphides the heat of the atomisation of sulphur is much higher than that of the metal and therefore polymers are frequently formed[6-8]. The positive electronegativity difference indicates the polarisation of the sulphide sulphur[8,9], which should also enhance the reactivity of the sulphides.

The interaction of these compounds is complicated by the presence in them of three types of bond: covalent, metallic, and ionic. The considerable ionic character of the bonds is typical for the sulphides of alkali and alkaline earth metals and lanthanides. The bonds in the sulphides of B group metals are covalent and those in the transition metal sulphides are of the covalent-metallic type[2,3,6,10-12].

The structures of the crystalline sulphides are various but most of them are highly symmetrical with close packing of the sulphide sulphur or the metal[13,14]. It has been noted[14] that structures of this type are deficient in the metal.

Furthermore, many sulphides tend to form two or more polymorphic modifications, the stability of which is determined not only by the temperature but also by the presence of another sulphide (sometimes even in insignificant amounts).

Thus the reactivity of sulphides should depend on the nature of the bond, the type of lattice, the dimensions of the atoms or ions of the metals whose compounds interact, and their polarising capacity.

It has now been established that sulphides interact with formation of solid solutions and complex sulphides. Nevertheless, so far there is no information which would make it possible to predict the nature of the interaction of simple sulphides.

II. INTERACTION OF SULPHIDES AT ELEVATED TEMPERATURES

1. The Formation of Solid Solutions

According to general hypotheses, the formation of solid solutions of metals or chemical compounds is observed when the crystals belong to the same or similar structural types, when the difference between the lattice constants and the radii of the interacting atoms are small, and when the chemical properties of the metals or the types of chemical bonds are also similar[15]. The failure of any one of the above conditions leads to the formation of a narrow range of solid solutions or their complete absence.

In their interpretation of experimental results, investigators usually compare either atomic or ionic radii (depending on the data obtained), without taking into account as a rule the type of bond. Thus Flahaut et al.[14] based their discussion of data for the formation of the solid solutions of the sulphides of aluminium, gallium, and indium, on the one hand, and magnesium, manganese, zinc, and cadmium, on the other, on the similarity of the atomic radii, and for the sulphides of the lanthanides and magnesium, the calcium subgroup metals, manganese, and lead on the similarity of the ionic radii. However, the bond in lanthanide sesquisulphides[16,17], and in the majority of sulphides in general, has considerable covalent character.

Table 1, which lists the available information about the existence of solid solutions in sulphide systems, shows that the difference between atomic radii cannot account for the formation of the more extensive region of solid solutions of gallium sulphide with Cu_2S than for the corresponding solid solutions with Ag_2S. This applies equally to the systems Cu_2S–Ag_2S, Ga_2S_3–MnS, etc. On the other hand,

germanium and tin sulphides form a continuous series of solid solutions, other conditions being equal. The above examples show that, using atomic or ionic radii alone, it is impossible to account for the presence or absence of a solid solution in the given system.

Table 1. Regions of existence of solid solutions in sulphide systems.

System	Difference between radii,%			Solubility, mole %	Type of lattice of solid solution	Refs.
	ionic	atomic	effective			
B_2S_3—BeS	41.2	19.4	—	nil	—	14
B_2S_3—MgS	74.4	43.1	—	nil	—	14
B_2S_3—ZnS	76.0	34.5	—	nil	—	14
B_2S_3—CdS	80.6	41.7	—	nil	—	14
Al_2S_3—Cu_2S	40.6	10.5	15.3	nil	—	18
Al_2S_3—Ag_2S	50.0	0.7	25.8	nil	—	18
Al_2S_3—MgS	27.0	10.6	9.8	nil on MgS side	—	14
Al_2S_3—ZnS	31.3	7.0	10.3	0–49.9 at.% Al	wurtzite	14
Al_2S_3—CdS	44.6	4.0	23.4	nil on CdS side	—	14
Al_2S_3—MnS	37.4	8.4	12.1	nil on MnS side	—	14
Ga_2S_3—Cu_2S	35.4	8.0	3.5	30 (Cu_2S)	cubic	18
Ga_2S_3—Ag_2S	45.1	3.5	9.8	15 (Ag_2S)	cubic	20
Ga_2S_3—MgS	20.5	13.1	8.8	up to 12 (MgS)	wurtzite	14
Ga_2S_3—ZnS	25.3	4.3	4.1	0–20 and 70–90 90–100 (ZnS)	cubic wurtzite	14, 19
Ga_2S_3—CdS	40.0	7.0	7.0	up to 16 (CdS)	wurtzite	14, 19
Ga_2S_3—MnS	31.2	6.0	6.5	up to 16 (MnS)	wurtzite	14
In_2S_3—Cu_2S	4.2	18.0	—	less than with Ga_2S_3	—	18
In_2S_3—Ag_2S	19.0	8.3	—	ditto	—	18
Y_2S_3—MgS	26.0	11.1	—	up to 23 (Y_2S_3)	cubic	14, 20 21
Y_2S_3—CaS	0.0	8.6	—	up to 5 (Y_2S_3)	cubic	14, 20 21, 22
Y_2S_3—SrS	16.3	16.5	—	very narrow range if any	—	14, 20
Y_2S_3—BaS	20.0	26.0	—	nil	—	14, 20
Y_2S_3—MnS	14.1	27.2	—	up to 23 (Y_2S_3)	cubic	14, 20, 21
Y_2S_3—PbS	20.0	3.3	—	up to 5 (Y_2S_3)	cubic	21
Cu_2S—Ag_2S	15.0	11.0	13.0	nil	—	23, 24
ZnS—MnS	7.7	1.5	2.0	0–52 (MnS)	hexagonal	25
CdS—MnS	11.6	10.7	12.9	continuous series	hexagonal	
Ag_2S—PbS	14.4	17.2	—	0.4 (Ag_2S at 700°C) 3.0 (PbS at 605°C)	—	26
Ag_2S—Bi_2S_3	3.0	20.9	—	4.0 (Bi_2S_3 at 615°C)	—	26
PbS—Bi_2S_3	9.1	4.4	—	9 (Bi_2S_3 at 800°C) 3 (Bi_2S_3 at 400°C)	—	26
GeS—SnS	4.0	11.4	—	continuous series	ortho-rhombic	27
ZnS—FeS	4.5	0.0	6.8	up to 16 (FeS)	NiAs, CdI_2 type	28
FeS—($TiS \cdot TiS_2$)	12.4	16.9	4.7		CdI_2 type	29
CoS—($TiS \cdot TiS_2$)	13.8	15.9	11.1		CdI_2 type	29
NiS—($TiS \cdot TiS_2$)	14.5	11.5	14.2			29

Therefore it is difficult to agree with the statement [14, 20] that the occurrence of a wide range of solid solutions is possible in systems where the ionic radii of the metals differ by 27–28%.

The presence of a covalent bond should reduce the miscibility of sulphides, since this entails the mutual substitution not of metal atoms or ions but of groups of the type $M_xS_y^{n(\pm)}$. However, since sulphide sulphur tends to form its own lattice, it may be supposed that in its formation the sulphur incorporated in a species of the type $M_xS_y^{n(\pm)}$ can also serve as a "constructional material". Therefore formally the dimensions of this species may be described by the radius of the metal.

The determination of the effective charges of the elements in sulphides showed that the ionic character of the bond differs appreciably for various metals and lies in the range 30–60%. [6,12] This value is fairly appreciable in calculations designed to establish the similarity of ionic or atomic radii of metals and therefore a correction allowing for it must be introduced. Hence we calculated "effective" radii (Table 2) defined as the sum

$$\frac{q \cdot r_{M^{n+}}}{n} + \left(1 - \frac{q}{n} \cdot r_{M\cdot}\right)$$

where n is the valence of the metal, q its effective charge in the sulphide, and $r_{M\cdot}$ and $r_{M^{n(\pm)}}$ are the atomic or ionic radii.

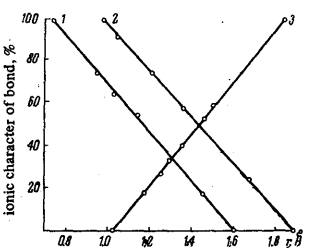
The validity of the calculations is confirmed by the fact that the calculated effective radii for both the cations and sulphide sulphur lie satisfactorily on the straight line drawn through the values of the ionic and atomic radii (Figure).

Table 2. "Effective" radii of metals in sulphides.

Sulphide	Effective radius, Å	Sulphide	Effective radius, Å	Sulphide	Effective radius, Å
Cu_2S	1.18	BaS	1.95	FeS	1.06
Ag_2S	1.35	ZnS	1.16	CoS	1.12
MgS	1.11	CdS	1.31	NiS	1.09
CaS	1.47	MnS	1.14	Al_2S_3	1.00
				Ga_2S_3	1.22

Comparison of the metal radii obtained in this way with the experimental values for gallium in Ga_2S_3 shows (Table 1) that they differ by not more than 9.8%. The following series of compounds with increasing size of the region of solid solutions of gallium sulphide with certain metal sulphides has been constructed on the basis of the calculated data: $Cu_2S > ZnS > MnS > CdS > MgS > Ag_2S$; it agrees satisfactorily with the experimental series [14,18,19]:

$$Cu_2S > ZnS > MnS \geqslant CdS \geqslant Ag_2S > MgS$$



Variation of the effective radius with the ionic character of the bond for sodium (curve *1*), magnesium (curve *2*), and sulphur (curve *3*) in their compounds.

Some deviation observed in the case of Ag_2S is evidently due to the fact that the range of existence of the solid solution in this system has been established only approximately. We believe that the solubility of Ag_2S in Ga_2S_3 should be less than 12 mole %.

The above hypothesis agrees well with the results of studies on systems consisting of FeS, CoS, NiS, and TiS. $.TiS_2$, [29] where the empirical series based on the range of existence of solid solutions—FeS ≫ CoS > NiS—agrees with the series based on the difference between the effective radii of the metals (Table 1). The calculation of the radii was made on the basis of the titanium radius in TiS, which is of decisive importance in this case. The sulphides CrS, VS, and MnS are even less capable of forming solid solutions with $TiS.TiS_2$.

Because of the lack of data on the effective charges of the metal and sulphur in lanthanide sesquisulphides, it is unfortunately impossible to make a similar comparison for their interaction woth the sulphides of magnesium, manganese, lead, and calcium subgroup metals[14,20,21]. However, the available effective charges for the latter compounds explain why in the experimental series based on the size of the solid solution regions–MgS > MnS > CaS > PbS > SrS > BaS–manganese sulphide occupies an intermediate position and strontium and barium sulphides altogether fail to form solid solutions or the solid solutions are formed only over a narrow range.

The introduction of the concept of the "effective" radius of the metals in sulphides permits the elimination of the contradictions existing in the literature. As an example, one may quote the data of Flahaut and coworkers[20], who failed to explain why the solid solution region in the systems Y_2S_3–MgS or Y_2S_3–MnS is greater than in the system Y_2S_3–CaS, although the ionic radii of calcium and yttrium are almost the same.

It is noteworthy that sulphide sulphur forms a close-packed sublattice with octahedral and tetrahedral vacancies, which are occupied by metals in a definite sequence. Since the dimensions of these sites are smaller than those of the majority of metals, a polarisation effect occurs when the vacancies are filled. Analysis of the data obtained shows that the formation of solid solutions should be most complete when the high symmetry of the crystals is further increased or maintained. This inturn is possible when the dimensions of the metals undergoing mutual substitution and the bond types are similar. Indeed the solid solutions obtained in the vast majority of cases crystallise in the cubic or hexagonal system (Table 1). The high symmetry of the crystals in the formation of solid solutions is also due to the tendency of the sulphide sulphur to give rise to its own intrinsic sub-lattice. Therefore the factors leading to its distortion alter the energy of the crystal, in consequence of which it becomes less stable. Conversely, if the addition of another sulphide favours the formation of an undistorted sulphur sublattice, miscibility is observed even when the initial substances differ considerably in symmetry type. As an example, one may quote the studies of Hahn et al.[18], who observed that the addition of small amounts of copper or silver sulphide stabilises the zinc blende structure, which is unstable for gallium sulphide at 900°C. An exception is the system GeS–SnS in which a continuous series of solid solutions is formed. However, X-ray diffraction studies showed that these sulphides form two types of solid solutions, on the basis of GeS and SnS.[27]

Since the nature of the chemical bond in sulphides is variable, the charges of the metal and sulphur should alter on formation of solid solutions. This favours an increase or decrease of the covalent character of the bond and a simultaneous deviation of the metal radii from those in the initial compounds. These changes are small, since mixed crystals are formed only when the type of chemical bond and dimensions of the metals in the initial sulphides are similar. Indeed, when aluminium sulphide is added to zinc sulphide, the Al–S interatomic distance decreases, while in the systems MS–L_2S_3 (L = lanthanide) the L–S distance increases. In the first example the addition of a more ionic compound (Al_2S_3) leads to an increase in the latter of the covalent bond character, as a result of which the interatomic distance Al–S is reduced. The addition of Ga_2S_3 to ZnS, the ionic character of the bond of which is similar, scarcely changes the Ga–S distance. The lack of data on charge distribution in lanthanide sulphides precludes an analogous comparison, but the increase of the L–S distance suggests that the covalent bond character in L_2S_3 is smaller than in the MS compounds investigated.

Apart from the systems described, some results in the literature cannot be arranged systematically in a similar manner because of the lack of essential data[30,31].

The miscibility of sulphides increases greatly when one of the system components is a double sulphide. Thus the sulphides of bismuth and lead are almost immiscible, but 1.7 and 10 mole % PbS dissolves in $AgBiS_2$ at 200°C and 615°C respectively. Bismuth sulphide forms mixed crystals with $AgBiS_2$, in which the maximum Bi_2S_3 content is 16 mole %, and 14 mole % $AgBiS_2$ dissolves in PbS at 195°C.[26] It is believed that the increased miscibility of the components is due to the replacement of Ag^+ and Bi^{3+} by $2Pb^{2+}$ with formation of a cubic structure. The replacement in $AgBiS_2$ of silver by thallium, the dimensions of which are closer to those of lead and bismuth, leads to the formation of a continuous series of solid solutions in the system PbS–$TlBiS_2$.[32] The lower miscibility of PbS and $AgBiS_2$ is probably due not only to the greater difference between the dimensions of the metal atoms but also the inadequate homogenisation of mixtures of the systems. The regions of solid solutions in the systems $CuGaS_2$–ZnS and $AgGaS_2$–ZnS correspond respectively to 40 and 5–10 mole % ZnS.[33] The investigators concerned believe that the smaller solid solution region in the system with $AgGaS_2$ is not due to steric hindrance to the replacement of silver by zinc but is caused by the greater departure of the unit cell from the pseudocubic form. The spinels $MgIn_2S_4$, $CrIn_2S_4$, $MnIn_2S_4$, $CdIn_2S_4$, and $CoIn_2S_4$ form with In_2S_3, and $ZnAl_2S_4$ with Al_2S_3, an almost unlimited region of solid solutions[14,34]. An exception is $CaIn_2S_4$. It has been noted that in the region rich in MS solid solutions are not formed[14]. This phenomenon is probably due to the fact that the lattice constants of the spinel and the trivalent metal sulphide differ less than for the sulphide MS.

$PbSnS_2$ forms a two-sided solid solution with the initial components in which the region of homogenisation corresponds to about 30–53 mole % PbS.[35-37] The existence of a more extensive region of solid solutions of $PbSnS_2$ with SnS than with PbS can be accounted for by the similarity of their lattice constants.

According to X-ray diffraction data, the thiochromate spinel systems $ZnCr_2S_4$–$CdCr_2S_4$ and $FeCr_2S_4$–$CdCr_2S_4$ form a continuous series of solid solutions, due to the similarity of the atomic radii of zinc, cadmium, and iron[28].

Complete miscibility of the components is also observed in the systems Ag_3AsS_3–Ag_3SbS_3 and Ag_8GeS_6–Ag_8SnS_6.[38,39] It can be supposed that in the system Ag_8SnS_6–Ag_8SiS_6, whose compounds are isomorphous, unlimited miscibility should be observed.

The ready formation of solid solutions with complex sulphides and the unlimited miscibility of the components suggest that in the compounds described the metals are not divided into cations and anions but are distributed statistically in the tetrahedral and octahedral vacancies in the sulphur sublattice.

As mentioned above, solid solutions of simple sulphides are formed when the crystal structures, chemical bond type, and the effective radii of the metals undergoing mutual substitution are similar. As the composition of the compounds becomes more complicated, the above criteria lose their value. For double sulphides, the following factor evidently limits the miscibility: the dimensions of the vacancies in the sulphur sublattice do not exceed 0.76 Å,[13] while the effective radii of the majority

of metals are much greater and therefore the incorporation of the latter leads to the deformation of the lattices and the polarisation of sulphur. The formation of a double sulphide is favoured by a high temperature and the unsaturation of the chemical affinity of the sulphide sulphur. At the same time the constant of the sulphur sublattice increases, which creates favourable conditions for a freer substitution of the metals. This is also facilitated by the absence of acid radicals from many double sulphides of the type $[M_2S_4]^{2-}$, $[MS_6]^{8-}$, etc.

2. The Formation of Complex Sulphides

Systematic studies of sulphide systems at high temperatures were carried out by Flahaut, Hahn, and their coworkers. The most complete studies have been made on complex sulphides formed by mono-, tri, or di-valent metals with the general composition $M^IM^{III}S_2$, where M^I = Li, Na, K, Rb, Cs, Cu, or Ag and M^{III} = B, Al, Ga, In, P, V, As, Sb, Bi, Cr, Ti, Fe, or Ni.[3,18,26,40,41,64-66,70,72-75,79,97,114,183,199-206] Some investigators are inclined to attribute to the above compounds the formula $M^I_2M^{III}_2S_4$ in order to draw an analogy with the double sulphides $M^{II}M^{III}_2S_4$, where M^{II} = Cu, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Mn, Fe, Co, Ni, Pb, Yb, Sm, or Eu and M^{III} = B, Al, Ga, In, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Ti, Zr, As, Sb, Bi, Cr, Fe, Co, or Ni.[3,14,19,21,22,26,42,44,46-63].

The chemical stability of the sulphides described in relation to acids and alkalis is much greater than that of the individual compounds. Thus, whereas Al_2S_3, Ga_2S_3, and Cr_2S_3 are readily hydrolysed in moist air, $Li_2Ga_2S_4$, $Li_2In_2S_4$, $Rb_2Ga_2S_4$, $Cs_2Ga_2S_4$, $Rb_2In_2S_4$, and $Cs_2In_2S_4$ are not decomposed by water[64-66] and $Na_2Ga_2S_4$ and $K_2In_2S_4$ form hydrates. The double sulphides $MBiS_2$ (M = alkali metal) are stable in relation to water and $CuAlS_2$ is actually stable in relation to dilute hydrochloric acid at normal temperatures.

Many of the sulphides quoted above are not decomposed at high temperatures, which permits their purification by recrystallisation from a melt of halide salts with the same cation M,[48] or with the acid of gas-transport reactions[46,48]. The stability of the compounds formed by the interaction of the sulphides of zinc subgroup metals and gallium increases on going from double sulphides containing mercury to those with zinc and from the double sulphides with aluminium to those with indium, but it is lower than the stability of the analogous oxygen compounds.

Sokolov[67] proposed an empirical rule to determine whether the formation of compounds in binary sulphide systems is possible; it assumed that the reactions occur when the interatomic distance between the anion and the complex-forming cation in the crystalline state is smaller than the distance between another cation and the anion. However, in many systems mutual coordination of the initial compounds is observed as a function of their relative amounts (for example, $4Cu_2S.Na_2S$ and $Cu_2S.9Na_2S$). The above deficiencies make it difficult to extend the rule to many sulphide systems and therefore it will not be employed in the present review.

There exist three types of sulphide crystal lattices: chalcopyrite, spinel, and salt-like.

Double sulphides containing mono- and tri-valent metals crystallise with a chalcopyrite structure, the position of the atoms corresponding to a distorted tetragonal zinc blende structure with a statistical distribution of the metals. According to the data of Hahn et al.[19], many simple sulphides tend to undergo tetrahedral coordination, but this is prevented when the metal : sulphur ratio is greater or smaller than unity. This obstacle is eliminated in the interaction of two sulphides ($M_2S + M_2S_3$) which form compounds with a zinc blende structure and the corresponding electron distribution. This increase in the symmetry of double sulphide crystals is probably caused (as was observed in the formation of solid solutions) by the tendency of sulphur to form its own sublattice. In most cases the metals in the compounds differ in their radii, charges, and polarisation properties and therefore the formation of a wurtzite or zinc blende structure is different. The chalcogenides of mono- and tri-valent metals frequently have the chalcopyrite structure, in which there is an ordered arrangement of the metals in accordance with their properties.

The spinels include double sulphides, the composition of which is described by the formula $M^{II}M^{III}_2S_4$; they have the wurtzite or zinc blende structures. The high symmetry of the crystals is caused, on the one hand, by the tendency of sulphide sulphur to form its own lattice and, on the other hand, by the presence in most metals of a filled d level, as a result of which they tend to form with non-metals covalent bonds with sp^3 orbitals and a tetrahedral configuration[19]. Spinels are divided into normal and inverse depending on the distribution of the metal in the vacancies of the sulphide sulphur lattice. In the first type M^{II} atoms are distributed in tetrahedral vacancies and M^{III} atoms in octahedral vacancies, while in the second type M^{II} and M^{III} occupy simultaneously both octahedral and tetrahedral sites. This phenomenon is due to the relative ionic radii of the metals[51]. Depending on whether the radius of M^{II} is greater or smaller than that of M^{III}, the normal or inverse spinel is formed. However, this rule, as well as the rule designed to determine the lattice energy, the polarisation of sulphur, or the relative bond energies, is not always obeyed in practice. For example, at normal temperatures the "thiogallate structure"[19] resembles that of β-Cu_2HgI_4, but at higher temperatures it undergoes a transition to a zinc sulphide lattice with a statistical distribution of the metals.

Furthermore, indium, tin, and lanthanides form sulphides with the composition M_3S_4. X-Ray diffraction and magnetic studies of these compounds confirmed the existence in them of di- and tri-valent metals, so that the phase can be regarded as the spinel $M^{II}M^{III}_2S_4$.[52,68,69]

Taken together the above data lead to the conclusion that double sulphides with the composition $M^IM^{III}S_2$ or $M^{II}M^{III}_2S_4$ are formed only in those cases where the initial sulphides M^I_2S, $M^{II}S$, and $M^{III}_2S_3$ crystallise in a system of high symmetry and the polarisation properties of the metals are very weak.

The polarisation of sulphide sulphur by metals in the formation of double sulphides has attracted much attention[19,51]. Indeed the radii of covalent or ionic sulphur are much greater than those of oxygen and therefore, under the action of multicharged ions, sulphur should be considerably polarised. Compairson of the polarising capacities of zinc subgroup and Group III metals shows that, on going from zinc to mercury, there is a tendency for metals to be polarised, while on going from indium to boron there is a considerable increase in the polarisability of sulphur. Thus both in the transition from indium to boron and from zinc to mercury the electron density in double sulphide crystals will deviate to the maximum extent from that for wurtzite or zinc blende, which in turn will tend to loosen the structure and ultimately will in general lower the

stability of the double sulphide. This factor readily accounts for the stability and the possibility of the formation of double sulphides with the compositions discussed. Thus so far, it has proved impossible to obtain the spinels MAu_2S_4 (M = Mg, Zn, Cu^{II}, Ti^{II}, Sn^{II}, Pb, Mn^{II}, or Fe^{II}), and also the compounds $MgAl_2S_4$, $CuAl_2S_4$, $FeAl_2S_4$, $CoAl_2S_4$, and $NiAl_2S_4$, which have been described for indium. The sulphides of elements in the lowest state of oxidation (VS, SnS, TiS, Ti_2S_3, etc.) also fail to form spinels with trivalent metals [29,51,55,70].

Triple sulphides with the composition Cu_2ZnSnS_4, Cu_2CdSnS_4, and Cu_2HgSnS_4 have the zinc blende structure and the compound $CuZn_2GaS_4$, the existence of which has not been quite convicingly demonstrated as yet, crystallises in the hexagonal system [33,71]. It is interesting to note that the analogous compound Cu_2FeSnS_4 has been described as a mineral.

Crystallographic studies of the sulphide $CuPS_2$ showed that this compound crystallises with a würzite lattice and its structure is analogous to that of $CuBS_2$, where sulphur and boron or copper atoms are believed to alternate [203].

On the basis of the above data, one may conclude that the statistical distribution of metals in the vacancies of the sulphur lattice is more likely than the salt-like structure. Thus the data quoted do not justify the classification of the compounds described above as salt-like, which means that they cannot be approached from the standpoint of the acid–base theory. Therefore one can hardly agree with the statement [64] that potassium thioindate can be regarded as the salt of the dibasic acid $H_2In_2S_4$. The absence of salt-like properties in these compounds is confirmed by the following data. If CuV_2S_4 is regarded as a salt, then copper should be replaced by other metals. In fact the attempts to replace copper by zinc, cadmium, or mercury proved to be unsuccessful [3,72,73]. Rüdorff and Stegemann [74] established that the formation of $K_2Cr_2S_4$ is much more difficult than the formation of $Na_2Cr_2S_4$. On the basis of the chemical and crystallographic properties of potassium thiochromite, it was concluded that its lower stability is due to the different polarising properties of the alkaline metals, which is hardly ever observed for salt-like compounds. When the sulphide $Na_2Fe_2S_4$ is treated with a solution of a silver salt, the silver replaces not only the sodium but also part of the iron [75].

Only a few compounds have been classified as salt-like double sulphides with the composition $M^{II}M^{III}S_2$ or $M^{II}M^{II}_2S_4$. Bokii et al. [76] and Betekhtin [77] suggest that the sulphides of trivalent arsenic, antimony, and bismuth be regarded as salts containing complex ions of the type $[ES_3]^{3-}$. However, as stated above, crystallographic study of such bismuth compounds showed that they have a structure of the sodium chloride type with a statistical distribution of the metal atoms. $SrAs_2S_4$, which crystallises with a zinc blende structure, evidently belongs to sulphides of the same type [73]. Furthermore, the double sulphides $Ag_{24}Sb_2S_{15}$, Ag_9SbS_6, Ag_5SbS_4, Ag_3SbS_3, and $Ag_2Sb_{12}S_{19}$, which occur in nature as minerals, cannot be readily regarded as derivatives of the corresponding acids. The behaviour of $PbBi_2S_4$, which crystallises in the orthorhombic systems with layers of bismuth and sulphur having the composition BiS_2^-, is somewhat unusual [78]. Alkali metal thioarsenites and thioantimonites may be classified as salt-like compounds.

The elements of the arsenic subgroup are known to form compounds in which they are present in the anionic form. On this basis, one might expect that in the interaction with sulphides the metal components of which tend to form cations, thio-salts should be formed. However, arsenic, antimony, and bismuth do not form double sulphides having the composition $M^{II}M^{III}_2S_4$ with metals of the calcium subgroup, zinc, beryllium, the iron-group metals, etc [73]. It is striking that As_2S_3, Sb_2S_3, and Bi_2S_3 crystallise in a system of lower symmetry (orthorhombic and monoclinic) than the other trivalent metal sulphides mentioned above. At the same time the products of their interaction with Cu_2S and Ag_2S crystallise with a lattice of the chalcopyrite type. Similiar phenomena were observed also for other sulphides, which leads to the conclusion that an increase in the symmetry of the low-symmetry crystals is possible only when two metal atoms, of different valence, can replace zinc atoms in the zinc blende structure without appreciable distortion of the latter. X-Ray diffraction studies of sodium and potassium thiochromites [74,79] led to the conclusion that –Cr–S–Na–S–Cr– layers in hexagonal positions form a close-packed structure of the sodium chloride type. The formation in this structure of CrS_2^- units permits the classification of these compounds as salt-like. It is interesting to note that the group of double sulphides with the composition $MNaS_2$ (M = Nd, Sm, Eu, Gd, Tb, Dy, Ho, or Er) have been assigned to this type of thio-compound [60].

Table 3. Composition of double sulphides containing Group IV elements.

ES_3^{2-}		ES_4^{4-}	ES_6^{8-}	$E_2S_5^{2-}$
Li_2SiS_3	$CaSiS_3$	Li_4SiS_4 Cd_2GeS_4 $La_4[GeS_4]_3$	Cu_8SiS_6	$Na_2Ge_2S_5$
Cu_2SiS_3	Cu_2SnS_3	Cu_4SiS_4 Hg_2GeS_4 $Ce_4[GeS_4]_3$	Ag_8SiS_6	$CaSi_2S_5$
Na_2GeS_3	K_2TiS_3	Mg_2SiS_4 Mn_2SiS_4 $Pr_4[GeS_4]_3$	Ag_8GeS_6	
Cu_2GeS_3	$SrTiS_3$	Ca_2SiS_4 Mn_2GeS_4 $Nd_4[GeS_4]_3$	Ag_8SnS_6	
$PbGeS_3$	$BaTiS_3$	Ca_2GeS_4 Pb_2SiS_4 $Sm_4[GeS_4]_3$		
K_2SnS_3	$BaZrS_3$	Ca_2SnS_4 Pb_2GeS_4 $Gd_4[GeS_4]_3$		

The sulphide of tetravalent elements form a series of compounds [39,61,70,75,80–96], which can be regarded as the salts of the corresponding acids (Table 3).

Comparison of X-ray diffraction data show that only the thio-compounds of silver crystallise in the cubic system [39,44], which is characteristic of simple compounds. The structure of double sulphides belongs to a system of lower symmetry—orthohombic and even monoclinic—but for the majority of sulphides it has not been elucidated at all.

Sulphides containing elements of the titanium subgroup and copper(I) are dimorphous. The existence of the anions $[SiS_3]^{2-}$ or $[SiS_4]^{4-}$ has been proved only for Li_2SiS_3 and Ca_2SiS_4. [80]

The presence in certain double sulphides of anions, the formal correspondence between these compounds and the usual salt-like compounds, the great tendency of Group IV elements to form anions, the low symmetry of the crystals of many of the compounds, and the more ready hydrolysis of Li_4SiS_4 and Ca_2SiS_4 compared with Li_2SiS_3 and $CaSiS_3$ permit the classification of these compounds as salt-like. Their greater basicity than that of salts of the corresponding oxygen acids can be accounted for by the greater size of sulphide sulphur compared with oxygen. However, the data quoted above do not explain the coordination of four, and even less so six, atoms (ions) of sulphur by silicon, germanium, and tin, the increase in crystal symmetry on going from double sulphides containing copper to those with manganese, the occurrence of hexagonal packing of

sulphide sulphur in Mn_2SiS_4 and Mn_2GeS_4 with the metal atoms distributed among the tetrahedral and octahedral vacancies, the decrease of reactivity in the series $SiS_2 > GeS_2 > SnS_2$, the acid properties increasing in the same sense, and the relatively high miscibility of silver thiostannate and thiogermanate over the entire concentration range, although the dimensions of the ions $[GeS_6]^{8-}$ and $[SnS_6]^{8-}$ should differ considerably.

The above group of compounds is located at the boundary between complex sulphides, which are typical for mono- or di- and tri-valent elements, and the thio-salts of metals of Groups V–VII. The complex sulphides containing alkali and alkaline earth metals and Group IV metals should probably also be classified as thio-salts. This conclusion is confirmed by data for the interaction between titanium or zirconium sulphides, on the one hand, and elements of the calcium subgroup and magnesium, on the other. Since the acid properties of zirconium disulphide are not very pronounced, a metal with very marked basic properties is required for the formation of a double sulphide. Among the metals enumerated above, barium has the most basic properties and this is why only $BaZrS_3$ is formed. Evidently the reaction with alkali metals will proceed much more readily, and hafnium sulphide will behave similarly. Titanium disulphide has more marked acid properties and therefore it forms two compounds—$SrTiS_3$ and $BaTiS_3$. The stability of the above sulphides increases from double compounds containing zirconium to those containing titanium. The findings described above agree well with data [70,95] showing the absence of interaction of TiS_2 with ZnS, CdS, HgS, MnS, FeS, and NiS.

These results are in conflict with the statement [95] that compounds of the type ABS_3 have a structure consisting of ions packed into groups $(AS_3)_n$, in which the radii of the ions A and S should not differ too much. The species B is disregarded. However, this explanation is not entirely satisfactory, since it is impossible to understand the reason for the higher reactivity of the sulphides of calcium subgroup metals with TiS_2 than with ZrS_2 or TaS_2.

Group V elements in the normal state of oxidation yield two series of double sulphides, which may be regarded as derivatives of mono- and tri-basic acids (Table 4). The compounds BPS_4 and $AlPS_4$ are isomorphous, crystallising in the orthorhombic system with formation of infinite chains, as in the case of SiS_2, aluminium and phosphorus being linked to one another via sulphur and each being surrounded by sulphur atoms distributed tetrahedrally. Monosubstituted sodium, silver, and thallium thiophosphates are polymeric [97]. X-Ray diffraction study of sulvanite [86,98] Cu_3VS_4 and infrared spectroscopic study of ammonium thiovanadate in solutions [101] showed the existence of the tetrahedra $[VS_4]^{3-}$, which are distributed as in β-K_2SO_4. In view of the short Cu–V interatomic distance in the crystal lattice, it is believed [86] that there is a bond between copper and vanadium. The diamagnetism of Cu_3VS_4, its low electrical conductivity at elevated temperature, and the fact that even part of the vanadium cannot be replaced by chromium, manganese, iron, cobalt, and nickel suggest the formula $Cu_3^{+}V^{5+}S_4^{2-}$. The diamagnetism of the sulphide Tl_3NbS_4 leads to the assignment of the formal valencies to the elements in the compound: $Tl_3^{+}Nb^{5+}S_4^{2-}$. As a result of the considerable asymmetry in the distribution of cations about sulphur, these ions are strongly polarised. Estimation of the degree of polarisation by calculating the electrostatic field confirmed that this energy constitutes a considerable part of the total lattice energy, which is greater than for the zinc blende structure. It is interesting to note that the analogous arsenic compound Cu_3AsS_4 has a covalent As–S bond, in contrast to sulvanite [86].

When vanadium in sulvanite is replaced by niobium and tantalum, which have greater atomic dimensions, the stability of the thio-compounds increases and the colour weakens, which can be accounted for by less intense polarisation of the elements.

Table 4. Composition of double sulphides containing Group V elements [76,86,97–100].

	ES_4^{3-}		ES_3^{-}
Cu_3VS_4	K_3VS_4	Tl_3VS_4	$(NaPS_3)_x$
Cu_3NbS_4	K_3NbS_4	Tl_3NbS_4	$CuVS_3$
Cu_3TaS_4	K_3TaS_4	Tl_3TaS_4	$CuTaS_3$
Cu_3AsS_4	BPS_4	$AlPS_4$	$(AgPS_3)_x$
Cu_3SbS_4			$(TlPS_3)_x$

The compound $CuTaS_3$ crystallises in the orthorhombic system, in which tantalum is surrounded octahedrally by six sulphur atoms with six bonds and a Cu–Ta metallic bond is present [86]. Similar double sulphides with thallium and potassium have been less investigated. In view of the isomorphism of K_3VS_4 and K_3TaS_4, it is believed that these compounds are also salt-like, but some investigators deny the isomorphism of KVS_3 and K_3VS_4 [sic], since in this case the tetrahedra should be combined in a different way.

The data quoted show that the double sulphides described above, containing Group V elements in the highest state of oxidation, are similar to the oxygen-containing compounds and may be classified as thio-salts containing the ions $[ES_3]^{-}$ or $[ES_4]^{3-}$. The compounds exhibit different stabilities towards moisture, acids, and alkali. Thus, while sodium, boron, and aluminium thiophosphates readily undergo complete hydrolysis in moist air, K_3VS_4 hydrolyses only after dissolution; $(TlPS_3)_X$ and $(AgPS_3)_X$ are oxidised only with nitric acid on heating, and sulvanite Cu_3VS_4 occurs as a mineral. It has been noted that the compounds Tl_3ES_4 (E = V, Nb, or Ta) are sparingly soluble in water [86]. The melting points of these double sulphides are in the range 300–500°C. Studies on the electrical conductivity of the sulphides suggest that they are semiconductors.

The data for the interaction of the sulphides of lanthanides (L_2S_3) and aluminium or gallium with formation of compounds having the composition $AlL^{III}S_3$ (L^{III} = La, Ce, Pr, Nd, Sm, Gd, or Y), $GaL^{III}S_3$ (L^{III} = La or Y) [102,103], and $YInS_3$ [103–105] are insufficient for their assignment to any of the classes described above. Most of them crystallise in the hexagonal system ($YInS_3$ crystallises in the orthorhombic system). With certain component ratios, glasses are produced. The compounds are stable towards water, alkalis, weak mineral and organic acids, and organic solvents [104]. It is suggested that a covalent–ionic bond is present in the molecule of the sulphide $ML^{III}S_3$. [105] In accordance with the type of crystal lattice and composition, the sulphides $FePS_3$, $CoPS_3$, and $NiPS_3$ may be included among these compounds [106].

Apart from the classes of compounds described above, there is much information in the literature concerning the existence of compounds with more complex chemical compositions (Table 5). The ratios of the initial sulphides in these compounds range mainly from unity to five. However, in some cases fractional ratios occur, for example

in $5Na_2S.2Fes$, $5Cu_2S.2Na_2S$, $5PbS.4Sb_2S_3$, and $2L_2S_3.3GeS_2$, where L is a lanthanide [40,83,107-110], reaching nine in only a few cases, namely in $9Na_2S.Cu_2S$. [107,108]. Their crystal structures are also different, but the most characteristic feature of all of them is the absence of acid and basic groups.

Table 5. Composition of complex sulphides obtained by the thermal method.

Composition of compound	No. of valence electrons	Composition of compound	No. of valence electrons	Composition of compound	No. of valence electrons	Composition of compound	No. of valence electrons
$Cu_2S\cdot 3Ag_2S$	8	$SnS\cdot 4FeS$	10	$CaS\cdot 2Y_2S_3$	14	$DyS\cdot 2Dy_2S_3$	14
$Rb_2S\cdot 3Bi_2S_3$	20	$CuS\cdot 2FeS$	6	$MgS\cdot 2Y_2S_3$	14	$TuS\cdot 2Tu_2S_3$	14
$3Cu_2S\cdot As_2S_3$	12	$ZnS\cdot 2BaS$	6	$SrS\cdot 2Y_2S_3$	14	$HoS\cdot 2Ho_2S_3$	14
$3Cu_2S\cdot Sb_2S_3$	12	$SnS\cdot PbS$	4	$BaS\cdot 2Y_2S_3$	14	$SiS_2\cdot 2Li_2S$	8
$3Cu_2S\cdot Bi_2S_3$	12	$SiS_2\cdot 2MgS$	8	$FeS\cdot 2Y_2S_3$	14	$SiS_2\cdot 2Cu_2S$	8
$Ag_2S\cdot 3Bi_2S_3$	20	$SiS_2\cdot 2CaS$	8	$MnS\cdot 2Y_2S_3$	14	$SiS_2\cdot 4Ag_2S$	12
$Li_2S\cdot 5Al_2S_3$	32	$SiS_2\cdot 2MnS$	8	$CdS\cdot 2Y_2S_3$	14	$GeS_2\cdot 4Ag_2S$	12
$Cu_2S\cdot 5Al_2S_3$	32	$SiS_2\cdot 2PbS$	8	$CrS\cdot 2Y_2S_3$	14	$SnS_2\cdot 4Ag_2S$	12
$Ag_2S\cdot 5Al_2S_3$	32	$GeS_2\cdot 2CaS$	8	$MgS\cdot 2Dy_2S_3$	14	$2PbS\cdot B_2S_3$	10
$Ag_2S\cdot 5La_2S_3$	32	$GeS_2\cdot 2CdS$	8	$CdS\cdot 2Dy_2S_3$	14	$2PbS\cdot Al_2S_3$	10
$Ag_2S\cdot 5Ce_2S_3$	32	$GeS_2\cdot 2HgS$	8	$MnS\cdot 2Dy_2S_3$	14	$2GaS\cdot Ga_2S_3$	10
$Ag_2S\cdot 5Pr_2S_3$	32	$GeS_2\cdot 2MnS$	8	$CrS\cdot 2Ho_2S_3$	14	$2PbS\cdot Sb_2S_3$	10
$Ag_2S\cdot 5Nd_2S_3$	32	$GeS_2\cdot 2PbS$	8	$MgS\cdot 2Ho_2S_3$	14	$2PbS\cdot Bi_2S_3$	10
$Ag_2S\cdot 5Sm_2S_3$	32	$SnS_2\cdot 2CaS$	8	$CdS\cdot 2Ho_2S_3$	14	$2FeS\cdot 5Na_2S$	14
$Ag_2S\cdot 5Gd_2S_3$	32	$Cu_2S\cdot ZnS\cdot SnS_2$	8	$MnS\cdot 2Ho_2S_3$	14	$3GeS_2\cdot 2La_2S_3$	24
$Ag_2S\cdot 5Dy_2S_3$	32	$Cu_2S\cdot CdS\cdot SnS_2$	8	$FeS\cdot 2Ho_2S_3$	14	$3GeS_2\cdot 2Ce_2S_3$	24
$5Cu_2S\cdot Fe_2S_3$	16	$Cu_2S\cdot HgS\cdot SnS_2$	8	$CrS\cdot 2Ho_2S_3$	14	$3GeS_2\cdot 2Pr_2S_3$	24
$3Cu_2S\cdot 5Bi_2S_3$	36	$Cu_2S\cdot Al_2S_3\cdot 2SnS_2$	16	$MgS\cdot 2Er_2S_3$	14	$3GeS_2\cdot 2Nd_2S_3$	24
$3Cu_2S\cdot Tb_2S_3$	12	$Cu_2S\cdot In_2S_3\cdot 2SnS_2$	16	$CdS\cdot 2Er_2S_3$	14	$3GeS_2\cdot 2Sm_2S_3$	24
$3Cu_2S\cdot Dy_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2SnS_2$	16	$MnS\cdot 2Er_2S_3$	14	$3GeS_2\cdot 2Gd_2S_3$	24
$3Cu_2S\cdot Ho_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2ZrS_2$	16	$FeS\cdot 2Er_2S_3$	14	$2GeS_2\cdot Na_2S$	10
$3Cu_2S\cdot Er_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2TiS_2$	16	$CrS\cdot 2Er_2S_3$	14	$GeS_2\cdot 2Na_2S$	8
$3Cu_2S\cdot Tu_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2HfS_2$	16	$MgS\cdot 2Tu_2S_3$	14	$3ZnS\cdot K_2S$	8
$3Cu_2S\cdot Yb_2S_3$	12	$Ag_2S\cdot In_2S_3\cdot 2SnS_2$	16	$CdS\cdot 2Tu_2S_3$	14	$3CdS\cdot K_2S$	8
$3Cu_2S\cdot Y_2S_3$	12	$Ag_2S\cdot Cr_2S_3\cdot 2SnS_2$	16	$MnS\cdot 2Tu_2S_3$	14	$3MnS\cdot K_2S$	8
$3Cu_2S\cdot Lu_2S_3$	12	$GeS_2\cdot 4CdS$	10	$FeS\cdot 2Tu_2S_3$	14	$3PbS\cdot Na_2S$	8
$Cu_2S\cdot Ag_2S$	4			$CrS\cdot 2Tu_2S_3$	14	$3InS\cdot In_2S_3$	12
$Al_2S_3\cdot La_2S_3$	12			$MgS\cdot 2Yb_2S_3$	14	$3ZnS\cdot In_2S_3$	12
$Al_2S_3\cdot Ce_2S_3$	12			$CdS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Pr_2S_3$	12			$MnS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Nd_2S_3$	12			$FeS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Sm_2S_3$	12			$CrS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Y_2S_3$	12						
$Ga_2S_3\cdot La_2S_3$	12						
$Ga_2S_3\cdot Y_2S_3$	12						
$In_2S_3\cdot La_2S_3$	12						
$In_2S_3\cdot Y_2S_3$	12						

Thus Flahaut et al. [111] and then Ballsstracci [112,113] obtained and investigated by X-ray diffraction compounds with the general formula $M_2S.5Al_2S_3$, when M = Li, Cu, or Ag, $Ag_2S.5L_2S_3$ (L = La, Ce, Pr, Nd, Sm, Gd, Tb, or Dy), and $3Cu_2S.L_2S_3$ (L = Tb, Dy, Ho, Er, Tm, Yb, Lu, or Y). They showed that aluminium-containing double sulphides crystallise with a spinel type of lattice, in which the monovalent metals and one fifth of aluminium are distributed in a random fashion among the tetrahedral vacancies. In the sulphide $Ag_2S.5L_2S_3$ the metal atoms are distributed statistically among the vacancies of the sulphide sulphur lattice.

Copper and iron sulphides interact with formation of the compounds Cu_5FeS_4 ($5Cu_2S.Fe_2S_3$), $CuFeS_2$ ($Cu_2S.Fe_2S_3$), and $CuFe_2S_3$ ($CuS.2FeS$), where the metal atoms in the crystal lattice occupy tetrahedral sites in a spinel type structure with a close-packed sulphide sulphur lattice [40,114].

The double sulphide Ba_2ZnS_3, [115] to which the incorrect composition $BaZnS_2$ was initially attributed [66] (this probably applies also to $SrZnS_2$), crystallises in the orthorhombic system. The Zn–S and Ba–S distances in this compound are almost equal to those in the initial sulphides, which also throws doubt on their salt-like structure. X-Ray diffraction confirmed the existence in the system PbS–Bi_2S_3 of double sulphides with the composition $Pb_2Bi_2S_5$ and $Pb_4Bi_2S_7$. [73,116] It has been established that the $Pb_2Bi_2S_5$ structure contains extensive regions of the zinc sulphide type [117].

Double sulphides with the composition MCu_4S_3 (M = K or Rb), which crystallise in the tetragonal system [118-120], have been described. The lattice consists of layers of –S–Cu–S–Cu–S– units, in which sulphur atoms form an almost regular tetrahedron. Copper is displaced from this tetrahedron into the layer formed by the alkali metal atoms. It is present in these compounds in the mono- and di-valent forms, but occupies identical positions regardless of valence, the layers constituting an integral whole and bearing a negative charge, i.e. $[Cu_4S_3]^-$.

Many of the sulphides listed in Table 5 have the sphalerite or zinc blende structure with a statistical distribution of metal atoms. This suggests that the compounds may be derived from the zinc sulphide structure, where the zinc sites are occupied by other metals and sulphide sulphur forms its own more or less distorted lattice. Goodman [121] and also Koshkin [122] believe that the chalcopyrite lattice of semiconductor compounds of the type $A^IB^{III}C_2^{VI}$, $A_2^IB^{IV}C_3^{VI}$, and $A^{II}B^{IV}C_3^{VI}$ resembles the sphalerite lattice, the difference being that the metal chalcopyrite sublattice contains atoms of two types. With a statistical distribution of metal atoms, the lattice of the three component compounds does not differ from that of sphalerite. The retention of the lattice properties in more complex sulphides suggests that the above hypotheses can be extended to the compounds under discussion.

However, the crystal-chemical properties of zinc sulphide requires that the following conditions be fulfilled. Since in the crystal lattice of the double sulphide the two metals must occupy at least two zinc positions, the number of valence electrons of the metal should be a multiple of four and the overall polarising capacity of the metals should be close to that of zinc in ZnS. Table 5 shows that all the compounds may be divided into two groups in accordance with the composition of the initial simple sulphides.

The first group includes the sulphides with metals having even or odd valences (for example $Cu_2S.Ag_2S$, $Li_2S.5Al_2S_3$, $GeS_2.2MS$, etc). The total number of valence electrons of the metals is a multiple of four. The data explain why in the sulphide systems where the metals have even or odd valences the initial components form only combinations in which the total number of valence electrons of the metals is a multiple of four and which have the composition $M_2S.M_2S_3$, $3M_2S.M_2S_3$, $M_2S.3M_2S_3$, and $M_2S.5M_2S_3$. The numbers of valence electrons in the molecules of the complex compounds are respectively 8, 12, 20, and 32, while the numbers corresponding to the compositions $2MS.M_2S_3$, $4M_2S.M_2S_3$, $M_2S.4M_2S_3$, and $M_2S.6M_2S_3$ are 10, 14, 14, 26, and 38 respectively. Therefore their existence is less likely.

A number of compounds with metals having different valences, where, as in the preceding case, the total number of valence electrons of the metals is a multiple of four, approach closely in their properties the sulphides of the above type. The thiospinels $M^{II}S.M_2^{III}S_3$, $3MS.K_2S$, and $3MS.In_2S_3$ should be included among them. As a rule, their crystals show high symmetry. Probably the combinations of these two factors is in fact decisive for the existence of compounds of this kind.

It is interesting to note that an increase in the complexity of the composition of sulphides of this type, for

example $Cu_2S.MS.SnS_2$ (M^{II} = Zn, Cd, or Hg), or $M^I_2S.M^{III}_2S_3.2M^{IV}S_2$ (M^I = Cu or Ag; M^{III} = Al, In, or Cr; M^{IV} = Ti, Zr, Hf, or Sn)[71,123] does not infringe the principle that the number of valence electrons of the metals must be multiple of four.

The second group includes complex sulphides consisting of elements with even and odd valences, the sum of the valence electrons of the metals of the coordinated sulphides being a multiple of four, for example $MS.2M_2S_3$, $2MS.M_2S_3$, etc., despite the different coordinating capacities of sulphides of this class.

Comparison of the available literature data shows that the coordination number of the simple sulphides combined in the complex depends on the position of the metals in the Periodic System; it increases with the atomic number of the complex-forming metal. As an example, one may quote the double sulphides which include Group I elements: $Na_2Mn_2S_4 \rightarrow K_2Mn_3S_4$; $Na_2Cu_3S_3 \rightarrow K(Rb)Cu_4S_3$; $M_2S.Bi_2S_3$ (M = Li, Na, or K) $\rightarrow Rb_2.3Bi_2S_3$; $Na_2S.Cr_2S_3 \rightarrow K_2S.2Cr_2S_3$; $Cu_2S.Bi_2S_3 \rightarrow Ag_2S.3Bi_2S_3$; etc. It has been noted that rubidium and bismuth sulphides do not form $Rb_2S.Bi_2S_3$. Thus, as the atomic number of the coordinating metal increases, the composition of stable double sulphides becomes more complicated.

III. INTERACTION OF SULPHIDES IN PRECIPITATION FROM AQUEOUS SOLUTIONS

As in fusion, the interaction of sulphides in their precipitation from solution reduces to the formation of solid solutions or double compounds, but the process itself takes place in a more complicated manner. This is because, apart from the conditions for the formation of solid solutions or complex sulphides described in the preceding sections, other factors influencing the process are the solubility of the sulphides (which varies within a wide range), the state of the metal in the initial solution, the stability of its complexes, and the presence of other substances which affect the formation of colloidal and crystalline particles.

For example the particular modification of cadmium sulphide obtained when it is precipitated from solutions depends both on the temperature and the composition of the initial salt[124].

One must agree with Feigl's view[7] that the above phenomena cannot be described solely in terms of the law of mass action or the solubility products. One of the main factors which influence the interaction of sulphides is the concentration in the solution of hydrogen sulphide and sulphide ions. This effect determines conditions for the formation of the precipitate and the acquisition of a charge by the latter. When the amount of hydrogen sulphide is insufficient, metal atoms are adsorbed on the surface of the precipitate by virtue of their high affinity for sulphur, and create a positive charge, while in the presence of an excess of hydrogen sulphide a negative charge is produced. In their discussion of the effect of hydrogen sulphide on coprecipitation, Kolthoff and coworkers[125,126] concluded that hydrogen sulphide and its ions favour the interaction of sulphides because their concentration is higher on the surface of the precipitate than in solution, which has been confirmed by the studies of Rudnev and Malofeeva[127-131]. The removal of hydrogen sulphide from the surface of the solid reduces or altogether suppresses the reactivity of the sulphides precipitated. The capacity for coprecipitation is partially or completely restored after repeated addition to the washed precipitate of water containing hydrogen sulphide. Therefore it is believed that the presence of hydrogen sulphide or its ions on the surface of the sulphide is an essential but not a decisive factor in coprecipitation. This hypothesis is confirmed by the studies of Vachnadze[132], which show that the existence of the compounds In_2S_3 and $MInS_2$ is determined by the relative amounts of In and M^I and not of the sulphide sulphur and indium, and also by the ion exchange between the sulphide precipitate and solution in the absence of adsorbed hydrogen sulphide. In the latter case the experiments were performed on columns containing freshly prepared sulphides of zinc, cadmium, and lead with solutions of copper, lead, manganese, cobalt, nickel, zinc, cadmium, and thallium(I) salts or the sulphides of iron, zinc, lead, cadmium, copper, and silver with solutions of mercury(II), copper(II), and silver salts[133-135]. It was shown that in all the experiments only copper was fully precipitated, while other ions either did not undergo quantitative exchange or their exchange was not consistent with the solubility products. It was noted that the exchange is retarded as the concentration of the precipitating metal in solution is reduced regardless of the solubility products of the sulphides, probably because diffusion of the metal ions through the layer of the corresponding sulphides is difficult. It is interesting to note that the rate of exchange with the less soluble cadmium sulphide is much higher than with the more soluble zinc sulphide, while complete exchange between As_2S_3 and silver ions is not achieved in practice. It is believed that in this case the double sulphide Ag_3AsS_3 is formed and is not decomposed by the excess silver ions. Mercury is precipitated in the form of the compounds xHgS.yHgHal$_2$. There is no ion exchange between zinc sulphide and arsenic, germanium, and indium salts, but the degree of precipitation of indium from solutions containing all the above metals increases under analogous conditions, while that of germanium falls[136], which we believe to be related to the formation of solid solutions of indium and arsenic sulphides or double sulphides. The investigators concerned have correctly noted that the absence of a rigorous relation between the results and the solubility products of the sulphides can be explained by the low reliability of the solubility products and the lack of data for their variation with the size of the precipitated crystals and the particular modification of the sulphide. Indeed, according to data in handbooks[137], the solubilities quoted for the same sulphide differ by 2–6 powers of ten. The results show that the suggestions by Ruff and Hirsch[138] to use as the criterion of the possibility of separation the ratio $SP_1 : SP_2 = K$, where SP_1 and SP_2 are the solubility products of the sulphides to be separated, is erroneous. For high values of K, the sulphides should be separated quantitatively and equilibrium should be attained rapidly. It has now been established that NiS ($SP = 10^{-21}$–10^{-28}) coprecipitates most readily with SnS_2, Bi_2S_3, and FeS, whose solubility products are smaller, and K for Bi_2S_3 is 10^{44}, while MnS ($SP = 10^{-15}$) is most readily coprecipitated with SnS_2 and HgS, where $K = 10^{28}$, the extent of coprecipitation with sulphides whose solubility products are much higher being appreciably less. Nor can one agree with the view put forward by Troitskii[139], who accounts for deviations of this kind by adsorption or by the presence in the precipitate of impurities more soluble than the element coprecipitated.

Many investigators noted long ago that the sorption capacity of the sulphides precipitated from solutions is different in the presence of organic compounds, where were therefore used to suppress coprecipitation[140-142]. The reason for this phenomenon is the interaction of the

oppositely charged colloidal particles of the organic substance and the sulphide sol with possible formation of chemical compounds [143,144]. Sulphides react most fully with triphenylmethane dyes and certain azine dyes, whereby it is possible to prevent completely the coprecipitation of metals with sulphides. This is also favoured by the formation of stable complexes of the coprecipitating metal with the organic compound.

The study of the sorption capacity of a group of sulphides, using as an example the dye Neutral Red, showed that the sorption capacity of bismuth, antimony, mercury, and tin sulphides increases with time, that of arsenic and lead sulphides decreases, and that of copper, silver, and cadmium sulphides remains unchanged [143,145]. The authors believe that this is due to a change in the state of aggregation of the sulphides. However, the results of studies on the coprecipitation of gallium subgroup metals with copper, cadmium, mercury(II), and thallium(I) sulphides and with Bi_2S_3 showed [146,147] that the attempts to extend these findings to the coprecipitation of metals were unsuccessful. Similar results were obtained in the study of the effect of the surface area of the sulphides formed and their charge on their reactivity [145,148,149].

It may be supposed that the degree of coprecipitation should be a minimum in the presence of organic substances and when organic sulphur-containing substances, which do not produce sulphide ions in the solution, are employed. Ion exchange can be successfully used to concentrate elements forming sparingly soluble sulphides.

The interaction of metal salts and hydrogen sulphide may take place via the formation of normal (MS), acid $[M(HS)_2]$ and mixed ($M^{I}SM^{II}$) compounds [150,151]. Furthermore, it is also complicated by the presence in the inner sphere of the complex cation of coordinated water and hydrogen sulphide, which are capable of forming stable hydrogen bonds [152-155].

Thus the data obtained by investigators attempting to find the physical causes of coprecipitation [138,139,156-160] yielded convincing proof of one of the first hypotheses put forward by Feigl [7,161], namely that the reason for the interaction between sulphides is the coordination unsaturation of sulphide sulphur, as a result of which the formation of solid solutions and double sulphides is possible. Physical factors merely increase or decrease the degree of coprecipitation but are not decisive for the reactivity of sulphides. Their interaction with formation of double compounds must be determined by the thermodynamic quantities which include in the first place the affinity of the metals for sulphur, the latter decreasing with enhancement of the non-metallic properties of the elements in the series Zn > Mn > (Co) > Cd > Cu > (Ni) > Fe > Rb > Sn > Ag > Sb > Bi. [162] Furthermore, as pointed out by Yatsimirskii [163], stable thio-salts are formed in those cases where the sulphides have pronounced electrostatic and covalent characteristics.

All the findings described above suggest that the most reliable results can be obtained only by employing the method of physicochemical analysis in combination with crystallographic hypotheses concerning the structure of the above class of compounds. The application of physicochemical analysis to coprecipitation processes, which was first justified by Rudnev and Malofeeva, permitted a deeper understanding of this phenomenon. However, we believe that, when phase diagrams are plotted, a somewhat arbitrary procedure is employed. Usually coprecipitation is studied under conditions excluding the deposition of an independent phase consisting of one of the sulphides. Therefore in the formation of complex compounds the ratio of the amounts of the metals in the precipitate is smaller than in the solution. As the equivalence point is approached, the degree of coprecipitation diminishes due to the decomposition by the medium of the double sulphide formed and the difficulty of attaining the true state of equilibrium because of the rapid precipitation of the solid phase. Therefore the coprecipitation curve obtained by plotting $M:M_1$ (solution) against the degree of precipitation of M(%) will describe the interaction processes only when a single stable complex sulphide is formed (Table 6). When several compounds exist in the system, the curves will reflect only the most stable compound, which is not the case when the results are represented by plots of $M:M_1$ (precipitate) against $M:M_1$ (solution). Therefore in order to avoid an incorrect interpretation of the results, experimental data should always be represented by plots of the latter type.

Table 6. Comparison of the results of interaction studies of sulphides on the basis of different plots.

System	Interaction of sulphides based on different plots		Refs
	$M:M_1$ (soln.)–degree of precipitation, %	$M:M_1$ (soln.)–$M:M_1$ (ppt.)	
$Tl_2S - Re_2S_7$	$TlReS_4$	$2Tl_2S\cdot Re_2S_7 - 3Tl_2S\cdot Re_2S_7$	127, 165
$In_2S_3 - Re_2S_7$	solid soln	$In_2S_3\cdot Re_2S_7$	180
$Tl_2S - PtS_2$	$TlPtS_3$	$Tl_2S\cdot 2PtS_2$	130
$Tl_2S - In_2S_3$	$TlIn_2S_3$	$Tl_2S\cdot 2In_2S_3$	167
$Tl_2S - GeS_2$	$TlGeS_3$	$3Tl_2S\cdot 2GeS_2$	164
$Tl_2S - Ru_2S_3$	$TlRu_2S_2$	$Tl_2S\cdot 2Ru_2S_3$	129
$In_2S_3 - SnS_2$	solid soln.	solid soln.	168, 169
$Tl_2S - Bi_2S_3$	$TlBiS_2$ or solid soln	$Tl_2S\cdot 2Bi_2S_3$	171
$CdS - HgS$	solid soln.	$CdS\cdot HgS$	172, 173
$In_2S_3 - GeS_2$	$InGe_3S_5$	$3In_2S_3\cdot 2GeS_2$ and $In_2S_3\cdot 6GeS_2 - In_2S_3\cdot 2GeS_2$	164
$Tl_2S - Sb_2S_3$	$Tl_3Sb_2S_2$	$2Tl_2S\cdot Sb_2S_3$ or Tl_3SbS_3	164
$Tl_2S - PdS$	$TlPd_2S_3$	$Tl_2S\cdot 4PdS$	164

The conclusions based on the results of the study of systems by the method of continuous variations alone are not sufficiently convincing, since this procedure involves the continuous variation of the amount of solid phase, which affects the degree of precipitation. This can probably account for the discrepancy between the results obtained in the study of the system Tl_2S–PbS by a thermal method, which indicates very limited miscibility [32], and by precipitation of the sulphides, which indicates unlimited miscibility of the solid solutions [164].

In connection with the formation in the system of several complex compounds or solid solutions and compounds, the method of preparation of double sulphides in the presence of a large excess of the coprecipitating metal is valid only if the formation of a single double sulphide has been proved. If the interaction takes place in a complex manner, the preparation of a stoichiometric sulphide requires the use of an acceptable excess, a more suitable acidity of the solution, or fusion.

1. Formation of Solid Solutions

A general defect of the studies relevant to this section is the lack of a rigorous proof of the individuality of the solid phases formed, as was the case in the fusion of the sulphides. Therefore sometimes, when the precipitation of solid solutions during coprecipitation is postulated, a clear distinction is not established between this process and the formation of double sulphides.

The possibility of the formation of a solid solution in the study of coprecipitation in the sulphide systems of zinc and manganese, cadmium and manganese, cadmium and mercury, manganese and mercury, and cobalt and tin was pointed out at an early stage by Feigl[7,161], who called such products "*misch*-sulphides", but this was disputed by Ruff and Hirsch.

The study of the interaction of the sulphides of indium and tin(IV), arsenic(III), bismuth, and cadmium[168,174] indicates the formation of solid solutions, the range of existence of which are various. The results have been explained by the similarity of the atomic radii and the crystallographic parameters, assuming the bonds in the sulphides to be covalent. However the conclusion[174] that "... with increase in the difference between the atomic radii of the metals replacing one another, the miscibility of the components in molecular solid solutions steadily diminishes" is controversial, since in reality similar degrees of coprecipitation have been obtained for pairs of metals differing appreciably in their radii.

The study of the interaction under similar conditions of the sulphides of gallium and tin(IV), copper(II), zinc, and cadmium[175-178] showed that the range of existence of the solid solutions depends on the similarity of the ionic radii of the metals and the ionic character of the metal–sulphur bond. Furthermore, it was established that the degree of precipitation of gallium is determined also by the concentrations of the metals in the initial solution when their relative amounts are kept constant. This is due to the concentration gradient of the coprecipitating element near the surface of the precipitate, caused by its rapid deposition. The subsequent equalisation does not have an appreciable influence on the process, since it is now determined by the diffusion coefficient of the coprecipitating metal in the solid phase. As an example, one may quote on the dissolution of indium coprecipitating with tin disulphide in hydrochloric acid of various concentrations, where it was established that, as the precipitate dissolves, the indium to tin ratio increases from 0.4 for the first portion to 0.8 when the precipitate has completely disappeared. The results suggest that, when solid solutions are formed, coprecipitation will be most complete in dilute solutions, since under these conditions a high degree of dispersion of the sulphide precipitate is maintained for a longer period. This creates favourable conditions for the system to approach a state of equilibrium. Indeed the degree of precipitation of gallium with zinc and copper sulphides increases as the concentration of the elements in the initial solution is reduced. Thus the above property of sulphide systems may serve as one of the criteria for the determination of the cause underlying the interaction of sulphides during their isolation from solution.

The results of the study of the interaction in the systems Tl_2S–As_2S_3 and Tl_2S–As_2S_5, where the existence of a limited region of solid solutions in the first system (100–62 mole % As_2S_3) and its absence in the second was demonstrated, confirm the conclusion of a significant role of metal ion dimensions in the process under discussion. The data concerning the unlimited miscibility in the systems Tl_2S–Sb_2S_3, Tl_2S–Sb_2S_5, and Tl_2S–SnS require revision, since the dimensions of the metal species differ appreciably from one another[179].

The lack of information about the ionic character of the bond for most of the sulphides described hinders the use of effective radii in the discussion of experimental data.

Thus in the formation of solid solutions of sulphides precipitated from solution the conditions established in the systems are not as severe as in fusion and therefore the degree of mutual replacement of the metals is less complete. This can probably explain the finding that in the region of solid solutions, even when the atomic or ionic radii and crystal chemical parameters are similar, the ratio of the metals in the precipitate does not exceed 1 : 0.1 (10%)[180,181].

The data on the effects of temperature on the interaction between sulphides in the formation of solid solutions are contradictory. Some workers believe that an increase of temperature reduces the degree of coprecipitation in the case of crystalline precipitates but has not effect if the sulphide is amorphous, while others think that it has no effect at all or increases the degree of coprecipitation[178,182,212].

The degree of coprecipitation of the metal depends to a considerable degree on the concentration of acid in the initial solution. This is because a decrease of acidity favours the precipitation of the second sulphide in consequence of secondary processes. In such cases the reason for the coprecipitation of the metal may be inferred only from X-ray diffraction data. Therefore sulphide systems must be studied under conditions such that the degree of coprecipitation is less than 100%. Then the formation of an independent or so called "colloidal" phase of the coprecipitating sulphide becomes impossible. The formation of the "colloidal" phase complicates the comparison of the conditions for the formation of solid solutions and double sulphides and the determination of the relations governing such processes. Evidently this can account for the discrepancy between the views of various workers on the effect of temperature and acidity of the medium on coprecipitation. The determination of the type of interaction of the sulphides from the chemical analysis of the solid phase precipitated is also doubtful[168].

Comparison of the data concerning the impurity content in minerals consisting of simple sulphides[183] confirms our earlier conclusion that the amount of impurities in compounds with a cubic lattice is much greater than for the same substances with a hexagonal lattice. Thus up to 26% of iron, 5% CdS, and 5.36% HgS have been found in cubic zinc sulphide, while in hexagonal zinc sulphide [the CdS content is (? Translator)] up to 8% and HgS was not detected. Manganese and zinc sulphides, which have similar effective radii and crystallise in the cubic system, contain a large number of metals at high concentrations. The impurities most frequently encountered are iron, copper, zinc, and manganese, which is probably due to the intermediate position of these metals in the series of effective radii.

An increase [decrease ? (Ed. of Translation)] in the content of isomorphous impurities in the series $Bi_2S_3 > Sb_2S_3 > As_2S_3$ takes place in parallel with the variation of the reactivity of the sulphides. This suggests that in this case complex sulphides and not solid solutions are formed.

The isomorphous substitution of elements in double sulphides can be followed most fully for compounds of the type $M_xE_yS_z$, where M^I = Cu or Ag, E^{III} = As, Sb, or Bi, $x = 1$ or 3, $y = 1$ or 3, and $z = 2$, 3, or 5. As the ratio M : E increases, there is an increase in the symmetry of the crystals of the complex sulphides, the impurity content, and the degree of mutual substitution of the E elements, but the degree of isomorphous substitution of the M elements diminishes.

Thus comparison of the relations obtaining in the formation of solid solutions formed by the fusion of sulphides or their precipitation from aqueous solution shows that in all cases the interaction in the systems is more complete when the radii of the metals corrected for the ionic charac-

ter of the M–S bond are similar and the crystal symmetry is high.

2. Formation of Complex Sulphides

There is less information about the interaction of sulphides during their precipitation from solutions (Table 7) than in the case of their heat treatment.

Hexavalent molybdenum and tungsten form thio-salts of the type $M^{I}_{2}ES_4$ derived from the corresponding acids H_2ES_4.[195,207-211] Infrared spectroscopic studies of the double sulphides in solutions and in the crystalline state showed that the existence of a tetrahedral configuration of sulphur atoms around the metal $[ES_4]^{n-1}$ is characteristic of elements in Groups V and VI, for which the existence of E=S double bonds has been demonstrated. The characteristic frequency of the E–S stretching vibrations is in the range 400–500 cm^{-1} [101,166,194]. Other elements, including rhenium(VII), do not form ions of this type, and therefore investigators [195,196] rejected the possibility of the formation of the thio-salts $KReS_4$ and $TlReS_4$. The absence of the E=S double bonds [194,197] in $[AsS_4]^{3-}$ and $[SbS_4]^{3-}$ also throws doubt on the salt-like nature of these compounds.

Table 7. Composition of double sulphides obtained by co-precipitation from solution [127,129,130,164,165,167-171,173,176-179,184-193,213].

Composition of compound	Sum of valence electrons	Composition of compound	Sum of valence electrons	Composition of compound	Sum of valence electrons	Composition of compound	Sum of valence electrons
$Ag_2S \cdot Au_2S$	4	$4CdS \cdot GeS_2$	12	$4ZnS \cdot In_2S_3$	14	$3ZnS \cdot Ga_2S_3$	12
$3Ag_2S \cdot Au_2S$	8	$4PbS \cdot GeS_2$	12	$4CuS \cdot Tl_2S$	10	$3CuS \cdot Ga_2S_3$	12
$Na_2S \cdot Fe_2S_3$	8	$2HgS \cdot SnS_2$	8	$4PdS \cdot Tl_2S$	10	$3SnS_2 \cdot Ga_2S_3$	18
$K_2S \cdot Fe_2S_3$	8	$CuS \cdot GeS_2$	6	$4Li_2S \cdot GeS_2$	12	$CaS \cdot Fe_2S_3$	8
$(NH_4)_2S \cdot Fe_2S_3$	8	$BaS \cdot CS_2$	6	$4Na_2S \cdot GeS_2$	12	$BaS \cdot Fe_2S_3$	8
$Tl_2S \cdot As_2S_3$	8			$4K_2S \cdot GeS_2$	12	$ZnS \cdot Ga_2S_3$	8
$Cu_2S \cdot In_2S_3$	8			$4Rb_2S \cdot GeS_2$	12	$CuS \cdot Ga_2S_3$	8
$Ag_2S \cdot In_2S_3$	8			$4Cs_2S \cdot GeS_2$	12	$CdS \cdot Ga_2S_3$	8
$Tl_2S \cdot In_2S_3$	8			$4Ag_2S \cdot GeS_2$	12		
$Bi_2S_3 \cdot Ga_2S_3$	24			$2CuS \cdot Tl_2S$	6		
$3Na_2S \cdot P_2S_5$	16			$2Tl_2S \cdot SnS_2$	10		
$K_2S \cdot Re_2S_7$	16						
$Tl_2S \cdot Re_2S_7$	16						
$Tl_2S \cdot Tl_2S_3$	8						
$H_2S \cdot B_2S_3$	8						
$3Tl_2S \cdot As_2S_5$	16						
$2Bi_2S_3 \cdot 3Ga_2S_3$	30						
$2Bi_2S_3 \cdot Ga_2S_3$	18						

Apart from the double sulphides quoted in Table 7, a number of others, where the metals are in an unusual valence state, have been described in the literature. These include $TlSnS_2$, $TlMoS_2$, $TlIn_2S_3$, $TlGeS_2$, $Tl_3Sb_2S_2$, Tl_3Ir_3S, $TlRh_2S_4$, $TlRu_2S_6$, $TlPd_2S_3$, $TlPtS_3$, $InGe_3S_5$, and ZnS.GaS.[166,198] According to data derived by physico-chemical analysis, the inflections in the coprecipitation curves reflect only the ratio of the metals in the compound formed. The sulphur content is determined by chemical analysis preceded by washing and drying of the precipitate, which can lead to a change in its composition. Indeed formulae for certain sulphides can be written assuming the metal to be present in different valence states, for example, $TlSnS_2$–$Tl_2S.SnS.SnS_2$, $TlIn_2S_3$–$Tl_2S.2InS.In_2S_3$, $InGe_3S_5$–$InS.2GeS.GeS_2$, etc. All the simple sulphides quoted here are obtained as a rule at elevated temperatures.

A general feature of the compounds listed in Table 7 is the fact that the sum of the valence electrons of the metal is a multiple of four (for the majority of the sulphides). As for the double sulphides obtained by the thermal method, these can be divided into two similar groups: metals with even or odd and mixed valences having analogous properties. It is interesting to note that some of the compounds listed have also been obtained by the thermal method, for example $Cu_2S.In_2S_3$, $Ag_2S.In_2S_3$, $Tl_2S.In_2S_3$, $ZnS.Ga_2S_3$, etc.

The results quoted show that, in their interaction, simple sulphides tend to form definite compounds regardless of the method used. The acid–base properties of the simple sulphides are not of decisive importance for their reactivity.

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