CHEMICAL DATA SERIES

MOLYBDENUM CHEMICALS

PROPERTIES OF MOLYBDENUM DISULFIDE
MoS₂ (Molybdenite)

Molybdenum disulfide is found in nature in the mineral molybdenite and in conjunction with copper sulfide ores. It may be prepared synthetically by treating pure molybdic oxide, MoO_3, with hydrogen sulfide. Subsequent reduction is required to obtain a pure molybdenum sulfide in the tetravalent state. The natural and synthetic MoS_2 materials differ substantially in crystal structure. The chemical and physical properties reported here pertain to natural molybdenite.

PHYSICAL PROPERTIES

Formula Weight	160.08
Color	Blue-gray to black
Specific Gravity	4.85–5.0
Melting Point	higher than 1600 C
Crystal Structure	Hexagonal. Alternate layers of Mo and S atoms. Each Mo atom surrounded by a trigonal prism of S atoms at distance 2.41 Angstroms.[1,2]

THERMODYNAMIC PROPERTIES[3]

Heat of Formation	$\Delta H^\circ_{298.16K} = -56.1$ kcal/mole
Free Energy of Formation	$\Delta F^\circ_{298.16K} = -54.0$ kcal/mole
Heat of Fusion	$\Delta H_{1458K} = 10.9$ kcal/mole

Although the melting point of pure MoS_2 is higher than 1600 C, a melting point of 1185 C has been reported for molybdenite. Accordingly, the heat of fusion of this material was estimated for the lower temperature.

Recent studies have produced new data relating to the low temperature heat capacity and entropy of molybdenum disulfide.[4]

ELECTRICAL AND MAGNETIC PROPERTIES

Molybdenum disulfide is diamagnetic. The magnetic susceptibility varies from specimen to specimen.[5,6,7] The susceptibility in the basal plane is smaller and decreases less rapidly with increasing temperature than the susceptibility perpendicular to the basal plane.[7]

Molybdenum disulfide is a linear photoconductor; i.e., the photo-current is characterized by exponential decay and growth, and the growth rate is proportional to the intensity of illumination.[8] Maximum photosensitivity is in the red. The threshold of photoconductivity is at about 2 microns.[9]

Conductivity in MoS_2 may be either *p*- or *n*-type.[10,11] Charge-carrier activation energies of 0.55, 0.14, 0.12, and 0.05 ev have been reported.[10,12] The conductivity and Hall constant of various specimens may differ widely. In a recent study, conductivity (in the basal plane) of 4 to 0.009 $(ohm-cm)^{-1}$ and Hall constant of 35 to 3000 cm^3/coulomb were found for various specimens of natural molybdenite.[11] The conductivity is ohmic over a wide current range. The charge-carrier mobility in the basal plane is of the order of 10^2 cm^2/volt-sec at room temperature. The mobility varies approximately as $T^{-3/2}$ (where T is the absolute temperature), above about 150 K, indicating lattice scattering. Conductivity and mobility are smaller in the direction normal to the basal plane.[11]

The transverse change in resistance in a magnetic field (with the field perpendicular to the basal plane) is similar for specimens of different conductivity. The coefficient α is about 2 x 10^{-12} $oersted^{-2}$ in the expression $\Delta\gamma/\gamma = \alpha H^2$, where γ is the conductivity, and H is the magnetic field strength. With the field parallel to the basal plane, no change in conductivity has been detected ($\alpha < 4$ x 10^{-13} $oersted^{-2}$).[11]

A study of the resistance-pressure characteristic of one specimen of natural molybdenite showed that the resistance decreased smoothly (with increasing pressure) to 56 per cent of the initial value at 20,000 kg/cm^2, then dropped abruptly, as a result of a transition, to 20 per cent of the initial value. With further pressure increase, the resistance decreased smoothly to 11 per cent at 100,000 kg/cm.[13]

The thermoelectric power of MoS_2 has been reported as 300 to 700 microvolts/degree at room temperature. It is essentially constant over a wide temperature range.[11,12]

Rectifier and transistor action have been observed in MoS_2.[14,15] A power rectifier with a barrier layer of MoS_2 is claimed to be usable at temperatures up to 250 C.[16] A stable electric resistance element comprising between 2 and 20 per cent molybdenum sulfide is also claimed.[17]

PREPARATION

Molybdenum disulfide can be prepared by direct combination of the elements at elevated temperatures, by heating molybdenum trioxide in hydrogen sulfide, or by fusing molybdenum trioxide with a mixture of sulfur and potassium carbonate.

CHEMICAL PROPERTIES

REACTIONS Molybdenum disulfide is quite unreactive chemically. It can be reduced to molybdenum by heating in an inert atmosphere, vacuum or hydrogen. The decomposition pressure of MoS_2 is given by the equation $\log P_{mm} = -A/T + B$, in which P_{mm} is the sulfur pressure in mm Hg, T is the temperature in deg K, and $A = 13,830$, $B = 6.35$ over the temperature range 1177 to 1379K.[18]

The equilibrium constant of the reaction $MoS_2 + 2H_2 = 2H_2S + Mo$ is as follows:[19]

t, °C	805	910	1005	1100
$\log_{10}K$	−2.235	−2.059	−1.863	−1.319

Heating in air oxidizes MoS_2 to MoO_3, in chlorine to $MoCl_5$.

SOLUBILITY Molybdenum disulfide is not soluble in ordinary solvents, but it dissolves in strong oxidizing agents (aqua regia and hot, concentrated HCl, H_2SO_4 and HNO_3) by oxidation to the hexavalent state. It dissolves in KCN solution by complex ion formation.

A study[20] of the rate of dissolution of MoS_2 in alkaline solution was carried out under carefully controlled conditions. Studies made in the temperature range of 100 C to 175 C and in the pressure range 0 to 700 psia of oxygen showed that the rate of leaching by KOH was a linear function of oxygen over-pressure and KOH concentration. Commercial application of this process to the production of ferromolybdenum and molybdenum chemicals is promising.

USES

LUBRICATING PROPERTIES Basic to the lubricating properties of molybdenum disulfide is its laminar structure. Each lamina is composed of two layers of sulfur atoms between which is sandwiched a layer of molybdenum atoms. Within each layer the atoms are arranged hexagonally, and all laminae have the same sandwich construction. The attractive forces between atoms in the same lamina are greater than the forces attracting sulfur atoms in one lamina to those in another. As a result of these weak bonds between layers, one lamina slides easily over the other, imparting low shear characteristics to the compound. This characteristic laminar structure of molybdenum disulfide can be observed with the electron microscope.[21] The lubricating characteristics of molybdenum disulfide are independent of adsorption films, a factor that indicates that it is more valuable than graphite as a lubricant under conditions unfavorable to formation and retention of adsorption films on cleavage faces.

The coefficient of friction of molybdenum disulfide is low, showing advantages over other solid lubricant additives. Experiments with graphite and MoS_2 conducted on a Kinetic Friction Apparatus show that at room temperature and low speed there is little choice between the two materials, but that at higher speeds, the friction coefficient of MoS_2 is lower. No welding occurred with the MoS_2 films and the MoS_2 was bonded to the surface In comparing MoS_2 and graphite, both in light motor oil, the coefficients of friction are .071 and .196, respectively.

CATALYTIC PROPERTIES Molybdenum disulfide is used as a catalyst in a variety of hydrogenation-dehydrogenation reactions involving complex hydrocarbon mixtures such as petroleum and coal tars. For maximum surface area, the disulfide is usually precipitated onto a carrier from ammonium molybdate and hydrogen sulfide or from ammonium thiomolybdate. However, difficult hydrogenation reactions have also been carried out over natural MoS_2 in a micronized form. The tetravalent form of the sulfide is usually preferred. To insure proper reduction, hydrogen activation of precipitated molybdenum sulfide catalysts is recommended.

REFERENCES

General: D. H. Killefer and A. Linz, *Molybdenum Compounds — Their Chemistry and Technology*, New York, Interscience Publishers, 1952.

Gmelin's Handbuch der anorganischen Chemie — Molybdän, System Number 53, Berlin, Verlag Chemie, 1935.

J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Volume XI, London, Longmans Green and Company, 1931.

N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Volume II, Oxford, The Clarendon Press, 1950.

1. R. G. Dickinson and L. Pauling *JACS 45*, 1466 (1923).
2. O. Hassel, *Z. Krist, 61*, 92 (1925).
3. K. K. Kelley, Thermodynamic Properties of Molybdenum Compounds, Bulletin Cdb-2, New York, Climax Molybdenum Company, 1954.
4. D. F. Smith et al, *JACS 78*, April 20, 1956, 1533-1536.
5. B. T. Tjabbes, *Proc. Acad. Amsterdam, 35*, 693 (1932).
6. A. K. Dutta, *Indian J. Phys. 18*, 249 (1944).
7. A. K. Dutta, *Nature 156*, 240 (1945).
8. D. B. Gurevich and N. A. Tolstoi, *Doklady Acad. Nauk S.S.S.R. 72*, 473 (1950).
9. W. W. Coblentz and H. Kahler, *Bureau of Standards Sci. Paper* No. 338 (1919).
10. F. Regnault, P. Aigrain, C. Dugas, and B. Jancovici, *Compt. rend 235*, 31 (1952).
11. R. Mansfield and S. A. Salam, *Proc. Phys. Soc.* (London) *B66*, 377 (1953).
12. B. M. Hokhberg, *J. Exptl. Theoret. Phys.* (U.S.S.R.) *7*, 1090 (1937).
13. P. W. Bridgman, *Am. Acad. Arts Sci. 81*, 265 (1952).
14. L. Lagrenaudie, *J. Phys. Radium 13*, 311 (1952).
15. T. H. Tonneson, *Proc. Phys. Soc.* (London) *B65*, 737 (1952).
16. F. R. Quinn, U. S Patent 2,541,832 (Feb. 13, 1951).
17. ibid USP 2,740,080 (July 12, 1952).
18. C. M. Hsiao and A. W. Schlechten, *J. Metals 4*, (1), 65 (1952).
19. N. Parravano and G. Malquori, *Atti. accad. Lincei, 7*, (6), 109 (1928).
20. Dreshen, W. H., Wadsworth, M. E., and Fassell, W. M., Jr. *Trans AIME*, Vol. 8, No. 6, 794-800, June 1956.
21. I-Ming Feng, "Lubricating Properties of Molybdenum Disulfide," *Lubrication Engineering 8*, 285, 288, 306-308 (1952).