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MOLYBDENUM CHALCOGENIDES

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1. INTRODUCTION

The investigation of the chemistry of molybdenum can be said to have begun in the first half of the XIXth century, when Berzelius obtained and described some of the principal compounds of molybdenum. Both the metal itself and various of its compounds find wide and diverse applications in industry and in chemical technology. However, several molybdenum compounds of theoretical and practical importance have been studied far too inadequately. These include the molybdenum chalcogenides, that is, the compounds of molybdenum with sulphur, selenium, and tellurium.

It is well known that the most widely distributed molybdenum-bearing mineral — molybdenite — exhibits specific electrical and photoelectric properties and is a semiconducting material.

The field of use of semiconducting materials requires from them the most diverse properties. Therefore an intensive search for new semiconducting substances with various electrical characteristics is now being carried out. In particular, there is now interest in semiconductors which exhibit high thermoelectric characteristics and are suitable for efficient thermoelectric generation.

Because the higher the junction temperature the higher the efficiency of the thermoelement, there is special interest in those materials which exhibit the thermoelectric effect and retain its positive properties at high temperatures. These are, above all, high-melting-point compounds. It is also known that the best thermoelectric materials were obtained from chalcogenides, or combinations of them, which have as constituents metals of high atomic weight. What has just been said explains the special

interest which has recently developed in the chalcogenides in general and in molybdenum chalcogenides in particular.

The practical importance of these compounds necessitates broadly based theoretical investigations, since to obtain semiconducting substances with reproducible properties it is necessary to know the mechanism of their formation, and also all their physicochemical characteristics. The character of the chemical bond, structure, valency state, distribution of electron density in the bonds, magnetic properties, thermodynamic and kinetic characteristics — these are the main directions for the theoretical investigation of thermoelectric materials, including the molybdenum chalcogenides.

A marked intensification of the work on the physicochemical investigation of molybdenum chalcogenides in recent years has led to the production of a series of new facts, which cardinally correct and supplement the old work, the results of which were inadequate, and frequently also erroneous.

In the well-known monographs and reviews [1-4] devoted to the chemistry and technology of molybdenum and its compounds, the information about the molybdenum chalcogenides is usually limited only to their mention and to some of the most general information, mostly out of date.

The authors hope that this review devoted to the chemistry of the molybdenum chalcogenides will make good these deficiencies and allow the reader to obtain exhaustive information, based on the most recent data, about this extremely interesting and promising class of compounds.

On the basis of an analysis of the known experimental data the authors have considered the methods of investigating the molybdenum chalcogenides and of determining the most promising and important regions (in theory and practice) of study of these compounds.

Table 1 gives the chalcogenides of the chromium subgroup elements that are known at present.

Berzelius [21,22] was the first to describe the method of production and some of the properties of the molybdenum sulphides.

The most stable of all the molybdenum chalcogenides is the disulphide MoS_2. It is also the most important sulphide of molybdenum from the practical standpoint. It is the main industrial source for the preparation of molybdenum metal and its compounds.

Molybdenum disulphide, whether natural or artificial, is used as a dry lubricant, forms part of anti-friction lacquer coatings, and allows the production of highly efficient lubricant systems capable of operating at high velocities and at elevated temperatures (up to 400°C), which is especially important in contemporary technology [23-30].

After molybdenum disulphide, the compound which is second in practical importance and the extent to which it has been studied must be the trisulphide MoS_3, which is widely employed in analytical chemistry [31].

The molybdenum atom has incomplete inner electron shells, which can bring about catalytic activity. The ease of transfer from one valency state to another allows molybdenum to function either as a donor or as an acceptor of electrons. Therefore many molybdenum compounds are used as catalysts for various chemical processes. An important point is that molybdenum compounds exhibit high catalytic activity and selectivity, and are also stable against such a common catalyst poison as sulphur. For example, molybdenum sulphides are used as catalysts in condensations, dehydrations, etc. [32-36].

Of the selenides and tellurides of molybdenum, $MoSe_2$ and $MoTe_2$ have been studied most. The interest in them is due above all to their semiconducting properties.

The following oxide chalcogenides and chalcogenide halides of molybdenum are known: MoO_2S [37], $MoO_2S.3H_2O$, $MoOS_2.3H_2O$ [33], $2MoS_3.MoO_3.9H_2O$, $MoS_3.5MoO_3.6.5H_2O$ [39], $MoCl_2S$ [40], $Mo_5Cl_9S_8$ [41].

TABLE 1. Chalcogenides of the elements of the chromium subgroup [1-20].

Chalcogen	Metal			
	Cr	Mo	W	U
S	$CrS, Cr_7C_8, Cr_5S_6, Cr_3S_4, Cr_2S_3$	Mo_2S_3, MoS_2, Mo_2S_5, MoS_3, (MoS_4)	WS_2, WS_3	U_4S_9, US, U_2S_3, U_3S_5, US_2, US_3
Se	$CrSe, Cr_7Se_8, Cr_5Se_6, Cr_3Se_4, Cr_2Se_3$	Mo_2Se_3, $MoSe_2$, Mo_2Se_5, $MoSe_3$	WSe_2, WSe_3	$USe, U_3Se_4, U_2Se_5, U_2Se_3, USe_2, USe_3$,
Te	$CrTe, Cr_7Te_8, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3$	Mo_2Te_3, $MoTe_2$	WTe_2	$UTe, U_3Te_4, U_2Te_3, UTe_2$

2. LOWER CHALCOGENIDES OF MOLYBDENUM

Of the lower molybdenum chalcogenides, the compounds corresponding to the sesqui-composition, Mo_2X_3, are known for all chalcogens.

The first information about the preparation and some properties of molybdenum sesquisulphide was published around 1900, when Guichard [42-44] isolated long steel-grey needles of Mo_2S_3 by brief heating of MoS_2 out of contact with air, at a high temperature. The reaction products were treated with a cold dilute mixture of nitric and hydrochloric acids.

Later Muthmann and Mai [45] obtained well-formed blue-black crystals of Mo_2S_3 on heating MoS_2 (previously boiled in hydrochloric acid) with a mixture of calcium oxide and calcium fluoride. The Mo_2S_3 crystals were separated from the sinter by treating it with concentrated hydrochloric acid followed by elutriation of the unreacted material.

Of the early works it is also worth remembering a low-temperature method of obtaining Mo_2S_3, based on the prolonged action of hydrogen sulphide on a sulphuric acid solution of Mo^{III}, leading to the formation of a black precipitate, which is evidently a hydrated form of molybdenum(III) sulphide [46].

The most contradictory opinions were held for a long time about the formation of molybdenum sesquisulphide from MoS_2 during its thermal decomposition. Thus Guichard [43,44], and later Parravano and Malquori [47], considered that the reduction of molybdenum disulphide in hydrogen proceeds to the metal without formation of intermediate compounds:

$$MoS_2 + 2H_2 = Mo + 2H_2S.$$

It has been reported [48-50] that the thermal dissociation of MoS_2 in a vacuum is also not accompanied by the formation of Mo_2S_3.

In view of the contradictory opinions and the absence of sufficient experimental data, the problem of the existence of Mo_2S_3 and the temperature range of its stability remained unsolved for a long time. A definitive solution of the problem became possible only recently after new precise data about the thermal decomposition of MoS_2 had been obtained, tensimetric investigations had been made, and some physicochemical properties of Mo_2S_3 had been studied.

It is now established that the thermal decomposition of MoS_2, whether in an inert atmosphere, in hydrogen, or in a vacuum, is accompanied by the formation of Mo_2S_3 as an intermediate; its existence has been shown chemically and by X-ray diffraction.

Zelikman and Belyaevskaya [51] showed that in argon MoS_2 rapidly decomposes at 1650–1700°C with formation of a lower sulphide.

The vapour pressure of sulphur over Mo_2S_3 in equilibrium with molybdenum has been measured [52] by the Knudsen method between 1025° and 1150°C and it has been found that not MoS_2 but Mo_2S_3 is in equilibrium with metallic molybdenum and sulphur vapour at these temperatures.

Stubbles and Richardson [53] have shown the error in earlier data [47] on the reduction of MoS_2 in hydrogen at high temperatures. They studied [53] the equilibrium in the Mo–S–H system between gaseous (H_2–H_2S) and solid (Mo–Mo_2S_3 and Mo_2S_3–MoS_2) mixtures at temperatures from 850° to 1200°C by the circulation method. The equilibria are described by the following equations:

$$^2/_3\,Mo + H_2S \rightleftarrows {}^1/_3\,Mo_2S_3 + H_2,$$
$$Mo_2S_3 + H_2S \rightleftarrows 2\,MoS_2 + H_2,$$

which show that the reaction of MoS_2 with hydrogen at high temperatures is accompanied by the formation of Mo_2S_3 as an intermediate. The method of studying the equilibria involves establishing equilibrium between the gases and heated solids on circulating hydrogen over the ground materials [54,55]. The constancy of the hydrogen sulphide pressure was determined by radiochemical determination of its concentration in the gas phase (radioactive sulphur was introduced during the preparation of the sulphides).

The following free energy equations were proposed [53] for the above equilibria:

$$^2/_3Mo(solid) + H_2S(gas) \rightleftharpoons {}^1/_3Mo_2S_3(solid) + H_2(gas),\ t = 850–1200°,$$
$$\Delta G^\circ = -21\,270 + 6.4T \text{ cal } (\pm 100 \text{ cal}),$$
$$Mo_2S_3(solid) + H_2S(gas) \rightleftharpoons 2MoS_2(solid) + H_2(gas),\ t = 1000–1200°,$$
$$\Delta G^\circ = -21\,610 + 8.23T \text{ cal } (\pm 100 \text{ cal}).$$

The free energy equations for the formation of each sulphide from diatomic sulphur and molybdenum are:

$$^4/_3Mo(solid) + S_2(gas) = {}^2/_3Mo_2S_3(solid),$$
$$\Delta G^\circ = -85\,700 + 36.41T \text{ cal}.$$

$$Mo(solid) + S_2(gas) = MoS_2(solid),$$
$$\Delta G^\circ = -85\,870 + 37.33T \text{ cal}.$$

It has been shown [56] that the vacuum thermal dissociation of molybdenum disulphide at 1280°C leads to the formation of the sesquisulphide.

The thermal dissociation of MoS_2 was brought about [56] by putting a few grammes of it in a thoroughly cleaned and previously outgassed quartz ampoule, which was evacuated to a residual pressure of 1×10^{-5} mmHg, sealed and put in a tube furnace in such a way that the end with the substance was in the furnace while the other end projected outside it and could be cooled. The material was heated to a known temperature and held there for a few hours. A sublimate of sulphur condensed in the cold end.

Heating MoS_2 at 1280–1300°C leads to the formation of steel-grey products with a marked metallic lustre, the composition of which corresponds to the formula $Mo_{1+x}S_2$, where x varies according to the time held at a given temperature. The crystal lattice of the phases of variable composition is based on hexagonal MoS_2 with slight distortion in the c direction.

Mo_2S_3 is formed when MoS_2 is heated for a long time under these conditions.

Gorokh and coworkers [57] synthesised Mo_2S_3 from the elements by direct heating of stoichiometric quantities of molybdenum and sulphur in an evacuated quartz ampoule to 500°C and holding at this temperature for 6 h, after which the temperature was raised to 900°C, held there for 14 h, heated again at 1400°C, and held at that temperature for 15 h.

Mo_2S_3 dissociates into the elements at 1600°C, that is, in an inert atmosphere at normal pressure it undergoes thermal dissociation before fusion [57]. Heating Mo_2S_3 with sulphur again leads to the formation of MoS_2. [43,44]

There is evidence that molybdenum sesquisulphide forms a non-stoichiometric compound of composition $Mo_{2.06}S_3$. [52,58,59]

The lower selenides and tellurides of molybdenum have been studied less than the sulphide.

The selenide Mo_2Se_3 is obtained by fusing a finely ground mixture of MoO_2, K_2CO_3, and Se†. The closed crucible with the mixture is put into a furnace at 800°C, the furnace temperature raised to 1200°C, and the mixture held at that temperature for ~1 h until fusion is complete. The cooled melt is treated with water in an atmosphere of nitrogen, to dissolve the potassium selenide. The residue — a steel-grey powder — is Mo_2Se_3. [60]

The telluride Mo_2Te_3 is obtained during the vacuum distillation of the alloy prepared by heating a mixture of molybdenum and an excess of tellurium in an evacuated sealed quartz ampoule. After the reaction the excess of tellurium is sublimed into the cooled upper end of the ampoule, by heating its lower end with the material for a few days at 815–890°C. [61]

Recent work [62,63] on the investigation of molybdenum chalcogenides showed that the lower selenides and tellurides of molybdenum are compounds of variable composition with narrow homogeneity regions. The authors [62,63] note that in composition the molybdenum lower selenides and tellurides do not correspond precisely with the sesqui--compounds, but correspond better with the formula Mo_3X_4 (where X is Se or Te).

As a result of the thermographic investigations and also the data on the vacuum-thermal decomposition of the dichalcogenides, the following general methods for preparing Mo_3Se_4 and Mo_3Te_4 were proposed: (a) thermal dissociation of the molybdenum dichalcogenides — $MoSe_2$ and $MoTe_2$ — in a vacuum at definite temperature ranges; (b) reaction of stoichiometric amounts of the elements in evacuated quartz ampoules; (c) reaction of metallic

† The mixture is covered with a layer of potassium carbonate.

molybdenum with the corresponding dichalcogenide in evacuated quartz ampoules according to the reaction:

$$Mo + 2MoX_2 = Mo_3X_4,$$

where X is selenium or tellurium.

All these reaction lead to temperature intervals which ensure the decomposition of the corresponding dichalcogenides to the lower compounds, that is, for selenides at 1180–1240°C, for tellurides at 770–920°C.

The lower molybdenum chalcogenides show great similarities in physical and chemical properties. They are grey crystalline substances, comparatively resistant to attack by acids. At ordinary temperature Mo_2S_3 does not react with hydrochloric and sulphuric acid, or with a mixture of dilute hydrochloric and nitric acids, but it dissolves readily on heating in nitric acid, with the formation of molybdic and sulphuric acids[42-44,57]. The dissolution is apparently due to the reaction:

$$Mo_2S_3 + 10HNO_3 = 2H_2MoO_4 + 3H_2SO_4 + 10NO.$$

The molybdenum lower selenide shows similar behaviour[60].

The molybdenum lower telluride is oxidised by nitric acid to MoO_3 and TeO_2, but boiling sulphuric acid is decomposed with the liberation of SO_2 and formation of a cherry-red product of unknown composition[61].

The behaviour of the lower chalcogenides of molybdenum on heating has been insufficiently studied. Such information as has been published[47-53,57] about the thermal stability of Mo_2S_3 has been given in detail above. The molybdenum lower selenides and tellurides are stable in a vacuum up to 1250° and 950°C respectively, above which they dissociate to the elements[61-63].

According to Wendehorst's results[60] the lower molybdenum selenide does not change composition on heating in a stream of H_2Se. However, this is doubtful in the light of subsequent results from studies of the equilibrium in the Mo–S–H system[53] and the great similarity between the properties of these compounds.

The hardness of Mo_2S_3 is somewhat greater than that of MoS_2, and is five on Mohs' scale; the density, determined pyknometrically, is 5.75 g cm^{-3}.[57] The density of the lower telluride is 7.35 ± 0.01 g cm^{-3} at 15°C.

The magnetic properties are known only for the lower telluride of molybdenum. It is paramagnetic, the magnetic susceptibility being $+(0.185 \pm 0.002) \times 10^{-6}$.[61]

A determination of the crystal structure of Mo_2S_3 by the powder method[53] showed that it is tetragonal with unit cell parameters c = 10.9 Å and c/a = 1.27. However, it was shown later[64] that Mo_2S_3 is monoclinic with parameters a = 8.6335 Å, b = 3.208 Å, c = 6.092 Å, β = 102°43′, Z = 2, space group $P2_1/m$, density calculated from the X-ray measurements 5.806 g cm^{-3}.

In the Mo_2S_3 structure each molybdenum atom is situated at a distance of 2.36 Å from three neighbouring sulphur atoms and at a distance of 2.57 Å from three other sulphur atoms (Fig. 1). The molybdenum atoms in direction b are displaced 0.32 Å relative to one another and form a zig-zag chain with Mo–Mo distance of 2.85 Å.

According to Gorokh and coworkers[57], Mo_2S_3 is orthorhombic with the rhombobipyramidal class of symmetry ($3L^23PC$). The Mo_2S_3 crystals are elongated prisms with a rhomb cross-section and angles of 40° and 140° between the adjacent faces. The Mo_2S_3 crystal lattice is similar to the Sb_2S_3 lattice.

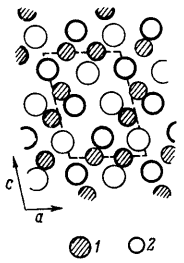


Fig. 1. Structure of Mo_2S_3 projected along axis b. The broken line marks out a unit cell. The atoms at $y = \frac{1}{4}$ are drawn with a light line, those at $y = \frac{3}{4}$ with a heavy line: 1) molybdenum atom; 2) sulphur atom.

TABLE 2. Structural data for Mo_3Se_4 and Mo_3Te_4.

Compound	Symmetry	Lattice parameters, Å			β	Z	Density, g cm^{-3}	
		a	b	c			X-ray	pyknometric
Mo_3Se_4	monoclinic	4.61	4.77	6.62	93°09′	1	6.88	6.75
Mo_3Te_4	monoclinic	4.87	5.09	7.04	93°46′	1	7.61	7.45

The crystal structure of the molybdenum lower selenides and tellurides has been investigated by the powder method. Mo_3Se_4 and Mo_3Te_4 are isostructural, their crystals are monoclinic. Table 2 gives the results of X-ray investigations[65].

The lower chalcogenides have been studied insufficiently, especially the selenides and tellurides. Probably one of the reasons is that until recently the methods for preparing them were not simple and reliable enough. The methods developed recently for the preparation of molybdenum lower chalcogenides will undoubtedly facilitate their more intensive study[57,62,63].

Structural information about the lower molybdenum chalcogenides is limited to studying them by the powder method. There is a future possibility of obtaining single crystals of these compounds to carry out thorough structural investigations.

Information on the chemical properties of the molybdenum lower chalcogenides is limited to the qualitative characteristics of the behaviour of these compounds in certain acids. It is evident that a study of their reaction with certain elements, with various acids and bases, and also with solid salts and salt solutions, allows interesting data to be obtained on the properties of these compounds, and this in turn opens a path for the preparation of new molybdenum compounds.

3. MOLYBDENUM DICHALCOGENIDES

The molybdenum dichalcogenides are the most stable, most fully studied, and most industrially important compounds of those considered in this review.

The properties of MoS_2 have been described more fully than those of $MoSe_2$ and $MoTe_2$ but the latter are now of special interest in connection with the rapidly developing investigations of semiconductors.

Molybdenum disulphide, molybdenite, is encountered in nature but can be made artificially by various methods. $MoSe_2$ and $MoTe_2$ are only made artificially.

Of the many methods for obtaining molybdenum dichalcogenides we will consider those which are the most general and important in practice (Fig. 2). Several different methods for making MoS_2 have been proposed, but $MoSe_2$ and $MoTe_2$ are made commercially only by the direct reaction of the elements. The exceptional position of MoS_2 is explained above all by the extent to which methods of preparing MoS_2, $MoSe_2$, and $MoTe_2$ have been studied. There is no doubt that further investigation of $MoSe_2$ and $MoTe_2$ will lead to the development of new methods for preparing them, both by methods similar to those for making MoS_2 and by original methods, specific for each of the compounds under consideration.

The method most frequently used for obtaining $MoSe_2$ and $MoTe_2$ — direct synthesis from the elements — apparently still attracts investigators because it allows the purest materials to be obtained, suitable for the investigation of their semiconducting properties without additional purification. However, the use of transport reactions [73,77,82], which not only allow the substances to be purified but also to be obtained in the form of single crystals, make the old preparative methods of interest today.

In addition to the methods for obtaining molybdenum chalcogenides shown in Fig. 2, mention must be made of a method of synthesising crystalline MoS_2, proposed by Spengler [83]. MoS_2 is obtained by the reaction of molybdenum metal or its compounds (molybdenum oxides, salts of molybdic acids, etc.) with sulphur or sulphur(II) compounds (for example, H_2S, alkali metal polysulphides, etc.), in an alkaline medium at 300–500° and at increased pressure in an atmosphere free from oxidising agents.

Methods for obtaining the molybdenum dichalcogenides from the gas phase are also known. Thus MoS_2 can be obtained by the direct reaction of H_2S and CS_2 with molybdenum [84] or by reaction of S and H_2S with volatile molybdenum compounds on heating [85]. The last method can also be used to make $MoSe_2$ and $MoTe_2$.

Of the methods for obtaining molybdenum dichalcogenides which are considered the following are used most often: to prepare MoS_2, the reaction of molybdenum trioxide with sulphur in molten potassium carbonate [70]; to prepare $MoSe_2$ and $MoTe_2$, direct synthesis from the elements [59,73–77].

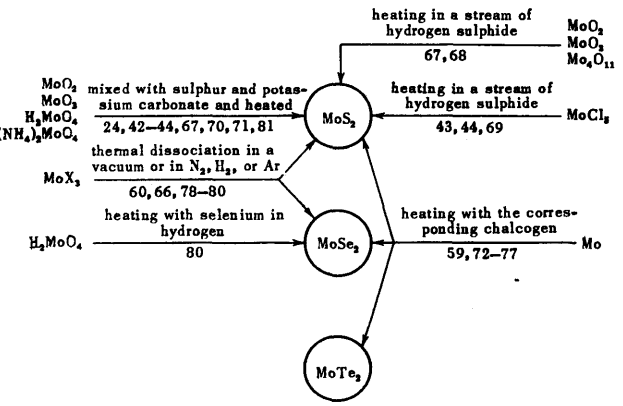


Fig. 2. Methods of preparing the molybdenum chalcogenides (the numbers underneath the arrows are literature references).

In the method of making MoS_2, the potassium carbonate plays a dual role: it serves as a solvent for the sulphur and is a flux, protecting the product formed from oxidation. To obtain MoS_2, four parts by weight of K_2CO_3 are fused with six of sulphur in a closed porcelain retort at 700°. The reaction continues until SO_2 is no longer lost, after which the retort containing the melt is removed from the furnace and cooled. One part by weight of pure MoO_3 (obtained as a sublimate) is added, the retort is heated to 900° and held at that temperature for 30 min. The operation is repeated until six parts by weight of MoO_3 have been added. On cooling, the whole mass solidifies.

The excess of the reagents and the impurities are removed by prolonged boiling in dilute ammonia solution, followed by washing with distilled water, boiling for 30 min in dilute hydrochloric acid, and thoroughly washing with water, alcohol, and ether successively. The product is dired in a vacuum at 75°C.

Bell and Herfert [86] think that the formation of MoS_2 takes place in two stages:

$$2\,MoO_3 + S \rightarrow 2\,MoO_2 + SO_2,$$

$$MoO_3 + 3\,S \rightarrow MoS_2 + SO_2$$

The disulphide obtained always contains MoO_2. These authors were unable to carry out the second reaction to completion by various methods, therefore they removed unreacted MoO_2 present as impurity by treating the material with dilute KCNS (similar to the method developed by Milbauer [87]) with subsequent treatment with dilute solutions of ammonia and hydrochloric acid. This operation almost completely frees the disulphide preparation from MoO_2 and a fairly pure product is obtained (< 0.01% MoO_2).

It is interesting to note that in the reaction of various molybdenum oxides (for example, MoO_3, MoO_2, Mo_4O_{11}) with hydrogen sulphide at 400–550°C, the final product always contains some MoO_2 as well as MoS_2. [68] The process takes place differently, depending on the initial substance. With molybdenum trioxide the following reactions are possible:

(a) exchange of oxygen with sulphur:

$$MoO_3 + 3\,H_2S \rightarrow MoS_3 + 3\,H_2O;$$

(b) reduction of the higher oxide to MoO_2:

$$MoO_3 + H_2S \rightarrow MoO_2 + H_2O + S;$$

(c) reaction of MoO_2 with hydrogen sulphide:

$$MoO_2 + 2\,H_2S \rightarrow MoS_2 + 2\,H_2O;$$

(d) decomposition of the sulphide obtained earlier (a) at 400–500°C:

$$MoS_3 \rightarrow MoS_2 + S.$$

The reaction of Mo_4O_{11} with hydrogen sulphide proceeds as follows:

$$Mo_4O_{11} + 3\,H_2S \rightarrow 4\,MoO_2 + 3\,H_2O + 3\,S,$$

and subsequently by scheme (c). When the initial substance is MoO_2 the reaction with hydrogen sulphide apparently leads only to reaction (c).

The reaction products always contain MoS_2 and MoO_2, the sum of the stoichiometric coefficients $(x + y)$ in the empirical formula MoO_ySx are often greater than two, which shows that either elemental sulphur or MoS_3 is present in the products.

As molybdenum disulphide has recently been widely used in technology as a lubricant, the problem arises as to the methods for obtaining pure MoS_2 containing $\gtrsim 0.2\%$ impurities. Quartz, 5–7% of which is present in molybdenite concentrates, is an especially harmful impurity. Therefore to obtain pure MoS_2 suitable for use as a lubricant the natural concentrates are subjected to many treatments, which greatly increases the cost of the product[24]. The use of flotation-leaching chemical purification in association with the grinding of molybdenite in ball mills enables a sufficiently pure (99.8%) MoS_2 to be obtained from natural molybdenite concentrates[88].

However, it is more economical to obtain pure MoS_2 by artificial means. A proposed[81] method of preparing MoS_2, by the reaction of MoO_3 or $CaMoO_4$ with sulphur in molten sodium carbonate at 700°C, allows a product with the theoretical ratio of the elements to be obtained.

The direct synthesis of the molybdenum dichalcogenides from the elements is carried out as follows. Stoichiometric amounts of the pure powdered elements are mixed well and put into a quartz ampoule which has previously been cleaned and thoroughly outgassed in a vacuum. The ampoule is outgassed to a residual pressure of 10^{-5} mmHg, sealed, and heat treated, to ensure completion of the reaction and to give a homogeneous product. The ampoule with the reaction mixture is heated slowly in a furnace having smooth temperature regulation. As Table 3 shows, the temperature and holding time in the thermal treatment are different for different authors.

Obviously a higher temperature in the preparation ensures a more rapid completion of the reaction and the best homogenisation of the product. However, in high-temperature preparations explosion of the ampoule is possible. Therefore it is more convenient to carry out direct preparation from the elements at low temperatures, when this is possible, as was suggested for the explosion-free preparation of compounds of the $A^{II}B^{VI}$ type[89].

Finally, in this instance the time of heat treatment to obtain a homogeneous product should be greatly increased.

All the molybdenum dichalcogenides are crystalline. As is known, the ions S^{2-}, Se^{2-}, and Te^{2-} have large radii (1.82, 1.93, and 2.11 Å respectively[90]), and consequently can readily be polarised. On the other hand, the Mo^{4+} ion, which has an ionic radius of 0.65 Å,[90] is a strongly polarising anion. Under such conditions, when the anion is readily polarised and the cation exhibits strong polarising properties, compounds of the type AX_2 show layer structures[91], which have a layer of the cation atoms situated between two layers of anion atoms, as a result of which a packet of three layers is formed. The bonds inside the three layers are considerably stronger than those between two three-layer packets. The molybdenum dichalcogenides are representatives of just this type of layer structure.

Natural molybdenite forms normally flat, thin, very flexible, soft, blue-grey flakes or scales, greasy to the touch and similar to graphite. Its crystals are hexagonal[92,93], space group $P6_3/mmc$–D_{6h}^4. The unit cell contains two MoS_2 molecules and has the following parameters[94]: $a_0 = 3.16$ Å, $c_0 = 12.32$ Å, $a_0/c_0 = 1:3.899$.

Molybdenite has the typical layer structure. The layers of molybdenum ions are situated between two layers of sulphide ions parallel to the $(000\bar{1})$ plane. The ions in the layers are joined by strong bonds and the slip forces between such triple packets are very weak and apparently are of the van-der-Waals type.

This also explains the properties of molybdenite, such as the exceptional ease of slip in the direction perpendicular to the c axis — cleavage is completely by $(000\bar{1})$, the predominant flaky form.

Molybdenum has a coordination number of six in MoS_2 but because of the peculiar electronic structure of molybdenum it corresponds to a trigonal prism and not an octahedron. A molybdenum atom is surrounded by six sulphur atoms at the apices of a regular isosceles trigonal prism (Fig. 3).

TABLE 3. Conditions for the preparation of molybdenum dichalcogenides from the elements in evacuated quartz ampoules.

Compound prepared	Heat treatment conditions		Reference
	temp., °C	time, h	
$MoSe_2$	700 anneal I	100	74
$MoSe_2$ / $MoTe_2$	600—700 anneal II 1000—1200	10—15	73
$MoTe_2$	1100	5—10	75
$MoTe_2$*	460	16	61
$MoTe_2$**	580	20	
	640	24	
	780	48	
	640	40	
	775	24	
$MoTe_2$	600	2 d	77

* After the reaction the product was crushed, passed through a 125 mesh sieve and heated at 600°C for 48 h in a vacuum.

** In preparing $MoTe_2$, an excess of tellurium was taken; after the reaction it was removed by sublimation at 580–815°C in a vacuum.

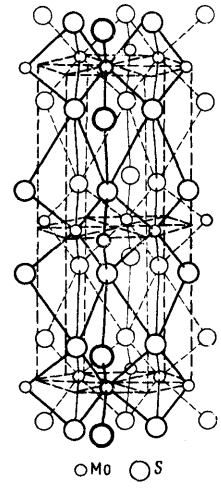


Fig. 3. Structure of hexagonal molybdenum disulphide, MoS_2.

The layer nature of the MoS_2 structure can be represented more graphically[95] as alternating layers of trigonal prisms with Mo^{4+} ions in their centres alternating with empty layers of octahedra (Fig. 4). The hexagonal axis c is perpendicular to the triangular surface of the prism. In MoS_2 the Mo–S distance is 2.35 Å, the S–S distance between two neighbouring layers is 3.66 Å, and the S–S distance in a trigonal prism is much less (2.98 Å)[96].

Synthetic MoS_2, $MoSe_2$, and $MoTe_2$ crystallise as blue-grey tablets or leaflets, and even in thin needles a few millimetres long[70,73,75].

For a long time the crystal structure of MoS_2 remained uncertain, since the preparation of the disulphide was confirmed mainly by chemical analyses, or sometimes microscopically. Although X-ray examination showed the preparation obtained from the elements in an iron tube[72] to have the structure of natural molybdenite, the identity of natural crystals with artificial ones obtained by other methods[67,69,70] was not established. It was suggested that there was a trigonal morphology of artificial MoS_2 crystals[92,97].

The polymorphism of MoS_2 which had been suggested earlier was demonstrated in 1957, when Bell and Herfert[86] obtained the X-ray diagram of synthetic molybdenum disulphide differing in structure from natural molybdenite.

It is now known that MoS_2 can exist in at least two, and possibly in three, polymorphic states[75,86,98–100].

Bell and Herfert[86], who first described a new crystalline form of synthetic MoS_2, obtained by the de Schulten method[70], concluded on the basis of X-ray investigations that the artificial MoS_2, unlike the hexagonal natural molybdenite, is tetragonal with a rhombohedral unit cell, parameters $a = 3.16$ Å, $c = 12.32 \times 1.5$ Å, that is, with the same a parameter, but with the c parameter 1.5 times that for the hexagonal form of the natural disulphide.

The authors[86] explained this difference as follows. Since the interatomic distances in the two modifications are equal, the structures differ in the disposition of the sulphur atoms in the packets, namely: in the hexagonal form a molybdenum atom is situated at the centre of a triangular prism with the three upper sulphur atoms directly above the three lower atoms (Fig. 5*a*), in the rhombohedral form one layer of sulphur atoms in the packet (for example, the upper) is turned 60° relative to the other (the lower) (Fig. 5*b*), which on a more thorough examination of the structure leads to octahedral coordination of the molybdenum atom[99].

Hence for the new modification of MoS_2 they proposed a structure with a centre of symmetry, which is described by

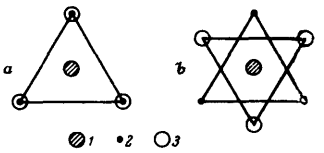


Fig. 5. Coordination of molybdenum atoms in molybdenum disulphide[86]:
a) natural hexagonal MoS_2; *b*) synthetic rhombohedral MoS_2;
1) molybdenum atom; 2) lower sulphur atoms; 3) upper sulphur atoms.

the space group $R\bar{3}m$–D^5_{3d}, that is, a $CdCl_2$-type structure, where the mutual orientation of the three layers is effected so that only the fourth layer of anions repeats the first, the fifth repeats the second, and so on.

However, this structure did not correspond sufficiently accurately with reality, because of the great discrepancies between the theoretical and experimental intensities of the reflections.

Subsequently a new rhombohedral MoS_2 structure was considered and worked out more precisely. A scheme was proposed[98] with triangular-prismatic coordination of the molybdenum (Fig. 6). The structure shown can be described by space group $R3m$–C^5_{3v} with the following distribution of atoms:

3 molybdenum atoms in 3 (*a*): 00*z* with $z = 0.000$
3 sulphur atoms I in 3 (*a*): with $z = 1/4.001/4$
3 sulphur atoms II in 3 (*a*): with $z = 5/12.005/12$.

This scheme for the rhombohedral modification of molybdenum disulphide agrees well with the experimental results.

Semiletov[99] confirmed this theoretically. He showed that a structure of the $CdCl_2$ type proposed by Bell and Herfert[86] for rhombohedral MoS_2 was wrong and the constructed a model of a structure with the molybdenum atoms distributed in a trigonal prism (and not in an octahedron, as they should be according to Bell and Herfert).

According to Semiletov[99] the rhombohedral modification is obtained from the hexagonal by rotating through 60° entire three-layer packets and not one of the layers of a single packet, which leads to a structure without a centre of symmetry and with space group $R3m$–C^5_{3v}.

Knop and MacDonald arrived at the same conclusion[75]. They considered both layer structures consisting of hexagonal layers of atoms of molybdenum and sulphur situated

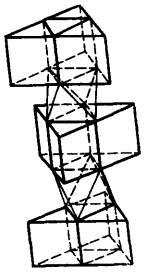


Fig. 4. Structure of MoS_2.[95]

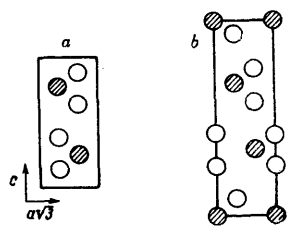


Fig. 6. Polymorphic structure of MoS_2:[98]
a) hexagonal form; *b*) rhombohedral form.

parallel to the basal plane as differing from one another in the sequence of periods of combination of packets with respect to one another, namely:

. . . AMA BHB/AMA BHB/AMA . . . for the hexagonal form,
. . . APA CMC BHB/APA CMC BHB/APA . . . for the rhombohedral form,

where *A*, *B*, *C* refer to sulphur layers and *M*, *H*, *P* to molybdenum layers. However, in both instances they give trigonal-prismatic coordination of the molybdenum atoms with the nearest atoms of sulphur.

Hence in hexagonal MoS_2 with parameter c = 12.32 Å there are two three-layer packets and in the rhombohedral, the lattice parameter of which is 1.5 times as much (a ratio of 3 : 2), there are three packets.

Apparently the rhombohedral form of MoS_2 is unstable and on prolonged heating it is converted into the stable hexagonal form[79].

Study of the chemical bonds in molybdenite, where the Mo^{IV} atom has a coordination number of six, leads to the conclusion that the six sulphur atoms do not form an octahedron around the molybdenum, but — by virtue of the special structure of the electronic cloud of the molybdenum atom — a triangular prism with a ratio of the axes equal to unity, and S–Mo–S angles of 82° and 136°.[92,101-103]. *dsp* orbitals participate in the bondformed. Most investigators think that d^4sp hybridisation occurs here, that is, 4*d*, 5*s*, and 5*p* electrons of the central atom participate in the formation of the bond and the only 4*d* orbital (fifth shell) not participating in the bond of the molybdenum atom is occupied by two electrons (one unshared pair)[104-106].

Barinskii and Vainshtein[104] confirmed the d^4sp hybridisation by investigation of the fine structure of X-ray absorption and emission *L* spectra of molybdenum in MoS_2. Knop and MacDonald[75] consider that the magnetic properties of MoS_2 confirm that bond; they think that this results in the diamagnetism and the considerable anisotropy of the diamagnetism of MoS_2 crystals, in which the negative susceptibility in a direction parallel to the hexagonal axis is almost twice that in the direction perpendicular to the axis. The marked temperature dependence of the magnetic properties of molybdenite crystals[107-109] and also the considerable electrical conductivity in the direction perpendicular to the hexagonal axis (that is, along the base of the plane)[110], is explained by the existence of strongly delocalised mobile π-electrons inside the layers, which can be understood, starting from d^4sp orbital configuration of the molybdenum atom.

Investigation of the structure of $MoSe_2$ and $MoTe_2$ began only recently. A hexagonal modification of MoS_2 type is known for these compounds, with space group $P63/mmc$–D^4_{6h}. Table 4 shows some structural characteristics of $MoSe_2$ and $MoTe_2$.

Fig. 7 shows the structure of the ditelluride schematically. The Te–Mo–Te angles[75,76] are respectively α 80.74° ± ± 0.50° and 80.4°; β 83.10° ± 0.60° and 83.5°; γ 134.95° ± ± 0.60° and 133.9°, which corresponds to d^4sp hybridisation[101].

Molybdenum diselenide and ditelluride are thought to be structurally isomorphous with molybdenum disulphide. As MoS_2 exhibits polymorphism, the structural data for $MoSe_2$ and $MoTe_2$ obtained by different methods should be considered incomplete.

TABLE 4. Structural characteristics of molybdenum diselenide and ditelluride.

Compound	Lattice parameter, Å		Density, g cm^{-3}		Interatomic distance	Unit cell volume, Å^3	Reference
	a_0	c_0	X-ray	pyk	Mo–X, Å		
$MoSe_2$	3.288	12.900	6.98	6.9		120.8	73
	3.284	12.88	7.0	6.9			74
	3.288	12.931	6.96		2.49		111
	3.289	12.921					118
$MoTe_2$	3.517	13.949	7.8	7.7		149.4	73
	3.518	13.974	7.78	7.68	2.71	149.79	75
	3.519	13.964	7.78	7.8	2.736		76
			7.78	6.85			77
				7.60			61

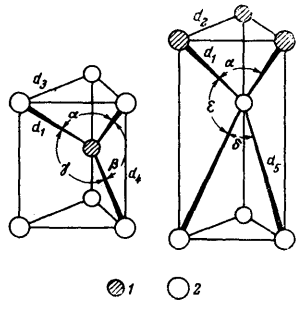


Fig. 7. Coordination of molybdenum and tellurium atoms in molybdenum ditelluride:
1) molybdenum atoms; 2) tellurium atoms.
d_1(Mo–Te) = 2.716 Å;
d_2(Mo–Mo) = d_3(Te–Te) = a_0 = 3.5182 Å;
d_4(Te–Te) = 3.603 Å;
d_5(Te–Te) = 3.945 Å;
d_6(Mo–Mo between layers) = 7.276 Å;
α(Te–Mo–Te) = α(Mo–Te–Mo) = 80.74°;
β(Te–Mo–Te) = 83.10°;
γ(Te–Mo–Te) = 135.95°;
δ(Te–Te–Te) = 52.96°;
ϵ(Mo–Te–Te) = 100.59°.

It is interesting that in the thermal dissociation of molybdenum trisulphide or ammonium thiomolybdate products of composition MoX_{2+x}, or sometimes $Mo_{1-x}S_2$, are obtained under definite conditions[78,79,112]. x decreases as the decomposition temperature is raised. Such products are considered as subtractional solid solutions based on hexagonal MoS_2 with disorder in the crystal lattice: the higher the value of x, the more distorted the structure in the direction of axis c. Above 800° ordering of the structure occurs and stoichiometric molybdenum disulphide is obtained.

The molybdenum dichalcogenides exhibit semiconducting properties. The quality of different thermoelectric materials is compared by use of the figure of merit, which is calculated by the formula[113]:

$$Z=\frac{\alpha^2\sigma}{\kappa},$$

where α is the Seebeck coefficient, σ the electrical conductivity, and κ the thermal conductivity.

At the same time the efficiency of the thermoelectric element increases with the temperature of the hot junction[114].

TABLE 5. Electrical and thermoelectric properties of the molybdenum chalcogenides.

Compound	Electrical conductivity, Ω^{-1} cm^{-1}	Electrical resistivity, Ωcm	Seebeck coefficient, mV deg^{-1}	Thermal conductivity, t*, cm^{-1} deg^{-1}	Figure of merit, deg^{-1}	Type of conductivity	Reference
MoS_2	–	–	72.7 (mean in range 20–80°)	–	–	–	115
	$4.2–9.0 \times 10^{-3}$ (in range 183–500°)	–	–	–	–	p	120
	–	–	–	4.75×10^{-4}	–	–	119
$MoSe_2$	–	3.44×10^3 at 25° 4.76×10^6 at −196°	900	0.023	1.02×10^{-5}	n	73
	1.23×10^{-4} at 22° 2.30×10^{-4} at 62°	–	610–430 (in range 25–150°)	–	–	p	74
	–	20.0 at 100° 1.0 at 600°	−900 at 100° +190 at 600°	–	–	n- at 100° p- at 600°	118
$MoTe_2$	–	8.5×10^3 at 25° 1.34×10^6 at −196°	780	0.020	3.66×10^{-6}	n	73
	–	25.0 at 100° 0.1 at 600°	−360 at 100° −104 at 600°	–	–	–	118

* t is presumably g cal s^{-1} (Ed. of Translation).

Consequently, to obtain large thermoelectric effects, materials with a high Seebeck coefficient and low thermal conductivity, capable of retaining these properties at high temperatures, are required.

Table 5 gives the electrical and thermoelectric characteristics of the molybdenum chalcogenides.

Interesting structural and thermoelectric investigations were made with compositions of the systems $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ and $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$.[116] It was shown that compositions of the first system at $x \leq 0.65$ have a space group of type $CdCl_2$ (D^5_{3d}); after this there is a narrow two-phase region with approximately the same intensity for both types, and with $x > 0.8$ all the compositions crystallise in the space group of MoS_2 type (D^4_{6h}). The pyknometric and X-ray densities of compositions in the system were compared.

A structural study of the $W_xMo_{1-x}Se_2$ system showed a linear dependence of lattice parameters (a, c, c/a, ρ_{X-ray}) on x: with successive replacement of molybdenum by tungsten a decreases c increases (Table 6). All the compositions in this system crystallise with MoS_2-type structures.

The thermoelectric characteristics for the composition of these systems have been given. Since the conductivity mechanism in $MoSe_2$ is electronic (n type), but that in WSe_2 is hole (p type), the solid solutions of these compounds of different conductivity types show high electrical resistivity, due to compensation of two opposing conductivity mechanisms. $TaSe_2$ has a comparatively high electrical conductivity and is a metal-like conductor[73,117]. Brixner and Teufer[116] showed that by varying the concentration of the individual components in the compositions of the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system, the optimal values of the parameters in which an investigator is interested can be found.

TABLE 6. Lattice parameters of compositions of the $W_xMo_{1-x}Se_2$ system.

Composition	a, Å	c, Å	c/a	ρ_{X-ray}, g cm^{-3}	Unit-cell volume, Å^3
$MoSe_2$	3.289	12.930	3.931	6.959	121.128
$Mo_{0.85}W_{0.15}Se_2$	3.289	12.935	3.933	7.318	121.175
$Mo_{0.75}W_{0.25}Se_2$	3.288	12.941	3.936	7.560	121.157
$Mo_{0.65}W_{0.35}Se_2$	3.288	12.945	3.937	7.799	121.195
$Mo_{0.25}W_{0.75}Se_2$	3.287	12.965	3.944	8.754	121.308
WSe_2	3.286	12.976	3.949	9.353	121.337

Guennoc[77] stated that solid solutions corresponding to the general formula (Mo, W)(Se, Te)$_2$ with additions of niobium or tantalum can operate as thermoelectric materials at 200–400°.

There is great interest in investigating thermoelectric materials in the problem of obtaining substances with thermal conductivities as low as possible. As Ioffe and coworkers showed[121], this can be achieved by fusing the thermoelectric material with an isomorphous element or alloy. Then in the solid solution of two isomorphous crystals the short-range periodicity of the lattice is destroyed, which leads to considerable scattering of phonons. Such destruction of the short-range order of the crystal lattice of the material (while retaining the long-range periodicity) gives a marked decrease in thermal conductivity at very small change in mobility of the charge carriers, which leads to a considerable increase in the figure of merit.

Brixner and Teufer[116] attempted to obtain such alloys based on the $W_xMo_{1-x}Se_2$ system. The results of measuring the thermal conductivity of these compositions show that the thermal conductivity of an alloy of the two isomorphous substances WSe_2 and $MoSe_2$ is less than the thermal conductivity of either of its components and is least when half the tungsten atoms have been replaced by molybdenum.

Study of various alloys of the molybdenum dichalcogenides MoS_2, $MoSe_2$, and $MoTe_2$ with the structurally isomorphous tungsten chalcogenides and also with additions of metals of the neighbouring groups of the Periodic System (for example, niobium, tantalum, rhenium, etc.) for thermoelectric purposes is a future problem of the chemistry of the molybdenum chalcogenides.

The coefficient of thermal conductivity of molybdenite MoS_2 at 80°C is $\kappa = 4.75 \times 10^{-4}$ cal cm^{-1} deg^{-1} s^{-1}.[119] Since the thermal conductivity of semiconductors is of great importance for determining the usefulness and quality of a material, such data are of great interest.

In semiconductors the thermal conductivity is made up of the transfer of heat by waves of thermal motion of the

molecules of the lattice (or phonons) κ_{ph} and from the transfer of the energy of the free charges (or electrons) κ_{el}. However, phononic thermal conductivity plays the principal part, since for semiconducting materials the part of the thermal conductivity which is determined by the diffusion of electrons is negligible.

In semiconductors with carrier current of a single sign the electronic constituent of the thermal conductivity κ_{el} is determined by the Wiedemann–Franz law:

$$\kappa_{el} = \frac{k^2}{e^2} A\sigma T,$$

where k is the Boltzmann constant, e the charge of an electron, A a coefficient (= 2 when undegenerate), σ the electrical conductivity, and T the absolute temperature.

The value $\sigma = 4.3\ \Omega^{-1}\ cm^{-1}$ was found for molybdenite at $T = 353°K$, and the electronic thermal conductivity was calculated to be $\kappa_{el} = 0.0557 \times 10^{-4}$ cal cm^{-1} deg^{-1} s^{-1}.[119] Consequently the phononic thermal conductivity is $\kappa_{ph} = \kappa - \kappa_{el} = 4.75 \times 10^{-4} - 0.0577 \times 10^{-4} = 4.69 \times 10^{-4}$ cal $cm^{-1} \times deg^{-1}\ s^{-1}$, which is ~ 84 times the electronic thermal conductivity. However, it is clearly evident that lattice vibrations make the main contribution to the mechanism of the thermal conductivity of MoS_2.

The Debye temperature for MoS_2 is $\Theta = 209°K$.[119] The dielectric constant of MoS_2 at -196°C is $\epsilon = 7.6$.[122]

The electrical conductivity of molybdenite has been measured over a wide range of temperatures: from 100° to 500°K.[110] It was shown that the electrical conductivity along the basal plane, that is, in the direction perpendicular to the c axis ($\sigma_\perp$), is approximately 10^3 times greater than that in the direction parallel to the hexagonal axis ($\sigma_\parallel$). Ohm's law is obeyed on passing current in the two directions at ~ 420°K, but at room temperature Ohm's law is not obeyed in either direction (Fig. 8).

Measurements of the electrical conductivity in molybdenite crystals at high temperatures show the electronic nature of the conductivity[110]. The mechanism of electronic conductivity in MoS_2 is confirmed by the measurements of the surface conductivity of thin plates of molybdenite cleaved off natural crystals. The surface conductivity rises in an atmosphere of ammonia vapour and falls in an atmosphere of nitric acid vapour. Apparently the adsorption of the vapours of these substances changes the mobility and concentration of the charge carriers[123–125].

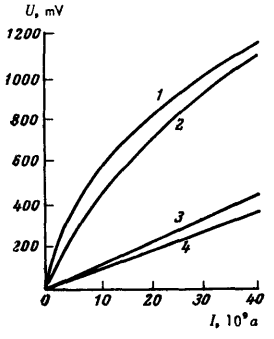


Fig. 8. Dependence of the electrical conductivity of crystals of molybdenite on the stress[110]:
1) $\sigma_\parallel$ at room temperature; 2) $\sigma_\perp$ at room temperature; 3) $\sigma_\perp$ at ~ 420°K; 4) $\sigma_\parallel$ at ~ 420°K.

An investigation of the magnetic properties of MoS_2 confirms the presence of free electrons in the planes of the crystal. Considerable anisotropy (~ 72%) of the diamagnetism of molybdenite crystals was found: the susceptibility in the direction parallel to the hexagonal axis is $\chi_\parallel = 87.1 \times 10^{-6}$, and that in the direction perpendicular to this axis is $\chi_\perp = -44.3 \times 10^{-6}$.[107] Such an increase in diamagnetism in the direction perpendicular to the basal plane is due to the presence of free electrons, which are completely free in the plane of the base but have restricted mobility in the perpendicular direction. A similar diamagnetism of free electrons was found earlier for graphite[126,127].

Still more conclusive facts in support of this were obtained on measuring the magnetic properties of MoS_2 at various temperatures[108,109]. It is known that the susceptibility of free electrons is very sensitive to a change in temperature. With weak magnetic fields and not very low temperatures the diamagnetic susceptibility of the electron gas is[128]:

$$(\chi_e)_{dia} = \frac{nN\mu_B^2}{3kT},$$

where n is the number of free electrons per unit volume, N Avogadro's number, μ_B the Bohr magneton, k the Boltzmann constant, and T the absolute temperature.

The results of measurements of the temperature dependence of the susceptibility of molybdenite shows that the observed electron susceptibility of MoS_2 equals the diamagnetic susceptibility of free electron gas having an electron density of 0.3 electron per atom[108]. The temperature dependence of the diamagnetic anisotropy resembles the behaviour of graphite single crystals on heating[129].

The above suggests that in MoS_2, where the bond between the molybdenum and sulphur atoms is covalent, bonds of partly metallic character are formed along the basal plane, which agrees well with the results of electric and magnetic measurements of molybdenite crystals. For $MoTe_2$ the specific magnetic susceptibility is 0.345×10^{-6}.[61]

The effect of pressure on the electrical resistivity of MoS_2 has been investigated[130]. At $P = 20$ kbar and 296°K the resistivity of MoS_2 is 300–600 Ω cm. The resistivity decreases considerably with increase in pressure. Phase transformations were not observed up to 500 kbar.[130]

The optical properties of single crystals of MoS_2 [131–134] and $MoTe_2$ [135] have been studied, using very thin crystals (thickness: MoS_2 100 Å, $MoTe_2$ 200–1000 Å), obtained by splitting at cleavage planes. The optical spectra give valuable information about the bond energies and the excited state in the crystal. Conclusions about the covalent nature of the bonds in crystals of MoS_2 and $MoTe_2$ can be drawn from the spectra.

The molybdenum dichalcogenides are rather stable. For a long time the melting point of molybdenite was thought to be 1185°.[97] Zelikman and Belyaevskaya[51] found, by subjecting MoS_2 to rapid and short-time (2–3 min) heating, that specimens of MoS_2 start to melt at 1650–1700°C; this is accompanied by intensive decomposition with formation of a lower sulphide. However, Cannon[136] considers that this temperature is depressed owing to the reaction of the material with the graphite vessel used in the work[51]. On

heating specimens of MoS_2 in molybdenum crucibles in a vacuum, he[136] observed fusion on heating for 10 min at 1800° ± 20°C. He concluded that if MoS_2 obeys Tammann's rule, that is, the temperature for the start of appreciable sintering is approximately one-half *Tf*, then the melting point of MoS_2 must be ~2375°C.

In view of the contradictory data[51,136], the problem of the melting point of MoS_2 requires further investigation. However, it is clear that the above experimental results[51,136] are erroneous. As shown recently[56], when heated in a vacuum MoS_2 decomposes before melting, and when heated for a sufficient time even at 1280°C the dissociation of MoS_2 is accompanied by the formation of the sesquisulphide. At 1400°C the thermal decomposition of MoS_2 goes to metallic molybdenum[137]. On heating MoS_2 to a temperature above 1000°C, sintering of the material occurs and the surface of the MoS_2 is covered with a dense, difficultly permeable scale, which retards the dissociation[56,138]. This may be the reason for the erroneous results[136].

Careful examination of Zelikman and Belyaevskaya's results[51] suggests that the dissociation of MoS_2 in an inert medium also starts before 1350°C, as is shown by the chemical analysis of the products. Although their X-ray diagrams do not differ from that of the original disulphide it is evident from the chemical analysis that the products of the heating are appreciably enriched in molybdenum. Probably there is formation of a phase of type $Mo_{1+x}S_2$, based on the hexagonal MoS_2 type which has been described[56]. The authors[51] concluded that MoS_2 had no phase transformations up to 1350°C according to the results of the heating curves recorded with a pyrometer; this is evidently due to a very small rate of dissociation of molybdenum disulphide and consequently an insignificant thermal effect.

It must be emphasised that both the formation and the dissociation of the chalcogenides take place rather slowly, especially at low temperatures. This must be remembered in considering various equilibria in chalcogenide systems. This is why the published results[51,136] obtained in short-time heating should be regarded critically.

$MoSe_2$ and $MoTe_2$ dissociate with formation of lower chalcogenides when heated in a vacuum to 1170° and 750°C respectively[61,62].

The thermodynamic characteristics of MoS_2 are known[139-141]. Smith and coworkers[140] carried out calorimetric measurements and calculated some thermodynamic quantities for solid MoS_2 at low temperatures (Table 7).

The free energy and heat of formation of MoS_2 from the elements have been calculated[53]:

$$\Delta G^\circ_{298} = -78\,420 \text{ cal}, \qquad \Delta H^\circ_{298} = -91\,340 \text{ cal}.$$

TABLE 7. Smoothed values of the molar thermodynamic functions for solid MoS_2.

T, °K	C_p, cal × ×mole^{-1} deg^{-1}	S°_T, e.u.	$\frac{-(G^\circ_T-H^\circ_0)}{T}$, cal mole^{-1} × × deg^{-1}	$\frac{(H^\circ_T-H^\circ_0)}{T}$, cal mole^{-1} × × deg^{-1}
20	0.28	0.140	0.055	0.085
30	0.63	0.315	0.110	0.205
40	1.12	0.560	0.190	0.37
50	1.74	0.870	0.290	0.58
60	2.46	1.25	0.420	0.83
70	3.24	1.69	0.570	1.12
80	4.07	2.17	0.740	1.43
90	4.97	2.71	0.930	1.78

The molybdenum dichalcogenides are quite stable in air at room temperature but the finely-divided ditelluride is reported[76] to oxidise slowly.

On heating in air all the compounds burn to form MoO_3 and the corresponding chalcogenide oxide.

Since the oxidation of MoS_2 is widely used industrially for the treatment of molybdenite concentrates the kinetics of the oxidation of molybdenite at 400°, 500°, and 600°C has been studied[142,143]. It is thought[142] that within the range 400–600°C molybdenum disulphide is oxidised by oxygen to MoO_3, without the stage of formation of MoO_2. The mechanism of the oxidation of MoS_2 is probably:

$$MoS_2 + O_{2ads} \rightarrow MoS_2O + O,$$
$$MoS_2 + O_{2ads} \rightarrow MoSO_2 + S,$$
$$MoS_2O + O_{2ads} \rightarrow MoO_3 + 2S,$$
$$MoSO_2 + O_{2ads} \rightarrow MoO_3 + SO.$$

The initial act of reaction of MoS_2 with oxygen consists in the adsorption of oxygen molecules on the surface of the molybdenite. The formation of intermediate compounds of the oxide sulphide type is facilitated by the presence on the surface of the MoS_2, which is a semiconductor, of active centres with free valencies[144]. Above 600°C the secondary reaction of MoS_2 with the MoO_3 occurs, with formation of MoO_2.[142]

Heating in the absence of air gives different results, depending on the conditions of the experiment, which has already been discussed in detail above. As the results of different authors show, the question of the thermal dissociation of molybdenum dichalcogenides under different conditions is still not completely clear. Taking into account that most of these investigations are comparatively old, the problem of the behaviour of the molybdenum chalcogenides on heating remains unsolved and requires repetition of the experiments on a contemporary level.

According to Wendehorst's results[60], when heated in hydrogen, molybdenum diselenide does not give a lower selenide but is slowly reduced to the metal if the temperature is high enough.

Not one of the chalcogenides of the MoX_2 type is converted into a compound richer in chalcogen by heating with the chalcogen concerned[42-44,60,61]. Apparently compounds of the MoX_3 type are always thermodynamically unstable, as Biltz and Köcher[145] found for MoS_3, and the reaction $MoX_3 \rightarrow MoX_2 + X$ must be considered irreversible. However, there have been reports of the possibility of obtaining molybdenum trisulphide by the reaction of the disulphide with elemental sulphur[53].

MoS_2 is rather inert chemically. It is insoluble in boiling water. It reacts with the halogens as follows. On gentle heating, fluorine reacts with crystalline MoS_2 with ignition[42-44]. Below 400°C, chlorine reacts very slowly, forming $MoCl_5$ and the intermediate compounds $MoSCl_2$ and $MoOCl_4$. The chlorination of the disulphide with $Cl_2 + 3O_2$ mixture is thermodynamically more favourable, MoO_2Cl_2 being formed. In the presence of nitrogen oxides or nitric acid fumes the reaction is appreciable even at 170°C.[40] Bromine vapour reacts very slowly; the composition of the reaction products has not been established[146].

When SF_4 is used as a fluorinating agent, molybdenum can be oxidised to the quinquevalent state. Thus the reaction of SF_4 with MoS_2 at 350°C gives MoF_4[147] and with the mixture 2NaF + MoS_2 at 400° the compound $NaMoF_6$ is formed[148].

$SOCl_2$ does not react with MoS_2 even on heating for a few days[149]. Gaseous hydrogen chloride does not react with MoS_2 at temperatures up to red heat[42-44]. Liquid anhydrous hydrogen fluoride also does not react with the disulphide in the temperature range -18° to -7°C.[150]

However, MoS_2 is completely soluble in *aqua regia*, is decomposed in boiling concentrated sulphuric acid, and is oxidised to MoO_3 in nitric acid.

Aqueous solutions of acids, alkalis, and salts react differently with molybdenum disulphide. Alkali solutions with pH 10 oxidise and dissolve MoS_2 most actively[151]. In acid, neutral, and weakly alkaline solutions the oxidation of MoS_2 is weaker[151]. This is confirmed by an investigation[152] of the anodic dissolution of molybdenite in 0.5–5% solutions of H_2SO_4 and NaOH. The results show that MoS_2 is almost insoluble in these solutions in the absence of current, but is electrochemically soluble. The rate of dissolution increases with increase in current density, increase in NaOH concentration, and decrease in H_2SO_4 concentration. Probably oxidation takes place by the following reactions:

$$MoS_2 + 9O + 3H_2O \rightarrow 2H_2SO_4 + H_2MoO_4,$$

$$MoS_2 + 9O + 6NaOH \rightarrow 6Na^+ + 2SO_4^{2-} + MoO_4^{2-} + 3H_2O.$$

In aqueous solutions of 3 *N* Na_2CO_3 and 8 *N* HCl, MoS_2 is almost insoluble up to 90°C.[153]

The reaction of finely dispersed MoS_2 with water vapour at 200–500°C showed that at 200–300°C a little hydrogen and traces of sulphur dioxide are formed, but at 400–500°C traces of hydrogen and measurable amounts of sulphur dioxide. The gaseous products of the reaction were identified mass-spectroscopically[154].

The reaction of MoS_2 with MoO_3 was studied at 400–700° in an inert atmosphere, in a vacuum, and in SO_2 at atmospheric pressure[155-159]. MoS_2 reacts with MoO_3 to form molybdenum dioxide:

$$MoS_2 + 6MoO_3 \rightarrow 7MoO_2 + 2SO_2.$$

Reaction starts even at 400°C and the reaction rate rises rapidly with the temperature. Below 550°C the reaction products contain (in addition to MoO_2) the intermediate oxide Mo_4O_{11}, which is formed by the reaction:

$$MoS_2 + 12MoO_3 \rightarrow 2Mo_4O_{11} + 5MoO_2 + 2SO_2.$$

This oxide reacts further with the disulphide to form MoO_2:

$$2Mo_4O_{11} + MoS_2 \rightarrow 9MoO_2 + 2SO_2.$$

The results were confirmed by chemical and X-ray analyses.

Solid molybdenum disulphide readily reacts with the alkali and alkaline earth metals dissolved in liquid ammonia[160]. From solutions which contain the alkali metals in excess, black homogeneous compounds of the composition:

$$Cs_{0.5}MoS_2;\ K_{0.6}MoS_2;\ Na_{0.8}(NH_3)_{0.2}MoS_2;\ Li_{1.1}(NH_3)_{0.6}MoS_2,$$

can be separated after filtration, washing with liquid ammonia, and removing the remaining ammonia in a vacuum at room temperature.

The last two compounds do not lose ammonia when held for a long time in a vacuum at room temperature.

All the compounds are extremely sensitive to heat and air. The potassium and caesium compounds glow in air, and react readily with water to form the sulphide and hydrogen, which contains a very slight amount of hydrogen sulphide. On heating in a vacuum a slight amount of alkali metal is detached. At 100°C the preparations decompose appreciably and give new compounds, which correspond to the polarised form of $K^+(MoS_2)^-$ type.

Such compounds are considered as interstitial compounds, in which a layer of alkali or alkaline earth metal is introduced between the molybdenum disulphide layers. The distance between the layers increases considerably with an insignificant increase in the Mo–Mo interatomic distances.

The reaction of liquid ammonia with MoS_2 has been described[161]. Under the influence of the NH_4^+ and NH_2^- ions present in liquid ammonia, at low temperatures there is a disturbance of the layers in molybdenum disulphide, as was shown by recording infrared spectra of thin layers of MoS_2. Adsorption of ammonia leads to far-reaching changes in the mechanical properties of the solid.

The adsorption of argon, krypton, and organic substances on MoS_2 has been studied[162-164].

Carbon dioxide and sulphur dioxide gases do not react with molybdenum disulphide at low temperatures; the reaction only takes place above 500°C and at ~ 800°C there is a sudden increase in the reaction rates. The final product of these reactions is MoO_2.[165]

The main reaction of MoS_2 with carbon dioxide is expressed by the following equation:

$$MoS_2 + 6CO_2 = MoO_2 + 2SO_2 + 6CO.$$

Apart from these products, a little COS, S, and MoO_3 are obtained, due to side reactions taking place.

The reaction of the disulphide with sulphur dioxide follows the equation:

$$MoS_2 + SO_2 = MoO_2 + 3S,$$

which is almost complete at 1100°C.

The molybdenum chalcogenides, like those of other transition metals, are capable of forming ternary phases. Heating MoS_2 with the sulphides of iron group metals at 500–1300°C in an inert atmosphere (argon or nitrogen) or in hydrogen sulphide leads to the formation of a new class of stable crystalline compounds of type $AMoS_y$, where A is the iron-group metal (Fe, Co, Ni) and y = 2.5–3. The $FeMoS_{2.5}$ crystals have strongly expressed ferromagnetic properties[166].

A thermoelectric material of composition Ag_2MoX_3 (where X is selenium or tellurium) is obtained by reaction of the components at 700–1100°C.[167] However, a study of the solubility of copper and silver in molybdenum disulphide by heating the components at 800°C in evacuated ampoules did not give positive results. Compounds similar to Cu_xNbS_2 ($\sim 0.6 \leq x \leq 0.8$) could not be prepared for molybdenum disulphide[168].

In the coprecipitation of thallium with molybdenum trisulphide, the formation of the compound $TlMoS_2$, which is amorphous to X-rays, was established[169,170].

A series of mixed chalcogenides is known for molybdenum[171].

There is only limited information about the chemical behaviour of $MoSe_2$. It is insoluble in hot concentrated hydrochloric acid, but is readily soluble in hot concentrated sulphuric acid with liberation of sulphur dioxide. The

diselenide is completely insoluble in ammonia, and in alkali metal sulphides and selenides, and dissolves very slightly on prolonged boiling in concentrated alkalis[60].

The chemical properties of $MoTe_2$ have been studied even less. Water and hydrochloric and sulphuric acids do not react with $MoTe_2$ on boiling, whereas dilute nitric acid breaks down the ditelluride even in the cold[61].

Finely ground $MoTe_2$ powder is gradually oxidised by atmospheric oxygen at room temperature[76].

4. HIGHER CHALCOGENIDES OF MOLYBDENUM

A. Molybdenum(V) Chalcogenides

Only the sulphide and selenide of molybdenum(V) are known. Mawrow and Nikolow[172] obtained Mo_2S_5 and described its properties. Their method of preparation will now be described.

A solution of 5 g $(NH_4)_2MoO_4$ in 150 ml water was mixed with sufficient concentrated sulphuric acid to give a concentration of 20% H_2SO_4. The acid solution was reduced with metallic zinc to give a dark red coloration, then diluted with an equal quantity of water, filtered, and saturated with hydrogen sulphide. The precipitate which separated was filtered off, washed with hot water until an acid reaction was no longer obtained, and then washed with alcohol. The precipitate was washed to remove free sulphur by repeatedly shaking with carbon disulphide, and was washed on the filter with ether. The moist brown-black precipitate was dried at 68–75°C, whereupon it became dark brown. The compound corresponded to the formula $Mo_2S_5.3H_2O$. Sufficiently pure preparations are obtained when the product is well washed with hot water (to give a negative reaction with H_2SO_4) and carbon disulphide and dried for a long time on a water-bath at 68–75°C in the finely dispersed state.

$Mo_2S_5.3H_2O$ is completely insoluble in water. On boiling with alkalis or ammonia it dissolves with a brown-yellow coloration and liberation of hydrogen sulphide. $Mo_2S_5.3H_2O$ dissolves well in alkali metal sulphides, especially on heating. On cooling, an orange-yellow precipitate separates from the solutions. When heated with concentrated hydrochloric acid the compound dissolves, with a green coloration, but with concentrated sulphuric acid a red-yellow liquid is formed, which gradually turns green with separation of free sulphur and sulphur dioxide.

When heated in air up to 135–140° $Mo_2S_5.3H_2O$ loses one molecule of water and gives the compound $Mo_2S_5.2H_2O$. However, on further heating to 195–200° in air, this compound is partly oxidised.

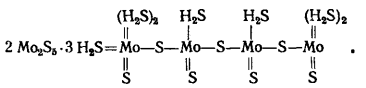
Very careful heating of $Mo_2S_5.3H_2O$ in a stream of carbon dioxide gives brown-black Mo_2S_5. The heating takes place so that the tip of the flame of a burner did not touch the tube which contained the compound.

The sulphide obtained in this way sometimes contains a slight amount of water of hydration, which is very difficult to remove, since at a higher temperature the compound is oxidised and then burns, but heating in a current of hydrogen, even at a very low temperature, leads to partial reduction to MoS_2.

In an attempt to dehydrate $Mo_2S_5.3H_2O$ by heating in a current of hydrogen sulphide the authors[172] obtained a brown-black compound corresponding to the formula $2Mo_2S_5.3H_2S$, which is evidently formed as a result of the replacement of water by hydrogen sulphide by the equation:

$$2(Mo_2S_5\cdot 3H_2O) + 3H_2S \rightarrow 2Mo_2S_5\cdot 3H_2S + 6H_2O.$$

The following structural model was proposed for this substance:



The compound is insoluble in water and hydrochloric acid, very difficultly soluble with a green coloration on boiling in sulphuric acid, and on boiling with alkalis and alkali metal sulphides it dissolves to give a yellow solution and separation of a dark green mass, which turns blue in air.

Wendehorst[60] obtained the molybdenum(V) selenide similarly. The precipitate of selenide is decomposed during drying, even in a stream of nitrogen, therefore it is analysed moist. The atomic ratio Mo : Se = 2 : 5 shows that the material obtained is molybdenum(V) selenide.

In its chemical properties the selenide is reminiscent of the corresponding sulphide, but even more unstable. On dissolution in alkalis, sulphides, and acids there is an intense coloration of the solutions.

B. Molybdenum(VI) Chalcogenides

The oldest method for obtaining MoS_3 and $MoSe_3$ consists in the decomposition of solutions of thio- and seleno-molybdates respectively with acids.

Thus Berzelius[21] first obtained a dark brown precipitate of MoS_3 by saturating with hydrogen sulphide a concentrated solution of alkali metal molybdate and then decomposing the thiomolybdic acid which was formed. $MoSe_3$ was obtained similarly[173].

Wendehorst[60] obtained $MoSe_3$ by saturating with hydrogen selenide a solution containing 5 g $(NH_4)_2MoO_4$ in 10 ml conc. sulphuric acid and 50 ml water. The excess of H_2Se was removed with a stream of nitrogen. The black fine-grained precipitate of $MoSe_3$ was washed successively with ice water, alcohol, and ether, and dried in a stream of nitrogen with slow heating.

The MoS_3 and $MoSe_3$ thus obtained always contain an excess of the chalcogen[60,174,175]. To obtain the sulphide in a purer form, an aqueous solution of pure thiomolybdate — for example, ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$ — is first obtained, which is then decomposed by the action of acid (for example, sulphuric acid). A method for obtaining pure solutions of H_2MoS_4 by passing dilute solutions of $(NH_4)_2MoS_4$ through a column with an anion-exchange resin in the H^+ form[176] is interesting.

The so-called "crystalline"‡ molybdenum trisulphide is obtained as fine gleaming black leaflets, resembling graphite, from salts of thiomolybdenic acid with some organic compounds — for example, that with piperazine, $C_4H_{10}N_2.H_2MoS_4$ — by decomposing them with hydrochloric or acetic acid[177].

Molybdenum trisulphide is obtained in the high-temperature reaction of KCNS with MoO_3.[178–181]

‡ Reported[78] to be amorphous to X-rays.

Another method of obtaining MoS_3 by dry means is the thermal decomposition of ammonium tetrathiomolybdate in the temperature range 190–200°C in a vacuum or inert medium[78,79,182].

It has been noted[79,112] that during the decomposition of $(NH_4)_2MoS_4$, stoichiometric MoS_2 is obtained at ~1000°C, but below 800°C the homogeneous phases MoS_{2+x} (x = 0–0.5), which have a distorted MoS_2 structure, are produced. The distortion grows with increase in x in the direction c but the lattice parameter a remains constant. Measurement of the density of such products shows that they must be considered as MoS_2 with insufficient metal, that is, they are best given the formula $Mo_{1-x}S_2$.[79]

In any of the above methods the molybdenum trisulphide obtained always contains some excess of sulphur and corresponds to the formula MoS_{3+x}, where $0 < x < 1$ and depends on the method of preparation: the value of x in the wet method reaches 0.7; in the dry method it is less[78].

Such compounds are considered either as polysulphides, whose composition is expressed, for example, by the formulae $MoS_3.S_2$ or $MoS_3.S_3$,[183] or as phases of variable composition based on MoS_3 with the addition of a certain amount of chemically unbound sulphur[78].

However, it is maintained[184–188] that molybdenum trisulphide with composition corresponding accurately to the formula $MoS_3.2H_2O$ can be obtained. For this, first 15 N ammonium sulphide or 2 N sodium sulphide is prepared by saturating the corresponding hydroxide with hydrogen sulphide below room temperature and then using the reagent obtained to treat ammonium molybdate solution. The solution of thiosalt $(NH_4)_2MoS_4$ formed is decomposed by an excess of dilute (6 N or 2 N) hydrochloric acid until completely decolorised and molybdenum sulphide is precipitated. The mixture is heated to boiling, gives a precipitate, and is filtered, the precipitate being washed successively with water, alcohol, ether, and then air is sucked through for 15 min. The precipitate, dried for 30 min in a vacuum dessicator, is reported to accurately correspond to the formula $MoS_3.2H_2O$, which enables us to use this method to determine molybdenum quantitatively. It is possible to obtain $MoSe_3$ by a similar procedure[189,190].

The thermal dissociation of air-dry preparations of $MoS_3.2H_2O$ proceeds as follows (Fig. 9). At 80–120°C the loss in weight is 1–2%. At 170–290°C the loss in weight corresponds with two molecules of water. At 290–390°C anhydrous MoS_3 is stable and at higher temperatures it is oxidised to MoO_3, which sublimes at 800°C.[187]

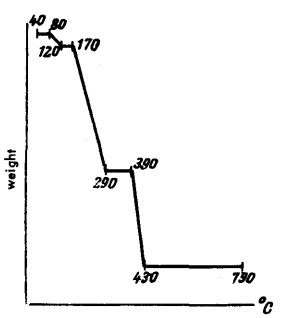


Fig. 9. Thermal dissociation curve of $MoS_3.2H_2O$.[187]

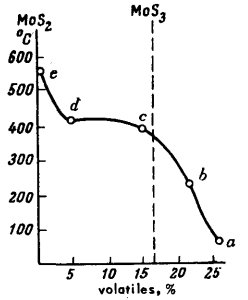


Fig. 10. Decomposition polytherm of a specimen of molybdenum trisulphide[78].

On heating in a non-oxidising atmosphere (for example, in nitrogen), molybdenum(VI) chalcogenides disproportionate into the dichalcogenide and the free chalcogen. The thermal decomposition of MoS_3 in nitrogen has the following result[78]: on heating a preparation of composition $MoS_{3+x}.yH_2O$ to 250°C there is a loss of hygroscopic and loosely bound water together with part of the sulphur in excess (Fig. 10, section a–b). Subsequently between 250° and 400°C sulphur in excess of the composition MoS_3 is removed, then the main mass of MoS_3 decomposes with simultaneous evaporation of sulphur formed during this decomposition (Fig. 10, section b–c–d). As a result, a new phase of variable composition is formed (with an excess of sulphur) based on MoS_2, which on further heating to 900–1000°C gradually loses sulphur and approaches molybdenum disulphide in composition (Fig. 10, section d–e).

Crystallisation of molybdenum disulphide has already started at 350°C, and when molybdenum trisulphide decomposes the disulphide produced crystallises as the hexagonal form. The suggestion[78] that the rhombohedral modification crystallises initially and changes into the more stable hexagonal modification as the temperature rises has not been confirmed[79].

The vapour pressure of sulphur on heating molybdenum trisulphide has been measured[80,191] between 350° and 500°C:

Temperature, °C:	355	390	418	475	480	500
Pressure, mmHg:	4.0	28.8	178.6	250	313	980

There is a difference of opinion about the reversibility of the process:[192]

$$MoS_3 \rightleftarrows MoS_2 + S.$$

For long it was thought that the decomposition of molybdenum trisulphide is reversible and that in the range 350–400°C there is an equilibrium with the disulphide[80]. However, Biltz and Köcher[145] showed the thermodynamic instability of molybdenum trisulphide. Despite this, some investigators tend to assume that it is possible to obtain the trisulphide by heating the disulphide with sulphur, if the reaction is carried out over several days at 400°.[53] Probably, such a reaction can be brought about by selecting suitable conditions.

In this connection, work[193] on the preparation of tantalum triselenide by direct synthesis from the elements is of interest. The authors[193] consider that with very slow cooling (~250 h) of the reaction products, heated to 820°C,

tantalum triselenide (which dissociates at 780°C) can be formed according to the equation:

$$TaSe_4 + Se \rightleftarrows TaSe_5.$$

They also obtained[193] tantalum trisulphide by heating the disulphide with sulphur for a week at 450–500°C.

It is interesting that tungsten trisulphide was obtained by heating the disulphide in sulphur vapour[194]. In view of the great similarity between the chalcogenides of molybdenum and tungsten, it seems quite probable that there would be similar results with the molybdenum chalcogenides.

On heating in hydrogen, the molybdenum(VI) chalcogenides are reduced to the dichalcogenides. In hydrogen selenide $MoSe_3$ does not change composition[60]. On heating in air, dry molybdenum triselenide is stable up to 410°C but at higher temperatures it is oxidised to MoO_3.[190]

The molybdenum(VI) chalcogenides are amorphous to X-rays. Evidently the chemical bond in molybdenum trisulphide is formed by d^2sp^3 hybridisation[104].

Molybdenum trisulphide readily dissolves in *aqua regia*, ammonium sulphide, and in alkali metal sulphides; it also dissolves in alkalis on heating[21]. On fusing the trisulphide with sodium carbonate the reaction is[37]:

$$MoS_3 + 2\,Na_2CO_3 \rightarrow Na_2MoO_2S_2 + Na_2S + 2\,CO_2.$$

Even in the cold molybdenum trisulphide dissolves in alkali metal sulphides and selenides, in concentrated alkali solutions, and even in concentrated ammonia. Molybdenum triselenide dissolves in concentrated sulphuric acid on heating[60].

It is interesting to note that dissolution of molybdenum triselenide, like the molybdenum(V) chalcogenides, is almost always accompanied by coloration of the solutions with a rich hue.

Molybdenum triselenide is a rather unstable compound. It reacts readily with many oxidants, but not with organic acids[60].

Molybdenum tritelluride has not yet been obtained. Apparently this compound is still more unstable than molybdenum triselenide.

The magnetic susceptibility of molybdenum trisulphide powder at 15°C is 0.361×10^{-6}.[195]

Oxide sulphides of molybdenum(VI) are known. MoO_2S is obtained by the reaction of MoO_2Cl_2 with Na_2S in alcoholic medium by the reaction[37]:

$$MoO_2Cl_2 + Na_2S \rightarrow MoO_2S + 2\,NaCl.$$

The MoO_2Cl_2 is obtained by passing dry gaseous hydrogen chloride over MoO_3 at 180°C; the alcoholic solution of the oxide chloride is kept in an atmosphere of carbon dioxide. The brown-black precipitate of MoO_2S, which resembles MoS_3, is filtered off, washed well with water (until there is no alkaline reaction), and dried in a vacuum.

There has been a report[196] of the preparation of $MoOS_2$ by the thermal dissociation of $(NH_4)_2MoO_2S_2$ in nitrogen at 300–400°C. As was found later, the decomposition of ammonium oxothiomolybdate under these conditions does not give an oxide sulphide[68]. The final product of the reaction is molybdenum disulphide with MoO_2 as impurity. Romanowski[68] has confirmed this not only by chemical analysis (which was used in the earlier work[196]) but also by X-ray and thermographic studies.

The oxide sulphides $MoO_3.2MoS_3.9H_2O$ and $MoS_3.5MoO_3.6.5H_2O$ are also known[39]. The method of obtaining these compounds consists in the reaction of solutions of Na_2MoO_4 and Na_2S followed by neutralisation with hydrochloric acid to pH 4.5. Then the mixture is heated to 90°C and held there for an hour with constant stirring, after which the solution and precipitate are kept another 12 h in a thermostat at 25° ± 0.1°C. The compounds are washed with alcohol and ether and dried at 140°C.

Particular note should be made that in these preparations the atomic ratio Mo : S plays an important part. Thus a pale brown oxide sulphide of composition $MoO_3.2MoS_3.9H_2O$ is obtained at Mo : S = 1 : 2 and 1 : 1 and the green $MoS_3.5MoO_3.6.5H_2O$ ratio at Mo : S = 2 : 1, 1.75 : 1, and 1.5 : 1. At Mo : S = 1 : 3 or over, MoS_3 is formed.

The oxide sulphides $MoO_2S.3H_2O$ and $MoOS_2.3H_2O$ are obtained by saturating a molybdate solution at pH 8.6 with hydrogen sulphide for 30 min and 12 h respectively, washing the precipitate with alcohol, and drying. On heating them to 200°C almost all the crystallisation water is lost and at higher temperatures they start to decompose[38].

Oxide compounds have not been obtained for molybdenum triselenide.

Only two molybdenum chalcogenide halides have been obtained: $Mo_5S_8Cl_9$ and $MoSCl_2$. The first of these is obtained on passing S_2Cl_2 vapour in a gentle stream of carbon dioxide over incandescent molybdenum powder. $Mo_5S_8Cl_9$ is formed as a red-brown amorphous sublimate, stable in air. It is insoluble in water and alkalis but dissolves completely in concentrated nitric acid[41].

$MoSCl_2$ was observed in the products of the chlorination of molybdenum disulphide at ~ 400°.[40]

Sulphides richer in sulphur than molybdenum trisulphide have been described[21,197,198]. Thus sulphides of the approximate composition MoS_4 and MoS_6 are obtained during the decomposition of alkali metal thiomolybdates with acids (hydrochloric or sulphuric). The compounds are insoluble at ordinary temperatures in water and acids but dissolve in alkalis and alkali metal sulphides. The authors[198] also regard such higher sulphides as anhydrides of perthio-acids of molybdenum. However, in view of insufficient experimental facts, the physicochemical properties of these products have hardly been studied at all and the homogeneity of the phases has not been established.

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Transition metal chemistry is now developing very rapidly. A series of new facts have now been obtained which are interesting not only from the practical aspect but are also of great importance theoretically. Therefore the chalcogenides of such a typical transition metal as molybdenum are undoubtedly of theoretical interest and their detailed study allows us to hope for new results of practical importance.

Study of the electrical, thermoelectric, magnetic, thermodynamic, and other properties of the transition metal chalcogenides has shown that "transition metal–chalcogen" systems are extremely complex. The tendency of chalcogenides to form compounds of non-stoichiometric composition has set the task of finding the reason for this departure, since even insignificant changes in composition lead to essential changes in some of the physical properties. Since the non-stoichiometry of the compounds is

the result of defects in the crystal lattice, the investigation of the chalcogenides is directed first to the determination of the crystal structure, to revealing the fine character of the interconnection between chemical impurities and lattice defects, and between the structure of the molecule and the physical properties of the substance.

The crystal structure of the molybdenum chalcogenides has been studied most fully only for the molybdenum(IV) compounds. However, the polymorphism of MoS_2 and the various interpretations of this phenomenon again emphasise the insufficiency of our knowledge in this region.

The information about the structure of Mo_2S_3 is little and contradictory. The structural study of the lower molybdenum selenide and telluride is restricted to the powder method. Therefore detailed structural investigation of the lower chalcogenides of molybdenum is one of the first tasks.

Data about the non-stoichiometric nature of the phases in the molybdenum–chalcogen systems confirms the necessity for a thorough study of the non-stoichiometric molybdenum chalcogenides.

The detailed determination of the structure of the compounds and the lattice defects, and of the regions and conditions of existence of the phases, requires modern physicochemical methods for the study of equilibrium diagrams. The volatility of the components and the decomposition of the compounds before melting create additional difficulties in the study of molybdenum–chalcogen systems. However, without knowledge of the physicochemical data it is impossible to correctly select methods of preparation especially in making materials suitable for semiconductor purposes. Therefore future investigation of the molybdenum chalcogenides should be directed above all to the detailed study of the physicochemical properties of systems which include these compounds.

Since the molybdenum dichalcogenides are widely used as thermoelectric materials their study in this direction is extremely promising. Good thermoelectric properties can be expected from various combinations of MoS_2, $MoSe_2$, and $MoTe_2$ with other transition metal chalcogenides.

We consider that the known molybdenum chalcogenides, oxide chalcogenides, and chalcogenide halides are only the first representatives of this class of materials. Molybdenum is known to be a rather reactive element. The variety of its chemical properties, expressed above all in its ability to vary its valency, suggest that the systematic investigation of the molybdenum chalcogenides will lead to a whole series of new compounds, not only of theoretical interest but also important for practical use.

Compounds in which the molybdenum has a lower valency should be especially reactive. The oxidation of molybdenum to higher valencies uncovers wide prospects for the preparation of new mixed compounds.

The different molybdenum compounds show greatest stability at different oxidation states. Thus in the compounds with oxygen or fluorine the most stable valency of molybdenum is six (MoO_3 and MoF_6); with chlorine, five ($MoCl_5$); with sulphur, four (MoS_2); with bromine and iodine, the most stable valency is apparently even lower. Such a selectivity of the valency of molybdenum in its compounds with different non-metals can be used to obtain new stable mixed compounds with a different degree of oxidation.

The chemical properties of the molybdenum chalcogenides have been quite inadequately investigated. The behaviour of the compounds in alkalis and acids has been described only qualitatively. Such an interesting problem as the solubility in salts has hardly received any attention. And yet here it is possible to obtain interesting results, to find possible paths for making new compounds, to find mechanisms for some reactions of molybdenum which are important to chemists.

There is great interest in carrying out the reactions in non-aqueous solvents. Such solvents as liquid ammonia, sulphur dioxide, dinitrogen tetroxide, nitrosyl chloride, hydrogen fluoride, bromine, interhalogen compounds, etc. unconditionally give rich material for theoretical investigations and allow a preparative route to be found for compounds with specially intended specific properties.

The study of the behaviour of the molybdenum chalcogenides on heating acquires special value in connection with the possibility of using them in thermoelectric assemblies. Therefore extensive thermographic analysis of the molybdenum chalcogenides in various media is urgently required.

What has been stated undoubtedly does not exhaust all the tasks which are presented by the chemistry of the molybdenum chalcogenides. However, the problems listed are the most pressing and their solution can be expected to give promising theoretical and practical information.

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KINETICS OF RECOMBINATION AND DISPROPORTIONATION REACTIONS OF ALKYL RADICALS

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The present review is an attempt to collect and systematise information from numerous Russian and non-Russian papers on the kinetic study of recombination and disproportionation reactions of free radicals.

Recombination and disproportionation of alkyl radicals

$$R_1+R_2- \begin{cases} \longrightarrow R_1R_2 & (1) \\ \longrightarrow P+O, & (2) \end{cases}$$

(R_1 and R_2 are alkyl radicals, P is a paraffin molecule, and O is an olefin molecule) are the main types of reactions in which chains are broken, or free valencies disappear, in numerous organic reactions that proceed by a radical chain mechanism in the gas or liquid phase. On the other hand, these reactions are thermodynamically linked with the dissociation of alkanes and the molecular dismutation of alkanes and alkenes, which are possible routes to radical initiation in conversions of hydrocarbons at high temperatures. Actually, the radical chain mechanism results from the competition between these reactions and chain-propagation reactions.

In the experimental study of substitution reactions

$$R+M \rightarrow RH+R_1, \quad (3)$$

the difficulty of setting up an experimental model of reaction (3) is encountered, since under experimental conditions with sufficiently complicated radicals (beginning with C_2H_5), reactions (1) and (2) occur to a great extent, and these require virtually no activation energy. This makes difficult the determination of the absolute rate constant of reaction (3) from experimental results. However, the relative value of the rate constant of reaction (3) may be determined experimentally, when it is expressed in the form of the rate constants of the recombination k_1 and disproportionation k_2 of radicals. The rate of disappearance of radicals by recombination and disproportionation in reactions (1) and (2) is

$$W = (k_1 + k_2)(R)^2. \quad (4)$$

Eliminating the concentration of radicals (R) from Eqn. (4) and Eqn. (5) for the rate of reaction (3):

$$W_3 = k_3(R)(M), \quad (5)$$

we obtain the relation

$$\frac{k_3}{(k_1+k_2)^{\frac{1}{2}}} = \frac{W_3}{W^{\frac{1}{2}}(M)}. \quad (6)$$

Since the right-hand side of Eqn. (6) contains values that can be calculated from the experimental kinetic curves for the accumulation of products (RH, R_1R_2, P, O) and for the disappearance of M, the relative value of the rate constant of reaction (3) can be calculated from experimental results.

As will be seen, by comparing reactions of the same radical R with different molecules it is possible to determine the relative values of the rate constants of radical reactions (3) without finding the concentrations of free radicals (R), which up to now has presented considerable difficulties. The essential feature of this determination forms the basis of the now well developed method of competitive reactions[1,2]. In the simplest type in the method of competitive reactions we are concerned with competing reactions of the same order, for example

$$R + M_1 = RM_1, \quad (7)$$

$$R + M_2 = RM_2. \quad (8)$$

The ratio of the rate constants of reactions (7) and (8)

$$\frac{k_7}{k_8} = \frac{W_7(M_2)}{W_8(M_1)}, \quad (9)$$

is determined from experimental measurements of the reaction rates W_7 and W_8 and the concentrations of the molecules taking part in the reactions. If the value of one of the rate constants (k_7 or k_8) can be determined (or calculated) by some independent method, the absolute value of the other constant can be determined from Eqn. (9).

However, it is not always possible successfully to choose a suitable competing reaction, and then Eqn. (6) must be used to determine the absolute rate constant of reaction (3). The solution of this problem requires independent experiments to measure absolute rate constants of the radical recombination (1) and disproportionation (2) reactions; at present these experiments present serious difficulties and must be supplemented by theoretical calculations.

Experimental difficulties are one of the reasons for the view long held that radical recombination reactions occur with every collision[3]. It should be mentioned that even