

SOME PRELIMINARY OBSERVATIONS ON THE
THEORETICAL GEOCHEMISTRY OF
MOLYBDENUM UNDER SUPERGENE
CONDITIONS

By

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INTRODUCTION

Recent work outlining the potential of molybdenum as a geochemical indicator has prompted further inquiry into the behavior of molybdenum in the zone of oxidation. A considerable literature, notably Russian, exists on various aspects of molybdenum geochemistry. Among such studies have been those relating to ore search and exploration (Baranova, 1957; Malyuga, 1958), solubilities and transport (Vinogradov, 1957a and 1957b), and trace content of molybdenum in water (Vinogradov, 1957b), rocks and soils (Kuroda and Sandell, 1954; Mikhailov, 1959; Rabinovich, et al., 1958; Studennikova, et al., 1957). However, no data have been found relating to the stability of molybdenum compounds, minerals, or ions under the wide variety of physical-chemical conditions found in the shallow oxidizing environment.

In the present study, the attempt has been made to define the stability fields of various molybdenum mineral and ionic species in terms of oxidation potential (Eh) and pH. This theoretical approach is the one utilized by Garrels (1954, 1960) in studies of the relationships of various minerals in the zone of oxidation. Use of this approach is particularly suited to the study of geochemistry in the zone of supergene processes because of the low temperatures, low pressures, and other relatively easily determined and duplicated factors that exist in the near surface environment.

Determination of stability fields is based upon application of the Nernst equation and utilizes the thermodynamic properties of the various ions and compounds considered. Certain elements and their compounds are relatively well suited to such an approach because of the large quantity of thermodynamic data available. The study of molybdenum and its compounds, however, is complicated by two factors. One of these is the fact that the strong amphoteric behavior of molybdenum makes possible a wide variety of substances and complexes whose exact chemical natures are unknown. The second factor is the dearth of thermodynamic data for many of the simplest of the possible compounds and ions important to this study.

For the purpose of this preliminary report, the first factor has been simplified and only the simpler possibilities of complexing have been treated. All the complexes considered have been suggested in the chemical (Deltombe, et al., 1956; Killeffer and Linz, 1952; Latimer, 1952; Pourbaix and de Zoubov, 1957) or geological (Goldschmidt, 1954; Rankama and Sahama, 1950) literature. To overcome the second difficulty, free energies have been calculated either by a process relating substances with known free energies of formation to substances of unknown free energies in a series of simultaneous equations, or by calculation of free energy from published (Killeffer and Linz, 1952; Latimer,

1952) electrode potential data.

While the complex behavior of molybdenum in acid solutions is well known, the complexes so formed are poorly understood (Killeffer and Linz, 1952; Latimer, 1952). In the calculations carried out and in the deductions made, the simpler complexes have been treated with full realization that these combinations may be gross oversimplifications of the actual character of the ions present. However, the complexes and their stability fields, as they have been determined, are probably accurate in terms of the stability of the ionic states of molybdenum complexes considered.

Free energy values used in the calculations and a sample of the method of calculation are shown on pages 105 and 106. The method has been presented and discussed in detail by Garrels (1954, 1960) and the reader is referred to those publications for further information. Free energy data have been taken from Latimer (1952), from Pourbaix and de Zoubov (1957), and Deltombe and coworkers (1956), or have been calculated.

In the present treatment, no attempt has been made to outline in detail the stability fields of naturally occurring molybdate compounds such as powellite, wulfenite, or lindgrenite. Their stability fields can, however, be delimited in a very general way. The study has been restricted, so far, to consideration of the behavior of molybdenum in water and dissolved sulfur.

GEOCHEMISTRY OF MOLYBDENUM

The geochemistry of this element is largely the chemistry of its hexavalent state. The principal primary mineral is the sulfide (molybdenite) of valence 4, but all of the secondary minerals are varied combinations of metals and quivalent molybdene cations with the molybdate anion. There have been numerous studies of molybdenum chemistry, a great number of these cited in Killeffer and Linz (1952) but only one definitive study of the geochemistry of the element (Kuroda and Sandell, 1954). Rankama and Sahama (1950) and Goldschmidt (1954) have summarized much of the pertinent data related to molybdenum in the geochemical cycle.

In this study, the thermodynamics suggest that the pentavalent and hexavalent states are the dominant ones to be considered as important in the restricted range of conditions of the ordinary zone of oxidation. Quadravalent and trivalent species exist but under conditions of negative pH and above the oxidizing conditions required for breakdown of water.

IONIC SPECIES

Hexavalent Molybdenum

Three possible complexes are considered. Molybdate (MoO_4^{2-}), the acid molybdate (HMoO_4^-) and the molybdene cation (MoO_2^{+2}) are all of some probable importance in nature. In all of the systems considered in the present work, molybdenum of the hexavalent state appears to be the stable valence over a large range of conditions. An approximate free energy of -47 kilocalories

FREE ENERGIES OF FORMATION (k cal)

		F°	Source
MoO ₂	c	-117.3	Latimer
MoO ₃	c	-161.95	Latimer
MoO ₄ ⁻²	aq	-205.4	Pourbaix
HMoO ₄ ⁻	aq	-213.6	Pourbaix
H ₂ MoO ₄	aq	-227	Latimer
MoO ₂ ⁺	aq	-122.8	Calc.
Mo ₃ O ₈	aq	-480	Calc.
MoS ₂	c	- 53.8	Latimer

EXAMPLE OF CALCULATIONS



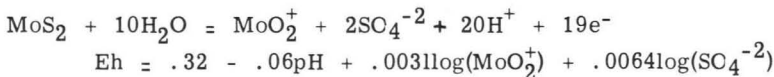
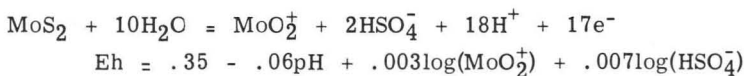
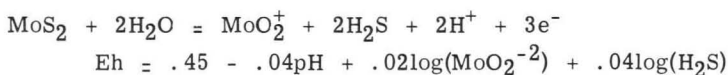
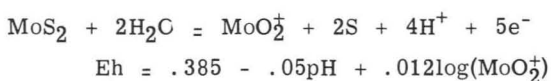
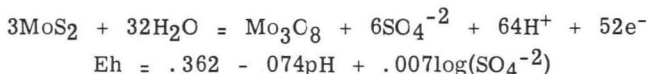
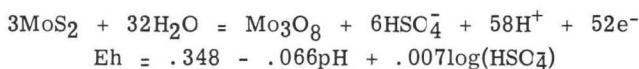
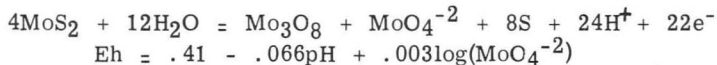
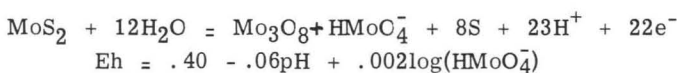
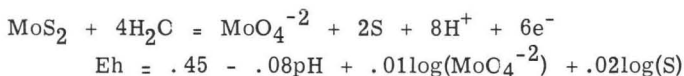
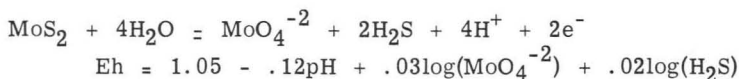
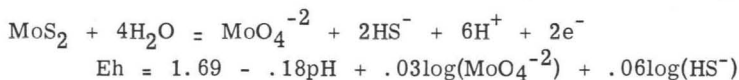
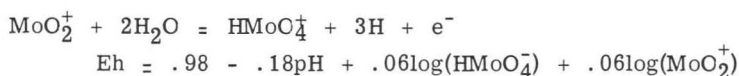
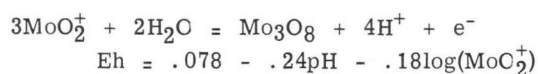
$$E^{\circ} = \frac{\Delta F_R^{\circ}}{n \times 23.06} = \frac{78.2}{46.12} = 1.69\text{v}$$

$$E_h = E^{\circ} + \frac{0.59}{n} \log K; \quad E_h = 1.69 - .18\text{pH} + .03\log[\text{MoO}_4^{-2}] + .06\log[\text{HS}^-]$$

$$\text{at } [\text{MoO}_4^{-2}] = 10^{-6} \text{ and } [\text{HS}^-] = 10^{-1},$$

$$\underline{E_h = 1.45 - .18\text{pH}}$$

SOME REACTIONS AND THEIR Eh-pH EQUATIONS
USED IN THE CALCULATIONS



(kcal) for the molybdene cation has been calculated which suggests it may be a stable species in the hexavalent field at pH values up to about 8.5. Because of lack of confidence in accuracy of the calculated values and lack of knowledge of its importance in the natural environment, however, the field of stability of the molybdene cation has not been plotted on the diagrams.

At pH of 6, equilibrium between molybdate and the acid molybdate ions is established. The diagram suggests that the molybdate complexes are stable over a wide range of pH conditions in the oxidizing environment.

Quinquevalent Molybdenum

The quinquevalent molybdene complex MoO_2^+ cuts away a portion of the hexavalent field at acid pH and in the field of oxidation. It is rather surprisingly stable in a significant portion of the field.

Trivalent Molybdenum

The molybdic ion Mo^{3+} appears to be stable at pH values less than zero. It does not fall within the conditions depicted on the diagrams, but instead appears to be stable only at negative pH. These are conditions that would appear to be unlikely in the great majority of natural environments.

MINERAL SPECIES

Molybdenite

This mineral, MoS_2 , is the only primary mineral of molybdenum considered in the study. It remains a remarkably stable species and constitutes a significant portion of the diagrams, even at low concentrations of dissolved sulfur species.

Ilsemannite

Lack of knowledge as to the precise character of this mineral makes its study somewhat difficult. Most of the literature, however, suggests its composition to be approximately Mo_3O_8 or $(\text{MoO}_2)_2\text{MoO}_4$ (Dana's System of Mineralogy, 1944; Staples, 1951). Rankama and Sahama (1950) suggest the oxide may be tied up with a sulfate ion. All studies indicate that water may be present in the structure. However, the free energy of the anhydrous substance has been determined from electrode potential data (Latimer, 1952). The stability field of ilsemannite is restricted to a narrow range of pH and Eh conditions which may explain its scarcity in nature.

Ferrimolybdate

Even though this mineral is the most important of the oxidized minerals of molybdenum, its nature is poorly understood. Dana's System (1944), following the work of Blanchard and Boswell (1930) and Schaller (1907), suggests its composition to be approximately $\text{Fe}_2(\text{MoO}_4)_3$. Russian workers (Malyuga, 1958; Vinogradov, 1957a) have suggested that an intermediate form of the non-sulfide exists and that its formula is nearly MoO_2SO_4 . Free energies have been approximated for both these compounds which suggests that they lie, in general, in portions of the molybdate stability field.

EXPLANATION OF THE DIAGRAMS

The Eh-pH diagrams have been constructed using solid-line boundaries to delineate fields of dissolved molybdenum species with a concentration of 10^{-6} moles per liter. This is an arbitrary figure, but is probably a close approximation for geologic situations. Thus, an equilibrium boundary between a solid and 10^{-6} concentration of dissolved species is considered as representative of the boundary of the insoluble compound. Dashed-line boundaries are used to indicate both direction of solubility and the enlarged stability field that would result from increased concentration of dissolved species.

The first diagram (Fig. 1) depicts the stability boundaries of the various solids as functions of the partial pressure of oxygen. The compound Mo_3O_8 appears to be the dominant species over a broad range of oxygen concentration. Molybdenum trioxide (MoO_3) is a stable species with respect to Mo_3O_8 only at high oxygen concentrations, while the dioxide is a metastable form under the conditions established. These data provide the basis for suggesting that neither MoO_2 nor MoO_3 are found in nature in the oxidizing environment.

The relationships among various molybdenum oxides and sulfides are shown in the second diagram (Fig. 2) which is a composite of stability fields with respect to partial pressures of oxygen and sulfur. It is of interest to note that the only "simple" oxide that might be found in nature is the ilsemannite type. Further, MoS_3 would be a stable species only at very high partial pressures of sulfur.

The third diagram (Fig. 3) illustrates a portion of the system $\text{Mo}-\text{H}_2\text{O}$. The metastable boundary between Mo_3O_8 and MoO_2 is shown. In this diagram as in the ones that follow, Mo_3O_8 occupies a very restricted portion of the diagram with respect to Eh and pH.

The fourth (Fig. 4) and fifth (Fig. 5) diagrams show the relationships of molybdenum oxides and sulfides under varying conditions of Eh and pH. The conditions shown differ only in the amount of sulfur considered in the dissolved state. Molybdenite remains a stable mineral species even under low concentrations of dissolved sulfur. It also appears to be unstable at the higher pH values. Ilsemannite retains its position on the diagrams as a stable substance whose boundaries are fixed only by the amount of dissolved molybdenum and to a lesser extent by the amount of dissolved sulfur.

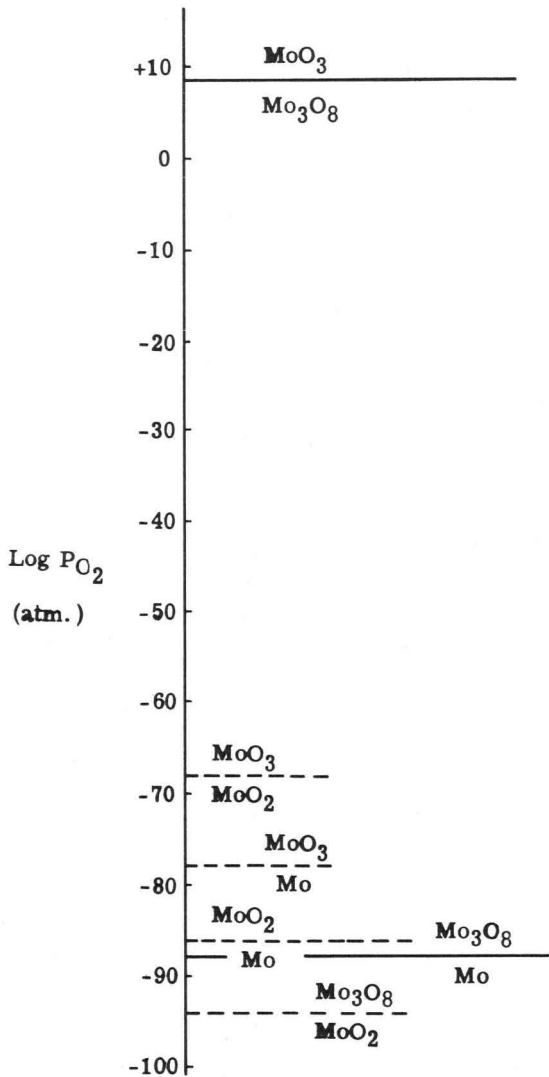


Figure 1. --Stability relations among some molybdenum compounds as a function of partial pressures of oxygen. Dashed lines indicate metastable boundaries.

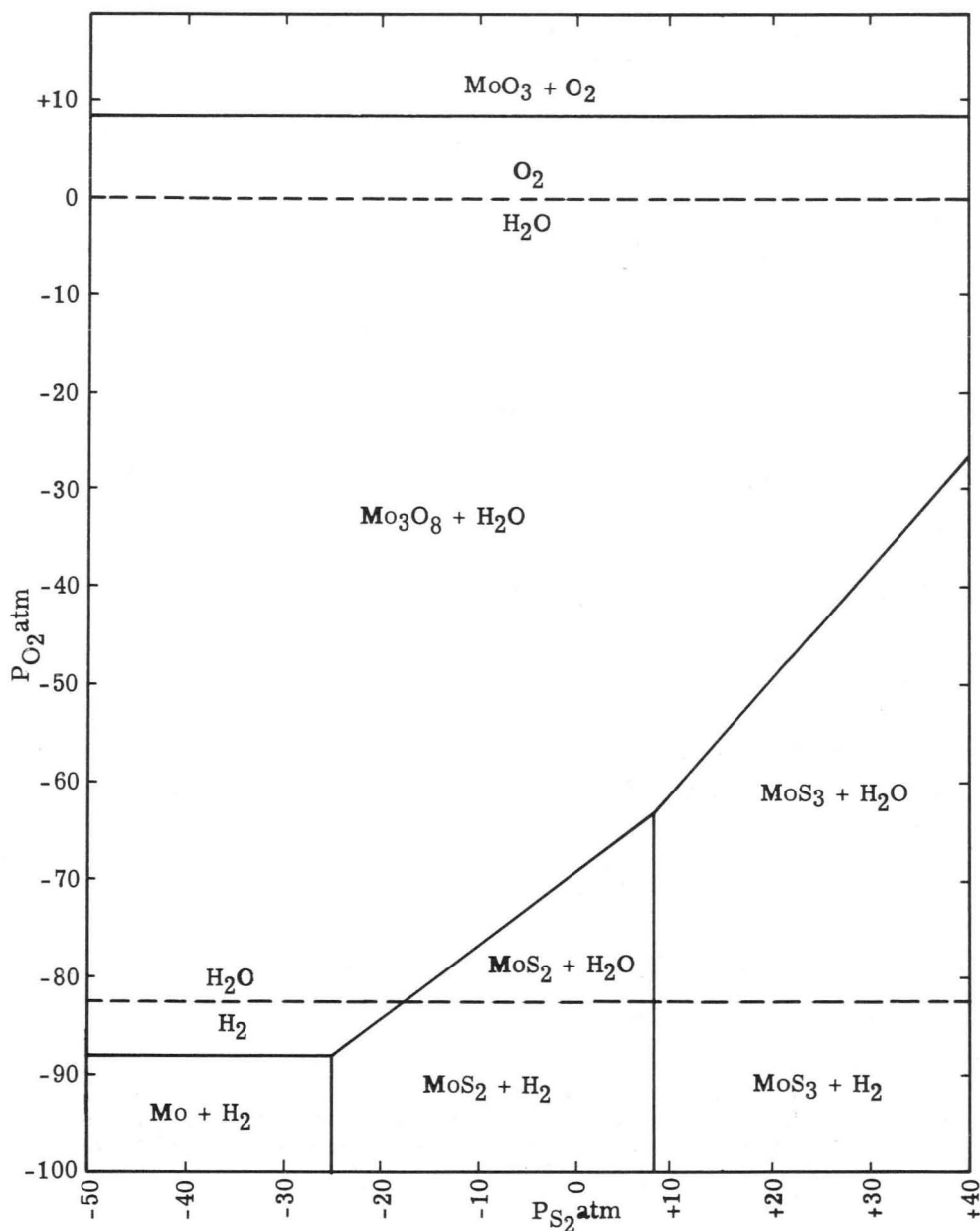
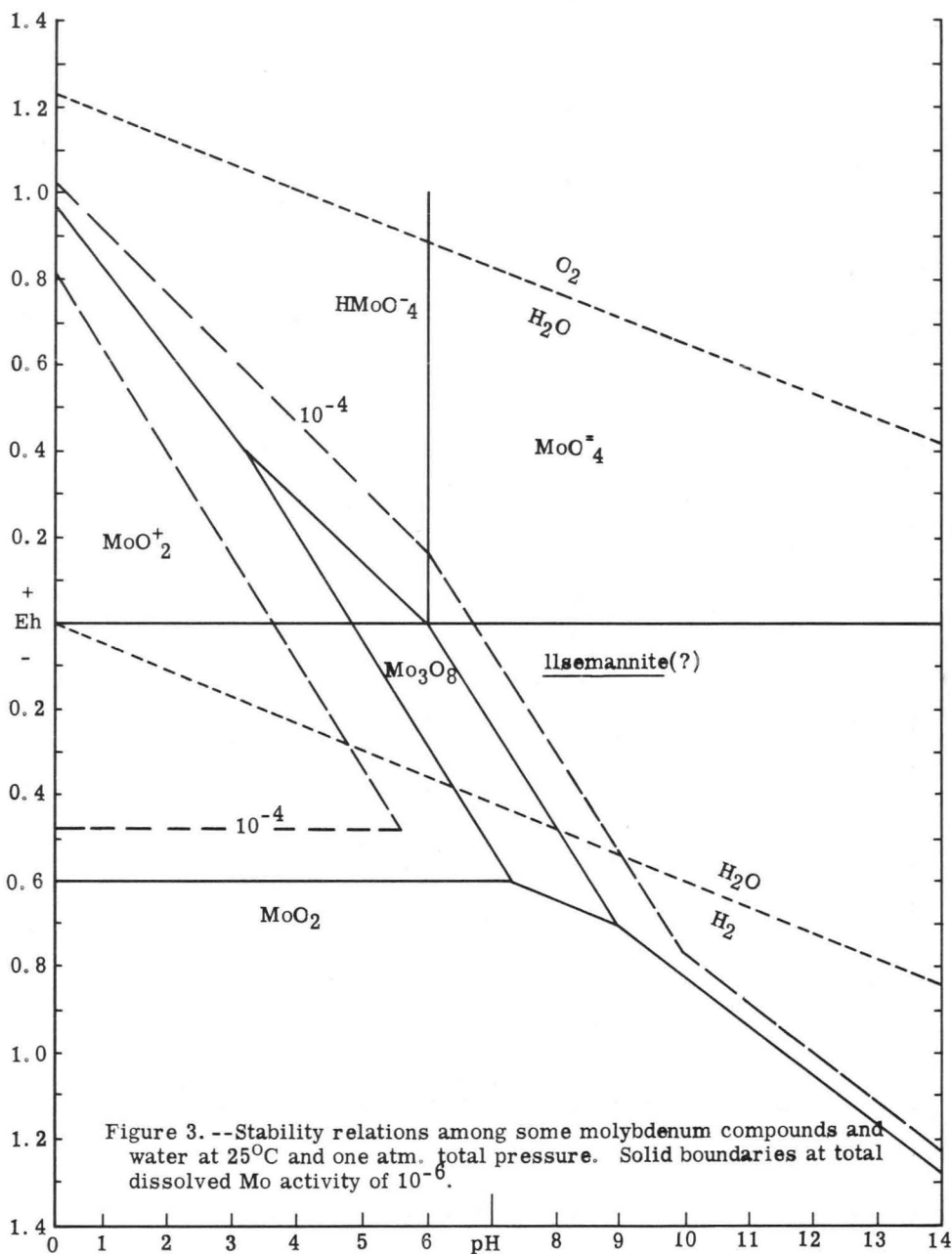


Figure 2. --Stability relations of some molybdenum compounds as functions of P_{S_2} and P_{O_2} at 25°C and one atm. total pressure.



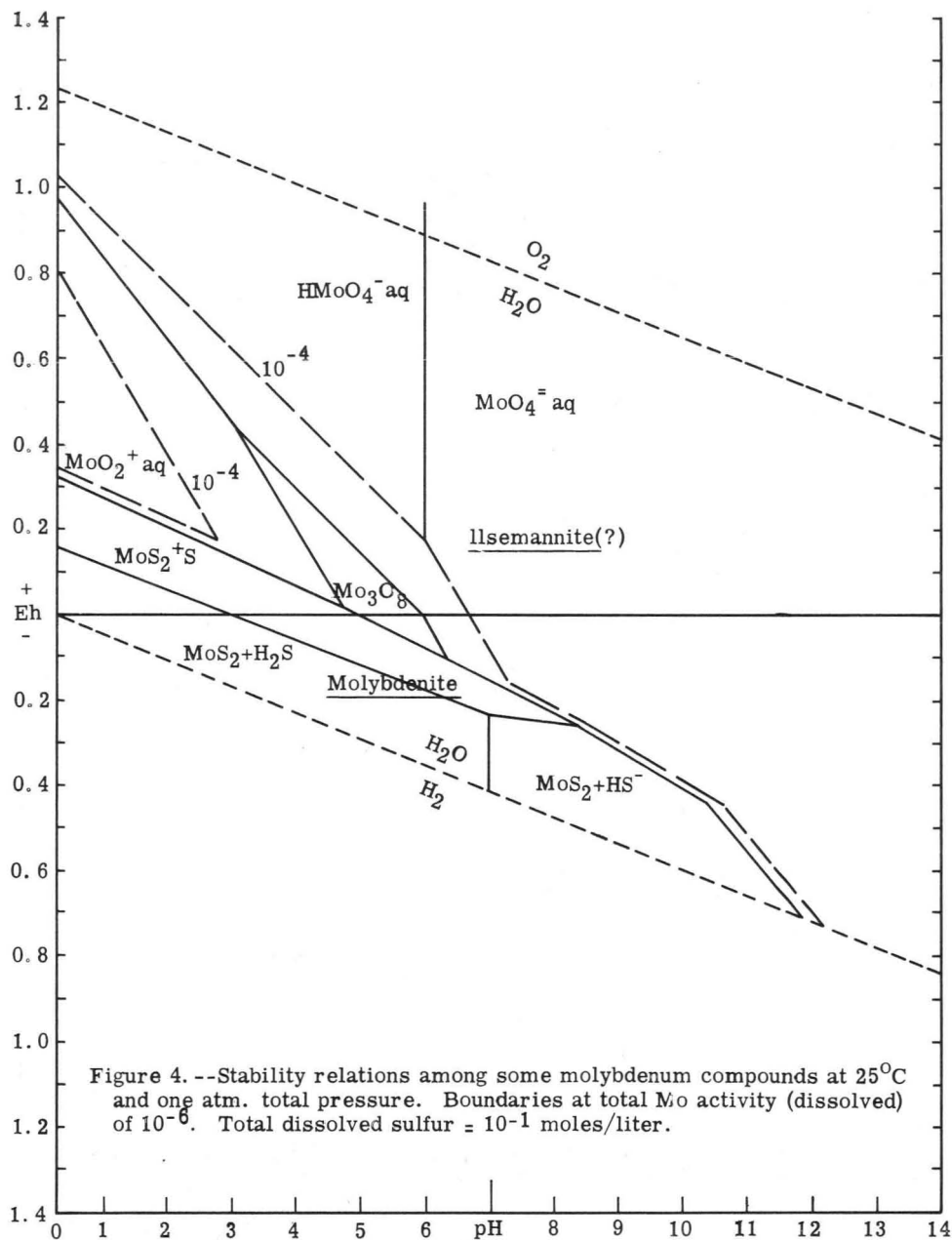
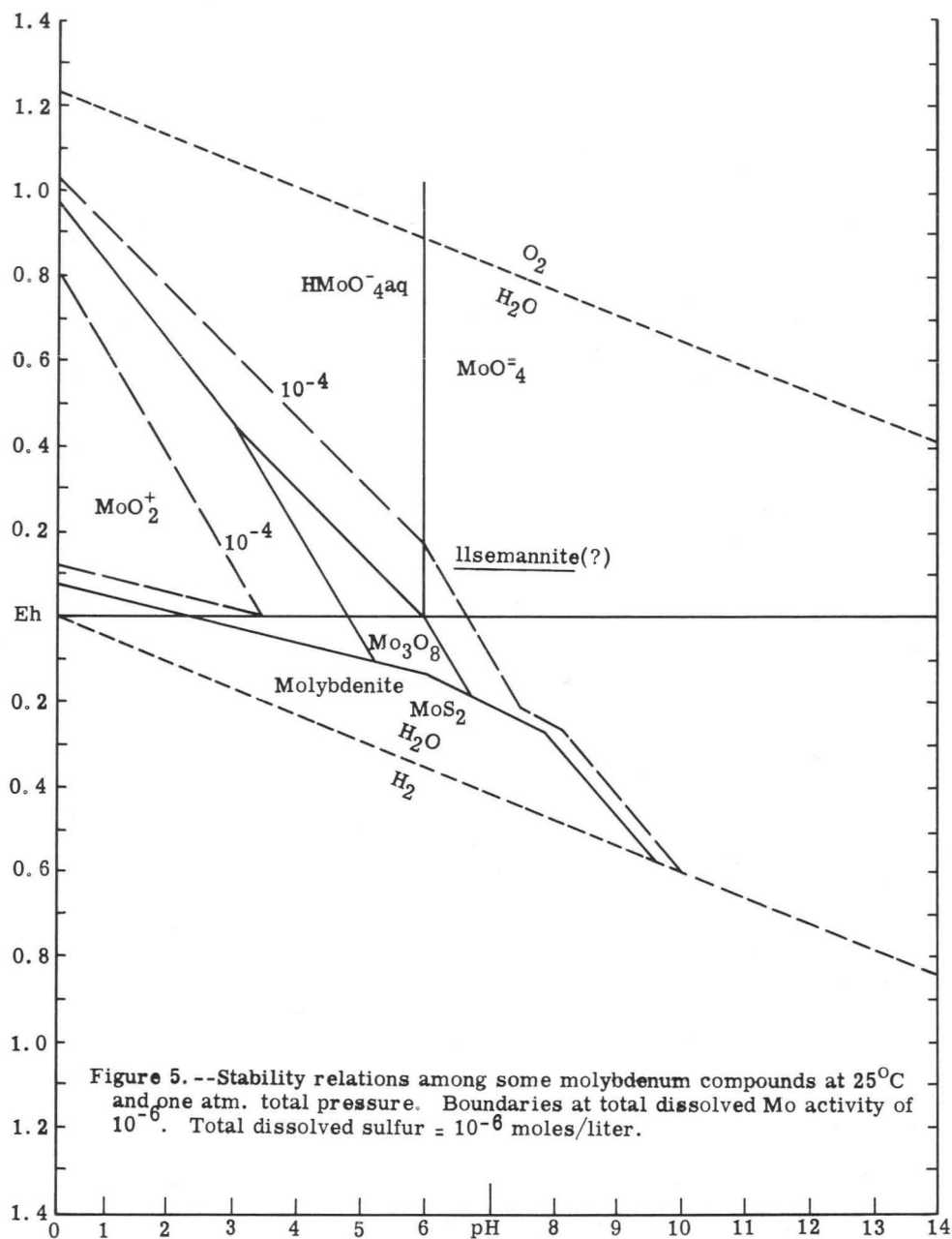


Figure 4. --Stability relations among some molybdenum compounds at 25°C and one atm. total pressure. Boundaries at total Mo activity (dissolved) of 10^{-6} . Total dissolved sulfur = 10^{-1} moles/liter.



CONCLUSIONS

While this work is largely theoretical and of only preliminary character, it is possible to make certain general deductions and to suggest certain conclusions. It should be emphasized that these conclusions are based upon the thermodynamics as calculated at 25°C and one atmosphere pressure which is an approximation of the conditions existing in the oxidizing environment.

The approach used in this study is that of thermodynamics and does not take into consideration any of the aspects of mechanisms of reaction. Thus, while molybdenite, for example, is indicated to be unstable at high pH values, the thermodynamics do not indicate the conditions under which breakdown might commence and proceed in the chemical system.

Molybdenite would appear to break down rather readily into molybdate ions and possibly form the intermediate compound MoO_2SO_4 under most conditions encountered in the supergene environment. It appears to be unstable under the higher pH conditions encountered. Rankama and Sahama have noted that molybdenite is precipitated from molybdenum-bearing solutions in a reducing environment such as a swamp. Theoretical considerations indicate this to be possible.

It should be noted that when the equilibrium boundaries for dissolved sulfur species are plotted (Garrels, 1960), the field of sulfate stability is approximately correlative with that of the molybdate ion and in part with the hexavalent molybdenum cation. It might be possible, therefore, that a number of possibilities exist for complexing hexavalent molybdenum with sulfate ions.

The molybdate ion can exist under a wide range of conditions and appears to be a possible soluble form. This appears to be especially important in suggesting an origin of wulfenite, a common mineral in the oxidized zone of a number of lead deposits in southern Arizona. While Takahashi (1960) implies that, in a great number of instances, the presence of both galena and molybdenite are requisite for the development of that mineral, the present work would suggest that the molybdenum need not be indigenous but can be transported to the site of deposition as a soluble anion. This possibility seems more in keeping with numerous observations of occurrence of wulfenite in deposits where molybdenite is either extremely scarce or totally absent.

It has not been possible to determine, thus far, what other factors contribute to the solubility of the molybdate ion. It is precipitated by either lead or calcium and more rarely by copper. What the conditions of precipitation are, can be only matters of speculation at this time.

Ilsemannite would appear to be an excellent geological indicator of conditions in the oxidized zone. Its restricted field lies at the acid and oxidizing extremes of conditions encountered in the zone of oxidation as depicted by Garrels (1954). Ilsemannite has been reported as a mineral associated with numerous uraninite deposits (Kerr, et al., 1957). It is quite probable that temperatures of formation in such environments were higher than those used in the present calculations. However, the location of uraninite on the diagrams shown by Garrels (1960) is correlative with a portion of the ilsemannite field.

Development of ferrimolybdate is probably closely associated with availability of the sulfate ion, and probably bears some relation to the presence

of pyrite in the mineral suite. In a number of environments in the southwest, the yellow oxidized mineral occurs in situations where pyrite is not present, suggesting that in the presence of excess iron, the non-sulfide is unstable. It has not yet been possible to place any confidence in the calculations because of inadequacy of data. However, any factor that would promote solubility of the sulfate ion, such as excess iron, would inhibit formation of ferrimolybdate. This would apply if the mineral is the sulfate. However, if it is the molybdate complex, then deficiency of sulfur would probably have to be invoked to explain its formation.

The results of this preliminary study underscore the usefulness of this type of approach to the study of supergene processes. While these data are far from complete and experimental work is indicated, the theoretical approach suggests answers and helps to define the major problems.

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