

PROPERTIES OF MOLYBDENUM DISULFIDE

MoS₂ (Molybdenite)

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The primary commercial source of molybdenum disulfide, as well as other molybdenum products is molybdenite, the mineral designation for MoS₂. Molybdenite is found in many parts of the world, but much of the world's supply originates in the Americas, either in primary deposits or as co-deposits with copper bearing minerals. The primary ores typically contain about 0.25% MoS₂, whereas in co-deposits, the MoS₂ content is <0.05%. The MoS₂ is recovered from the ore and purified by physical methods to a level of 99% for lubricant applications. In addition to its natural occurrence, MoS₂ can be prepared synthetically by several routes including direct union of the elements in pure nitrogen at 800 C,¹ thermal decomposition of ammonium tetrathiomolybdate or molybdenum trisulfide,² and by reaction of MoO₃ with H₂S or H₂S/H₂ mixtures at 500 C.³ These preparative techniques result in hexagonal crystalline MoS₂, by far the most common form, but the rhombohedral form has been found in nature,⁴ and prepared synthetically.² Natural and synthetic MoS₂ of both crystalline types possess lubricant properties, but the natural hexagonal material is preferred when cost and overall performance are considered. The properties of MoS₂ described in this bulletin are for hexagonal (2H) MoS₂ either naturally occurring or synthetically produced.

CRYSTAL STRUCTURE

Molybdenum disulfide exists in two crystalline forms, hexagonal and rhombohedral. The hexagonal form is by far the most common, being the only type found in commercial ores, but the rhombohedral form has also been found to occur in nature.

The hexagonal form is characterized by MoS₂ layers in which the Mo atoms have trigonal prismatic coordination of six sulfur atoms, with two molecules per unit cell. The crystal structure consists of "sandwiches" in which one planar hexagonal layer of molybdenum atoms is interspersed between two layers of sulfur atoms as shown in Figure 1.^{5,6} Within the crystal, each S atom is equidistant from three Mo atoms and each Mo atom is surrounded by six equidistant S atoms at the corners of a trigonal prism with altitude and edge dimensions of 3.17 Å and 3.15 Å respectively, and a Mo to S spacing of 2.41 Å as shown in Figure 2.

The rhombohedral modification of MoS₂ also has trigonal prismatic coordination and differs from the hexagonal form only in the method of stacking. There are three molecules per unit cell. A schematic

comparison of the hexagonal and rhombohedral modifications of MoS₂ is shown in Figure 3.

Molybdenum disulfide is classified as a transition

metal dichalcogenide (TMD) which includes the disulfides, diselenides and ditellurides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. These compounds exist in various crystalline forms but only the Mo and W compounds form the MoS₂ hexagonal type crystal structure.⁷ Thus the excellent lubricant properties of MoS₂ are attributable to the large spacing (and weak Van der Waals bonding) between S-Mo-S sandwich layers. In supporting this statement, Jamison⁶ has postulated that differences in lubricating behavior among the TMD compounds are attributable to the distribution of electrons on the constituent atoms. In MoS₂, there are six non-bonding electrons which can completely fill a band which physically confines the electrons within the crystal structure. This creates a net positive charge on the surface of the S-Mo-S sandwich layers which promotes easy shear through electrostatic repulsion. Gardos states that the ability of TMD particles to serve as building blocks of low shear strength surface layers is manifested by two

simultaneously exhibited properties: low *inter-planar* attraction accompanied by high-strength *intra-planar* chemical bonding. The former attribute leads to the low shear strength of the lubricant film, whereas the latter helps resist asperity penetration of the more or less aligned basal planes under the enormously high micro-Hertzian stresses that develop between contacting asperities.⁸ Measurements of hexagonal MoS₂ lattice parameters and compressibilities have been measured over the pressure range of 0.001 to 90 kbar (1,305,000 psi). A strong anisotropy was observed where the c-compressibility was more than seven times greater than the a-compressibility.⁶⁷ This anisotropy provides useful elastic cushioning of bearing surfaces in addition to prevention of metal-to-metal contact.

PHYSICAL PROPERTIES

Some of the various physical properties of molybdenum disulfide are summarized in the accompanying table. The color of MoS₂ varies from lead gray to black depending on the degree of crystal orientation and particle size. Although a melting point of 1185 C has been reported in the older literature^{9,10}, it is most likely incorrect. No melting was observed when MoS₂ was heated under high vacuum at 1800 C for ten minutes¹¹, although it is doubtful that MoS₂ remains intact at that temperature. MoS₂ has been shown to dissociate in two stages, first to Mo₂S₃ + S₂ and then to the elements at 1100 C.¹² Similar more recent work has shown that at 1.3×10^{-7} Pa (10^{-9} Torr), the onset of the thermal dissociation of MoS₂ is detected at 927 C (by TGA) and at 1093 C (by mass spectrometry).¹³

THERMODYNAMIC PROPERTIES

The thermodynamic properties of MoS₂ have been studied extensively. Low temperature heat capacities of molybdenite conform to the T³ limiting law¹⁴ and were used to evaluate the following functions at 298.15 K: $C_p = 15.19 \pm 0.03$ cal/K/mole and $S_{298}^0 = 14.96 \pm 0.02$ cal/K/mole. Data on the heat of formation ΔH_f^0 and free energy of formation ΔG_f^0 have been reported^{15,16} (see table). ΔG_f^0 over the temperature range 867 K to 1209 K for MoS₂ was expressed by the equation $\Delta G_f^0 = -97.681 + 43.76 \times 10^{-3} T \pm 0.538$ kcal/mole where T is in degrees K¹⁶.

MAGNETIC, ELECTRICAL, OPTICAL AND THERMAL EXPANSION PROPERTIES

Molybdenum disulfide is diamagnetic. Magnetic susceptibility in the basal plane is smaller and decreases less rapidly with increasing temperature than in the plane perpendicular to it.¹⁷ The magnetic susceptibility varies from specimen to specimen and measurements at 298 K show that this variation is

caused by variations in three dimensional structures.¹⁸

The average magnetic susceptibility of several commercial samples of MoS₂ was found to be 0.25×10^{-6} emu/g as received and 0.32 emu/g after purification with HCl.¹⁹

Molybdenum disulfide is a linear photoconductor. Maximum photoconductivity is in the red color area, and the threshold of photoconductivity is about two micrometers.²⁰ Reflectivity spectra over a wide energy (wavelength) range on MoS₂ single crystals have been generated at high vacuum (1.3×10^{-4} Pa) at room temperature and at 78 K.^{21,22} Energy loss functions derived from Kramers-Kronig analysis showed sharp peaks at 8.8 and 23.3 eV.²¹

Molybdenum disulfide is classified as a semiconductor and may be either the p or n type.²³ Data on the electrical transport properties of p-type single crystals of molybdenite has been obtained.²⁴ Electrical conductivity at room temperature for several single crystals ranged from 0.16 to $5.12 \Omega^{-1} \text{cm}^{-1}$ along the cleavage plane and from 1.02×10^{-4} to $5.89 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ parallel to it. Volume resistivity of single crystals at 300 K was $2 \times 10^3 \Omega \text{cm}$ parallel to the basal plane and $12 \Omega \text{cm}$ perpendicular to it.²⁵ Average values for electrical conductivity at other temperatures are given in the accompanying table. The electrical conductivity along the cleavage plane slowly increases with temperature up to about 400 K, then decreases with further increase in temperature. Above 700 K, it again begins to increase. Hall coefficients in this same study²⁴ were found to range from 15 to 450 cm³/coulomb at room temperature increasing at lower temperatures, while thermoelectric power ranged from 350 to 580 $\mu\text{V}/\text{K}$ at room temperature both along the cleavage plane and parallel to it. Both Hall coefficient and thermoelectric power values become negative at about 750 K, and remain negative at higher temperatures. All the preceding electrical transport values were measured in vacuum and in the absence of light.

Electron spin resonance measurements on MoS₂ suggest that the signal obtained is due to mobile charge carriers rather than free radical centers.²⁶

The thermal expansion properties of MoS₂ have been reported for both single crystals and polycrystalline compacts formed at high pressure. Synthetically prepared single crystals of MoS₂ exhibited thermal expansion coefficients of $\alpha_a = 4.922 \times 10^{-6}/\text{K}$ and $\alpha_c = 18.58 \times 10^{-6}/\text{K}$ in the temperature range of 10 to 300 K.²⁷ In the range from 300 to 1100 K, the values were $\alpha_a = 1.9 \times 10^{-6}/\text{K}$ and $\alpha_c = 8.65 \times 10^{-6}/\text{K}$ respectively.²⁸ Compacts prepared from commercial high purity MoS₂ compressed to 95% of theoretical

density exhibited a thermal expansion coefficient of 5.84/K over the temperature range 300 - 810 K.²⁹

Thermal conductivity measurements have been made on the bulk MoS₂ powder and also on compacts as listed in Table 1. Values range from 0.13 to 1.82 W m⁻¹K⁻¹ depending on the degree of compaction and temperature.^{30,31}

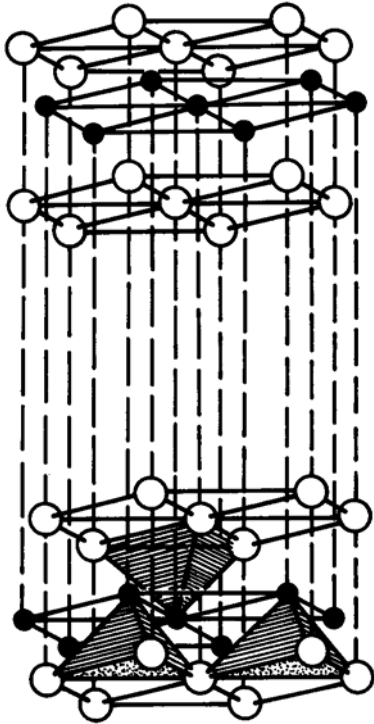


Figure 1. The crystal structure of MoS₂. Molybdenum atoms are small filled circles; sulfur atoms are large open circles. (adapted from Ref. 7).

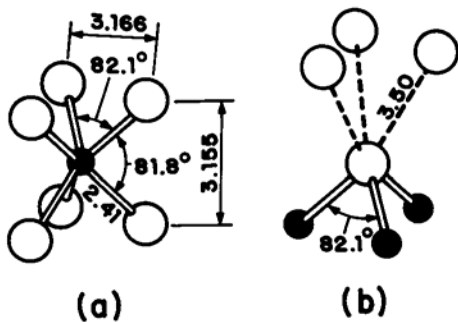


Figure 2. Atomic coordination in MoS₂ (after Takeuchi and Nowanki⁴). (a) Configuration of MoS₂ trigonal prism; (b) surroundings of sulfur atom. Mo and S are shown by solid and open circles respectively.

CHEMICAL PROPERTIES

Molybdenum disulfide in its naturally occurring hexagonal modification is quite unreactive chemically. It dissolves in strong oxidizing agents such as aqua regia, hot concentrated sulfuric and nitric acids to give hexavalent molybdenum species. Molybdenite (MoS₂) is converted on a commercial

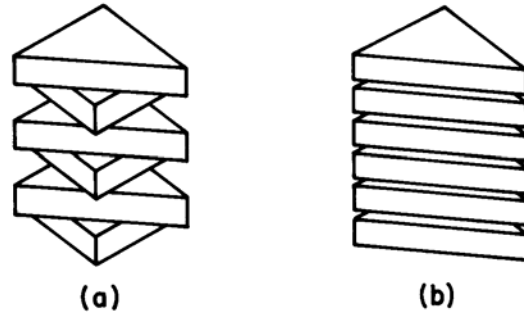


Figure 3. Schematic comparison of MoS₂ crystal structure modifications: (a) hexagonal MoS₂ - adjacent layers in anti-parallel orientation; (b) rhombohedral MoS₂ - all layers in parallel orientation (Reference 2).

scale to MoO₃ via highly exothermic oxidation reactions in air at 500-600 C.³²

The oxidation characteristics of lubricant grade natural MoS₂ have been studied by several researchers. The thermal oxidation rate of MoS₂ in air studied by x-ray diffraction showed that below 300 C, the rate is very slow and difficult to measure accurately, and that below 388 C, MoS₂ oxidized at a slower rate than WS₂.³³ The dependence of temperature on oxidation rate conformed to the Arrhenius reaction rate with a derived activation energy of 54 kcal/mole.³³ The oxidation behavior of MoS₂ in dry air has also been studied by thermogravimetric analysis.³⁴ It was determined that 10%, 50% and 90% MoO₃ was formed at temperatures of 435 C, 466 C and 516 C respectively. Chlorine gas reacts in the absence of air with natural MoS₂ at elevated temperatures to yield MoCl₅ and in air at 550 C to yield the volatile products MoO₂Cl₂ and MoOCl₄.³⁷ Carbon dioxide reacts with natural molybdenite slowly at 250 C increasing to a maximum rate at 900-1000 C to form MoO₂ and some MoO₃ along with SO₂, CO, S and COS.³⁶ A low-carbon, low-oxygen molybdenum metal is produced by the reduction of MoS₂ with metallic Sn beginning at around 500 C.³⁷ No nitrides are formed when formed when MoS₂ is heated in nitrogen.³⁸ Reduction of MoS₂ by hydrogen gas proceeds to the metal via the intermediate compound Mo₂S₃.³⁹ Molybdenum disulfide is not soluble in ordinary aqueous or organic solvents. However, MoS₂ is oxidized slowly by sodium hypochlorite solutions,⁴⁰ and has very slight (0.89 x 10⁻³ mole/L) solubility in

sodium sulfide solutions.⁴¹ It also dissolves by complex formation in potassium cyanide.⁴²

Intercalation Compounds and Nanoparticles of MoS₂

Like graphite, the lamellar structure of MoS₂ permits it to form interlamellar compounds. For example, powdered MoS₂ absorbs ammonia from -63.5 to -78 C up to about 50 mole percent.⁴³ Intercalation compounds of molybdenum disulfide (and some other transition metal dichalcogenides) with alkali metals have been prepared by reacting the MoS₂ with liquid ammonia in which the metal has been dissolved. An example of this type of intercalation compound is Li_{0.8}(NH₃)_{0.8}MoS₂.⁴⁴ Molybdenum disulfide has been intercalated with Lithium by reacting MoS₂ with n-butyl lithium in hexane. The insertion of Li in the MoS₂ lattice markedly changes its superconducting properties,⁴⁵ and the layers can subsequently be separated (exfoliated) and restacked with other materials, e.g., polymers, between the layers, forming nanocomposites.⁴⁶

Multi-walled hollow nanoparticles of MoS₂ and WS₂ have been synthesized and studied.⁴⁷ These particles are hollow and are said to resemble the outer layers of an onion. They are claimed to offer good tribological performance in liquid lubricants.

USES

Lubricants - Natural molybdenite, purified by flotation and/or other techniques to 98+ percent is used as a solid lubricant by itself, as an additive to conventional fluid lubricants, and in bonded lubricant coatings.^{48,49} The excellent lubricating properties of MoS₂ are intrinsic to its unique crystal structure and electron configuration.⁶ In contrast, graphite, while possessing a layered crystal structure, depends on the presence of condensable vapors (water, hydrocarbons, etc.) to promote easy cleavage and low friction.⁵⁰

The friction coefficient of dry burnished films of MoS₂ may range from 0.01 to 0.20 depending on the substrate metal, sliding speed and relative humidity, but typically, values in the 0.03 to 0.06 range are observed. Factors influencing the performance of MoS₂ as a lubricant are discussed in three reviews.^{48,49,51} Small variations in purity among commercial lubricating grades of MoS₂ do not affect performance.⁵² These commercial grades contain 98+ percent MoS₂ with carbon being the major impurity along with minor amounts of iron, acid insoluble substances and MoO₃.⁵³ Increasing humidity generally increases the friction coefficient of dry films of MoS₂ while higher loads or speeds reduce the friction.⁵⁴ Early work on the effect of environment on friction suggested that the lowest friction values were obtained in the absence of condensable vapors in ultra high vacuum,⁵¹ but

subsequent work at high vacuum (1.3×10^{-6} Pa) showed that with the admission of certain vapors, lower friction can occur due to vapor adsorption at crystalline edge sites (rather than on basal plane surfaces).⁵⁵ It should be emphasized that that the foregoing information relates to natural MoS₂ applied to substrates by mechanical means. Films applied by sputtering or ion plating techniques can possess significantly different friction values.^{56,57}

Molybdenum disulfide has been used successfully over a wide temperature range - from cryogenic (-190 C)⁵⁸ to 1200 C (inert atmospheres) for short time periods.⁵¹ While MoS₂ begins to oxidize to MoO₃ in the vicinity of 350 C *in air or oxygen*, it can be used as a lubricant at or above this temperature as long as some unoxidized MoS₂ remains in the lubricant film.⁵⁹ Molybdenum trioxide produced when MoS₂ oxidizes, is not abrasive⁶⁰ and while exhibiting a relatively high friction coefficient (0.8) at room temperature, has been proposed as a high (700 C) temperature lubricant because its friction decreases to about 0.3 at elevated temperatures.⁶¹

The lubricating behavior of MoS₂ is not affected by exposure to nuclear radiation. Most of this work has been conducted on compounded solid film lubricants containing MoS₂, other solid lubricants and binders (phenolic resins, sodium silicate, etc.). A film composed of MoS₂-graphite-sodium silicate was resistant to a gamma dose of 5×10^9 R⁵⁸, and likewise, the friction and wear-life of a MoS₂-phenolic film was unaffected by gamma doses up to 2×10^8 R. A similar film containing sodium silicate as the binder exhibited increased friction after the same exposure.⁶² The limiting factor in these bonded film evaluations appears to be the binder rather than MoS₂. Graphite has been reported to suffer lattice distortion when exposed to a neutron dose of 3.66×10^{20} nvt in a mixed reactor flux, while MoS₂ exposed similarly was unaffected.⁶³

Unrelated to radiation stability, work conducted for the U.S. Nuclear Regulatory Commission has cautioned against the use of MoS₂ in threaded fastener and turbine disc applications at nuclear powered electricity generating stations.^{64,65} This work suggests that MoS₂ may increase the stress corrosion cracking susceptibility of high strength steels subjected to high stress in steam at 280 C as a result of an hydrolysis reaction where H₂S is formed. Frequently however, torque specifications for the tightening of threaded connections are based on an assumed friction coefficient for unlubricated surfaces. If a MoS₂ lubricant is used, the desired stress is obtained at a lower torque value, thus causing the connection to be overstressed and making the material more susceptible to cracking.⁶⁶

In commercial applications, molybdenum disulfide is used in various forms including dry burnished (rubbed-on) films, as an additive in pastes and greases, gear oils, as a filler in self-lubricating plastics and powder metal parts, and in metalworking compounds.⁶⁸ Summaries and reviews of MoS₂ have been published for specific applications in the steel industry,⁶⁹ greases,^{70,71} rubber,⁷² motor oils,⁷³ and bonded coatings.⁷⁴

Natural and synthetic MoS₂ has catalytic activity in a variety of petrochemical processes including hydrotreating, hydrogenation/dehydrogen-ation and olefin oxidation.

Other Uses - Molybdenum disulfide reacts with azides of alkali and alkaline earth metals to rapidly generate nitrogen gas in large volume at relatively low temperature. This reaction is utilized for the inflation of passive restraint "air bags" for passenger cars and light trucks.⁷⁸ Flame and smoke suppression activity in PVC and polyvinylidene chloride compositions has been reported for MoS₂, although MoO₃ and ammonium octamolybdate are almost exclusively used in these applications.⁷⁹

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Properties of Molybdenum Disulfide

<i>Molecular Weight</i>	160.06	Synthetic single crystal (2H) ²⁸												
<i>Color</i>	lead gray to black	300 K: $0.03 \Omega^{-1}\text{cm}^{-1}$ 1170 K: $7.5 \Omega^{-1}\text{cm}^{-1}$												
<i>Density</i>	4.8 to 5.0 (natural molybdenite) 4.96 ± 0.03 (repurified MoS ₂ , computed from x-ray diffraction measurements ⁸⁰)	Hot pressed bar ⁸⁷ $1.17 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$ (synthetic, 200 C, 206.9 MPa)												
<i>Melting Point</i>	air: none; oxidizes to MoO ₃ vac: dissociates (927 C) ¹³	<i>Volume Resistivity</i> (300 K) ²⁵ $2 \times 10^3 \Omega\text{cm}$ (c axis) $12.0 \Omega\text{cm}$ (\perp c axis)												
<i>Hardness</i>	1-1.5 Mohs Scale (basal plane) ⁸¹ 60 Knoop (basal plane) ⁸² 32 kg/mm^2 (001 plane) 900 kg/mm^2 (100 plane) ⁸³	<i>Modulus of Elasticity</i> ^{4,88} $2.0 \times 10^{-7} \text{ Pa}$												
<i>Wettability</i>	60 degree contact angle with water ⁸⁴	<i>Surface Energy</i> ⁸³ $2.4 \times 10^{-2} \text{ joule m}^{-2}$ (001 plane) $7.0 \times 10^{-2} \text{ joule m}^{-2}$ (100 plane)												
<i>Specific Heat</i>	$15.19 \text{ cal mole}^{-1}\text{K}^{-1}$ (Ref. 85)	<i>Bulk Density</i> (Scott Density) ⁸⁶ $3 \mu\text{m}$ avg. (Fisher) 1.4 g/cm^3 $0.7 \mu\text{m}$ avg. (Fisher) 0.4 g/cm^3 $0.4 \mu\text{m}$ avg. (Fisher) 0.3 g/cm^3												
<i>Heat of Formation</i>	$(\Delta H^0_f)^{15} 56.1 \text{ to } 55.5$ kcal/mole	<i>Thermal Conductivity, W m⁻¹K⁻¹</i> bulk powder ³⁰ 40 C: 0.13 430 C: 0.19												
<i>Free Energy of Formation at 1000 K</i>	$(\Delta G^0_f)^{16} 52.91 \text{ kcal/mole}$	compact (12.7Φ x 12.7 mm long) ⁸³ <table border="0"> <tr> <td></td> <td><u>-192C</u></td> <td><u>32C</u></td> <td><u>588C</u></td> </tr> <tr> <td>77 % dense</td> <td>0.540</td> <td>0.781</td> <td>0.500</td> </tr> <tr> <td>88 % dense</td> <td>1.38</td> <td>1.82</td> <td>1.19</td> </tr> </table>		<u>-192C</u>	<u>32C</u>	<u>588C</u>	77 % dense	0.540	0.781	0.500	88 % dense	1.38	1.82	1.19
	<u>-192C</u>	<u>32C</u>	<u>588C</u>											
77 % dense	0.540	0.781	0.500											
88 % dense	1.38	1.82	1.19											
<i>Electrical Conductivity</i>	Natural single crystal (2H) ²⁴ 300 K: $1.58 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ (\perp basal plane) $0.63 \Omega^{-1}\text{cm}^{-1}$ (basal plane) 523 K: $5.01 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$ (\perp basal plane) $0.50 \Omega^{-1}\text{cm}^{-1}$ (basal plane) 100 K: $1.6 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ (\perp basal plane) $0.02 \Omega^{-1}\text{cm}^{-1}$ (basal plane)	<i>Thermal Expansion Coefficient</i> Compact: (6.35 mm Φ x 12.4 mm lg, 95% dense) ²⁷ , 300 K to 810 K $\alpha = 5.84 \mu\text{m m}^{-1}\text{K}^{-1}$ Single Crystal (300K to 1100K) ²⁸ $\alpha_a = 1.9 \times 10^{-6} \mu\text{m m}^{-1}\text{K}^{-1}$ $\alpha_c = 8.65 \times 10^{-6} \mu\text{m m}^{-1}\text{K}^{-1}$												

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