The total volume of ethane which may be chemisorbed appears (by comparison of Figs. 3 and 5) to be a little under half the volume of ethylene which may be chemisorbed. This result suggests that hydrogen dissociated during the chemisorption of ethane cannot (at room temperature) migrate to class (B) sites.

Figure 6 confirms the view that the relatively slow exchange reaction of paraffins with deuterium is due to the strong chemisorption of hydrogen on all sites which might otherwise be accessible to the paraffin molecules.[12]

Preparation and Characterization of a New Crystalline Form of Molybdenum Disulfide

BY RONALD E. BELL AND ROBERT E. HERFERT

During an investigation involving preparation of a quantity of synthetic molybdenum disulfide, X-ray techniques were applied to evaluate purity where ordinary wet chemical methods could not be used. The X-ray examinations indicated diffraction patterns differing from the pattern of natural molybdenite. An intensive study by single crystal X-ray techniques revealed that instead of the customary hexagonal molybdenum disulfide structure a hitherto unreported rhombohedral form of the compound had been prepared.

Introduction

The synthesis of molybdenum disulfide by chemical means has been described by a number of early researchers.[1–9] Such various methods of preparation as that proposed by Berzelius,[1] wherein molybdenum trisulfide is decomposed by vacuum heating; or the method of Svanberg and Struve,[2] involving reaction of molybdenum trioxide with hydrogen sulfide gas at red heat; the procedure of heating molybdenum and sulfur in an iron tube as proposed by van Arkel[3]; the procedure of de Schulten,[4] in which molybdenum trioxide, sulfur and potassium carbonate are fused together; the method used by Milbauer,[5] wherein molybdenum dioxide reacted with molten potassium thiocyanate; finally, Lander and Germer deposited molybdenum disulfide coatings from molybdenum carbonyl in atmospheres containing rather critical ratios of hydrogen sulfide and carbon monoxide; are among those listed in the literature.

In these earlier experiments evidence that molybdenum disulfide had been prepared synthetically was based on chemical analysis and, in some cases, also on microscopic examination. Van Arkel[3] reported Debye–Scherrer patterns identical to those obtained with natural molybdenum disulfide for his synthetic product. Other than this, there are no references in which the crystal structure of synthetic molybdenum disulfide has been established by modern crystallographic techniques.

A quantity of molybdenum disulfide of a purity that was not readily obtained by purification of the natural product was required at the authors' laboratory for standardization as to physical, chemical and mechanical properties; therefore, it was proposed to prepare the material by chemical synthesis.

As will be shown, it developed that the material eventually prepared differed from natural molybdenum disulfide in that the crystal structure was not the same.

Experimental

Preparation.—After experimenting with several of the procedures described in the literature and finding them to yield products unsatisfactory for this investigation, the procedure described by de Schulten[4] was applied to the preparation of the subject material. Briefly, this procedure is as follows: four parts by weight of potassium carbonate (reagent grade) are fused with six parts of flowers of sulfur in a 250-ml. covered porcelain crucible at 675°, the reaction being conducted in a gas-fired furnace until evolution of sulfur dioxide is complete. The crucible and contents are removed from the furnace (taking precaution to avoid thermal shock) and allowed to cool. One part of sublimed molybdenum trioxide is added and the crucible is reheated at 900° for 30 minutes. Additional molybdenum trioxide is added in the same manner and the contents of the crucible are reheated at 900° after each addition, until a total of six parts by weight of molybdenum trioxide has been added. The entire mass is solidified, and the excess reagents and impurities are removed from the molybdenum disulfide by prolonged boiling with dilute ammonia, followed by washing with distilled water, boiling for a short time (20 to 30 min.) in dilute hydrochloric acid, and finally, by thorough washing with water, alcohol and ether. The material is then vacuum dried at 75°. The above treatment will not remove the MoO_2 impurity.

Purification.—The chemical reaction involved in de Schulten's method for synthesizing molybdenum disulfide is believed to proceed in two steps

$$2MoO_3 + S \longrightarrow 2MoO_2 + SO_2 \qquad (1)$$
$$MoO_2 + 3S \longrightarrow MoS_2 + SO_2 \qquad (2)$$
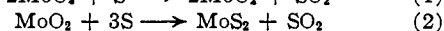
(It is assumed that potassium carbonate merely acts as a flux without actually entering into the reaction.)

The procedure just described includes measures which were intended to remove all ammonia and acid-soluble impurities. Upon X-ray diffraction examination of the product, the only detectable impurity not removed by this treatment was molybdenum dioxide.

The presence of molybdenum dioxide as an impurity in the product may be attributed to inhomogeneities in the fusion mass which resulted in local deficiencies of available

(1) J. J. Berzelius, *Pogg. Ann.*, **7**, 261 (1826).

(2) L. Svanberg and H. Struve, *J. prakt. Chem.*, **44**, 257 (1848).

(3) A. E. van Arkel, *Rec. trav. chim.*, **45**, 442 (1926).

(4) A. de Schulten, *Bull. soc. mineral. France*, **12**, 545 (1889).

(5) J. Milbauer, *Z. anorg. Chem.*, **42**, 441 (1904).

(6) M. Guichard, *Compt. rend.*, **129**, 1239 (1899).

(7) H. Arctowski, *Z. anorg. Chem.*, **8**, 213 (1895).

(8) M. Guichard, *Anal. Chem. Phys.*, [7] **23**, 498 (1901).

(9) J. J. Lander and L. H. Germer, *AIME TP*, 2259 (1947).

sulfur with subsequent failure of the reaction to go to completion.

A satisfactory method was not developed, despite many attempts, which would result in complete reaction of the MoO_2 with sulfur (eq. 2) to form MoS_2. The products of all the experiments contained various amounts of molybdenum dioxide with the molybdenum disulfide product.

No suitable method was found for detecting and estimating the molybdenum dioxide content by chemical means. However, by means of X-ray diffraction examination, the presence of molybdenum dioxide was determined readily (Fig. 2A).

In order to utilize X-ray methods for quantitative determinations of molybdenum dioxide in molybdenum disulfide, mixtures of known molybdenum dioxide and molybdenum disulfide contents were prepared. A direct reading X-ray spectrometer with copper radiation at 50 kvp.-16 ma. and a nickel filter was used to obtain X-ray diffraction patterns for samples containing 2.135, 5.31 and 9.36% molybdenum dioxide by weight. The X-ray intensity for the molybdenum dioxide phase was based on the absolute intensity of the (110) reflection from the molybdenum dioxide phase.

To reduce the lower limit of detection of the molybdenum dioxide phase in a mixture with molybdenum disulfide, specimens containing known amounts of the dioxide and the disulfide were compressed into pellets at a stress of 12,000 p.s.i. The application of stress to the powder mixture resulted in preferred orientation of the phases present. Preferred orientation of the dioxide phase resulted in greater intensity of the (110) planes compared to that of the randomly distributed powder. The development of preferred orientation in the powder mixture is, of course, highly dependent upon such factors as powder particle size, purity, method of compression and the total stress exerted on the mixture.

X-Ray diffraction data on pellets containing preferredly oriented molybdenum dioxide yielded a sensitivity of 325 counts per second per per cent. molybdenum dioxide contained in the mixture. Thus, the lower limit of detection

was placed at about 3.25 counts per second, or 0.01% molybdenum dioxide. Figure 1 represents a plot of the absolute intensity of the (110) reflection from molybdenum dioxide as a function of concentration of molybdenum dioxide in a mixture with molybdenum disulfide.

In order to remove the molybdenum dioxide present as impurity in the synthetic product, a procedure similar to that developed by Milbauer[5] was employed. Briefly, this consists of digesting the synthetic molybdenum disulfide in molten potassium thiocyanate, followed by digestion with dilute aqueous ammonia and dilute hydrochloric acid as previously described. This method was successful in decreasing the molybdenum dioxide content to a level below 0.01%, the limit of X-ray diffraction analysis. This treatment did not affect the crystallinity of the product.

Chemical Analysis of the Product.—A total of about 1500 g. of synthetic molybdenum disulfide was prepared and purified as described above. On the basis of the amount of molybdenum trioxide used, this represents a recovery of about 45%.

The product was analyzed by quantitative chemical methods for total molybdenum, total sulfur, carbon, titanium, insolubles and silica. The titanium was believed to result from the decomposition of the glaze on the porcelain crucibles. The results of these analyses are summarized in Table I.

TABLE I

CHEMICAL ANALYSIS OF SYNTHETIC MOLYBDENUM DISULFIDE

	Assay, %
Total molybdenum	60.17
Total sulfur	39.87
Carbon	0.04
Titanium	.005
Insolubles (including Ti as TiO_2 and most of the SiO_2)	.16
Silica	.10

X-Ray fluorescence analysis of the synthetic molybdenum disulfide showed the material to contain 59.9% molybdenum, which is in close agreement with the value obtained by chemical analysis as shown above.

Silicon and titanium in small amounts were the only impurities revealed by a semi-quantitative optical spectrographic analysis.

Crystallographic Examination.—During the processes of verifying the purity of product and determining of crystallinity by X-ray diffraction techniques, a marked difference was noted between the diffraction patterns obtained from the natural molybdenum disulfide and the synthetic molybdenum disulfide. The synthetic molybdenum disulfide exhibited differences in the reflections occurring in the vicinity of the (10 l + 2) reflections of the natural material (Figs. 2B and 2C). Instead of the (103), (105) and (107) reflections characteristic of the natural MoS_2, the synthetic material had doublets centered about the normal reflection position for the (103), (105) and (107) planes.

Crystallographic data describe natural molybdenum disulfide as a hexagonal layered structure. It has a dihexagonal dipyramidal unit cell with two molecules per unit cell. It is further characterized as a "P" Bravis lattice with a P6/mmc. symmetry. Under these limitations no reflections could occur at the positions found in the diffraction pattern from the synthetic molybdenum disulfide. Either an abnormality exists in the atomic positions of the unit cell or there is an entirely different crystal structure present. Due to the complexity of the diffraction pattern, structure determination from the powder patterns was not attempted.

Since crystal structure is determined most readily by single crystal X-ray techniques, an attempt was made to obtain crystals large enough for analysis. A single crystal platelet with a trigonal outline was obtained from one of the melts. A transmission Laue pattern was obtained from this crystal. This showed a threefold symmetry, instead of the sixfold symmetry characteristic of the naturally occurring molybdenum disulfide. This same crystal was used for obtaining both 0-level and 1-level Weissenberg photographs with rotation about an axis parallel to one of the edges of the three-sided crystal and also a rotation and 0-level Weissenberg photograph about an axis normal to one of the edges.
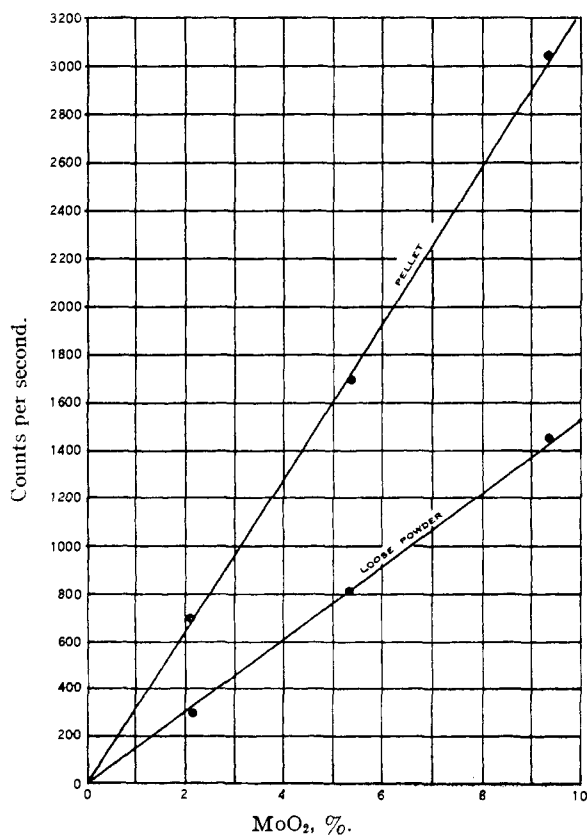

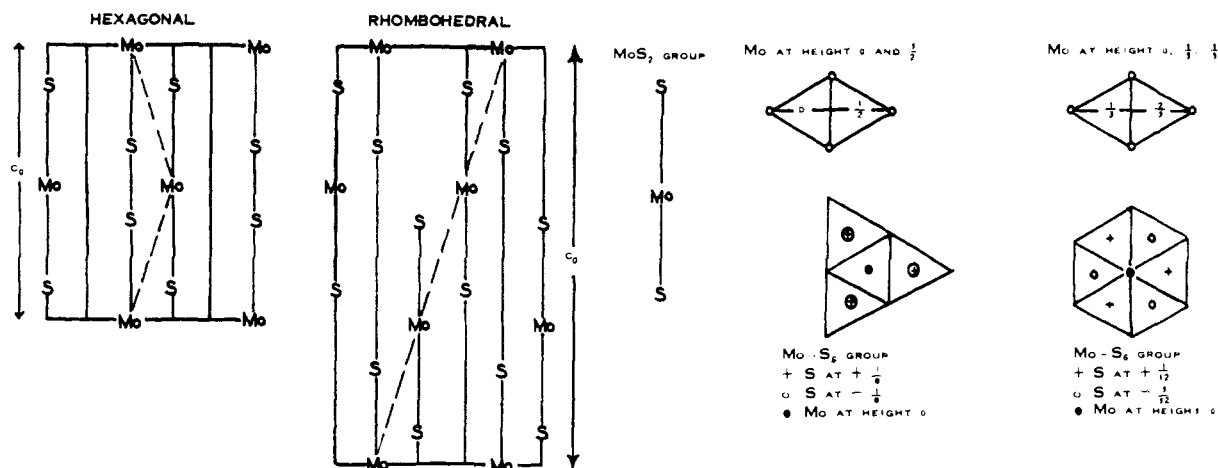Fig. 1.—X-Ray calibration curve for determination of MoO_2 in MoS_2.

Fig. 2A.—X-Ray diffraction pattern of synthetic molybdenum disulfide containing molybdenum dioxide (copper radiation, 50 kvp-16 ma. nickel filter).

Fig. 2B.—X-Ray diffraction pattern of purified naturally occurring molybdenum disulfide.

Fig. 2C.—X-Ray diffraction pattern of synthetic molybdenum disulfide with (hkl) as designated.

Indexing of these photographs showed that only reflections with $h + k + l = 3n$ were present. This indicated the presence of a rhombohedral lattice which is also in harmony with the threefold axis symmetry of the Laue photograph. Therefore, the crystal was assigned an "R" Bravis lattice with a "3m" symmetry. Referred to the hexagonal lattice, the a-axis was found to be identical with that of natural molybdenum disulfide. However, the c-axis of the rhombohedral was found to be 1.5 times greater. This means that the (002), (004) and (006) reflections of the hexagonal type would now correspond to (003), (006) and (009) for the rhombohedral lattice. The transformation from hexagonal to rhombohedral axis is H = h, K = k and L = 3/2 l.

The appearance of the doublets in the Debye–Scherrer pattern for the (103), (105) and (107) reflections of the natural molybdenum disulfide are now fully explained by the rhombohedral symmetry. The (101) plane of the hexagonal symmetry now becomes the (101) and (012) reflections of the rhombohedral planes. Similarly, the (103) is replaced by (104) and (015), and the (105) by (107) and (018).

The (001) reflections of the rhombohedral type show a very slight displacement away from the zero beam. Positional measurements of the powder photograph peaks of hexagonal (008) and rhombohedral (0012) reflections are, respectively, 1.540 and 1.533 Å.

The unit cell of the molybdenum disulfide has two molybdenum atoms at $^2/_3$, $^1/_3$, 0; and $^1/_3$, $^2/_3$, $^1/_2$, which places them on the two vertical axes. Pairs of sulfur atoms are on these same vertical axes, one above and one below each molybdenum atom at a distance of $^3/_8$ (equivalent to 4.61 Å.), as

shown in Fig. 3. The three molybdenum atoms in the rhombohedral unit would have to lie on three vertical threefold axes and could be placed at 000; $^2/_3$, $^1/_3$, $^1/_3$; and $^1/_3$, $^2/_3$, $^2/_3$, with a sulfur atom above and below each molybdenum atom at a distance of $^1/_4$ (equivalent to 4.61 Å.). Both types would have the same interatomic distances, but in the hexagonal form the molybdenum atom would lie at the center of a trigonal prism, with the three upper sulfur atoms directly above the three lower sulfur atoms. In the rhombohedral form, the three sulfur atoms above would be in alternate positions with respect to the three below, that is, rotated 60°.

There is also an alternative description possible for the hexagonal molybdenum disulfide atoms. The molybdenum atoms could be located on the threefold symmetry axes alternating with pairs of sulfur atoms 3.08 Å. apart. However, this description does not apply to the rhombohedral form—there are no sulfur pairs.

In order to compare the relative intensities obtained from the powder patterns, theoretical determinations were made for the atomic contributors to the (00 l) reflections. Using the parameter ($^1/_4$) for the sulfur atoms the contributors to the (00 l) reflections of the synthetic molybdenum disulfide would be

(003)	Mo
(006)	Mo − 2S
(009)	Mo
(0012)	Mo + 2S
(0015)	Mo
(0018)	Mo − 2S
(0021)	Mo

There is reasonably good correlation between the theoretical values obtained from the structure factor determinations for intensities and those observed on the powder patterns. A comparison of the "d-values" and relative intensities for the natural and synthetic molybdenum disulfides is presented in Table II.

TABLE II

COMPARISON OF THE "d-VALUES" AND RELATIVE INTENSITIES FOR HEXAGONAL MOLYBDENUM DISULFIDE AND RHOMBOHEDRAL MOLYBDENUM DISULFIDE

Molybdenum disulfide (hexagonal)			Synthetic molybdenum disulfide (rhombohedral)		
hkl	d, Å.	I/I₁	hkl	d, Å.	I/I₁
002	6.16	100	003	6.18	100
004	3.00	50	006	3.05	3
100	2.71	70	100	2.72	19
101	2.63	50	101, 012	2.64	14
102	2.52	70			
103	2.26	100	104	2.359	18
			015	2.205	20
006, 104	2.04	50	009	2.051	11
			107	1.897	9
105	1.83	70			
			018	1.766	5
106	1.75	20			
			109	1.703	1
110	1.58	50	110	1.586	15
112, 008	1.54	70	0012, 1010	1.534	18
107	1.48	20			
			0111	1.429	1
200	1.36	20	200	1.369	2
			203	1.314	2
202	1.29	70			
			204	1.286	2
203	1.25	50		1.253	5
116	1.22	50		1.228	3
0010	1.19	50		1.217	2

Density of Rhombohedral and Hexagonal Molybdenum Disulfide.—Since it has been established definitely that synthetic molybdenum disulfide prepared by the procedures described has a crystal structure related to, but decidedly different from, that of natural molybdenum disulfide, the

Fig. 3.—Comparison of single crystal structures of hexagonal (natural) MoS₂ and rhombohedral MoS₂.

theoretical density of the newly discovered crystallographic form was computed from X-ray measurement of the interplanar spacings. Computation of the theoretical density is based on the relation

$$\rho = \frac{1.6602 \times M \times \text{at. wt.}}{\text{volume}}$$

where $M = 3$, the number of atoms per unit cell. Lattice parameter measurements permit determination of the volume of the unit cell. The lattice parameters and theoretical density of rhombohedral molybdenum disulfide are presented in Table III.

TABLE III

DENSITY OF RHOMBOHEDRAL MOLYBDENUM DISULFIDE

X-Ray reflections for lattice parameter meas. (hkl)	Angle of diffraction 2θ, deg.	Lattice parameters, Å. c-axis	a-axis	Density, g./cm.³
0021	123.35	18.375		
118 and 0021	88.82	18.375	3.16	5.025
0018	97.90	18.390		Av. = 5.024
118 and 0018		18.345	3.171	5.022 ±0.002

Hexagonal

Natural MoS₂[a]			5.05	
Natural MoS₂[a]			4.9951	±0.008
Repurified MoS₂ obtd. from molybdenite, computed from X-ray diffraction measurements			4.96	±0.03

Gmelin's "Handbuch, System No. 53, Molybdän," p. 183.

Conclusion

In the course of preparing molybdenum disulfide by synthetic methods, a product has been made which resembles natural molybdenum disulfide, but is of higher chemical purity. However, the synthetic sulfide has a crystal form different from that of the natural sulfide. Although the chemical composition of the synthetic sulfide coincides with the theoretical composition, the crystallographic structure of the synthetic sulfide, as determined by X-ray diffraction studies, does not have the normal hexagonal, sixfold symmetry of natural molybdenum disulfide. Single-crystal X-ray studies indicate that the synthetic sulfide has a threefold trigonal symmetry with a rhombohedral unit cell. The lattice parameter of the a-axis is identical for the two crystal forms, but the parameter of the c-axis for the rhombohedral form is 1.5 times that of the hexagonal form. Various other compounds (silicon carbides, for example) are known to occur in allotropic forms such as these, where one axis remains constant and the other increases by some integral factor. Layer structured graphite shows marked similarity with the molybdenum disulfide, in that a naturally occurring allotropic form is rhombohedral with its c-axis 1.5 times greater than the hexagonal form. This is the first indication, however, of the existence of allotropic forms of molybdenum disulfide.

In view of the crystal structure, it is suggested that other crystallographic forms of the sulfide could exist, depending upon the mode of preparation.

The various lubrication studies performed in an attempt to compare naturally occurring molybdenum disulfide and synthetic molybdenum disulfide showed the two had essentially the same lubricating qualities.

For all practical purposes, the theoretical densities of the synthetic disulfide and the natural hexagonal disulfide are equal.

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