THE REDUCTION OF THIO-MOLYBDATE IN
AQUEOUS SOLUTIONS

by

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ABSTRACT

The high temperature behaviour of the molybdenum (VI) -sulphur (-II) -water system in the presence of an ammoniacal buffer was studied.

At 150°C. all species of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$ were shown to exist and the stability constants of mono-, di-, tri-, and tetra-thiomolybdate were $2.3 \times 10^2 \text{ M.}^{-1}$, $3.5 \times 10^5 \text{ M.}^{-2}$, $2.7 \times 10^8 \text{ M.}^{-3}$, $7.0 \times 10^{10} \text{ M.}^{-4}$, respectively. There were strong indications of the formation of protonated species, $\text{Mo}(\text{SH})_6$, in solutions containing low concentration of free ammonia.

Application of reducing gases to this system produced a mixture of a sulphide and an oxide of molybdenum, whose composition depended on the initial composition of the solution.

Under hydrogen, the reduction reaction was autocatalytic, rate being first order in product amount and hydrogen pressure. A mechanism was proposed in which the rate determining step was heterogeneous activation of hydrogen on the surfaces of precipitates followed by two paths, one to produce the sulphide and the other to produce the oxide. The proportion of the sulphide to the oxide was dependent on the solution composition, the higher the fractional distribution of tetra-thiomolybdate and the higher the concentration of hydrogen ion, the more the sulphide being produced.

Under carbon monoxide the reduction reaction was found to have an induction period. The molybdenum in solution then followed a linear decrease in concentration with time. The slope of this plot showed Langmuir type of dependence on both molybdenum concentration and pressure. A mechanism was proposed in which the rate determining step was a slow decomposition of some complex between thiomolybdates and carbon monoxide adsorbed strongly on catalytic precipitate which was produced during the induction period.

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To my wife I say thank you.

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INTRODUCTION

1. General

Molybdenite, MoS_2 , is well known to be an excellent lubricant, particularly for high temperature applications¹. It is usually manufactured by a complex process involving mineral dressing of molybdenite concentrate and leaching with hydrofluoric acid to remove abrasive materials such as silica². Owing to increasing demand, many attempts have been made to produce molybdenite synthetically³. Most of the attempts have involved direct fusion of molybdenum compounds and sulphur, with varying results, but no attempts to produce it from an aqueous system have been reported except in some experiments of geochemical interest.

Nominally molybdenite is a compound of tetra-valent molybdenum with sulphur. As the usual and most stable state of molybdenum is +6, production of molybdenite is likely to involve reduction and sulphidization. The present work was undertaken to study the reduction of aqueous solutions containing molybdenum in the hexa-valent state in the presence of sulphide ion with the object of producing MoS_2 and of developing a recovery technique for molybdenum from process solutions.

In the literature survey below, the following subjects are reviewed:-

1. The technology of the molybdenum industry.
2. The hydrometallurgical treatment of molybdenum ores and intermediates.
3. The reduction of aqueous solutions of molybdenum.
4. The Mo(VI) - S(-II) - water system.
5. The synthesis of MoS₂.

2. Literature Survey

2-1 Technology of the molybdenum industry

Molybdenum is known to improve the quality of iron and steel alloys⁴. It is classified as a strategic material and its use is increasing in spite of its relative scarcity in nature (3/10,000 of iron)⁵. Although the major use of molybdenum is in the iron and steel industry, the corrosion resistance of molybdenum metal, the special lubricating properties of MoS₂ and the chemical usefulness of molybdenum compounds as pigments, catalysts and reagents have established molybdenum as an indispensable element of modern industry.

The technology of molybdenum production is summarized in Fig. 1, in which materials underlined represent the product forms traded with the percentages listed as the limits of the specification. More than 90% of molybdenum produced comes from molybdenite, of which about half comes as a by-product of copper concentrate production⁶. Owing to the fact that no more purification is done for the majority

%-use is in terms of molybdenum content, in U.S.A. in 1966. ref. "Mineral Yearbook"

Fig. 1. Technology of molybdenum, (underlined are commercial forms with specifications below)

of uses, molybdenite concentrate must meet stringent purity requirements. Although the mineral dressing of molybdenite is termed simple⁷, several cleaning and re-cleaning steps with intermediate low temperature roasting or steaming and grinding are necessary, sometimes at the expense of recovery, in order to meet the specifications⁸. If purity specifications are not met after these treatments, hydrometallurgical or other processing techniques must be used. Hydrometallurgical processing is essential in the treatment of oxidized ores of molybdenum. Lubricant grade molybdenite must meet even more stringent purity requirements since it must be free of all abrasives, particularly silica, which is normally removed by treatment with hydrofluoric acid². Majority of molybdenite concentrates are roasted to remove sulphur and the resulting technical molybdic oxide is used mainly in ferroalloys and foundries without further purification. For production of metal and chemicals another step of purification is necessary. Sulphur and other impurities are removed by sublimation or hydrometallurgical treatments, thus producing pure molybdenum trioxide, which is further processed to produce the desired end products^{1,9,10}.

2-2 Hydrometallurgical treatment of molybdenum ores and intermediates.

Hydrometallurgical methods are currently employed in the purification of technical molybdic oxide and the processing of oxidized ores. The former involves 1) disso-

lution in dilute ammonia to remove sulphides, silica and other insolubles 2) precipitation and filtration of heavy metals such as copper as sulphides by addition of ammonium hydrosulphide 3) precipitation of ammonium molybdate by acidification 4) recrystallization and 5) calcination into molybdic oxide¹¹. The second application of hydro-metallurgy which is more recent is in the processing of oxidized ores of molybdenum, found overlaying sulphide ore bodies as finely dispersed ferric-molybdates etc., mostly in iron minerals. It involves 1) dissolution in acid 2) adsorption on charcoal 3) stripping with an aqueous ammonia 4) crystallization of ammonium molybdate and 5) calcination to produce technical grade molybdic oxide¹².

The leaching of molybdenite concentrates has come to be a subject of interest because it offers the potential of processing lower grade concentrates and gives a choice of purification methods. The leaching methods proposed are:-

- (a) in acid media: $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ^{13,14}, $\text{H}_2\text{SO}_4 + \text{NaClO}_3$ ¹⁴,
 $\text{H}_2\text{SO}_4 + \text{MnO}_2$ ¹⁵
- (b) in alkaline media: $\text{Na}_2\text{CO}_3 + \text{HClO}$ ^{16,17,18}, $\text{KOH} + \text{O}_2$
 (high temperature)¹⁹
- (c) bacterial leaching.

Although leaching was successful, the oxidants employed were found costly.

Various stripping and concentration methods from the leached solution were suggested, e.g. precipitation as ferricmolybdate^{13,14}, molybdenum tri-hydroxide²⁰ and ammonium molybdate^{17,21,23}, ion exchange using anion exchange resins^{18,24,25} and solvent extraction using TBP²⁶, charcoal¹² and others²⁷.

2-3 Reduction of aqueous solution of molybdenum

Reduction of molybdenum complexes in acid solution is known to be possible²⁸, although it is reported that molybdate ion is reduced infinitely slowly in alkaline media²⁹. An industrial method has been suggested for recovery of molybdenum from acid solutions as $\text{Mo}(\text{OH})_3$ after reducing Mo^{6+} with iron metal²⁰.

Paal and Buetter³⁰ studied the absorption of gaseous hydrogen at atmospheric pressure and at room temperature in solutions ($\approx 0.05\text{M.}$) of ammonium molybdate in the presence of a very active palladium hydrosol added as a catalyst. Absorption was noted to occur initially very rapidly (within 30 min.) up to about 50~60% of the theoretical value of reduction from +6 to +4, followed by a very slow process, complete reduction being achieved only after three days. They also reported that the reduction proceeded further, when heat ($\approx 60^\circ\text{C.}$) and slight overpressure of hydrogen was applied, until reaching the theoretical value equivalent to the reduction of hexa-valent to tri-valent. From the precipitate in the initial stage, they could, after careful drying,

obtain Mo(OH)_4 , MoO(OH)_2 , and MoO_2 , successively.

Lyapina and Zelikman³¹ studied the hydrogen reduction in acid solution. They reported that the batch reduction by hydrogen was two to four times as fast when "primed" by molybdenum powder (7% of stoichiometric amount) to form MoO_2 seed crystal. The recoveries in four hours at 200°C. from solutions containing 43.62 g./l. of molybdenum with the initial pH of 2 were 99, 82, 70 and 34%, respectively, for the hydrogen pressure of 60, 40, 20 and 10 atm. (final pH were 7.0, 6.56, 3.94 and 2.67, respectively). At 200°C, 60 atm. and in four hours, an initial pH of 3, 5 and 7 gave 81.1, 38.3 and 11.7% recovery, respectively. At 100°C. even an initial pH of 2 gave only 41% precipitation under the same condition. At 200°C., 60 atm. and in one hour, the recovery increased from 78% to 99% when initial concentrations of molybdenum were decreased from 43.6 to 5.33 g./l. In a subsequent paper³² they reported the selective reduction of tungsten from a solution containing tungsten and molybdenum. When a solution containing 41.0 g.Mo/l. and 5 g.W/l. at initial pH of 2 was reduced at 200°C. and $P_{\text{H}_2} = 20$ atm. for 90 min., the solution contained 38.9 g.Mo/l. and 0.5 g.W/l. and the precipitate was 47% and 40% in Mo and W respectively. When the solution was reduced subsequently at 200°C. and $P_{\text{H}_2} = 60$ atm. with Mo powder added as an accelerator, the solution contained 0.3 g./l. of Mo and W respectively. As the pH value varied considerably their data are difficult to analyse.

A somewhat different approach to the reduction in an acid solution was adopted by Dodonova³³ who studied the photolysis of acidified sodium molybdate solutions (made pH = 2 by HCl addition) under various atmospheres such as H₂, CO, CO₂, He, vacuum, H₂ + O₂ and CO + O₂. He noted the appearance of blue color due to the reduction of Mo⁶⁺ to Mo⁵⁺ under H₂ and CO and no appearance under the others. He attributed the latter fact to the oxidation of Mo⁵⁺ by the photolysis products of water, which would otherwise combine with H₂ and CO to form H₂O and HCHO thus avoiding the rapid reoxidation of Mo⁵⁺. When O₂ was increased in H₂ + O₂ mixture, the blue colour disappeared.

Reduction of molybdenum with hydrogen in ammoniacal solution was studied, with an industrial application in mind, by Kunda and Rudyk⁸. The effects of catalyst, solution recycling, concentrations of ammonium ion, free ammonium and initial molybdenum, hydrogen partial pressure and temperature, on the rate and extent of precipitation were determined. They again found palladium very effective (added as 0.5% PdCl₂ solution) as a catalyst, as well as metallic molybdenum powder, metallic nickel and graphite, at 177°C. and 24.5 atm. H₂ for a solution containing 1 M. Mo, 1~1.5 M. (NH₄)₂SO₄ and 1.5~2 M. NH₃. They found an approximate linear increase of the rate of precipitation with the concentrations of catalysts and (NH₄)₂SO₄ and with partial pressure of hydrogen (below 23 atm.), and a linear decrease of the rate of precipitation with the initial concentration

of molybdenum. Increase of free ammonium decreased the rate of reduction. The temperature dependence of the rate of precipitation at certain values of variables was studied with PdCl_2 and Mo metal powder as the catalyst. In both cases the apparent activation energy was found to be 16.4 Kcal./mole. Their precipitates contained 60-65% Mo and 4-5% NH_3 , suggesting that the reduction had proceeded partly to the trivalent state (67% Mo in $\text{Mo}(\text{OH})_3$).

2-4 The Mo(VI)-S(-II)-water system

In the Mo(VI)-water system, under weak acid conditions, large isopoly ions are formed, e.g., $\text{Mo}_7\text{O}_{24}^{4-}$ ³⁴ and a large family of heteropoly ions with many metallic and non-metallic ions, e.g.,

etc.³⁵. But under sufficiently alkaline conditions these complex ions decompose into the simple molybdate ion, MoO_4^{2-} .

When sulphide ion, S^{2-} , is introduced into the Mo(VI)-water system, interchange of oxide ion, O^{2-} , with sulphide ion can be expected because of the similarity of these ions. Most of the studies of this system up to 1928 were reviewed by Meller³⁶ and up to 1963 by the Chemical Society of London³⁷. The more recent studies are reviewed in the following order:

- (a) salts of tetra-substituted species, MoS_4^{2-} ,
- (b) salts of di-substituted species, $\text{MoO}_2\text{S}_2^{2-}$,
- (c) salts of mono- and tri-substituted species,
 $\text{MoO}_3\text{S}^{2-}$, MoOS_3^{2-} ,
- (d) species other than of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$
 $(x = 1-4)$,
- (e) studies of the equilibria between the complex species,
- (f) acid decomposition of the complex species.

2-4-a Salts of tetra-substituted species, MoS_4^{2-}

Salts of the tetra-substituted species (or tetra-thiomolybdate) MoS_4^{2-} , have been claimed by a number of workers³⁶. The ammonium salt $(\text{NH}_4)_2\text{MoS}_4$ was prepared as a blood-red, needle-like crystal by Kruess³⁸ in 1884 by saturating an ammoniacal ammonium paramolybdate solution with hydrogen sulphide gas. Tridot and Bernard³⁹ also prepared it similarly for their visible and U.V. spectroscopic study. Alkali metal salts have been obtained³⁶. Spacu and co-worker⁴⁰ prepared the salts of complex metallic amine of Cu and Cr:

and stated that these salts were more stable than the simple alkali metal salts. They also prepared the salts of organic

bases such as those of aminopyridine, ethylenediamine, hexamethylenetetramine and 1,10-phenanthroline. Perel'man and co-workers⁴¹ employed the solubility method to study the sodium salts system. After dissolving Na_2MoO_4 , Na_2S and NaOH at $60-70^\circ\text{C}$. in water to make up the composition range of $\text{Mo}^{6+} = 3-30\%$, $\text{S}^{2-} = 6-13\%$ and $\text{NaOH} = 5-40\%$, the mixtures were kept at 25°C . for 24 hours and solid and liquid phases were analysed. They reported that Na_2MoS_4 did not exist below 27% NaOH concentration perhaps due to the instability of the Na_2MoS_4 lattice. Bock and Langrock⁴² prepared an unstable compound, tetra-thiomolybdic acid, H_2MoS_4 , by passing a solution of the ammonium salt through the H^+ form of a cation exchange resin. Clark and Doyle⁴³ confirmed the K^+ and NH_4^+ salts but denied the existence of the salts of Co(II) , Ni(II) , Cu(II) and Zn(II) , stating them to be mixtures of sulphides of these metals with molybdenum trisulphide. Leroy and co-workers⁴⁴ prepared quaternary ammonium salts by the reaction of molybdic acid with NX_4OH ($\text{X} = \text{Me}$ or Et .). The solution was saturated with hydrogen sulphide and after a few days crystals of $(\text{NMe}_4)_2\text{MoS}_4$ and $(\text{NEt}_4)_2\text{MoS}_4$ were formed at -5°C . They also prepared $(\text{PPh}_4)_2\text{MoS}_4$ and $(\text{AsPh}_4)_2\text{MoS}_4$ by reaction of the ammonium salt with the chloride of the corresponding tetraphenyl complex. Saxena and co-workers^{45,46} confirmed the formation of PbMoS_4 by amperometric titration of $\text{Pb(NO}_3)_2$ and thiomolybdate solution.

Crystallographic study of the salts of tetra-thiomolybdates and spectroscopic study of the tetra-thiomolybdate ion in solution have been reported by several workers. Kruess³⁸ grew large crystals of $(\text{NH}_4)_2\text{MoS}_4$ and K_2MoS_4 and from the measurements of angles between habit planes, Haushofer reported them as having rhombic symmetry with $a:b:c = 0.7846:1:0.5692$ ³⁸. Gattow⁴⁷ made an X-ray study of the ammonium tetra-thiomolybdate crystal and reported it to be orthorhombic with the unit cell length as $a = 9.599$, $b = 12.288$, $c = 7.000$ Å, and its space group to be D_{2h}^{16} - Pnam, iso-morphous with K_2SO_4 type crystal, in which NH_4^+ ion and MoS_4^{2-} tetrahedral ion are packed rather loosely⁴⁸. Gattow and Franke summarized their X-ray data for K^+ , Rb^+ , Cs^+ and NH_4^+ salts⁴⁹. Schaeffer et al.⁵⁰ reported the same experiment and stated that MoS_4^{2-} tetrahedra are slightly distorted.

The Mo-S bond strength has been studied by I.R. and Raman spectroscopy. Gattow, Franke and Mueller⁵¹ measured the I.R. spectra of M_2MoS_4 crystals, where $\text{M} = \text{K}^+$, Rb^+ , Cs^+ , NH_4^+ and Tl^+ ⁵², and reported that the band frequencies observed for complex anions are practically unchanged by the various cations. Bands were found at 460, 480, 155, 195 and 280 cm^{-1} , and the first three of these were assigned to ν_1 , ν_3 and ν_4 vibration of MoS_4^{2-} tetrahedra. Clark and Doyle⁴³ studied the crystals of K^+ and NH_4^+ salts along with MoO_4^{2-} salts and reported the existence

of discrete MoS_4^{2-} ions and the effect of substitution of O^{2-} by S^{2-} was to approximately halve the vibrational frequencies. The theoretical treatment by Mueller and co-workers⁵³ revealed the higher double bonding character of Mo-S bonds. Leroy, Kaufman and Charlionet⁴⁴ stated that they did not observe much shift in bands nor appearance of new bands in I.R. spectra of their quarternary ammonium salts, by the change of the size of cation.

The electronic state of the tetra-thiomolybdate ion can be studied by the visible and U.V. spectroscopy of the aqueous solution. Tridot and Bernard³⁹ studied the spectrogram between 200 and 500 m μ of the aqueous solutions, (1.25×10^{-4} M.), obtained by dissolving crystals of ammonium salt which they prepared by Krüss's method. They reported the absorption peaks at 210, 240, 325 and 465 m μ and the molar extinction coefficients at 392.5 and 465 m μ as 700 and 10,800 $\text{M}^{-1}\text{cm}^{-1}$, respectively. Yatsimirski and Zakharova⁵⁴ did not observe the peaks, stated by Tridot and Bernard³⁹, in their spectrophotometric study of dilute solutions obtained by mixing ammonium molybdate solution and sodium sulphide solution. This disagreement may be due to the slowness of the rate of approach to the equilibrium noted by Tridot and Bernard. Companion and Mackin⁵⁵ interpreted the absorption peaks as the charge transfer of an electron on the sulphide ion to a molecular orbital localized on the metal ion.

Mueller, Ritter and Nagarajan⁵⁶ compared the

electron absorption spectra of MoO_4^{2-} and MoS_4^{2-} and stated that π -bonds must also be assumed in the thioanion. Later Mueller and Ekkehard⁵⁷ summarized their spectroscopic study on MX_4 anions where $\text{M} = \text{V}, \text{Mo}, \text{W}$ and $\text{X} = \text{O}, \text{S}, \text{Se}$. They interpreted that the band corresponded to $t_1 \rightarrow 2e$, transition of electron from the non-bonding molecular orbital t_1 to a weak anti-bonding molecular orbital $2e$ which is essentially localized on the metal atom, and that the strongly-bonding molecular orbital $1e$ is stabilized by the increase in anti-bonding character of molecular orbital $2e$.

2-4-b Salts of di-substituted species, $\text{MoO}_2\text{S}_2^{2-}$

The ammonium salt of the di-substituted species, or di-thiomolybdate $\text{MoO}_2\text{S}_2^{2-}$, was prepared by Krüss³⁸ by the same procedure as for the salt of the tetra-thiomolybdate except that a chilled solution having a slightly higher ammonium concentration was used. He obtained yellow crystals which reddened on exposure to air. Recently Hofmeister and Gattow⁵⁸ prepared it by the same method. Perel'man et al.⁴¹ postulated the existence of $\text{Na}_2\text{MoO}_2\text{S}_2$ to explain their results of a solubility investigation at low Na_2S and NaOH concentration. Tridot and Bernard³⁹ prepared the ammonium salt by Krüss's method, except that they added the ammonium chloride to facilitate the crystallization. From the U.V. spectrogram of the aqueous solution they reported the molar extinction coefficient of $\text{MoO}_2\text{S}_2^{2-}$ ion at 290 mμ of 6,950 $\text{M}^{-1} \text{ cm}^{-1}$. Yatsimirskii and Zakharova⁵⁴ proved the existence

of $\text{MoO}_2\text{S}_2^{2-}$ ion from a spectrographic study of dilute solution, when sodium sulphide to ammonium molybdate ratio is greater than 4 to 1 in 2×10^{-4} M. Mo solution. Mueller and Gattow⁵⁹ investigated the I.R. spectroscopy of the ammonium salt and reported the fundamental frequencies to be 836, 800, 488, 305 and 200 cm^{-1} . They compared these with the spectrum of MoO_4^{2-} salt and stated that the entry of two sulphur atoms into MoO_4^{2-} decreased the M-O bond strength. Leroy and Kaufman⁶⁰ observed the Raman spectrum of the ammonium salt using a He-Ne laser as the excitation source. The recorded lines were indexed on the assumption that $\text{MoO}_2\text{S}_2^{2-}$ has C_{2v} symmetry.

2-4-c Salts of mono- and tri-substituted species, $\text{MoO}_3\text{S}^{2-}$ and MoOS_3^{2-}

Few studies of the mono- and tri-substituted salts, or mono- and tri-thiomolybdate $\text{MoO}_3\text{S}^{2-}$ and MoOS_3^{2-} , have been reported. Krüss³⁸ claimed to have prepared the sodium salt of mono-thiomolybdate, $\text{Na}_2\text{MoO}_3\text{S}$. Perel'man et al.⁴¹ postulated both mono- and tri-thiomolybdate to explain their stability data. Hofmeister and Glemser⁶¹ stated that the tri- and mono-thiomolybdate were the product of hydrolysis of tetra- and di-thiomolybdate, respectively. Tridot and Bernard⁶² studied the absorption of hydrogen sulphide by alkaline molybdate solution and from the spectrograms of the solutions at different degrees of sulphidization, they concluded that mono-thiomolybdate did not exist but that tri-thiomolybdate exists and has the absorption peak at $392.5 \text{ m}\mu$.

with the molar extinction coefficients at 392.5 and 465 m μ of 9,850 and 400 M.⁻¹ cm.⁻¹, respectively. Yatsimirskii and Zakharova⁵⁴ studied more dilute solutions by Job's method and claimed to have proved the existence of mono-thiomolybdate in the solution of (Mo) + (S²⁻) $\approx 1 \times 10^{-3}$ M. Leroy, Kaufman and Charlionet⁴⁴ succeeded in preparing tri-thiomolybdate as quaternary ammonium salts, (NX₄)₂MoOS₃ where X = Et and Me. They also prepared the cesium salt Cs₂MoOS₃ by the reaction of (NH₄)₂MoO₂S₂ with CsCl at -5°C. Their U.V. and visible spectrum of MoOS₃²⁻ revealed three significant bands at 317, 392.5 and 465 m μ and I.R. spectrum of the crystals gave three strong absorption bands at 467, 477 and 857 cm.⁻¹. The first two and the last were attributed to Mo-S and Mo-O vibration, respectively. It was proven later⁶³ that MoOS₃²⁻ has C_{3v} symmetry in the crystal.

2-4-d Species other than those of the form MoO_{4-x}S_x²⁻
(x = 1-4)

A form of ionic species other than MoO_{4-x}S_x²⁻ (x = 1-4) has been claimed by various workers³⁶. Recently Srivastava and Ghosh⁶⁴ stated that, at lower pH values, yellow (H₆MoS₈)⁴⁻ and orange (H₈MoS₈)²⁻ were formed in solutions of [Mo] = 0.025 M. and [Mo]:[S] ratio greater than 1:8. Yatsimirskii and Zakharova⁵⁴ suggested the presence of Mo₂O₆S²⁻ from the fact that the absorbance of isomolar solution (0.1M.) at 465, 500 and 520 m μ passed through a maximum at S:Mo = 1:2, which is rather dubious because of the high

molarity and also the possible inadequacy of the wavelength chosen. Saxena, Jain and Mittal⁶⁵ studied the acidification of sodium thiomolybdate with HCl by pH and conductometric measurements and suggested the formation of three different polymerized species $(\text{Mo}_4\text{S}_{15})^{6-}$, $(\text{Mo}_2\text{S}_7)^{2-}$ and $(\text{Mo}_4\text{S}_{13})^{2-}$ at pH of 8.5-7.5, 5.3-4.2 and 3.3-2.8, respectively.

2-4-e Studies of the equilibrium between the complex species

A detailed study of the equilibrium between the complex species of Mo(VI) -S(II)-water system has not been performed. Hofmeister and Glemser⁶¹ studied the hydrolysis reaction of tetra- and di-thiomolybdate according to the equations (a) and (b):-

at temperatures of 20 to 60°C. They reported that the rate was independent of the hydrogen ion concentration between pH of 7 to 9. They gave the activation energy for the hydrolysis reaction of tetra- and di-thiomolybdate as 19.7 and 26.5 Kcal./mole, respectively, but no further details are available from their report.

Bernard and Tridot⁶² performed the most extensive work. They measured the absorption of hydrogen sulphide gas at one atmospheric pressure and at 19°C. during certain time

intervals, by 10 ml. of a solution containing 0.06 M. $(\text{NH}_4)_2\text{MoO}_4$ and 0.06 M. or 0.12 M. ammonia in a closed vessel, and spectrophotometrically determined the concentrations of tetra-, tri-, and di-thiomolybdate using the values of molar extinction coefficients they had previously determined³⁹. They also calculated the concentration of molybdate and total free sulphide concentration by the mass balance assuming that mono-thiomolybdate did not exist. They also used a solution containing 0.06 M. $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ and 0.06 M. ammonia. They did not report the equilibrium constants that could have been calculated from the data but reached the conclusion that:-

- (a) thiomolybdates are not stable below $\text{pH} = 7$,
- (b) in alkaline solution the substitution of oxygen by sulphur is quantitative and occurs in three steps:
 - i) initially di-thiomolybdate ion forms, quantitatively, especially at sulphide concentrations up to the limit of $\text{S/Mo} = 2$ in 0.001 M. Mo solution;
 - ii) second step being the formation of tri-thiomolybdate ion, marked by the appearance of an absorption peak at 392.5 m μ which goes through a maximum as sulphidization proceeds;
 - iii) thirdly tetra-thiomolybdate ion occurs as the final end product of sulphidization.

Their data was processed by the present author to obtain the consecutive constants using the literature values

for the dissociation constants of ammonium ion, aqueous hydrogen sulphide and hydrosulphide ion. The results showed that a) there is a doubt about their equilibrium condition, b) if equilibrium is assumed, mono-thiomolybdate must be assumed to exist and the logarithms of the consecutive constants (in M^{-1}), $k_4 = (MoS_4^{2-}) / (MoOS_3^{2-})(H_2S)$, $k_3 = (MoOS_3^{2-}) / (MoO_2S_2^{2-})(H_2S)$, $k_2 = (MoO_2S_2^{2-}) / (MoO_3S^{2-})(H_2S)$ and $k_1 = (MoO_3S^{2-}) / (MoO_4^{2-})(H_2S)$ are 2.7, 3.4, 4.4 and 5.5 respectively.

Yatsimirskii and Zakharova⁵⁴ used a rather dilute solution. But their data are not processable for the consecutive constants because Job's method is not reliable in the complex system in which many species are existing in equilibrium with each other. Around their concentration range and wavelengths employed, mono- and di-thiomolybdate and a small amount of tri-thiomolybdate can be expected to exist from Tridot's data.

2-4-f Acid decomposition of the complex species

Acid decomposition of thiomolybdates was observed to occur³⁶. When acid was added to a tetra-thiomolybdate solution, molybdenum trisulphide precipitated, liberating hydrogen sulphide gas. However, a di-thiomolybdate solution yielded no hydrogen sulphide³⁸.

Zvorykin, Perel'man and Tarasov⁶⁶ studied the equilibrium composition of precipitates with acidified solutions (made pH = 4.5 with HCl) of the $Na_2MoO_4 - Na_2S$ -water system by the solubility method. The precipitated phases

in relation to the starting molar ratio, $r = (S)/(Mo)$, were found to be:-

The last two can be written tentatively as $3MoS_2 \cdot 0.4MoO_3$ and $3MoSO_2 \cdot 3MoO_3$, respectively, suggesting the simple replacement of O with S in molybdenic oxide, MoO_3 .

Hofmeister and Glemser⁶¹ studied the acid decomposition reactions, equation (c) and (d), between

pH = 1 and 4 and stated that the rate determining steps were step 2, that the decomposition reactions were of the first order, and that the pH dependence of the first order rate constants suggested pre-equilibrium step 1. The reaction products suggested in equation (c) as HS^- and in equation (d) as H_2S are contrary to previous knowledge³⁸.

Srivastava and Ghosh⁶⁷ studied the precipitation of molybdenum sulphide from a solution containing 0.025 M. molybdate by the addition of 2N HCl and found that precipitation was complete only when the amount of sulphide added as 0.05 M. NaHS exceeded the molar ratio of Mo:S = 1:8. He proposed the possible form of the precipitate as $3\text{MoS}_3 \cdot \text{H}_2\text{S} \cdot \text{H}_2\text{O}$. He also stated that only the thiosalt of the form $\text{H}_4\text{MoS}_8^{6-}$ could be decomposed by acid to give molybdenum sulphide. Saxena, Jain and Mittal⁶⁵ stated that tetra-thiomolybdate decomposed into $\text{MoS}_3 \cdot \text{H}_2\text{O}$ at pH of less than 2.5.

2-5 Synthesis of molybdenum disulphide

The first synthesis was made by Berzelius in 1826; he stated that when an aqueous solution of tetra-thiomolybdate was boiled in a closed vessel, molybdenum disulphide precipitated along with other complex sulphides³⁶. Since then many syntheses of molybdenite have been made. Arutyunyan and Khurshudyan⁶⁸ reviewed the methods reported up to 1966 and the following information is abstracted partly from their work.

Most of the molybdenum disulphide found in nature is reported to be of the hexagonal modification with elongated bi-molecular unit cells except for a few rare examples having a rhombohedral structure with a tri-molecular hexagonal cell⁶⁹. The sulphur atoms surrounding molybdenum in MoS_2 are at the corners of right equilateral trigonal prisms which share vertical edges with one another to build

up complete MoS_2 layers normal to the c_0 axis. In the hexagonal modification the crystal is built up by repeating these complete layers on one another according to the alternating requirements of hexagonal close-packing, and in a rhombohedral modification, according to those of the three layer cubic close-packing. By denoting sulphur positions with capital letters and molybdenum positions with small letters, the former can be described as $\begin{smallmatrix} | \\ \text{AbA/BaB/A} \\ | \end{smallmatrix}$ and the latter as $\begin{smallmatrix} | \\ \text{AbA/BcB/CaC/A} \\ | \end{smallmatrix}$ ⁶⁸, where slashes indicate the positions of double layers of sulphur. The distance between these sulphur atoms is larger than the distance between the sulphur atoms forming the trigonal bi-pyramids (3.66Å against 2.98Å in hexagonal modification)⁷⁰. The weak bonding between the sulphur double layers is said to be the source of the lubricating properties of this material¹. The lubricating qualities of the two modifications were reported to be essentially the same⁷¹. There can be other modifications which may result from alternating combinations of hexagonal and rhombohedral packings⁷².

The methods of synthesizing MoS_2 were classified by Arutyunyan and Khurshudyan⁶⁸ into four groups:-

1. Reaction in a gaseous medium: the initial components are volatile molybdenum chlorides and hydrogen sulphide gas, reacting at a temperature of 700-800°C.
2. Reaction in molten salts: the initial components may be $\text{MoO}_3 + \text{S}$, $\text{CaMoO}_4 + \text{Na}_2\text{CO}_3 + \text{S}$, or $\text{MoO}_3 +$

$\text{Na}_2\text{CO}_3 + \text{S}$. The usual temperature of synthesis ranges from 700° to 900°C .

3. Reaction between the molybdenum compounds in solid phase with sulphur vapour or hydrogen sulphide gas at a temperature of $700\text{--}800^\circ\text{C}$.
4. Decomposition of molybdenum trisulphide at a high temperature, (over 500°C . in an inert atmosphere).

A further method which should be added is

5. Thermal^{73,74} or hydrothermal⁶⁸ decomposition of molybdenum thio-complex salts.

Almost all the synthetic molybdenum disulphides subjected to X-ray analysis are reported to be rhombohedral except for a few hexagonal examples prepared under extreme conditions or after prolonged annealing at high temperatures. This point was made clear by Arutyunyan and Khurshudyan⁶⁸ from their study of the hydrothermal decomposition of thio-molybdates. Their experiments consisted of sealing aqueous solutions, containing maximum of 0.5 M. MoS_4^{2-} with pH of 8-12 with NaOH, in a glass bottle and heating at $300\text{--}700^\circ\text{C}$. for 1~100 hours. Their results were summarized along with those of the other workers, as follows:-

Crystal Modification	Temperature	Conditions
amorphous	20-300°C	pH<6~7
colloformic	200-300°	
rhombohedral	250-900°	short duration of heating
hexagonal	600°C	22 days
hexagonal	1300°C	2 hours in silicate melt

They demonstrated the transition to the higher level of crystallization by the use of X-ray diffraction.

3. Scope of Present Work

From a review of the literature, the following points seem clear:-

1. The demand for molybdenum is growing, leading to a search for processes to treat lower grade ores.
2. Hydrometallurgical methods can treat low grade sulphide oxide ores to produce pregant molybdenum solution.
3. Reduction of aqueous solutions of molybdenum with hydrogen gas can proceed at elevated temperatures with the aid of catalysts to produce tetra- or tri-valent molybdenum compounds.
4. A fairly extensive study has been performed of the Mo(VI)-S(-II)-water system especially for the preparation and characterization of thio-complex salts.

The study of equilibrium in the system is incomplete and no studies on the system at elevated temperatures have been reported.

5. Synthesis of molybdenum disulphide has been mostly performed in non-aqueous media and when thiomolybdate was used as starting material, the process used was simple thermal and hydrothermal decomposition. Therefore, no positive effort has been made to reduce the molybdenum in solution prior to precipitation of the sulphide.

In view of the above facts the following was taken as the scope of the present work:-

1. To study the equilibrium of the Mo(VI)-S(-II)-water system at elevated temperatures with the object of establishing the equilibrium constants between complex species.
2. To investigate the reduction of the Mo(VI)-S(-II)-water system with hydrogen and carbon monoxide and to analyse reduction products and kinetics.

PART I: STUDY OF EQUILIBRIUM IN THE Mo(VI)-S(-II)-WATER SYSTEM

1. Principles of the experiment

From a review of the previous works on this system, the following facts seem to have been established:-

- (a) In crystals and in alkaline solutions thio-complex species of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$ ($x = 1-4$) exist.
- (b) Predominant absorption bands in the visible and near U.V. range of the above species are:-

- (c) In acidic solutions, there can be various complex condensed forms.
- (d) Establishment of equilibrium between the complex species in alkaline solutions is rather slow at room temperature but the formation of the thio-anion is highly favoured in the presence of a very dilute concentration of sulphide ion.

Therefore, when conducting experiments in an ammoniacal solution at higher temperatures, the following simple equilibrium between the species of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$ ($x = 1-4$) can be expected:-

where k 's are the consecutive constants.

In general, a complex system with one central metal ion, M , and a maximum co-ordination number of N is fully described by the concentrations of total metal, M_T , total ligand, L_T , or free ligand, L , and by a set of stability constants, β_i .

$$\beta_i = \prod_{j=1}^i k_j, \quad i = 1 \sim N$$

$$\begin{aligned} M_T &= [M] + [ML] + [ML_2] + \dots + [ML_N] \\ &= [M][1 + \beta_1 L + \beta_2 L^2 + \dots + \beta_N L^N] \end{aligned}$$

$$\begin{aligned} L_T &= L + [ML] + 2[ML_2] + \dots + N[ML_N] \\ &= L + [M][\beta_1 L + 2\beta_2 L^2 + \dots + N\beta_N L^N] \end{aligned}$$

An alternative is to use the formation function of the system, $\bar{n}$, defined by Bjerrum⁷⁵ as the average number of ligands per atom when the concentration of free ligand is L , and is unique for a particular system. Once $\bar{n}$ is obtained as a function of L , β_n can in turn be calculated by several

$$\begin{aligned}\bar{n} &= (L_T - L)/M_T \\ &= (\sum_{n=1}^N n \beta_n L^n) / (1 + \sum_{n=1}^N \beta_n L^n) \quad \dots (1)\end{aligned}$$

methods described by Rossotti and Rossotti⁷⁶.

Consideration of equation (1) shows that $\bar{n}$ is given from the fractional distribution of the species ML_c , α_c , against the free ligand concentration, L , by the equation (2):-

$$\bar{n} = c - (d \ln \alpha_c / d \ln L) \quad \dots (2)$$

$$\text{where } \alpha_c = [ML_c]/M_T = \beta_c L^c / (1 + \sum_{n=1}^N \beta_n L^n)$$

The usual method to use equation (2) is at first by putting $L = L_T$ followed by successive approximations and graphical differentiations to obtain final sets of $\bar{n}$ and L . If, however, the concentrations or some properties proportional to the concentrations of two successive species, ML_{m-1} and ML_m , are known, equation (2) can be further simplified by substituting the equilibrium relationship between these species, i.e.

$$ML_{m-1} + L = ML_m, \quad k_m = \alpha_m / \alpha_{m-1} L$$

By differentiation

$$d \ln L = -d \ln (k_m \alpha_{m-1} / \alpha_m) = -d \ln \alpha_{m-1} + d \ln \alpha_m$$

Therefore equation (2) will be rewritten as equation (3)

$$\bar{n} = c - (d \ln \alpha_c) / (d \ln \alpha_m - d \ln \alpha_{m-1}) \quad (3)$$

For the present system, α_3 and α_4 can be obtained by measuring Mo_T and absorptions at 395 m μ and 465 m μ and using the molar extinction coefficients given by Bernard and Tridot^{39,62}. Thus equation (4) applies.

$$\bar{n} = 4 - 1 / (1 - d \ln \alpha_3 / d \ln \alpha_4) \quad (4)$$

Therefore $\bar{n}$ can be calculated from the slopes of the plot of $\log \alpha_3$ against $\log \alpha_4$ by graphical differentiation. Preliminary calculations showed the breakdown of equation (4) at low α_4 and for such cases equation (5) was used:-

$$\bar{n} = 3 - 1 / (1 - d \ln \bar{A}_2^{315} / d \ln \alpha_3) \quad (5)$$

where $\bar{A}_2^{315}$ is a specific absorption by species ML_2 at 315 m μ and will be discussed later. Equation (2) with successive approximation was also used when α_3 was too low to obtain $\bar{n}$.

From $\bar{n}$ value, the concentration of free sulphide, S_f , was calculated using total concentration of molybdenum, and sulphide, Mo_T and S_T , by equation (6):-

$$S_f = S_T - \bar{n} Mo_T \quad (6)$$

2. Experimental

2-1 Apparatus and Procedure

Experiments were conducted in a stainless steel autoclave, series 4500, manufactured by Parr Co. Ltd., equipped with a titanium liner (inside volume 1990 ml. at room temperature) and a stainless steel lid to which the following were attached: a stirrer mechanism, two thermocouple wells, a solution injection system, a sampling system, a gas inlet and a gas outlet. All the parts in contact with the solution were titanium.

The stirrer was belt-driven by an electric motor. Heating was provided by a Bunsen burner for rapid heating and a ring type burner controlled by a solenoid valve activated by a Thermistemp temperature controller, Model 71 (Yellowsprings Instrument Co.) in conjunction with a thermistor probe in one thermocouple well. Temperature was measured by the e.m.f. of a Alumel-Chromel thermocouple in another thermocouple well with ice-water as a cold junction and was usually within $\pm 0.5^\circ\text{C}$. of the set value.

As the temperature selected for experimentation was above the boiling point of water, a pressurized solution injection system was constructed with Type 316 stainless

steel parts as shown in Figure 2. The whole system was positioned vertically.

Injectons were carried out by first flushing the system with distilled water through S, V_1 , V_3 and trap with V_2 and V_4 closed. V_1 was then closed and the system was evacuated. After attaining a suitable vacuum solution was sucked into B from S by closing V_3 and opening V_1 . Then V_1 was closed and V_2 was opened to apply a nitrogen pressure of higher value than the inside pressure of the autoclave, which was measured with a 1500 psi. helicoid gauge with a scale of 10 psi. per division. By opening V_4 solution was flushed into the autoclave through the stainless tubing, the tip of which was slightly above the surface of the solution inside the autoclave. The completion of injection was detected by a sharp drop of pressure measured in the gas system. V_4 was closed and one cycle of the injection process was completed. By this method an approximately constant amount (≈ 10 ml.) of solution was injected.

Although the decomposition reactions of tetra- and di-thiomolybdate at room temperature were reportedly slow, sample solutions were quenched to freeze the equilibrium existing at the elevated temperature.

The sampling system consisted of the following sequence: a 1/16 in. O.D. titanium tubing immersed in the solution inside the autoclave, a stainless steel valve with Teflon packing attached to the lid and a cooling coil of

V_1, V_2, V_3, V_4 : high pressure valves, 316 SS.

A : autoclave.

B : high pressure bottle, 316 SS.

T : trap.

S : container of solutions
to be injected, glass.

Fig. 2. SOLUTION INJECTION SYSTEM.

1/16 in. O.D. stainless steel tubing immersed in a cold water bath (7~10°C.). The inside volume of the sampling line from end to end was approximately 1.5 ml. The high temperature section of the system was about a quarter of its length.

Solutions of molybdenum or sulphide were injected. Operations for the latter case are described below. One litre of sodium molybdate solution in a $\text{NH}_3 - (\text{NH}_4)_2 \text{SO}_4$ buffer and 100 ml. of sodium sulphide solution in the same buffer composition were prepared fresh from stock solutions. Molybdenum solution was charged in the autoclave, the atmosphere was replaced with nitrogen gas and the system was sealed, heated and equilibrated while stirring. Sulphide solution was then injected through the injection system, the solution-mixture was allowed to stand for 30 minutes to attain equilibrium between the species, and the sample solution was then withdrawn while stirring. The first 5 ml. of the sample solution quenched by the cooling system was discarded and subsequently 10 ml. was filtered through a dry glass filter (Pyrex "Fine" grade) to remove any precipitates, into a dry glass bottle and stored for analysis. The injection and sampling were repeated successively.

2-2 Reagents

The experimental solutions were made from stock solutions of 1 M. Na_2MoO_4 (stored in a polyethylene bottle), 0.4 M. Na_2S (stored in a dark glass bottle), 10 M. NH_3 and

4 M. $(\text{NH}_4)_2\text{SO}_4$ using reagent grade chemicals.

All the reagents used in analysis were of reagent grade and were used as purchased. De-ionized water was used for all purposes.

The nitrogen gas was the low oxygen grade supplied commercially in a cylinder and used without further purification.

2-3 Analytical methods

The concentrations of total molybdenum, total sulphide, total ammonium and complex species in the sample solution were determined.

Total molybdenum was determined colorimetrically using a Beckman Model B spectrometer according to Buchwald and Richardson's method⁷⁷, in which the molybdenum content of the solution was calculated from the absorbance of a solution at 420 m μ by complexing in a 0.05 M. acetate buffer (pH = 5.2) with sodium -2,3-dihydroxy-naphthalene-6-sulfonate (after oxidizing sulphide in a sample solution with H_2O_2 in NaOH alkaline, adding Na_2SO_3 to reduce excess H_2O_2 , adding HNO_3 to drive off excess SO_2 , boiling to expel the lower nitrogen oxide, and neutralizing to pH=5.2 with NaOH).

The analysis of total sulphide in the thiomolybdate system is known to be difficult. In Part 1 the analysis was done by a modified Volhard method, which was also employed by Perel'man et al.⁴¹. An aliquot of sample solution was added to a known excess amount of AgNO_3 standard solution in

ammoniacal solution to precipitate sulphide ion as Ag_2S . The solution was heated to agglomerate Ag_2S precipitates which were filtered off after cooling and washed with a dilute ammonium solution. The filtrate and washings were combined and acidified by adding 5N HNO_3 and the Ag^+ remaining in the solution was titrated with a standard KCNS solution using Fe^{3+} solution as an indicator, and the sulphide amount was calculated by the difference from the blank.

Total ammonium content was determined by a distillation method. An aliquot of a sample solution was fed into the Kirk's apparatus, which contained an aqueous solution of KMnO_4 in H_2SO_4 , the former to oxidize sulphide into sulfate and the latter to fix the free ammonia. After waiting a few minutes to allow the oxidation and neutralization to be completed, concentrated NaOH was added and ammonia was distilled into a known amount of the standard H_2SO_4 solution. The remaining acid was titrated with a standard NaOH solution to $\text{pH} = 5$ using Beckman pH meter and the total ammonium content was calculated by the difference from the blank.

The concentration of complex species was determined colorimetrically. The spectrogram of the sample solution was taken between 600 and 260 $\text{m}\mu$ with a Beckman DK-2 spectrometer using a 0.1 cm. quartz cell, without dilution, and with distilled water as a reference. Bernard and Tridot^{39,62} gave molar extinction coefficients of the tetra- and tri-thiomolybdate at 19°C . as follows:-

$$\epsilon_3^{392.5} = 98.5 \times 10^2 \quad \epsilon_3^{465} = 4 \times 10^2$$

$$\epsilon_4^{392.5} = 7 \times 10^2 \quad \epsilon_4^{465} = 108 \times 10^2$$

where ϵ_i^λ is a molar extinction coefficient ($\text{M}^{-1}\text{cm}^{-1}$) of a species i ($\text{MoO}_{4-i}\text{S}_i^{2-}$) at wavelength $\lambda(\text{m}\mu)^{78}$. From the absorbances at wavelength λ , A^λ , ($\lambda = 392.5$ and $465 \text{ m}\mu$) of the solution, the concentrations of tetra- and tri-thiomolybdate, C_4 and C_3 , respectively, were calculated by equations (7) assuming no interference by the other ions.

$$C_3 = (1.018 A^{392.5} - 0.066 A^{465}) \times 10^{-3} \text{ M.} \quad \dots (7)$$

$$C_4 = (0.928 A^{465} - 0.038 A^{392.5}) \times 10^{-3} \text{ M.}$$

The concentration of di-thiomolybdate was not calculated from the absorbance at $290 \text{ m}\mu$ as there was a doubt about ϵ given by Bernard and Tridot⁶². Instead the specific absorbancy of di-thiomolybdate at $315 \text{ m}\mu$, $\bar{A}_2^{315}$, which is proportional to the fractional distribution of di-thiomolybdate, was calculated by equation (8).

$$\bar{A}_2^{315} = \bar{A}^{315} - 2.01 \times 10^4 \alpha_4 \quad \dots (8)$$

where $\bar{A}^{315} = A^{315}/\text{Mo}_T$, $\alpha_4 = C_4/\text{Mo}_T$ (the constant will be discussed later).

For most cases fixing of sulphide and ammonia for analysis was performed immediately after sample withdrawal. The spectrogram was taken within 10-20 minutes. Only a slight change was observed when the spectrogram of a sample was taken repeatedly (= 10 minutes later). (see Appendix C)

3. Results and Calculations

3-1 Observed Spectrogram

Figure B1 in Appendix B shows an example of a series of spectrograms where sulphide solution was injected successively. It is clear that no absorption peak exists other than those at 465, 395, 315 and 290 m μ reported by Bernard and Tridot^{39,62} and other authors⁵⁴, etc. It also shows that the peak at 290 m μ increases, reaches a maximum and decreases as the total sulphide concentration increases. The same is true for the peak at 395 m μ . The peak at 465 m μ increases as sulphide concentration increases.

In a series where the concentration of free ammonium was small (Series D), variation in position and magnitude of the absorption peak was observed as shown in Figure B2 in Appendix B. The peak at 465 m μ , corresponding to the tetrathiomolybdate, reached maximum at a small total concentration of sulphide and decreased as more sulphide was added. The magnitude was also smaller. The peak at 395 m μ degenerated after reaching a maximum and a new peak at around 380 m μ was observed at higher sulphide concentration.

A new peak was also observed at around 270 mμ, although this was obscured by a general increase in absorption around this wavelength range. A scan to 210 mμ showed no other peak than the one at around 230 mμ, due to free sulphide ion. In view of the fact that when free ammonium was kept high, no such peak was observed at high sulphide concentration, the new peaks were considered to be caused by protonated species of thiomolybdate.

3-2 Calculation of $\bar{n}$ and S_f

At first α_3 and α_4 were calculated and plotted in log-log scale to obtain $\bar{n}$ values graphically. This was found to give too large values of $\bar{n}$ at low values of α_4 resulting in the inconsistency of material balance. Because α_4 had too low a value, the equation (4) was not meaningful.

Bernard and Tridot³⁹ stated that the absorption at 315 mμ is caused by di- and tetra-thiomolybdate without giving the molar extinction coefficients, i.e.,

$$A^{315} = \ell \epsilon_2^{315} C_2 + \ell \epsilon_4^{315} C_4 ; \ell: \text{path length, (9)}$$

If the equilibrium is assumed between di-, tri- and tetra-thiomolybdate, equation (9) can be rewritten as equation (10):

$$A^{315} C_4 / C_3^2 = (\ell \epsilon_2^{315} k_4 / k_3) + \ell \epsilon_4^{315} (C_4 / C_3)^2 (10)$$

Thus from the plot of $A^{315} C_4/C_3^2$ against $(C_4/C_3)^2$, ϵ_4^{315} can be obtained. Figure 3 shows an example of such a plot of Series A. Good linearity was found for the others giving the results below:-

Series	ϵ_4^{315} M. ⁻¹ cm. ⁻¹	$\epsilon_2^{315} k_4/k_3$ M. ⁻¹ cm. ⁻¹	Temperature °C.	Nominal Concentrations M.
A	1.96×10^4	41.4×10^2	150	NH ₃ = 1.0, NH ₄ ⁺ = 1.0
B	2.04×10^4	40.5×10^2	150	NH ₃ = 0.5, NH ₄ ⁺ = 1.0
C	1.95×10^4	44.6×10^2	120	NH ₃ = 1.0, NH ₄ ⁺ = 1.0

From this table the molar extinction coefficient of tetra-thiomolybdate at 315 mμ was taken as 201×10^2 M.⁻¹ cm.⁻¹. Then absorption due to di-thiomolybdate at 315 mμ is given by equation (11):

$$A_2^{315} = A^{315} - 201 \times 10^2 \ell C_4 \quad (11)$$

Dividing this with Mo_T gives the specific absorption $\bar{A}_2^{315} = A_2^{315}/Mo_T$, which is proportional to the fractional distribution of di-thiomolybdate, α_2 , needed in $\bar{n}$ calculation by equation (5).

Figure 4 shows an example of the plot of α_4 and $\bar{A}_2^{315}$ against α_3 . By graphical differentiation of the smoothly fitting curves and by using equations (4) and (5) for high and low values of α_3 respectively, $\bar{n}$ was calculated for each experimental point. The calculated $\bar{n}$ and S_f are plotted in Figure 5 and listed in Appendix A, Table A-1-1.

Fig. 3 PLOT OF EQUATION (10) TO OBTAIN ϵ_4^{315}

Fig. 4 CALCULATION OF π , 150°C., SERIES A

Fig. 5 $\bar{n}$ vs. S_f

3-3 Conversion of free sulphide concentration to aqueous hydrogen sulphide concentration

The free sulphide concentration must be converted to the aqueous hydrogen sulphide concentration in order to calculate the consecutive constants and the stability constants. Since the dissociation constants of aqueous hydrogen sulphide are not known with great accuracy for high temperatures, the following method was employed for calculation.

The relationship between aqueous hydrogen sulphide concentration and free sulphide concentration is given by the mass balance equation,

$$[\text{H}_2\text{S}]_{\text{aq}} = S_f / (1 + (K_{s1}/[\text{H}^+]) + (K_{s1}K_{s2}/[\text{H}^+]^2))$$

Usually $\text{p}K_{s2}$ is estimated to be larger than $\text{p}K_{s1}$ by 3.5 and consequently the last term in the denominator is negligible in weak alkaline solution³⁷. Hydrogen ion concentration is proportional to the ratio of ammonium ion concentration and free ammonia concentration. Therefore the above equation is reduced to,

$$[\text{H}_2\text{S}]_{\text{aq}} = S_f / (1 + m [\text{NH}_3]/[\text{NH}_4^+]) \quad \dots (12)$$

$$\text{or } [\text{NH}_4^+]/[\text{NH}_3] = (1/[\text{H}_2\text{S}]_{\text{aq}}) (S_f [\text{NH}_4^+]/[\text{NH}_3]) - m$$

where m is a constant.

Therefore by plotting $[\text{NH}_4^+]/[\text{NH}_3]$ against $S_f [\text{NH}_4^+]/[\text{NH}_3]$

for the constant value of $[H_2S]_{aq}$, m can be obtained as the intercept.

At first concentrations of free ammonia and ammonium ion were calculated from the pH and total ammonium, N_T , of the quenched solutions at room temperature, knowing that for the series of experiments at 150°C. the same amount of ammonium sulphate was added. From material balance and equilibrium equations,

$$N_T = [NH_4^+] + [NH_3] = [NH_4^+] + ([NH_4^+] K_N) 10^{pH}$$

where K_N is the dissociation constant of ammonium ion at room temperature. Thus the plot of N_T against 10^{pH} would be a straight line and the intercept at $10^{pH} = 0$ gives the value of ammonium ion and, consequently, free ammonia. The proportion of ammonium ion and free ammonia thus obtained was considered not to change with temperature considering that the amount of molybdenum and sulphide were a magnitude smaller. (Ammonia loss due to flushing at the outlet of sampling line was found negligible).

Secondly free sulphide concentrations at the constant $\bar{n}$ -values were read from Figure 5 for different $[NH_4^+]/[NH_3]$ values. Since the formation function is a unique function of the free ligand concentration for the mono-nuclear complex system, constant $\bar{n}$ is equivalent to constant $[H_2S]_{aq}$ at the present case.

Figures 6a and 6b show the plots of N_T vs. 10^{pH} and $[NH_4^+]/[NH_3]$ vs. $S_f[NH_4^+]/[NH_3]$, respectively, and Table A-1-2 in Appendix A gives the relevant data. From Figure 6b m was obtained to be 5.8 and S_f was converted to $[H_2S]_{aq}$ by equation (12). Figure 7 shows the plot of $\bar{n}$ vs. $[H_2S]_{aq}$ at $150^\circ C$. $\bar{n}$ values of Series D at high free sulphide concentrations were not included in this figure since the interference by the appearance of new peaks became large and accuracy of the determination of α_4 became less.

3-4 Calculation of stability constants from the formation curve

3-4-a Bjerrum's Half- $\bar{n}$ Method

Bjerrum suggested the use of the reciprocal ligand concentration at all half- $\bar{n}$ values for consecutive constants, namely,

$$k_n = 1/L_n$$

where k_n is the consecutive constant for the step- n :

$$ML_{n-1} + L = ML_n$$

and L_n is the ligand concentration at

$$\bar{n} = n - 1/2$$

The principle is based on the fact that a solution with a $\bar{n}$ -value of $(n - 1/2)$ must contain approximately equal amount of the ML_{n-1} - and ML_n - complexes⁷⁵.

This method was applied to the present case. The following values were read from Figure 7:-

Fig. 6a, 6b CONVERSION OF S_f TO $[H_2S]_{aq}$, PLOT FOR m

Fig. 7 THE FORMATION CURVE OF THE THIOMOLYBDATE SYSTEM, 150°C.

$\bar{n}$	L
1/2	$0.35 \times 10^{-3} \text{ M.}$
3/2	$1.4 \times 10^{-3} \text{ M.}$
5/2	$2.3 \times 10^{-3} \text{ M.}$
7/2	$8.0 \times 10^{-3} \text{ M.}$

The calculated stability constants are given in Table 1. When $\bar{n}$ -values were calculated with equation (1) using the stability constants thus obtained, the result did not agree with the observed values except at the mid point as shown in Figure 7 line-1.

Rossotti and Rossotti⁷⁶ discussed the validity of the Bjerrum's Half- $\bar{n}$ method and concluded that the necessary condition was $k_{n-1}/k_n > 10^4$. Since none of the two neighbouring consecutive constants were found to be different enough to satisfy the condition, this method was not adequate.

3-4-b Two-parameters approximation

A system containing many complexes of different degree of complexing may be described in terms of only two parameters. One parameter gives the magnitude of the overall stability constant of the system and the other the ratio of the neighbouring consecutive constants⁷⁶.

Dyrssen and Silln assume that the ratio of the neighbouring consecutive constants is constant:

$$R_n = k_n/k_{n+1} = R = \text{constant}$$

Bjerrum assumes that R_n depends on n in a statistical way:

$$R_n = ((N - n + 1)(n + 1)/(N - n)n)x^2$$

where N is the maximum coordination number and x is the "spreading factor", defined by Bjerrum as a constant and unique parameter for a complex system and related to the mid-point slope of the formation curve.

For the case where the maximum coordination number is four, the above two methods lead to the following equations:-

Dyrssen and Sillen:

$$\bar{n} = (R^3a + 2R^4a^2 + 3R^3a^3 + 4a^4) / (1 + R^3a + R^4a^2 + R^3a^3 + a^4) \dots (13)$$

$a = vL$, v : constant

$$\beta_1 = R^3v, \beta_2 = R^4v^2, \beta_3 = R^3v^3, \beta_4 = v^4$$

Bjerrum:

$$\bar{n} = (4x^3b + 12x^4b^2 + 12x^3b^3 + 4b^4) / (1 + 4x^3b + 6x^4b^2 + 4x^3b^3 + b^4) \dots (14)$$

$b = kL$, k : constant

$$\beta_1 = 4x^3k, \beta_2 = 6x^4k^2, \beta_3 = 4x^3k^3, \beta_4 = k^4$$

Families of normalized diagrams of $\bar{n}$ - a and $\bar{n}$ - b were constructed for various values of R and x , respectively,

and the best fit values were sought by placing Figure 7 above them. The following values gave the most satisfactory results and the calculated values of stability constants by equation (13) and (14) are given in Table 1.

Dyrssen and Silln: $R = 1.05$, $v = 0.57 \times 10^3 \text{ M}^{-1}$

Bjerrum: $x = 0.65$, $k = 0.57 \times 10^3 \text{ M}^{-1}$

Both the Dyrssen and Silln method and the Bjerrum method gave approximately the same values of stability constants. The line 2 in Figure 7 represents the values of $\bar{n}$ calculated by the Dyrssen and Silln method using the values given above. Clearly this method gave a better fit than the Half- $\bar{n}$ Method although the fits at the highest and the lowest values of free ligand concentrations were poor.

3-4-c Calculation of k_4

From the equilibrium relationship between tetra- and tri-thiomolybdate, the ratio of the concentration of the tetra-thiomolybdate to that of the tri-thiomolybdate is proportional to the concentration of the aqueous hydrogen sulphide:

$$C_4/C_3 = k_4 [\text{H}_2\text{S}]_{\text{aq}}$$

Figure 8 shows the plot of the data at 150C. The linearity was considered good. The slope gives the value

Fig. 8 CALCULATION OF k_4 , PLOT OF $[H_2S]_{aq}$ AGAINST C_4/C_3

for k_4 as $2.6_2 \times 10^2 \text{ M}^{-1}$.

Figure 9 shows the similar plot for the data at 120°C ., where C_4/C_3 were plotted against the free sulphide concentration instead of the concentration of the aqueous hydrogen sulphide since the conversion factor was not obtained experimentally at this temperature. The linearity was also good (slope: $0.43_9 \times 10^2 \text{ M}^{-1}$). Fairly reliable data of K_N , the acid dissociation constant of the ammonium ion, are available in the literatures and at 120° and 150°C . $\text{p}K_N$ are 7.0_8 and 6.6_0 , respectively³⁷. Since m in the conversion equation is the ratio of the first acid dissociation constant of the aqueous hydrogen sulphide, K_{s1} , to K_N , $\text{p}K_{s1}$ at 150°C . was calculated to be 5.8_4 . By interpolation with the value at 25°C . (7.0_0) in the literature³⁷, $\text{p}K_{s1}$ at 120°C . was estimated to be 6.0_5 . This yielded the value for m at 120°C . as 10.7 and combined with the slope from Figure 9, k_4 at 120°C . was obtained as $5.3_5 \times 10^2 \text{ M}^{-1}$.

3-4-d Numerical calculation of stability constants (1)

When k_4 is known, the equation (1) can be handled with the least squares method by transforming it as follows:

$$Y = \beta_3 + \beta_2 X_2 + \beta_1 X_1$$

where $Y = \bar{n}/Z$, $X_2 = (2-\bar{n}) L^2/Z$, $X_1 = (1-\bar{n}) L/Z$

and $Z = (3-\bar{n}) L^3 + k_4(4-\bar{n}) L^4$

By making use of the "multiple linear regression program" of the HP9100A calculator, the best fit values of

Fig. 9 CALCULATION OF k_4 , PLOT OF S_f AGAINST C_4/C_3 , 120°C.

the consecutive constants were sought using k_4 values obtained in section 3-4-c. When the points at the lowest three values of the concentration of the aqueous hydrogen sulphide in Figure 7 were taken into consideration, β_1 became negative and the calculated $\bar{n}$ -values deviated greatly at the higher values of the ligand concentrations. Thus these points were neglected for the calculation and the line 3 in Figure 7 shows the formation curve thus calculated. β -values are listed in Table 1.

Similar calculations were performed to $\bar{n}$ and free sulphide concentrations for the Series C, 120°C. The dotted line in Figure 5, Series C, 120°C. shows the calculated formation curve and β -values are listed in Table 1.

3-5 Numerical calculation of stability constants (2)

The calculation methods so far described made use of the formation function obtained by the graphical differentiation of the plots of the fractional distributions of the tetra- and tri-thiomolybdate. The following semi-numerical method was derived to eliminate the graphical differentiation process.

From the definition of the fractional distribution of the mono-nuclear complex system,

$$\alpha_i = \beta_i L^i / U, \quad U = 1 + \sum_{j=1}^N \beta_j L^j$$

and $\alpha_i / \alpha_{i-1} = k_i L$

Defining a function F_0 as

$$F_0 = \frac{\alpha_{i-1}}{\alpha_i} / \frac{\alpha_i}{\alpha_{i-1}} = \left(\frac{\beta_{i-1}}{\beta_i} / \frac{\beta_i}{\beta_{i-1}} \right) U$$

Substitution of the above relationships yields

$$F_0 = \sum_{k=0}^N a_k g^k$$

where $g = \alpha_i / \alpha_{i-1}$ and $a_k = (\beta_k / \beta_{i-1}) k_i^{i-1-k}$

For the case where $i = 4$,

$$a_0 = k_4^3 / k_1 k_2 k_3$$

$$\beta_0 = 1$$

$$a_1 = k_4^2 / k_2 k_3$$

$$\beta_1 = (a_1 / a_0) k_4$$

$$a_2 = k_4 / k_3$$

$$\beta_2 = (a_2 / a_0) k_4^2$$

$$a_3 = 1$$

$$\beta_3 = (1 / a_0) k_4^3$$

$$a_4 = 1$$

$$\beta_4 = (1 / a_0) k_4^4$$

$$a_5 = k_5 / k_4$$

$$\beta_5 = (a_5 / a_0) k_4^5$$

$$a_6 = k_6 k_5 / k_4^2$$

$$\beta_6 = (a_6 / a_0) k_4^6$$

etc.

etc.

F_0 and g can be obtained from the experimental values of the fractional distributions of the neighbouring species. By finding a set of coefficients of the polynomial of g , and a value of k_4 , stability constants can be calculated without the graphical differentiation.

Noting that a_3 and a_4 in the function F_0 are unity by definition, working functions F_1 and H , defined as following, were used

$$\begin{aligned}
 F_1 &= F_0 - g^3 - g^4 \\
 &= a_0 + a_1g + a_2g^2 + \sum_{k=5}^N a_k g^k \\
 &= (C_4/C_3)^3 (M_{oT} - C_3 - C_4)/C_3 \\
 H &= F_1/g^2 \\
 &= a_2 + a_1h + a_0h^2 + \sum_{k=5}^N a_k h^{-(k-2)}
 \end{aligned}$$

where $h = 1/g$.

Since the summation in the function H contains all the polynomial forms of the inverse of h , the plot of H against h will diverge into infinity as h approaches zero if there were any appreciable amount of complexes of higher coordination than the tetra-substituted species. Therefore the plot of H vs. h can be used as the detector of higher complex formation.

Figure 10 shows the plots of F_1 vs. g and H vs. h for the data of series B where the nominal ratio of free

Fig. 10 NUMERICAL CALCULATION OF STABILITY CONSTANTS, F_1 vs. g & H vs. h

ammonia to ammonium ion was 0.5 and the temperature was 150°C. As the function H concaves-up at low h values, the need of a higher complex term is indicated. Judging from the observation in section 3-2 that new absorption bands appeared in the spectrum when the free ammonia concentration was low and that the peaks corresponding to the tetra-substituted species stopped increasing although the total sulphide concentration was increased and that the new peaks increased as the sulphide concentration was increased, a protonated species $\text{Mo}(\text{SH})_6$ was postulated:

$$\text{Then } F_1 = a_0 + a_1g + a_2g^2 + a_6g^6 \quad \dots (16)$$

The best fitting values of a 's were obtained graphically using the extrapolation method similar in principle to the method of Fronaeus for the treatment of $\bar{n}$ as a function of the free ligand concentration⁷⁶.

At low values of g , F_1 tends to a straight line of intercept a_0 and of slope a_1 . After a_0 was known (or estimated) the function

$$F_2 = (F_0 - a_0)/g = a_1 + a_2g + a_6g^5$$

was calculated and plotted against g , to give a_1 as an intercept and a_2 as the limiting slope. Similarly the function

$$F_3 = (F_2 - a_1)/g = a_2 + a_6 g^4$$

was calculated and plotted against g^4 to give a_2 as an intercept and a_6 as the slope.

Since the error accumulates in the value of a_6 , calculation procedure was reversed by calculating and plotting a function

$$G_1 = F_1/g^6 = F_1 h^6 = a_6 + a_2 h^4 + a_1 h^5 + a_0 h^6$$

against h^4 to obtain a_6 as the intercept. Subsequently functions

$$G_2 = (G_1 - a_6)/h^4 = a_2 + a_1 h + a_0 h^2$$

$$G_3 = (G_2 - a_2)/h = a_1 + a_0 h$$

were calculated and plotted against h to obtain a_2 , a_1 and a_0 . Then the successive approximation was used to match two sets of a 's. After a_0 , a_1 , a_2 and a_6 were obtained and refined, stability constants were calculated using the value of k_4 obtained in section 3-4-c.

Figures 11a and 11b show the example of such plots for the data of Series B. The best fit values of a_0 , a_1 , a_2 and a_6 were 0.072, 0.037, 0.68 and 0.27 respectively. Equally good fit was obtained by putting a_1 as zero, or

Fig. IIa, IIb PLOT FOR NUMERICAL CALCULATION (2)

assuming that mono-substituted species did not exist and the values obtained for a_0 , a_2 and a_6 were 0.080, 0.70₈ and 0.27₀ respectively. The calculated stability constants are given in Table 1. The calculated values of $\bar{n}$ from these stability constants are plotted in Figure 7 as line 4. Good fit was observed between $\bar{n}$ of 1 and 3 but fit was poor at high and low values of ligand concentration.

Similar calculation for the Series A, or 150°C. and nominal ratio of free ammonia to ammonium ion being 1:1, indicated a small amount of higher complex formation. Series C, 120°C. and 1:1, indicated no formation of higher complex. The best fit values of a_0 , a_1 , a_2 and a_6 for Series A and Series C were 0.105, 0.045, 0.58 and 0.30, and 0.085, 0.025, 0.87 and 0.00 respectively. The calculated values of stability constants using the values of k_4 in section 3-4-c are given in Table 1.

$\bar{n}$ values were calculated for Series C using the stability constants thus obtained and compared with the values obtained by graphical differentiation method. The agreement was not so good compared with the one obtained by the numerical method (1). (Solid line in Figure 5, C)

4. Discussion and Conclusions

Table 1 shows the summary of the calculated stability constants obtained by the various methods already described.

Since a good linearity was observed for the plot of C_4/C_3 against aqueous hydrogen sulphide concentration in

TABLE 1
Summary of Stability Constants Calculated
By Various Methods

150°C.							
Method	β_1 M. ⁻¹ x10 ⁻³	β_2 M. ⁻² x10 ⁻⁶	β_3 M. ⁻³ x10 ⁻⁹	β_4 M. ⁻⁴ x10 ⁻¹²	β_6 M. ⁻⁶ x10 ⁻¹⁸	k_4 M. ⁻¹ x10 ⁻³	Line in Figure 7
Half- $\bar{n}$	2.9	2.0 ₆	0.89	0.11 ₅	-	0.13	1
Two-parameter Dyrssen	0.66	0.40	0.22	0.11	-	0.49	2
Two-parameter Bjerrum	0.63	0.35	0.21	0.11	-	0.52	-
k_4 calcn.	-	-	-	-	-	0.262	-
Numerical (1)	0.23	0.35	0.27	0.070	-	0.262 (set)	3
Numerical (2)							
Series B	0.13	0.65	0.25	0.065	0.0012	0.262 (set)	4
Series B	0.00 (set)	0.61	0.22	0.059	0.0011	0.262 (set)	-
Series A	0.11	0.38	0.17	0.045	0.0009 ₄	0.262 (set)	-
120°C.							
Numerical (1)	4.2 ₆	9.8 ₀	3.4 ₉	1.8 ₇	-	0.53 ₅ (set)	dot
Numerical (2)	0.16	2.9	1.8	0.96	0.0 (set)	0.53 ₅ (set)	solid
k_4 Calcula- tion	-	-	-	-	-	0.53 ₅	

Line in Figure 5.

k_4 was obtained by using the estimated value of dissociation constant of aqueous hydrogen sulphide at 120°C.

the calculation of k_4 in section 3-4-c (Figure 8), the general method of calculation of $\bar{n}$, and the estimates of molar extinction coefficients of tetra- and tri-thiomolybdates given by Tridot and Bernard³⁹ were considered to be correct. Therefore Figure 7 was used for the comparison of methods employed.

No simple method of calculation yielded a result fitting the total range of the ligand concentration. Calculated values of $\bar{n}$ were generally too high at the highest values of aqueous hydrogen sulphide concentration and too low at the lowest values of the aqueous hydrogen sulphide concentration. However at lower values of ligand concentration, all the methods gave approximately the same values of $\bar{n}$. Therefore it was concluded that $\bar{n}$ values obtained by the graphical differentiation method were rather in error and too large in the lowest region of aqueous hydrogen sulphide concentration. This is plausible since the slope at the lowest values of α_3 in Figure 4 was extrapolated from the higher values and may be too large.

The validity of the Half- $\bar{n}$ Method has been discussed, already, and its inadequacy for the present system outlined.

Although the Two-parameter Approximation gave a "good fit", the calculated k_4 values were twice the values obtained in section 3-4-c as shown in the column 7 in Table 1. Therefore the Two-parameter Approximation method was considered not to be adequate to describe this system.

In the numerical calculation (1), k_4 value obtained in the section 3-4-c was used. The $\bar{n}$ values calculated by using the stability constants obtained by this method agreed fairly well with the values obtained by the graphical differentiation in the section 3-2, as can be seen by a dotted line in Figure 5 curve C and by the line 3 in Figure 7. When the fractional distributions of various species were calculated, it was observed that (a) simple molybdate and tetra-thiomolybdate were the dominant species, (b) monothiomolybdate was less significant in all range of the ligand concentration, and (c) tri- and di-thiomolybdate were fairly significant (around 20%) around the ligand concentration range where simple molybdate and tetra-thiomolybdate were of the same amount. From the calculated values of fractional distribution of di-thiomolybdate and the measured values of the specific absorption of the di-thiomolybdate at 315 m μ , $\bar{A}_2^{315}$, the molar extinction coefficient of the di-thiomolybdate at 315 m μ was calculated to be $0.9_5 \times 10^4 \text{ M.}^{-1} \text{ cm.}^{-1}$ (Table A-1-1 in Appendix A).

In the numerical calculation (2) it was necessary to postulate a protonated species of higher coordination, which was not necessary in the other methods. The accuracy of experiment was not high enough to confirm the validity of this assumption. However this protonated species offers an explanation for the observation in Series D, in which the concentration of tetra-substituted species stopped far short of the values expected from the other series and also

new peaks appeared and increased in intensity as the amount of total sulphide was increased. Since the stability constant β_6 for the protonated species $\text{Mo}(\text{SH})_6$ contains the square of the hydrogen ion concentration, β_6 would increase in proportion to the square of the hydrogen ion concentration, or to the square of the ratio of ammonium ion concentration to free ammonia concentration, and at a very high value of this ratio, the term containing β_6 would dominate the whole complex system decreasing the fractional distribution of all the other species, which agrees with the observation.

The protonated species of the forms

were rejected on the ground that by the equilibrium equations

the concentrations of these species would be proportional to the fourth power of the ligand concentration. Therefore the plot of function H against h in the numerical calculation (2) would not concave up as h approaches to zero, which is contrary to the observation.

The protonated species proposed by Ghosh et al.⁶⁴,

$\text{H}_6\text{MoS}_8^{4-}$ and $\text{H}_8\text{MoS}_8^{2-}$, were also rejected since by the equilibrium equations

the concentration of these species would not be affected or would be adversely affected by the increase of hydrogen ion concentration.

There might be a formation of polynuclei species proposed by Saxena et al. to explain the results of their experiments where thiomolybdate solutions were titrated with HCl ⁶⁵. However, in their work the pH was on the acid side. The present experimental data in ammoniacal solution appear to be adequately explained without the necessity of postulating polynuclei species.

Consequently the molybdenum (VI)- sulphur (-II) -water system may be described as a resultant of the interaction of the following two formation curves:

(a) A curve representing the equilibria between the species of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$, which does not vary with the hydrogen ion concentration. (Curve 1)

(b) A curve representing the equilibrium between molybdate ion and the protonated species, $\text{Mo}(\text{SH})_6$, which varies with the hydrogen ion concentration. (Curve 2)

Figure 12 shows the schematic description of the above statement.

Therefore at a very low value of hydrogen ion concentration, or in a fairly high alkaline solution, curve 2 will be completely suppressed and high fractional distribution of the species of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$ would be expected. This was confirmed by an experiment in Part 2 section 3, where the following concentrations were realized when a reaction mixture in a shaking autoclave at 150°C. was quenched to room temperature within 20 minutes.

NH_3	0.86 M.	C_3	0.00012 ₂ M.
$(\text{NH}_4)_2\text{SO}_4$	0.49 M.	C_4	0.00056 ₅ M.
Na_2S	0.33 ₁ M.	Mo_T	0.00067 M.

There was no appearance of the "new peaks" observed in Series D. The calculated values of $\bar{n}$ and aqueous hydrogen sulphide concentration with the method described in section 3-3 were 3.82 and 27×10^{-3} M., respectively, assuming that the high temperature equilibrium was frozen. This point is shown in Figure 7 with a double circle. The agreement was considered good.

The actual structure of the protonated species may be a colloidal molybdenum trisulphide, $\text{MoS}_3 \cdot 3\text{H}_2\text{S}$, instead of a molecule in which six hydro-sulphide ions are coordinated to molybdenum atom, since (a) the experimental mixtures

Fig.12 SCHEMATIC DIAGRAM OF THIOMOLYBDATE SYSTEM

Curve 1 :

Curve 2 :

in Series D passed through the finest grade glass filter (Pyrex) to give the same amount of molybdenum concentration originally charged, but (b) the absorption of the new peaks did not seem to follow the Beer's Law.

In Table 2 the logarithm of the consecutive constants are listed for various temperatures. The values at 120° and 150°C. are from the results of the numerical calculation method (1). The values at 19°C. are calculated from the experimental data by Tridot and Bernard^{39,62}. The rough estimates of enthalpy and entropy changes for the exchange of oxide ion with sulphide ion in the thiomolybdate species were performed using these data and listed in the column 5 and 6.

The enthalpies of the exchange were negative and decreased in magnitude as the coordination of sulphide ion increased. It is reported that "step-wise ligantional enthalpies for association with ionic ligands in aqueous solution are usually between 0 and ± 5 kcal./mole, but may be as large as -10 kcal./mole, for reactions of e.g. silver (I) or mercury (II) with cyanide or iodide ions. The values are usually between 0 and -5 kcal./mole for neutral undentate ligands, but may be as large as -20 kcal./mole with neutral multi-dentate ligands"⁷⁹. The present values were within the values for the neutral ligands. The large negative value for the exchange of one oxygen ion with sulphide ion and subsequent decrease in magnitude as more

TABLE 2.

Effect of Temperature on the Consecutive Constants

	Temperature (°C.)			ΔH Kcal. /mole	ΔS e.u.
	19	120	150		
$\log k_1$	5.20 5.81	3.63	2.36	-11.9	10.1
$\log k_2$	4.08 4.74	3.36	3.18	- 5.5	- 3.4
$\log k_3$	3.30 3.51	2.55	2.89	- 3.4	- 5.5
$\log k_4$	2.68 2.76	2.73	2.41	- 0.8 ₀	- 9.9

k values at 19°C. were calculated from the experimental data by Tridot and Bernard, ref. 39.

k values at 120° and 150°C. were from the results of numerical method (1).

The effective figures of $\log k$ and ΔH , and ΔS would be two and one.

oxygen ions were exchanged indicates clearly the formation of stronger covalent bonds by the exchange and subsequent decrease in effect as the exchange becomes saturated. This trend is in good agreement with the observation that the first absorption peaks moved to longer wavelength as the exchange advanced. The formation of covalent bonds is attributed to be the cause of the appearance of absorption peaks in the visible range when ions ClO_4^- , CrO_4^{2-} and MnO_4^- were compared⁸⁰.

The entropies of exchange decreased as the exchange advanced. If there is no contribution from the thiomolybdate species, the entropy of exchange for each step would be the difference of entropy between water and aqueous hydrogen sulphide, namely -12.5 e.u. ⁸⁰. The entropy of exchange for the step between tri- and tetra-molybdate approached close to this value and the difference increased as the step decreased. Since the entropies of thiomolybdate ions would be similar, the difference was interpreted as the difference in the entropies of hydration. In other words the amount of water molecule bound to the thiomolybdate ions decreased as the substitution of sulphide ion advanced. This is understandable since the "iceberg"⁸² around the ions would become smaller as the covalent nature of the molybdenum-ligand bonds increases, releasing more water molecules.

In conclusion

1. The experiments at 150°C. showed the existence of the species of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$ and the stability constants of mono-, di-, tri-, and tetra-thiomolybdate were $0.23 \times 10^3 \text{ M.}^{-1}$, $0.35 \times 10^6 \text{ M.}^{-2}$, $0.27 \times 10^9 \text{ M.}^{-3}$, and $0.070 \times 10^{12} \text{ M.}^{-4}$, respectively.
2. There were strong indications of the formation of protonated species, $\text{Mo}(\text{SH})_6$, as the pH of the solution decreased. This species may be the colloidal form of molybdenum trisulphide.
3. Molar extinction coefficients at 315 mμ of tetra- and di-thiomolybdate were estimated to be 2.01 and $0.95 \times 10^4 \text{ M.}^{-1} \text{ cm.}^{-1}$, respectively.
4. A calculation of thermodynamic parameters indicated the compensating effect of enthalpy and entropy for the step-wise substitution of oxide ion by sulphide ion.

PART 2: STUDY OF REDUCTION IN THE Mo-S-H₂O SYSTEM

Hydrogen and carbon monoxide were chosen as reducing gases because of their ready availability for any industrial process that might be developed. Some studies were made of stability in the system at high temperatures under an inert atmosphere (N₂) because some decrease of molybdenum in solution was noted under this latter condition. Since reduction processes with hydrogen and carbon monoxide appear to differ, the reactions under the three gases, N₂, H₂ and CO will be discussed separately. Products of any reaction and the kinetics of the reactions were studied in each case.

1. Experimental

1-1 Apparatus and procedures

A series of experiments was performed with the same apparatus and procedures described in Part 1. After the temperature was equilibrated, a sample was withdrawn from the autoclave. Agitation was stopped and reducing gas was introduced to the desired partial pressure. Agitation was resumed and time was measured from then on. The reaction was followed by withdrawing samples at certain time intervals. The total pressure in the autoclave was maintained constant by admitting more gases manually.

In the case of two stage runs, the end of the first stage was noted by the disappearance of an orange-

yellow color from the solution. Agitation was stopped and molybdenum solution was injected with the injection system. A sample was withdrawn immediately and agitation was resumed to continue the reaction. At the end of the run the autoclave was quenched in cold water.

A series of batch experiments using hydrogen as the reducing gas was performed in a stainless steel shaking autoclave described by McAndrew⁸⁴. Experimental solutions were prepared at room temperature from stock solutions. In some cases sodium sulphide and/or ammonium sulphate was added in crystalline form. A constant volume of the experimental solution was charged, then the system was sealed, flushed with nitrogen gas, heated and equilibrated to the desired temperature while shaking. Agitation was then stopped temporarily and hydrogen gas was introduced. The reaction was initiated by resuming the shaking and the pressure change of the whole system was followed by the reading of a helicoid gauge (0 - 1500 psi., 10 psi./div., filled with silicone oil to minimize the dead volume). At the end of each run when the pressure drop ceased, calibration was performed by introducing more hydrogen from a bottle of a known volume and measuring the pressure variations of the system and the bottle.

After calibration the autoclave was quenched by applying a water cooling coil around its head. Quenching the reaction in the middle of the run was performed by the

same cooling method. The temperature dropped from 160°C. to 120°C. in less than 5 minutes.

After the system was cooled to room temperature, the slurry was filtered and the precipitate was washed thoroughly with water, dried overnight at room temperature in a vacuum dryer, and stored in a bottle in a desiccator for analysis.

As the precipitates were found to catalyze the reduction reaction, the surfaces of the autoclaves were cleaned each time by boiling with a dilute nitric acid solution or a dilute sodium hydroxide-hydrogen peroxide solution.

By the procedure employed the thermal history of the solutions before starting the reduction reaction was approximately the same.

1-2 Analytical procedure

1-2-a Analysis of the solution

The analysis of sample solutions taken during the run was performed by the same procedure described in Part 1, except for sulphide, where in some cases the following method was employed:-

A suitable aliquot of the sample solution was taken into a beaker containing 10 ml. of 1 N.NaOH. Then 25 ml. of 0.05 N.NaClO solution, and 100 ml. of distilled water was added, followed by 10 ml. of 2 N.H₂SO₄ to make the pH of the solution approximately 2. The solution was swirled around and 1g. of KI crystals was added. The resulting I₂

was titrated by 0.05 N. $\text{Na}_2\text{S}_2\text{O}_3$ solution, standardized immediately before use against KIO_3 standard solution. The sulphur content was calculated from the difference from the reagent blank assuming that sulphur was oxidized from -2 to +6 valence state.

In some cases the spectrogram was taken with a quartz cell of 1cm. light path and samples were diluted so that they could be accommodated on the scale. Although the spectrogram of the $\text{Mo-S-H}_2\text{O}$ mixture made up at room temperature changed rapidly with time and dilution, the spectrogram of the solutions from the reduction experiments did not show appreciable change with time and dilution.

1-2-b Analysis of the precipitates

Several methods were employed for the analysis of precipitates, namely,

- a) Chemical analysis for Mo, S, NH_4^+ , and Na.
- b) Thermogravimetric analysis in both Ar and air.
- c) Differential thermal analysis in both Ar and air.
- d) X-ray diffraction.
- e) Optical and electron microscopy.
- f) Infrared spectroscopy.
- g) Magnetic susceptibility measurements.
- h) Others.

a) Chemical analysis

Molybdenum: A weighed amount of sample was oxidized with $\text{KBr} - \text{Br}_2$ solution and HNO_3 and then heated to dryness

after concentrated HCl addition. The residue was dissolved in water and the resulting solution was neutralized to phenolphthalein with NaOH and then acidified with HCl to 5% by volume. The solution was cooled to 5~10°C., a suitable amount of 2% α -benzoinoxime solution was added, and the resulting Mo- α -benzoinoxime precipitate was filtered, washed (filtrate and washings were kept for S analysis) dried, and ignited at 525°C. in a weighed porcelain crucible. The increase in weight of the porcelain crucible was taken as MoO_3 and the amount of Mo in the sample was calculated.

Sulphur: The filtrate and washings from the Mo analysis were neutralized with NaOH to make 0.1 N.HCl, heated to near boiling, 10% BaCl_2 solution added, and the BaSO_4 precipitates filtered hot after aging overnight. The precipitate was washed, dried, and ignited in a muffle furnace at 800°C., cooled and weighed; and the sulphur amount was calculated after subtracting the blank.

Nitrogen: A measured amount ($\approx 20\text{mg.}$) of sample was placed in a micro-Kjeldahl flask and digested with hot concentrated H_2SO_4 . After complete dissolution, the solution was cooled, diluted with water, and charged into a Kirk's micro-distillation apparatus and the ammonia distilled into 0.01 N.HCl solution after adding concentrated NaOH. The HCl remaining was titrated with standard 0.01 N.NaOH to pH = 5.2 using Beckman zeromatic pH-meter. The difference in HCl consumption from the reagent blank gave the NH_3

amount, hence the N% of the sample.

Sodium: Sodium was determined flame-photometrically after dissolving the sample with hot HNO_3 .

Oxygen: Oxygen analysis was performed by Gulf General Atomic Inc. (San Diego, California, U.S.A.). According to their description of the procedure, a sample in a polyethylene bottle, prepared and sealed by the customer, was irradiated with neutrons and the intensity of the 6.13 Mev. gamma-ray photopeak of N^{16} , which was formed by the interaction with neutrons via the $^{16}\text{O}(\text{n},\text{p})\text{N}^{16}$ reaction, was compared against the standard.

For a series of experiments under hydrogen atmosphere using the shaking autoclave, where the total amount of precipitate was small and stayed mostly on the autoclave walls, $\text{NaOH-H}_2\text{O}_2$ solution was added after thorough washing with water to remove free sulphate, to dissolve the precipitates. Analysis of molybdenum and sulphur was performed on the leached solutions.

For the chemical analysis of the precipitates during the run, sample weight was determined indirectly as follows: The precipitate on the fritted glass funnel was washed with distilled water ($\approx 50\text{ml.}$). The precipitate and the funnel were left in the atmosphere until dry and the overall weight was measured. The precipitate on the funnel was dissolved with KBr-Br_2 solution and HNO_3 , and washed, filtrate and washings being set aside for Mo and S analysis.

The funnel was dried as before and weight was measured. The difference from the value before treatment was taken as sample weight. In some instances a normal filter paper was used to collect the precipitate. Subsequent treatment was the same but accuracy was much lower in these cases. Molybdenum was determined spectrophotometrically as described in the analysis of the sample solution, and sulphur was determined gravimetrically as BaSO_4 .

b) Thermogravimetry

A sample was mounted in a quartz vessel, hung from one arm of a chemical balance with a thin quartz fibre in a Vycor (30 mm. I.D.) furnace tube at the centre of a vertical electric furnace. The weight change of the sample was recorded on a chart against time through a photometric zero-balancing mechanism. Constant argon gas flow, dried and deoxygenated by passing through a heated (500°C.) tube containing copper turnings, was passed for at least one hour before the heating started. The temperature of the furnace was raised linearly ($\sim 6^\circ\text{C./min.}$) and the temperature of the sample was calculated from the e.m.f. reading of a Chromel-Alumel thermocouple in a quartz thermocouple tube, the tip of which was exactly centered in the Vycor tube and 2~4 mm. from the bottom of the quartz vessel. The weight change recording was on ≈ 80 mg. full scale, with $\pm 2\sim 3$ mg. vibration due to a zero-balancing time lag. The balance was calibrated each time by placing

known weights on the other side of the arm of the chemical balance.

After the run the sample was cooled to room temperature in Ar flow. The subsequent run in air was performed with the same procedure except by passing a constant flow of dry air.

c) D.T.A.

Differential thermal analysis of the precipitates was performed with apparatus made in this department. The sample was diluted with Al_2O_3 powder and compared against Al_2O_3 in a reference cell. In the case of the run under argon atmosphere a Pt-Pt 10% Rh thermocouple was used in place of the Alumel-Chromel thermocouple which was found corroded by the gas evolved. (The furnace temperature was raised approximately linearly at 11.6°C./min.) Argon gas, deoxygenated by passing through heated copper turnings, was passed through the system at least one hour before heating was started. After the run the furnace was cooled to room temperature in the argon atmosphere and a subsequent test in air was performed by allowing free access of air.

d) X-ray analysis

X-ray diffraction pattern was taken with a conventional X-ray diffractometer using a copper $\text{K}\alpha$ radiation with a nickel filter. The samples were mounted on silicone

grease packed in a window of an aluminum sheet sample holder. Three sharp peaks at 2.14, 1.85 and 1.56 Å. were observed but the blank run of the silicone grease showed the same peaks and thus they were discarded from consideration.

e) Micrographs

A Zeiss metallurgical microscope and a Hitachi electron microscope were used to take micrographs of precipitates.

Samples were first dispersed in water taking care not to grind to cause a change in particle size and shape. Then a portion of the suspension was dropped on a microscope glass or on a carbon film and dried for inspection with an optical or electron microscope, respectively.

f) Infrared spectroscopy

Infrared spectrograms were made using the KBr disc method with a Perkin-Elmer grating I.R. spectrometer 621. Samples were ground and mixed with KBr crystals in a mortar under atmospheric conditions.

g) Magnetic susceptibility

Magnetic susceptibility was measured with a Gouy balance in the Chemistry Department. Samples were placed in a small Pyrex glass tube hanging on the arm of the automatic balance. The weight change before and after application of the magnetic field was measured and magnetic

susceptibility was calculated after subtraction of the blank reading. Calibration was made with mercury (II) tetra-thiocyanate cobaltate (II), $\text{Hg}(\text{Co}(\text{NCS})_4)$, which was supplied by Mr. B. Califord of the Chemistry Department.

h) Other methods

Other methods employed were digestion of the samples in various media and will be discussed elsewhere in the text.

2. Precipitation in an Inert Atmosphere

During the experiments in Part 1, a small but significant decrease of the total molybdenum concentration in the solution was noted in the series where the total concentration of sulphide ion was increased. [See Appendix A-1-1, Series A, No. 8.] The decrease slowed down at the high concentrations of sulphide indicating some equilibria between the solution and the precipitate.

The equilibration is clearly demonstrated in Figure 13 which was the result of a batch run under a nitrogen atmosphere. Figure B-3 in Appendix B shows the change in the spectrogram corresponding to this run. A regular decrease in transmission with time is clearly seen. The broken line shows the spectrogram of the initial solution mixture at room temperature, indicating the difference in the extent of complexing from the solutions at high temperature.

Fig.13 VARIATION OF CONCENTRATION UNDER N_2 , $158.8^\circ C$

Apparently a good linearity is obtained when $\log [X - X_e]$ is plotted against time as shown in Figure 14, where X and X_e are instantaneous and equilibrium concentrations, X_e 's were assumed. Table A-2 in Appendix A lists the best fit values of k and X_e calculated by using the integrated form:

$$X = X_e + a_x e^{-k_x t} \quad \dots (17)$$

(X - X_e) When the calculated k_x was divided by X_e , a number was found which was roughly constant, except for $[Mo]_T$, which showed constancy when $k_{Mo}/[Mo]_e[S]_e$ was calculated, as shown in Table A-2 line 13-16 in the Appendix A. Thus the empirical rate equation was assumed to be

$$d [Mo]_T / dt = -k_{Mo} [Mo]_e [S]_e ([Mo] - [Mo]_e) \quad \dots (18)$$

$$\text{and } d [X] / dt = -k_X [X]_e ([X] - [X]_e)$$

$$X = S_T, C_4, C_3$$

From the empirical equation (17) for sulphur and molybdenum, the molar ratio of sulphur and molybdenum in the precipitate was calculated by equation (19)

Fig. 14

$$r_{s \text{ calc}} = \Delta[S]_T / \Delta[Mo]_T = ([S]_0 - [S]) / ([Mo]_0 - [Mo])$$

Fig.14 FIRST ORDER PLOT

$$= (a_s/a_{Mo})(1 - e^{-k_s t})/(1 - e^{-k_{Mo} t}) \quad (19)$$

substituting the values of time, t , at the end of the experiments. The last line of Table A-2 in Appendix A shows the results. The agreement with the observed values was considered good.

The empirical rate constants k_x for molybdenum and sulphur were found to be almost the same. This implies that there was a stoichiometric precipitation, i.e.

$$\begin{aligned} d[S]/d[Mo] &= (d[S]/dt)/(d[Mo]/dt) \\ &= k_s([S] - [S]_e)/k_{Mo}([Mo] - [Mo]_e) \\ &= ([S] - [S]_e)/([Mo] - [Mo]_e) \end{aligned}$$

Integration gives for the instantaneous values of $[S]$ and $[Mo]$;

$$\log ([S] - [S]_e) = \log ([Mo] - [Mo]_e) + \text{constant}$$

Therefore

$$[S]_0 - [S] = u([Mo]_0 - [Mo]),$$

where u is a constant.

Chemical analysis of the precipitates revealed that fairly large amounts of substances other than molybdenum and sulphur were present. The X-ray analysis showed

broad diffraction between $2\theta=30^\circ$ and 60° , which was also observed for the precipitates of both hydrogen and carbon atmospheres. Thermogravimetric analysis showed a rapid weight loss [-10%] at around 280° C. in argon and another 12% in subsequent tests in the air at about 330° C. No molybdenum thio-oxy compound is reported to have this property and thus the precipitate is most likely a mixture of a sulphide and an oxy- or hydroxy- compound⁸⁹.

From the concentrations of tetra- and tri-thiomolybdate ions coupled with the other analytical data, the consecutive constant k_4 was estimated to be $0.29_5 \times 10^3 \text{ M.}^{-1}$. The conversion factor m at 158.8° C. in the equation (12) was estimated as 4.9 with the same method described in Part 1, section 3-4-c. The agreement in magnitude with the value at 150° C. ($0.26_2 \times 10^3 \text{ M.}^{-1}$) was fair.

The mechanism of the precipitation in the inert atmosphere may be the same as the acid decomposition of thiomolybdate observed by various authors (See Introduction - Literature survey - section 2-4-f). However since there was a concentration of aqueous sulphide in the equation (18), a slow reduction reaction might be taking place consuming a part of divalent sulphide. The calculation of the valency of molybdenum in the precipitates assuming that sulphur was in the hydrosulphide form and the large unaccounted residuals were hydroxide, indicated that molybdenum was reduced slightly.

3. Precipitation with Hydrogen

3-1 Reduction products

3-1-a Aqueous phase

The absorption spectrograms of the solutions during reduction were observed to be the same as those described in Part 1 (Study of the equilibrium). No new absorption peaks were evident between 700 and 260 m μ as shown in Appendix B, Figure B5. The regions 210-260 m μ and above 700 m μ were found also the same as those observed in the equilibrium study.

Therefore it was concluded that soluble complexes of molybdenum in lower oxidation state than 6 was not produced in sufficient concentration to be detected and that if a reduction intermediate existed it must be short lived.

3-1-b Precipitates

Precipitates were fine black powders similar in appearance to carbon black. When they were heated in Ar atmosphere, a white volatile material evolved. A total identification of this volatile material, was not attempted but the qualitative observations listed in Table 3 suggest that it was some compound of sulphide and nitrogen.

Optical and electron micrographs of precipitates showed that:

- (a) Particle shapes were very irregular and agglomeration seemed extensive.

Table 3

Properties of the volatile material produced by heating

(a) Produced in Ar atmosphere at around 150°C.

Solidifies at room temperature and trapped completely in a cold trap (around -10° C.).

Evaporates slowly in the air at room temperature.

(b) Dissolved easily in 0.1 N HCl solution and the resulting solution reduced an I₂-starch solution, oxidized a Fe²⁺ solution and reacted with the Nesler reagent to give a similar but slightly different absorption spectrum from that given by ammonium.

(c) Corroded an Alumel-Chromel thermocouple wire in Ar atmosphere at around 300° C. The corrosion did not occur in the air indicating that this material was not produced in oxidizing atmosphere.

- (b) There was no apparent size change of particles with variation of hydrogen pressure.
- (c) There was no apparent change in size and shape of particles, when the initial conditions were $([S]/[Mo])_i > 2$ and large $([NH_4^+])_i$.
- (d) When $([S]/[Mo])_i < 2$, and/or low $[NH_4^+]$, an increase in the size of the final products was observed as the $([S]/[Mo])_i$ decreased. The size of particles from runs interrupted halfway was found to be smaller than the size of particles from the duplicate runs which was allowed to go to completion, indicating particle growth during the run.

X-ray diffraction patterns of the precipitates did not give any sharply defined peaks. There was a general increase of reflection between $2\theta = 30$ and 60 degrees and, when the precipitates were heated in Ar, two distinct peaks were noted in this area ($d = 2.68$ and 1.56 Å). Also a broad peak at $d = 6.4$ Å was developed (Figure 15). These peaks roughly correspond to those of the rhombohedral modification of MoS_2 reported by several authors (See Table 4). MoS_3 synthesized by Chiya's method⁸³ did not give any reflection. The diffraction patterns of $(NH_4)_2MoS_4$ were completely different. Some electron diffraction pictures of the precipitates showed a hexagonal symmetry, which is

TABLE 4

X-ray Diffraction Data for MoS_2 and Precipitates

Rhombohedral MoS_2			Precipitates by Hydrothermal Decomposition of Thiomolybdate						ppts by H_2	
			(1)		(2)		(3)			
d A	I	hkil	d A	I	d A	I	d A	I	d A	I
6.2	100	0003	6.1	10	6.0	10	6.0	5	6.4	w
3.05	3	0006	3.02	1	-	-	-	-	-	-
2.72	19	10 $\bar{1}$ 0	2.77	9b	2.72	9b	2.71	10b	2.68	b
2.64	14	-	-	-	-	-	-	-	-	-
2.359	18	10 $\bar{1}$ 4	2.345	4	-	-	-	-	-	-
-	-	-	-	-	2.254	5b	-	-	-	-
2.205	20	10 $\bar{1}$ 5	2.198	5	-	-	-	-	-	-
2.051	11	0009	2.053	6	2.050	2	-	-	-	-
1.857	9	10 $\bar{1}$ 7	1.874	4	-	-	-	-	-	-
-	-	-	-	-	1.824	4b	-	-	-	-
1.766	5	10 $\bar{1}$ 8	1.754	3	-	-	-	-	-	-
1.704	1	10 $\bar{1}$ 9	-	-	-	-	-	-	-	-
1.586	15	11 $\bar{2}$ 0	1.578	8	1.578	10	1.568	10b	1.56	b
1.524	18	000,12	1.528	8	1.529	8	-	-	-	-
1.429	1	0 $\bar{1}$ $\bar{1}$,11	-	-	-	-	-	-	-	-
1.360	2	20 $\bar{2}$ 2	1.353	1	1.361	2	1.362	3	-	-
1.314	2	20 $\bar{2}$ 2	-	-	1.297	2	-	-	-	-
1.253	5	11 $\bar{2}$ 9	1.246	5	1.248	5	-	-	-	-
1.228	3	000,15	-	-	-	-	-	-	-	-
1.217	2	20 $\bar{2}$ 7	-	-	-	-	-	-	-	-
-	-	11 $\bar{2}$,12	1.094	7	1.097	8	-	-	-	-
-	-	000,18	1.029	1	1.034	4	1.033	2	-	-

Rhombohedral MoS_2 ; After Bell and Herfert, ref. 71.

Hydrothermal decomposition; After Arutyunyan and Khurshudyan, ref. 68.

Conditions: (1) 640°C., 20 hours.

(2) 550°C., 3 hours.

(3) 380°C., 4 hours.

Precipitates by hydrogen:

158.8°C., 500 psi., $[\text{Mo}]_T = 0.01 \text{ M.}$, $[\text{S}]_T = 0.05 \text{ M.}$, $[\text{NH}_3] = 1.0 \text{ M.}$, $[\text{NH}_4^+] = 1.0 \text{ M.}$, titanium autoclave.

Precipitation completed within one hour.

1. SILICONE

3. CO, HEATED

5. H₂, HEATED

2. CO

4. H₂

6. N₂

Fig. 15 X-RAY DIFFRACTION PATTERNS OF PRECIPITATES

reported to be the characteristic of the Mo-S network seen in both modification of MoS_2 . Therefore it was suggested that the sulphide form in the precipitated products is a very fine particle of the molybdenum disulphide.

A precipitate produced by hydrogen reduction showed an apparent weak paramagnetism amounting to approximately 0.32 unpaired electron per mole of molybdenum. The natural disulphide is reported to have a very weak diamagnetism, and MoO_2 and MoO_3 a weak paramagnetism. The observed paramagnetism disappeared completely when the precipitates were heated in Ar atmosphere at 300°C .

Infrared spectrum of precipitates were compared with MoS_2 and MoS_3 . The natural MoS_2 did not show any specific absorption band. Its absorption decreased gradually as the frequency decreased until it was almost transparent at around 650 cm^{-1} . MoS_3 synthesized by decomposition of $(\text{NH}_4)_2\text{MoS}_4$ solution with acid ⁸³ gave weak absorption around 1650, 1425, 1125, 950, and 900 cm^{-1} . The precipitates under hydrogen atmosphere gave the following absorptions: 620(sh), 880-935(s), 1020(sh), 1115-1190(b), 1395(s,sh), 1600(b), and 3450(b), where s, sh, b means strong, sharp, and broad respectively. They disappeared completely when the sample was heated in Ar atmosphere. Therefore the peaks observed were considered to be due to the volatile material.

Figure 16 shows the results of the thermogravimetric analysis of precipitates from a series of experiments where

Fig.16 TGA OF PRECIPITATES, WEIGHT LOSS vs. TEMPERATURE. CONDITIONS OF PRECIPITATION ; 158.8°C., 600psi., $\text{NH}_3 = 0.8\text{M.}$, $\text{NH}_4^+ = 1.0\text{M.}$, $\text{Mo} = 0.1\text{M.}$, $\text{S} = \text{varies}$ (($\text{S}/\text{Mo} = 1$) 0.66, 2) 0.97 3) 1.30 , 4) 2.01 , 5) 2.84 , 6) 5.77 , Initially))

the initial concentration of sulphide ion was varied. The weight loss in Ar atmosphere varied in position and magnitude starting at around 150°C. and ending at around 350°C. The samples which had been heated in Ar atmosphere showed a weight gain at 350°C. (for low $([S]/[Mo])_i$ cases) and a weight loss at around 450°C. when they were re-heated in air.

Figure 17 shows the results of the differential thermal analysis of precipitates. The natural MoS_2 gave peaks at higher temperature than synthetic MoS_3 and the precipitates produced in these experiments. The peaks observed for MoS_3 and the precipitates were similar, but the difference in the ratio of peaks at around 350°C. and 500°C. indicates some difference in nature is involved. When the D.T.A. was performed in Ar atmosphere there was no peak observed, and when the experiment was repeated in air successively the peak at 350°C. disappeared. Therefore the decomposition reaction in Ar to produce volatile material apparently took place at a comparatively low temperature.

Chemical analysis of precipitates revealed that the composition varied depending on the composition of the experimental solutions from which those precipitates were obtained. Tables 5a, 5b show some of the results of analysis, in which results of analysis of the precipitates from nitrogen and carbon monoxide atmosphere were included.

In all cases there was a large residual when the molybdenum and sulphur amount was subtracted. Analysis for nitrogen and sodium indicated that these were only minor constituents.

Fig.17 DTA. OF PRECIPITATES FROM H_2 RUNS

Curve 1. natural molybdenite, in air

2. synthetic molybdenum trisulphide, in air

3. precipitate under hydrogen, in air

4. " , in Ar

5. " , in air after Ar

TABLE 5a
Compositions of Precipitates

No.	Gas	Compositions			Main Variables	Other Conditions
		Mo%	S%	X%		
46	N ₂	44.9	39.8	15.3	-	(Mo _T = 0.020M., S _T = 0.056M., NH ₃ = NH ₄ ⁺ = 1.0M., 158.8°C.)
40	H ₂	48.0	32.7	19.3	P = 500psi. 300 100	(Mo _T = 0.020M., S _T = 0.056M., NH ₃ = NH ₄ ⁺ = 1.0M., 158.8°C.,)
42	H ₂	47.7	34.4	17.9		
44	H ₂	47.2	36.8	16.0		
86	H ₂	47.4	33.3	19.3	S _T = 0.195M. 0.096 0.065	(Mo _T = 0.1M., NH ₃ = 0.9M., NH ₄ ⁺ = 1.0M., 158.8°C., P _{H₂} = 600psi.)
85	H ₂	50.2	20.8	29.0		
83	H ₂	53.9	14.4	31.7		
106	H ₂	49.8	32.5	17.7	NH ₄ ⁺ = 0.98M. 0.39	(Mo _T = 0.1M., S _T = 0.2M., no NH ₃ , 151.6°C., P _{H₂} = 880psi.)
108	H ₂	53.4	29.4	17.2		
61	CO	33.4	22.2	44.4	Mo _T = 0.001M.	(S _T = 0.023M., 151.6°C., P _{CO} = 700psi., NH ₃ = NH ₄ ⁺ = 1.0M.)
23	CO	49.0	30.7	20.3	S _T = 0.011M. 0.033 0.089	(Mo _T = 0.020M., P _{CO} = 500psi., NH ₃ = NH ₄ ⁺ = 1.0M.)
25	CO	48.6	33.6	17.8		
26	CO	44.7	33.7	21.5		

$$X\% = 100 - Mo\% - S\%.$$

TABLE 5b

Detailed Analysis of a Precipitate

Conditions of precipitations: Run 64.

$\text{Mo}_T = 0.010\text{M.}$, $\text{S}_T = 0.049\text{M.}$, $\text{NH}_3 = \text{NH}_4^+ = 1.0\text{M.}$, $\text{P}_{\text{H}_2} = 500 \text{ psi.}$,
two-stage run in titanium autoclave, no catalyst addition

	as precipitated ^a	after heating ^b
Mo	47.1%	59.0%
S	32.7	32.8
N	2.5	0.3
Na	0.0	0.0
difference	17.7	7.9
	<hr/> 100.0	<hr/> 100.0
equivalent/mole Mo^c	15.0	15.6
%Mo dissolved ^d		
by 0.2M NH_4Cl	18.5	n.d.
by $(1 + 1)^4 \text{HCl}$	33.7	n.d.
by water	19.3	n.d.
by 2 N NaOH	83.	n.d.

a - washed with water and vacuum dried.

b - 300°C., 2 hours in Ar.

c - reducing equivalent with NaClO .

d - 60°C., 1 hour in Ar.

TABLE 6

Analysis of Oxygen in the Precipitates

Sample No.	Mo	S	X	O
64	47.1	32.7	20.2	28.1
64d	59.0	32.8	8.2	12.6
102	50.1	32.3	17.6	20.0
105	58.3	17.6	24.1	23.2
106	49.8	32.5	17.7	22.8
108	53.4	29.4	17.2	24.9

Content in %, $X = 100 - \text{Mo} - \text{S}$, Mo and S are by the author and O by G.G.A.

The results of the oxygen analysis with the neutron activation method performed by Gulf General Atomic, California, U.S.A., were compared with the residual stated above in Table 6. Although activation analysis results and chemical analysis results (by the difference from 100%) did not agree exactly and the former gave higher values in general, the trend agreed. Therefore it was concluded that the residuals were predominantly oxygen.

The ratio of molybdenum to sulphur in the precipitates depended primarily on the ratio of molybdenum and sulphide concentration in the initial solutions. Figure 18 shows the plot of the ratio of molybdenum to sulphur in the precipitate, $r_s = (S/Mo)_{ppt}$, against the ratio of the concentrations of molybdenum and sulphide in the initial solution, $([S]/[Mo])_i$, when the solution was well buffered. Clearly $r_s = ([S]/[Mo])_i$ (dotted line) when $([S]/[Mo])_i$ is smaller than 2 and when larger than 2, r_s approaches some limiting value.

Variation of the pH of the solution by varying the amount of $(NH_4)_2SO_4$ addition to the mixture of Na_2MoO_4 and Na_2S solution yielded a variation of r_s . At low level of $(NH_4)_2SO_4$ addition the precipitation was not complete but above the equivalent amount of $(NH_4)_2SO_4$ to neutralize sulphide, the precipitation was complete and r_s approached that for the highly buffered solution (Figure 19).

The consumption of hydrogen varied also primarily with the ratio of the concentration of sulphide and molybdenum

Fig.18 COMPOSITION OF PRECIPITATES BY H₂ REDUCTION
 r_s DEPENDENCE ON THE INITIAL SOLUTION COMPOSITION

in the initial solution. This is shown more clearly when $(r_H + r_S - 3)$ is plotted against r_S as shown in Figure 20, where r_H is the ratio of hydrogen consumption to molybdenum consumption. It is clear that when r_S approaches zero, i.e. no sulphide formation hypothetically, r_H approaches 1. In other words molybdenum in oxide and/or hydroxide was in tetra-valent state. The empirical equation was given by:

$$r_H = 1 + 0.18r_S \quad (20)$$

Assuming that the oxide (or hydroxide) and the sulphide (or hydrosulphide) in the precipitate are expressed by MoO_xH_z and MoS_yH_u , respectively, r_H and r_S have the following relationships:

$$r_S = y[\text{MoS}_y\text{H}_u]/([\text{MoS}_y\text{H}_u] + [\text{MoO}_x\text{H}_z])$$

$$r_H = ((3 - x + 1/2 z)[\text{MoO}_x\text{H}_z] + (3 - y + 1/2 u)$$

$$[\text{MoS}_y\text{H}_u])/([\text{MoO}_x\text{H}_z] + [\text{MoS}_y\text{H}_u])$$

$$\text{Then } [r_H + r_S - 3] = -[x - 1/2 z] + [(x - 1/2 z + 1/2 u)/y]r_S$$

$$\text{or } r_H = [3 - x + 1/2 z] + [([x - 1/2 z] - [y - 1/2 u])/y]r_S$$

By comparing with the empirical equation (20) the following relationships were derived:

Fig.19 r_s DEPENDENCE ON ACIDITY Fig.20 $(r_H + r_s - 3)$ vs. r_s

$$x - 1/2 z = 2$$

$$y - 1/2 u = 2 - 0.18 y = 1.6_9 - 0.07_6 u$$

This indicates that molybdenum in the sulphide (or hydro-sulphide) has the valency of less than 3.4 on the average, and that the sulphide may be composed of a mixture of tetra- and trivalent molybdenum depending on the value of u . If $u = 3$, $y = 2.92$, close to the value of molybdenum tri-hydro sulphide, $\text{Mo}(\text{SH})_3$.

The composition of the precipitate was further studied by comparing the results of T.G.A. with those from chemical analysis. Figure 21 shows the plot of various weight loss in gram per mole of molybdenum in the precipitates measured by T.G.A., against r_s . Three weight losses were considered:

ΔW_1 : weight loss in Ar at 200°C.

ΔW_2 : weight loss in Ar at 650°C.

ΔW_3 : weight loss in air at 550°C. after performing T.G.A. in Ar.

ΔW_1 and ΔW_2 are expected to show the effect of decomposition reactions in the inert atmosphere. ΔW_3 is expected to show the oxidation characteristics of the sample after decomposition was complete in inert atmosphere.

Fig.21 TGA RESULTS, WEIGHT LOSS vs. r_s
 WEIGHT LOSS IN g./mole Mo in precipitates

Although ΔW_2 showed a considerable scatter when r_S was greater than 1.7, all three values showed linear dependences on r_S . The intercepts at $r_S = 0$ give the hypothetical behaviours of the oxide (or hydroxide) and agree fairly well with those of hydrated molybdenum dioxide as shown below.

Weight Loss	Found g./mole Mo	Decomposition Reaction	Weight Loss g./mole Mo
ΔW_1	16	$\text{Mo(OH)}_4 \rightarrow \text{Mo(OH)}_2 + \text{H}_2\text{O}$	18
ΔW_2	36	$\text{Mo(OH)}_4 \rightarrow \text{MoO}_2 + 2 \text{H}_2\text{O}$	36
ΔW_3	-19	$\text{MoO}_2 \rightarrow \text{MoO}_3 - \frac{1}{2} \text{O}_2$	-16

ΔW_3 increased by 18g. for each addition of a mole of sulphur to a mole of molybdenum in the precipitate. The replacement of oxygen with sulphur in the precipitates at constant amount of molybdenum should yield the difference in molecular weight between sulphur and oxygen, namely 16g., slightly smaller than the value observed. Therefore the sulphur addition must be associated with the partial reduction of tetravalent molybdenum to trivalent, in agreement with the observation of hydrogen consumption. But the gross value agreed fairly well with the simple replacement of molybdenum dioxide with molybdenum disulphide in agreement with the observation of X-ray pattern.

ΔW_2 , below $r_S = 1.7$, and ΔW_1 decreased by 12 and

4g., respectively, for each addition of a mole of sulphur to a mole of molybdenum in the precipitate. This suggests the simple replacement of oxygen with sulphur below $r_S = 1.7$, and production of volatile material above $r_S = 1.7$.

As r_S and r_H varied with the change of the initial conditions, variation of r_S and r_H during the run was suspected. Several duplicate runs were conducted in which one experiment was stopped at halfway and compared with the other which was allowed to go to completion. Table 7 shows the results. When $([S]/[Mo])_i > 2$ and $[NH_4^+]$ was high, r_S and r_H of the runs stopped halfway agreed with those of the runs allowed to go to completion. But when $([S]/[Mo])_i < 2$ and/or $[NH_4^+]$ was low, r_S of the runs stopped halfway was larger than those of the runs allowed to go to completion. These facts indicate that there are two (or more) paths of molybdenum precipitation: one to form sulphide and the other to form oxide, and that under conditions $([S]/[Mo])_i > 2$ and high $[NH_4^+]$ both paths were followed in a certain proportion until molybdenum precipitation was complete, whereas under the condition $([S]/[Mo])_i < 2$ and/or low $[NH_4^+]$ the sulphide path proceeded faster than the oxide path completing the depletion of sulphide ion from the solution.

3-2 Kinetic study

The investigation of the final products described in section 3-1 indicated that, apparently, the reactions

TABLE 7

Variation of r_S and r_H by the Extent of Reaction

No.	%	r_S	r_H	T °C.	Initial Condition				
					[Mo] _T M.	[S] _T M.	[NH ₃] M.	[NH ₄ ⁺] M.	P _{H₁} psi.
102	100	1.93	1.22	151.6	0.099	0.211	0.86	0.98	858
111	57	1.98	1.37a	151.6	0.097	0.195	0.86	0.98	865
113	100	2.03	1.45	160.0	0.100	0.195	0.86	0.98	821
112	81	1.98	1.52a	160.0	0.100	0.195	0.86	0.98	826
85	97.5	1.23	1.39	158.8	0.098	0.096	0.85	0.97	600
114	71	1.42	1.46a	160.0	0.100	0.097	0.86	0.98	824
110	85	1.66	1.35	151.6	0.097	0.211	0.00	0.98	884
115	51	1.83	1.70a	160.0	0.098	0.195	0.00	0.98	840

% - Per cent of molybdenum disappeared from solution.

a - r_H for the runs interrupted in halfway were obtained by extrapolating the pressure drop curves until the times when the temperatures of the system dropped 20°C.

b - [NH₄⁺] was added as ammonium sulphate.

could be classified into two types, depending on the initial concentration ratio of sulphide to molybdenum and the amount of ammonium sulphate present in solution: type (1) - ratio of sulphide to molybdenum larger than 2 and high NH_4^+ concentration, giving no variation in the product during the reduction reaction and the final products having a limiting value of sulphur to molybdenum ratio; type (2) - ratio of sulphide to molybdenum less than 2 and/or low NH_4^+ concentration, precipitating the sulphide first followed by the oxide and/or the hydroxide.

Analysis of the solution produced during the runs conforming to the type (1) showed that there was in fact no variation in the ratio of the consumption of molybdenum and sulphur from the solution during the whole process of precipitation. Figure 22 shows the plot of total molybdenum concentration against total sulphide concentration in the solution. The linearity was considered good in view of the rapidly accelerating molybdenum depletion as shown by the solid triangles which correspond to the open triangle.

3-2-a Effect of pressure

The effect of the partial pressure of hydrogen for the type (1) was first investigated since no change of mechanism was expected during the run considering the constancy of the ratio of consumption of molybdenum and sulphide discussed above.

Fig. 22 Mo_T vs. S_T & TIME, 150°C. , $P_{H_2} = 500\text{psi.}$, $NH_3 = NH_4^+ = 1.0$ M.

Figure 23 shows the variation of the total concentration of molybdenum under constant pressure at 158.8°C. Pressure was varied. The rate of disappearance of molybdenum from the solution increased as the reaction proceeded. No simple order of reaction on molybdenum concentration describes this phenomenon. But when the logarithm of the amount of molybdenum removed from solution was plotted against time, a good linearity was observed except for the initial parts as shown in Figure 24. The integrated equation describing this removal is:-

$$\log ([\text{Mo}]_0 - [\text{Mo}]) = st + \log i \quad (21)$$

where s and $\log i$ are slope and intercept of the plot discussed above. The pressure dependence of s and i are shown in Figure 25. Linearity of s vs. pressure and i vs. $1/(\text{pressure})$ were observed. Therefore the empirical formula for the molybdenum concentration was given by

$$\log ([\text{Mo}]_0 - [\text{Mo}]) = c_1 Pt + \log (c_2 + c_3/P) \quad (22)$$

Differentiation of this equation with respect to time at constant pressure yields:

$$-d[\text{Mo}]/dt = c_1 P ([\text{Mo}]_0 - [\text{Mo}]) \quad (23)$$

Fig. 23 VARIATION OF TOTAL Mo IN SOLUTION, UNDER H_2

Fig.24 $\text{Log}(\text{Mo}_o - \text{Mo})$ vs. Time

Fig.25 SLOPE & INTERCEPT vs. PRESSURE

The equation (23) implies that the reaction is autocatalytic and that molybdenum and sulphide concentrations do not come directly into the rate process of molybdenum depletion. In order to clarify more of this aspect, two-stage experiments were conducted, in which the first stage was allowed to go to completion, the end point being detected by the disappearance of the colour of thio-molybdate complexes. Then a fresh molybdenum solution was injected and the rate of molybdenum depletion was followed as before.

Figure 26 shows the results, where the pressure of the second stage was decreased to 200 psi. from 500 psi. of the first stage. The depletion of molybdenum in the second stage was almost linear against time until completion while the ratio of sulphur to molybdenum of the precipitates remained practically constant. This indicates that in the second stage molybdenum was acting simply as a substrate which was easily reduced. The rates of depletion of molybdenum at the end of the first stage and at the beginning of the second stage were found to be 2.6 and 6.2×10^{-5} M. min.⁻¹, respectively. In the other run where the pressure of both stages were kept constant at 500 psi., the rate of molybdenum depletion at the initial part of the second stage was found to increase by 5.3-fold compared with that at the end of the first stage. This increase was interpreted to be caused by the activation of the precipitate from the first

Fig. 26 TWO STAGE RUN, H_2 , 500psi., 158.8°C.

stage by dissolved hydrogen during the time interval between the two stages. Assuming that the rate constant in the equation (23) was proportional to pressure, the rate of depletion of molybdenum at the initial part of the second stage was calculated from the rate of depletion at the end of the first stage correcting the activity change mentioned above. The calculated value was $5.5 \times 10^{-5} \text{ M. min.}^{-1}$ in close agreement with the observed value.

Figure 26 also includes the concentration changes of other species. The variation with time was similar to the total molybdenum concentration variation.

The distribution of complex species during the reduction reaction was investigated by plotting the fractional distribution of tri-thiomolybdate (α_3) against that of tetra-thiomolybdate (α_4) in log-log scale with the same reasoning given in Part 1 (Study of equilibrium). Figure 27 shows the results where data from the same run are indicated by the same symbol. Also the lines representing the equilibrium obtained in Part 1 at 150° and 120°C. are reproduced. Although there is scatter, the points representing the samples during the reduction reactions at 158.8°C. lie in close agreement and tendency with the equilibrium relationship. Therefore it was concluded that the complex species were in equilibrium with each other during the reduction reaction and exchange reactions between the complex species were not rate controlling.

Fig. 27 PLOT OF α_3 v.s. α_4 , DURING PRECIPITATION IN HYDROGEN ATMOSPHERE

Since the reduction reaction accelerated rapidly towards the end of the reaction, it was difficult to obtain a convenient sampling method to follow the reaction. Therefore another experimental method was employed in which the experiment was conducted in a constant volume autoclave described in the experimental section and the reaction was followed by reading the total pressure drop of the system.

Pressure decreases with time were similar to the decreases of the total molybdenum concentration with time discussed above as shown in Figure 28, namely the rate of hydrogen consumption increased as the reaction proceeded.

If the same rate equation as equation (23) applies, the rate equation in terms of hydrogen pressure would be of the form

$$-dP/dt = kP(\gamma(P_0 - P) + \delta) \quad (24)$$

where γ and δ are constants representing the stoichiometric relationship between molybdenum and hydrogen, and the initial condition of the system, respectively. Upon integration,

$$\ln [P/(\underline{a} + P_0 - P)] = -k\gamma(P_0 + \underline{a})t + \ln(P_0/\underline{a}) \quad (25)$$

where $\underline{a} = \delta/\gamma$.

Fig.28 VARIATION OF TOTAL PRESSURE, H₂ atms.

Figure 29 shows the plot of the left hand side of equation (25) against time where $\underline{a}$ was taken as 10 psi. Fluctuation of points was caused by the temperature fluctuation of approximately 0.3°C . Good linearity was observed and the slopes were found to be proportional to $(P_0 + \underline{a})$ as predicted by the equation (25) as shown in the inserted Figure in Figure 29. Therefore the equation (24) was considered to hold and further analysis of experimental data was performed by plotting the reduced rate $(1/P)(-dP/dt)$ against hydrogen consumption, $(P_0 - P)$. The instantaneous rates of hydrogen consumption, $-dP/dt$, were obtained by graphical differentiation of smoothly fitting curves of the pressure readings against time.

3-2-b Effect of temperature

The effect of temperature on the reaction was compared for the two experimental methods employed, namely
(A) 2l.-titanium autoclave, pressure maintained constant and
(B) 120ml. stainless-steel autoclave, pressure varied as the reaction proceeded.

Table 8 shows the results in which the rate constants for (A) are the slope of the plot of the equation (23) and for (B) the slope of the reduced rate against the amount of hydrogen consumed. In spite of the difference in the experimental methods and the concentration range employed, the activation energies were found almost the same, indicating that the same rate controlling step was operating and the

Fig. 29 PLOT OF $\ln(P/(a + P_0 - P))$ vs. TIME

TABLE 8

Effect of Temperature on the Rate

A. $[\text{NH}_3] = 1.0 \text{ M.}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.5 \text{ M.}$,

$\text{PH}_2 = 27.2 \text{ atm.}$ Initial concentrations:

$[\text{Mo}]_T = 0.020 \text{ M.}$, $[\text{S}]_T = 0.056 \text{ M.}$

No.	Temperature	k	
41	158.8°C.	$3.03 \times 10^{-2} \text{ min.}^{-1}$	
45	151.6°C.	$2.03 \times 10^{-2} \text{ min.}^{-1}$	$E_A = 20 \text{ kcal. /mole}$

B. $[\text{NH}_3] = 0.9 \text{ M.}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.45 \text{ M.}$,

Initial conditions:

$[\text{Mo}]_T = 0.10 \text{ M.}$, $[\text{S}]_T = 0.20 \text{ M.}$, $\text{P}_{\text{H}_2} = 57 \text{ atm.}$

No.	Temperature	k	
111	151.6°C.	$1.12 \times 10^{-3} \text{ atm.}^{-1} \text{ min.}^{-1}$	
112	160.0°C.	$1.74 \times 10^{-3} \text{ atm.}^{-1} \text{ min.}^{-1}$	$E_A = 21 \text{ kcal. /mole}$

step did not depend on the concentrations of molybdenum and sulphide in solution.

3-2-c Effect of catalyst

By dividing equation (24) with pressure, equation (26) was derived.

$$-d \ln P / dt = k(\gamma(P_o - P) + \delta) \quad (26)$$

The value inside the bracket in the right hand side corresponds to the amount of catalyst existing, under the same conditions of solution composition. Addition of catalyst at the beginning of the runs would be expected to cause a change in only δ .

When precipitates from the other run were added, there was an increase in total consumption of hydrogen as the amount was increased. However the plot of reduced rates against hydrogen consumptions showed a good parallelism when the end points were matched as shown in Figure 30. The slope that fitted well to the run 118 (no addition) was taken to draw best fit lines to the run 117 (200 mg.) and the run 116 (400 mg.). The intercepts at zero hydrogen consumption for the run 118 were plotted against amount of precipitates added in the insert of Figure 30. A good linearity was observed. Therefore δ in the equation (26) did in fact correspond to the initial condition of catalyst and γ was identical for solutions of the same compositions.

Fig. 30 EFFECT OF CATALYST,

The initial high values in Figure 30 were considered to be caused by the dissolution of precipitates and exchange of oxide with sulphide in the precipitates. This is in agreement with the empirical equation (20).

3-2-d Effect of solution conditions

From the analysis of the final products, described in section 3-1, it was found that the composition of precipitates varied with the initial solution conditions. Since it was shown that the rate of molybdenum depletion from solution was primarily controlled by the hydrogen pressure and the amount of precipitate, there appear to be steps (or a step) following the rate controlling step which determine the composition and the nature of the precipitates.

Several series of experiments were performed to clarify this aspect.

Figure 31 shows the effects of the variation of the concentration of molybdenum at constant amount of sulphide and at high concentrations of free ammonia and ammonium sulphate. Clearly when the initial molar ratio of sulphide to molybdenum, S/Mo , were above 2, the reduced rate dropped sharply to zero after reaching the maximum, whereas when S/Mo were less than 2, tails were observed after reaching the maximum at approximately the same amount of hydrogen consumption. From the experiments described in section 3-1 where the run was interrupted in halfway and the resulting solution was analyzed, it was found that

Fig. 31 EFFECT OF SOLUTION CONDITION, Mo_{Ti} VARIATION, IN H_2

sulphide depleted first when S/Mo was less than 2. Therefore the portions before the maximum were considered to correspond to the sulphide precipitation.

Figure 32 shows the effects of the variation of ammonium sulphate concentration where the initial molar ratio of sulphide to molybdenum was slightly above 2. Molybdenum and sulphide were added as sodium salts. There was a variation in the rate curves with the amount of the ammonium sulphate, namely when the amount was less than the equivalent to neutralize the sodium sulphide long induction periods were observed, whereas at above the equivalent value, high initial rate of hydrogen consumption was observed.

From the above two series of results, it was indicated that the distribution of various complex species and the pH of the solution seemed to play important roles in determining the compositions of the precipitates.

From the equation (25), it is suggested that the slope of the plot of $-\ln P/dt$ vs. $(P_o - P)$ would represent the effect of solution conditions on the composition of precipitates.

Initial compositions of the solution were calculated by using the results obtained in Part 1, as follows:-

Formation function was assumed as:

$$\bar{n} = \bar{n}(L), \quad L = [H_2S]_{aq} \quad (27)$$

Fig. 32 EFFECT OF SOLUTION CONDITION, IN H_2
 $(\text{NH}_4)_2\text{SO}_4$ AMOUNT VARIATION

The material balance for sulphide yielded

$$S_T = \bar{n}M_T + S_f = \bar{n}M_T + [H_2S] + [S^{2-}]$$

The charge balance equation yielded, noting the same charge for all molybdenum species,

$$[Na^+] + [H^+] + [NH_4^+] = 2M_T + 2[SO_4^{2-}] + [OH^-] + [HS^-] + 2[S^{2-}]$$

By neglecting H^+ , OH^- and S^{2-} , as being small in comparison with the other ionic species and substituting the relationships:

$$[H_2S] = S_f / (1 + m[NH_3]/[NH_4^+])$$

$$[HS^-] = [H_2S]m(N_T - [NH_4^+])/[NH_4^+]$$

the following equations were derived for $\bar{n}$ and L as functions of the concentration of ammonium ion, N_1 ;

$$\bar{n} = S_T/M_T - (1 - m + mN_T/N_1) L/M_T \quad (28)$$

$$L = (N_1 - 2M_T - 2[SO_4^{2-}] + [Na^+]) N_1 / m (N_T - N_1) \quad . . (29)$$

Assumption was made that the formation function at 150°C. applies also at 151.6°C. Then $\bar{n}$ and L were calculated from equation (28) and (29) selecting a suitable value of N_1 to satisfy the equation (27) by the method of successive approximations for a set of values of M_T , S_T , N_T ,

$[\text{Na}^+]$, and $[\text{SO}_4^{2-}]$. The value of m was taken as 5.8 as obtained in Part 1. After obtaining the value of the aqueous hydrogen sulphide concentration, L , the fractional distributions of various thiomolybdate species were calculated by using the stability constants obtained in Part 1.

Figures 33a and 33b show the plots of the slopes of Figures 31 and 32 against fractional distributions and the ratio of ammonium ion to free ammonia, respectively. Since the experiments of Figures 31 and 32 were conducted at the same temperature, the slopes from these two series could be combined and expressed by an appropriate function of the fractional distributions and the ratio of the ammonium ion to free ammonia.

After trial and error, it was found that Figures 33a and 33b could be combined only when the slopes were plotted against the products of the fractional distribution of tetra-thiomolybdate, α_4 , with the hydrogen ion concentration, or the ratio of ammonium ion to free ammonia, as shown in Figure 34. The low values of the slopes in the pH series were considered due to the same effect by the initial precipitates as were observed in the case where precipitates from a previous run were added to the initial solution. (section B-2-3) The increase in the slopes at large amounts of consumption of hydrogen seen in Figure 32 seem to support the assumption.

$\circ : \alpha_0$, $+$: α_1 , Δ : α_2 , $\square$: α_3 , $\bullet$: α_4 ,
 ∇ : $(\text{NH}_4^+)/(\text{NH}_3)$

Fig. 33 PLOT OF SLOPE vs. α AND $(\text{NH}_4^+)/(\text{NH}_3)$.

Fig. 34 SLOPE vs. $Q_4(\text{NH}_4^+)/(\text{NH}_3)$, COMBINED

Fig. 35 PLOT OF $1/\text{Slope}$ vs. $1/(Q_4(\text{NH}_4^+)/(\text{NH}_3))$

Figure 34 indicates a saturation effect at the large value of the product stated above. When the inverse of the slope was plotted against the inverse of the product, a good linearity was observed as shown in Figure 35, namely,

$$1/\text{slope} = A_1 + A_2/(\alpha_4[\text{NH}_4^+]/[\text{NH}_3])$$

where A_1 and A_2 constants. Therefore

$$\text{slope} = (\alpha_4[\text{NH}_4^+]/[\text{NH}_3])/[A_2 + A_1(\alpha_4[\text{NH}_4^+]/[\text{NH}_3])]$$

Noting that $[\text{NH}_4^+]/[\text{NH}_3]$ is proportional to hydrogen ion concentration, $[\text{H}^+]$, the above relationship can be written as

$$\text{slope} = k'[\alpha_4[\text{H}^+]/(k'' + \alpha_4[\text{H}^+])]$$

This treatment of the data was also successful when it was applied to the results of a series where amount of sodium sulphide was varied while keeping the concentrations of molybdenum, ammonium sulphate and ammonia constant. Figure 35a shows the plot of slope against α_4 and $[\text{NH}_4^+]/[\text{NH}_3]$, where stability constants at 150°C. were used for the calculation. Figure 36b shows the plot of slope against the product of the two variables.

Therefore the empirical rate equation was assumed to be:

Fig.36 EFFECT OF SOLUTION CONDITION , S VARIED.

$$-d \ln P/dt = k[\alpha_4[H^+]/(k'' + \alpha_4[H^+])](P_0 - P) + k''' \quad (30)$$

3-3 Discussion and conclusions

The experimental results are summarized as follows:

1. The precipitates obtained were mixtures of molybdenum tetra-hydroxide and possibly molybdenum tri-hydrosulphide.
2. The molar ratios of hydrogen consumed, and sulphur in the precipitates, to the molybdenum were related with the following equation:-

$$r_{H_2} = 1 + 0.18 r_S \quad (20)$$

3. The empirical rate equations were for the molybdenum consumption:-

$$-d [Mo]/dt = k P ([Mo]_0 - [Mo]) \quad (23)$$

and for hydrogen consumption:-

$$-d \ln P/dt = k(\alpha_4[H^+]/(k'' + \alpha_4[H^+]))(P_0 - P) + k''' \quad (30)$$

4. The various complex species of molybdenum in the solution are in rapid equilibrium with each other.

5. The activation energy of the rate of molybdenum depletion from solution was around 20 kcal./mole.

The above observations are consistent with the following mechanism:

- (1) Precipitation of catalytic material through the same reaction path as the one observed in the inert atmosphere. ... initiation.
- (2) Rapid and strong adsorption on the catalyst of various thiomolybdate species which were in equilibrium each other in the solution as well as on the surfaces of the catalyst.
- (3) Weak adsorption of hydrogen on the catalyst surfaces.
- (4) Activation of the adsorbed hydrogen. ... rate determining step.
- (5) Consumption of the activated hydrogen through two paths;
 - (a) Reaction with the protonated tetra-thiomolybdate to produce the sulphide, consuming 1.5 mole of hydrogen per mole of molybdenum.
----- catalyst generation.
 - (b) Reaction with simple molybdate adsorbed to produce the oxide or hydroxide consuming one mole of hydrogen per mole of molybdenum.

The initiation step was necessary to explain the slow reduction at the beginning of reaction. Since this slow

part disappeared when precipitates were added or when the surfaces of the autoclave were not cleaned, the delay was considered to be due to an inherent slowness of any homogeneous reactions.

The step (2) assumes that the fractional distribution of various thiomolybdate is the same both in the solution and on the surfaces of the catalyst. The equilibrium between tetra-thiomolybdate and its protonated form gives:-

or $[\text{HMoS}_4^-] = K [\text{MoS}_4^{2-}][\text{H}^+]$, (Where K is the equilibrium constant).

Therefore the fraction of adsorbed protonated tetra-thiomolybdate on the catalyst surfaces is given by

$$\gamma' = \alpha_4 [\text{H}^+] / (k_1 + \alpha_4 [\text{H}^+])$$

where k_1 contains concentrations of all the other species.

The step (3) assumes that the amount of hydrogen on the surfaces of the catalyst is proportional to the partial pressure of hydrogen.

$$[\text{H}_2]_{\text{ads}} = k_2 C_s P \quad (31)$$

where C_s is the number of active sites.

The step (4) assumes that the rate equation is expressed by

$$-dP/dt = k_3[H_2]_{ads} \quad (32)$$

Substitution of equation (31) into equation (32) yields

$$-dP/dt = k_2 k_3 C_s P \quad (33)$$

The step (5) assumes that the amount of catalyst produced is proportional to the product of the amount of hydrogen consumed with the fraction of protonated tetra-thiomolybdate on the catalyst surface existing. Namely

$$dC_s/dt = \epsilon \gamma' (-dP/dt) \quad (34)$$

where ϵ is the conversion factor to relate the pressure drop into mole/l. when the active site number is expressed by mole molybdenum in the precipitate per liter of suspension. If γ' does not vary much during the reduction reaction, the equation (34) can be integrated to give the amount of catalyst as

$$C_s = \epsilon \gamma' (P_0 - P) + C_{s0}$$

and substitution into the equation (33) yields the equation (26).

When γ' varies as the reaction proceeds the integration of equation (34) and (33) becomes difficult but qualitatively the variation of Figure 34 can be explained with this mechanism. As the depletion of molybdenum proceeds two mole of ammonium ion would be consumed to keep the charge balance, making the pH of the solution larger. This causes also the decrease of α_4 and γ' would become increasingly smaller.

The step (5) also indicate that r_H and r_S are related to γ' by

$$r_H = 1.5 \gamma' + (1 - \gamma') = 1 + 0.5 \gamma'$$

$$r_S = 3 \gamma'$$

$$\text{hence } r_H = 1 + 0.167 r_S$$

The coefficient is in close agreement with the one in equation (20).

The activation energy of 20 kcal./mole is reasonable for the heterogeneous activation of hydrogen on various catalyst surfaces^{85 86}

4. Precipitation in Carbon Monoxide Atmosphere

4-1 Reduction products

The absorption spectra of the solutions during the experiments were the same as those observed in the experiments with hydrogen as shown in Figure B-4 in

Appendix B. No new absorption peak was observed in the visible range. Therefore the soluble carbonyl complexes of molybdenum, if they existed, were considered to be of very small quantity and short-lived.

As the D.T.A. curves of the precipitates (discussed below) were found to be similar to those of the precipitate from the hydrogen reduction, no insoluble carbonyl complex was considered to form. The simple carbonyl of molybdenum, $\text{Mo}(\text{CO})_6$, was not expected to form since its synthesis is possible only under anhydrous conditions.^{1,87} No precipitate corresponding to this carbonyl was observed.

The total concentrations of both molybdenum $[\text{Mo}]_T$ and sulphide, $[\text{S}]_T$, in the solution decreased as the reaction proceeded when the initial ratio, $[\text{S}]_T/[\text{Mo}]_T$, was small. But as can be seen in Figure 37, where $[\text{S}]_T$ was plotted against $[\text{Mo}]_T$, a good linearity was observed throughout the reaction, indicating the existence of stoichiometry between molybdenum and sulphide during the precipitation process. For the different initial conditions, the slope of the curve varied, but linearity was observed.

Variation in the composition of the precipitates is also shown by the D.T.A. results shown in Figure 38, where total sulphide concentration was varied. The peak around 550°C . corresponds to the oxidation of the molybdenum compound to form MoO_3 in agreement with literature values⁸⁹. The peak at around 390°C . increased as the sulphide concen-

Fig. 37 VARIATION OF $[Mo]_T$ AND $[S]_T$ UNDER CO

Fig. 38 D.T.A. RESULTS

tration increased, which is in agreement with the increase of S/Mo ratio of precipitates and suggests the mixture of sulphide and hydroxide stated in section 3-1.

4-2 Kinetic study

The mode of decrease of the total concentration of molybdenum against time varied according to the initial condition of the solution.

Figure 39 shows the results of a series at high values of initial concentrations of molybdenum and sulphide, $[Mo]_{Ti}$ and $[S]_{Ti}$, where the partial pressure of carbon monoxide was varied. The curves show approximately the same initial induction period followed by linear decrease until the depletion was complete.

Figure 40 shows the results of a series at low $[Mo]_{Ti}$ and high $[S]_{Ti}$ where the partial pressure of carbon monoxide was varied. The curves show rather short induction periods followed by the depletion of total molybdenum concentration with a steady decrease of the slope.

Figure 41 shows the results of a series at high $[Mo]_{Ti}$ and constant partial pressure of carbon monoxide, where $[S]_{Ti}$ was varied. The curves showed large variation of the induction period followed by linear decrease of total molybdenum concentration. At lowest concentration of sulphide studied, the linear decrease part was not even clear within the experimental period.

Fig. 40 VARIATION OF CONCENTRATION UNDER CO , LOW $[Mo]_T$, P VARIES

Fig.4.1 VARIATION OF CONCENTRATION UNDER CO, HIGH $[Mo]_T$, $[S]_T$ VARIES

The kinetics were analyzed in two sections, the induction period and the linear portion. The induction time was obtained by extrapolating the linear portion back to the initial molybdenum concentration. When the linear part was not clear, the induction reaction rate constant was calculated by the method discussed below.

4-2-a Induction period

When $[\text{Mo}]_T$ values in the initial part were plotted against the square of time, a good linearity was observed, i.e.

$$[\text{Mo}]_0 - [\text{Mo}] = (kt)^2 \quad (35)$$

and the inverse of the rate constant, k , was found to be proportional to the induction time, τ , obtained by the extrapolation method.

$$\tau \propto 1/k$$

Therefore for the cases where the linear portion was not clear enough to use the extrapolation method, these rate constants were used for the analysis of the induction reaction.

The pressure dependence of the induction time is shown in Figure 42. There was no apparent dependence on the pressure in the range investigated. Therefore the induction period is concluded not to depend on the reduction reaction by carbon monoxide.

The sulphide concentration varied the induction period greatly as is shown in Figure 43. This showed roughly that

$$k \propto [S]_T, \text{ or } \tau \propto 1/[S]_T \quad (36)$$

The precipitation under nitrogen atmosphere follows equation (18). Thus the initial rate of precipitation under nitrogen is given by substituting the initial concentration of molybdenum, namely,

$$(-d[Mo]_T/dt)_0 = k_M [Mo]_e [S]_e ([Mo]_0 - [Mo]_e)$$

The time Δt required to yield a constant amount $\Delta[Mo]$ of precipitate at this rate is given by

$$\begin{aligned} \Delta t &= \Delta[Mo]_T / (-d[Mo]_T/dt)_0 \\ &= \{\Delta[Mo]_T / k_M [Mo]_e ([Mo]_0 - [Mo]_e)\} / [S]_e \propto 1/[S]_{Te} \end{aligned}$$

which is of the same form as equation (36).

Therefore the induction period is concluded to be caused by the slow precipitation of catalyst with the same reaction stated in Part 2, section 2.

Fig. 42 INDUCTION PERIOD, VS. PRESSURE

Fig. 43 INDUCTION PERIOD, k vs. $[S]_T$

4-2-b Growth (linear portion)

4-2-b-1 Effect of sulphide concentration

The initial sulphide concentration also varied the slope of the linear portion, rate, of the rate curve. But when the rate was plotted against the induction reaction rate constant, k , for the series where only the sulphide concentration was varied, a good linearity was observed, as shown in Figure 44. Therefore it was concluded that the sulphide concentration varies only the amount and quality of catalyst produced during the induction period and has no direct effect on the linear portion, i.e., the growth part. In other words, sulphide ion does not come into the rate determining step.

4-2-b-2 Effect of partial pressure of carbon monoxide

The effect of partial pressure of carbon monoxide on the rate was studied under various conditions. When the slopes of the linear portion of the series with high initial concentration of molybdenum and sulphide and the initial slopes of the series of the low initial concentration of molybdenum were plotted against the partial pressure of carbon monoxide, a non-linear dependence was observed approaching some limiting value at high pressure region as shown in Figure 46. This type of curves may be expected to follow the relationship,

$$\text{rate} = B_1 P / (1 + B_2 P) \quad (37)$$

Fig. 44 RATE vs. INDUCTION PERIOD

Fig. 45 EFFECT OF $[Mo]_T$ ON RATE, 160°C.

thus

$$1/\text{rate} = (B_2/B_1)(1/P) + (1/B_1)$$

Figure 47 shows the plot of $1/\text{rate}$ against $1/P$. A good linearity is observed in this plot, indicating a dependence of the rate on partial pressure of carbon monoxide as given in equation (37). The calculated values of B_1 and B_2 are also listed in Table A-4 in Appendix A.

4-2-b-3 Effect of total molybdenum concentration

When $[S]_T$ is very large compared to $[Mo]_T$, a slight variation in $[Mo]_T$ does not change appreciably the concentration of free sulphide. Consequently the degree of complexing does not change appreciably in such a case. Therefore the effect of the total molybdenum concentration was investigated under such conditions.

In Series C in Table A-4-1 in Appendix A, where the partial pressure of carbon monoxide was varied, $[S]_T = 0.022$ M., and $[Mo]_T = 0.0010 \sim 0.0008$ M. Hence, the condition stated above was fulfilled. The initial rate determined at $P_{CO} = 20.4$ atm. was the result from $[Mo]_T = 0.0008$ M. The interpolated value of the initial rate at $P_{CO} = 20.4$ atm. from the results of a series of experiments with $[Mo]_T = 0.0010$ M., is compared in the table below.

Fig.46 GROWTH UNDER CO, RATE vs. PRESSURE

Fig.47 $1/\text{RATE}$ vs. $1/P_{\text{CO}}$ PLOT

$[\text{Mo}]_T$	Initial Rate	k'
M. $\times 10^3$	M. min. ⁻¹ $\times 10^5$	min. ⁻¹ $\times 10^2$
0.8	1.44 (found)	1.80
1.0	1.81 (interpolated)	1.81

where $k' = (\text{Initial Rate})/[\text{Mo}]_T$

Fair agreement is noted for the first order rate constant calculated, indicating the pseudo first order dependence of the rate on the total molybdenum concentration when the sulphide concentration was in large excess.

The dependence of the rate on the molybdenum concentration was further studied by analyzing the rate curves of the series of high sulphide to molybdenum ratio. When $([\text{Mo}]_T/\text{Rate})$ was plotted against $[\text{Mo}]_T$ for the P series, where $[\text{Mo}]_T$ and $\text{Rate} = (-d[\text{Mo}]_T/dt)$ are the instantaneous values, good linearity was observed with all the lines at various pressures having a constant intercept as shown in Figure 45. Therefore the rate equation for this series was assumed to be

$$[\text{Mo}]_T/(-d[\text{Mo}]_T/dt) = a + b [\text{Mo}]_T$$

or $-d[\text{Mo}]/dt = ([\text{Mo}]_T/(a + b [\text{Mo}]_T))$

The integration gives

$$Y = \ln [\text{Mo}]_T + at = -b [\text{Mo}]_T + \text{constant}$$

The left-hand side was calculated by putting $a = 0.11 \text{ min.}^{-1}$ obtained from Figure 45, and plotted against $[\text{Mo}]_T$ to obtain the slope b . The values of the slope b were found to be proportional to the inverse of pressure. The plottings are shown in Figure 48. Therefore the rate equation is given by

$$-d [\text{Mo}]_T / dt = [\text{Mo}]_T / [a + (b'/P)[\text{Mo}]_T] \quad (38)$$

where b' is a constant.

For the initial rate equation (38) is reduced to equation (39).

$$(-d[\text{Mo}]_T / dt)_i = [\text{Mo}]_{Ti} P / (aP + b'[\text{Mo}]_{Ti}) \quad (39)$$

4-3 Discussion

The experimental observations are shown by equation (35) to (38).

A mechanism consistent with the above observations for growth is proposed as follows:

- (i) Fast equilibrium between various molybdenum complexes

Fig.48 INTEGRAL PLOT, $Y = \ln (Mo)_T + at$,

- (ii) Fast and strong adsorption equilibrium of a molybdenum complex and carbon monoxide on catalyst surfaces, C_s ,

- (iii) Fast equilibrium between adsorbed species to form an adduct

- (iv) Slow decomposition of the adduct

- (v) Rapid neutralization to cause the growth of the precipitates.

The rate of molybdenum precipitation given from the above assumption is

$$-d [Mo]_T / dt = k [MoO_n S_{4-n}^{2-} \cdots CO]_{ads} \quad \dots (40)$$

The strong adsorption equilibrium between CO_{ads} , $[MoO_n S_{4-n}^{2-}]_{ads}$ and $[MoO_n S_{4-n}^{2-} \cdots CO]_{ads}$ yields

$$[\text{MoO}_n\text{S}_{4-n}^{2-} \cdots \text{CO}]_{\text{ads}} = C_S \epsilon_{\text{MCO}} [\text{MoO}_n\text{S}_{4-n}^{2-} \cdots \text{CO}] / (\eta_{\text{CO}} P_{\text{CO}} + \eta_{\text{M}} [\text{MoO}_n\text{S}_{4-n}^{2-}] + \eta_{\text{MCO}} [\text{MoO}_n\text{S}_{4-n}^{2-} \cdots \text{CO}]) \dots\dots\dots(41)$$

assuming the Langmuir type of adsorption, where η 's are adsorption coefficients. The equilibrium at the step (ii) and (iii) gives

$$[\text{MoO}_n\text{S}_{4-n} \cdots \text{CO}] = K' [\text{MoO}_n\text{S}_{4-n}] P_{\text{CO}} \dots\dots\dots(42)$$

where K' is an equilibrium constant.

Using the fractional distribution of species, $[\text{MoO}_n\text{S}_{4-n}]$ is related to the total concentration of molybdenum by

$$[\text{MoO}_n\text{S}_{4-n}] = \alpha_n [\text{Mo}]_T \dots\dots\dots(43)$$

Substitution of equations (41), (42) and (43) into (40) yields:

$$-d [\text{Mo}]_T / dt = k C_S \epsilon_{\text{MCO}} K \alpha_n [\text{Mo}]_T P_{\text{CO}} / (\alpha_{\text{CO}} P_{\text{CO}} + \eta_{\text{M}}' \alpha_n [\text{Mo}]_T + \eta_{\text{MCO}} K' \alpha_n [\text{Mo}]_T P_{\text{CO}}) \dots\dots\dots(44)$$

For large values of $[Mo]_T$ the first term in the denominator is negligible versus others and equation (44) reduces to

$$-d [Mo]_T/dt = (kC_S \epsilon_{MCO} K) P_{CO} / (\eta_M + \eta_{MCO} K P_{CO})$$

which is equivalent to the equation (37). For low values of $[Mo]_T$, the last term in the denominator is negligible versus others and equation (44) reduces to

$$-d [Mo]_T/dt = (kC_S \epsilon_{MCO} K \eta_n) P_{CO} [Mo]_T / (\eta_{CO} P_{CO} + \eta_M \alpha_n [Mo]_T)$$

which is equivalent to the equation (38), (39).

The actual $[Mo]_T$ -time curve is the result of the combination of the molybdenum depletion by a) the catalyst production process, which will be denoted M_1 , and by b) the catalytic reduction process which will be denoted M_2 .

i.e., initial total molybdenum = $[M]_{Ti} = [M] + [M_1] + [M_2]$

The rate equations obtained for (a) and (b) are in simplified forms,

$$\frac{dM_1}{dt} = k_1 (M_{10} - M_1) \quad \dots \dots (45)$$

$$\frac{dM_2}{dt} = k_2 \frac{C_s [M] P}{P + k_3 [M] + k_4 [M] P} \quad \dots \dots (46)$$

If we assume

$$C_s = \gamma'' M_1 \quad \text{where } \gamma'' = \text{shape factor}$$

the equations (45) and (46) can be combined to give the rate equation for the molybdenum concentration in aqueous phase:-

$$\begin{aligned} \frac{d[M]}{dt} &= \frac{dM_1}{dt} + \frac{dM_2}{dt} \\ &= k_1 (M_{10} - M_1) + k_2 \frac{\gamma'' M_1 [M] P}{P + k_3 [M] + k_4 [M] P} \\ &= k_1 M_{10} e^{-k_1 t} + k_2 \frac{[M] P}{P + k_3 [M] + k_4 [M] P} \\ &\quad \gamma'' M_{10} (1 - e^{-k_1 t}) \quad \dots \dots (47) \end{aligned}$$

For large values of [M] and small values of t, equation (47) is reduced, on expansion, to

$$-\frac{d[M]}{dt} = k_1 M_{10} + k_1 M_{10} \left(k_2 \frac{P}{k_3 + k_2 P} \gamma'' - k_1 \right) t$$

This is the same form as equation (35), if the first term, i.e., k_1 , is small. For large values of t , $e^{-k_1 t} \approx 0$, thus,

$$-\frac{d[M]}{dt} = k_2 \frac{[M] P}{P + k_3 [M] + k_4 [M] P} \gamma'' M_{10}$$

in agreement with the observed rate equation.

The assumption of adsorbed adduct of thiomolybdates and carbon monoxide in the step (iii) is reasonable in view of the existence of various organo-molybdenum complexes containing carbon monoxide as a ligand⁸⁷. Halverson also postulated the adsorbed adduct of cobaltic ammine with carbon monoxide in his study of the reduction of cobaltic sulphate solution with carbon monoxide⁸⁸.

GENERAL SUMMARY AND CONCLUSION

1. Equilibrium study of molybdenum (VI) -sulphur (-II) -water system was made at 120° and 150°C. Species of the form $\text{MoO}_{4-x}\text{S}_x^{2-}$ existed for all values of x between 1 and 4, although mono-thiomolybdate was less significant at all ranges of aqueous hydrogen sulphide concentration. Rough estimation of thermodynamic parameters indicated that exchange of oxide ion in the molybdate ion with sulphide ion causes a strong covalent bond formation yielding negative enthalpy of exchange and positive entropy production which may not be compensated by the negative difference in entropy between aqueous hydrogen sulphide and water.

2. In the inert atmosphere at elevated temperature the thiomolybdate system was not stable and decomposed to approach equilibrium. There was an indication of reduction of molybdenum by sulphide ion in the ammoniacal alkaline solution.

3. Under hydrogen atmosphere the reduction reaction was found to be autocatalytic, rate being first order in the amount of molybdenum which has left solution and hydrogen pressure. A mechanism was suggested in which the rate determining step was the activation of the adsorbed hydrogen on the sulphide precipitates, followed by two alternative paths, one to produce sulphide in which molybdenum was tri-valent and the other to produce oxide

in which molybdenum was tetra-valent. The sulphide produced by the former path was considered catalytically active and the proportion of sulphide to oxide in the product was determined by the solution conditions.

4. Under the carbon monoxide atmosphere the reduction reaction was found to have an induction period followed by a linear decrease in concentration. A mechanism is suggested in which the induction period produces a catalyst. This catalyst is then active for a main reaction where slow decomposition of adducts between strongly adsorbed thiomolybdates and carbon monoxide was rate determining. The catalyst amount was considered not to change significantly during the main reaction.

SUGGESTED FUTURE WORK

1. Use of the tri- and tetra-thiomolybdate couple as an indicator of aqueous hydrogen sulphide concentration

(a) Determination of thermodynamic properties of aqueous hydrogen sulphide at elevated temperatures is possible by the experimental method described in Part 1, after determining more accurately the consecutive constant k_4 at various temperatures.

(b) Solubility products of heavy metal sulphides at elevated temperatures can be determined by measuring the activity of aqueous hydrogen sulphide by adding small amount of molybdenum to the solutions. In this case the investigation of co-precipitation of molybdenum with heavy metal may be required.

2. Catalytic material produced during the hydrogen and carbon monoxide reduction may be worth investigation for their natures as a general hydrogenation catalyst.

3. Stripping of molybdenum from the solution by the method was found complete. Thus the study of the potential of this system for the processing in molybdenum industry can be worthwhile.

4. Reduction of hexavalent molybdenum to tetra- and/or tri-valent was found to proceed. Thus by controlling the extent of reduction, molybdenum disulphide may be

produced. In this case carbon monoxide would be preferred in view of the difficulty of controlling the reaction in hydrogen reduction.

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A P P E N D I X

APPENDIX A

Experimental Data

Table A-1 The Study of Equilibrium

Table A-1-1 Analytical Data

Series A. 150°C., $[\text{NH}_3] = 1 \text{ M.}$, $[\text{NH}_4^+] = 1 \text{ M.}$, (nominal Concentration)

No.	Mo_T M. $\times 10^3$	S_T M. $\times 10^3$	α_3	α_4	$\bar{A}_2^{315}$ $\text{M.}^{-1}\text{cm.}^{-1}$ $\times 10^{-4}$	$\bar{n}$	S_f M. $\times 10^3$	$[\text{H}_2\text{S}]_{\text{aq}}$ M. $\times 10^3$	α_2 calcd.
22	0.49	12.73	0.233	0.105	0.221	1.54	11.98	1.893	0.231
3	.97	12.26	.216	.091	.208	1.47	10.83	1.711	.234
4	1.47	12.23	.201	.076	.208	1.41	10.16	1.605	.234
5	2.13	12.13	.181	.060	.188	1.32	9.32	1.473	.231
32	0.50	5.36	0.098	0.020	0.148	0.84	4.94	0.781	0.138
3	1.05	5.87	.088	.014	.138	.78	5.05	.798	.142
4	1.61	5.90	.073	.012	.125	.69	4.79	.757	.132
6	2.69	6.03	.060	.008	.113	.59	4.44	.702	.119
42	0.50	23.81	0.329	0.327	0.110	3.16	22.23	3.512	0.152
3	1.01	24.38	.334	.311	.123	3.10	21.25	3.358	.159
4	1.54	24.28	.323	.291	.132	3.03	19.61	3.098	.172
5	2.07	24.14	.314	.256	.151	2.93	18.07	2.855	.185
72	2.008	2.82	0.017	0.001	0.054	0.47	1.88	0.297	0.028
3	1.973	5.84	.063	.010	.115	.60	4.66	.736	.127
82	0.998	2.49	0.017	0.001	0.052	0.47	2.02	0.319	0.032
3	.930	5.39	.065	.011	.121	.61	4.82	.762	.134
4	.880	7.38	.125	.031	.171	1.06	6.45	1.019	.186
5	.871	10.47	.207	.079	.212	1.42	9.23	1.458	.230
6	.854	14.37	.282	.145	.229	2.07	12.60	1.991	.228
7	.828	16.93	.319	.199	.224	2.52	14.84	2.345	.212
8	.821	19.84	.334	.250	.195	2.82	17.52	2.768	.189
9	.817	22.44	.340	.286	.172	2.99	20.00	3.160	.169

SERIES B

150°C., $[\text{NH}_3] = 0.5 \text{ M.}$, $[\text{NH}_4^+] = 1 \text{ M.}$

(Nominal Concentrations)

No.	$[\text{Mo}]_T$ M. ₃ $\times 10^3$	$[\text{S}]_T$ M. ₃ $\times 10^3$	α_3	α_4	$\frac{-315}{\text{M.}^{-1}\text{cm.}^{-1}} \frac{\text{Å}^2}{\times 10^{-4}}$	$\bar{n}$	$[\text{S}]_f$ M. ₃ $\times 10^3$	$[\text{H}_2\text{S}]_{\text{aq}}$ M. $\times 10^3$	α_2 calcd.
92	0.995	2.41	0.043	0.003	0.098	0.57	1.84	0.440	0.057
3	.916	5.40	.163	.044	.194	1.13	4.37	1.044	.196
4	.946	8.44	.253	.104	.237	1.79	6.75	1.613	.234
5	.956	11.38	.301	.172	.226	2.58	8.91	2.129	.223
6	.944	14.26	.327	.235	.203	2.80	11.62	2.777	.189
7	.912	17.23	.337	.295	.172	3.10	14.40	3.442	.155
8	.910	19.80	.322	.326	.146	3.21	16.88	4.034	.130
9	.882	22.16	.316	.355	.124	3.29	19.26	4.603	.110

SERIES C

120°C., $[\text{NH}_3] = 1 \text{ M.}$, $[\text{NH}_4^+] = 1 \text{ M.}$

(Nominal Concentrations)

No.	$[\text{Mo}]_T$ M. ₃ $\times 10^3$	$[\text{S}]_T$ M. ₃ $\times 10^3$	α_3	α_4	$\frac{-315}{\text{M.}^{-1}\text{cm.}^{-1}} \frac{\text{Å}^2}{\times 10^{-4}}$	$\bar{n}$	$[\text{S}]_f$ M. ₃ $\times 10^3$	
52	0.465	8.16	0.215	0.060	0.192	1.83	7.31	
3	.865	6.30	.116	.029	.170	1.28	5.19	
4	1.407	4.68	.053	.008	.108	.89	3.43	
5	2.000	4.38	.038	.004	.089	.84	2.70	
62	0.498	-	0.319	0.285	0.136	2.61	-	
3	1.019	-	.322	.279	.151	2.61	-	
4	1.494	-	.324	.262	.172	2.51	-	
5	2.000	-	.320	.242	.200	2.43	-	
122	1.036	3.44	0.018	0.004	0.065	0.81	2.60	
3	1.068	6.64	.095	.027	.139	1.15	5.41	
4	1.028	10.39	.178	.073	.186	1.62	8.73	
5	.967	14.10	.246	.130	.201	1.97	12.20	
6	.852	17.21	.295	.193	.191	2.33	15.22	
7	.742	20.78	.328	.257	.175	2.50	18.93	
8	.671	24.28	.351	.331	.133	2.66	22.50	

TABLE A-1-1

Study of Equilibrium
(continued)

SERIES D

150°C. Nominal Ratio $(\text{NH}_3)/(\text{NH}_4^+) = 0.1/1$

No.	M_{oT} $M. \times 10^3$	S_T $M. \times 10^3$	α_3	α_4	$\bar{A}_2^{315}$	$\bar{n}$	S_f $M. \times 10^3$	$(\text{H}_2\text{S})_{aq}$ $M. \times 10^3$
102	1.054	2.34	0.095	0.013	0.177	0.82	1.48	0.75
3	1.051	4.75	0.201	0.076	0.255	1.42	3.26	1.66
4	1.044	7.17	0.195	0.114	0.266	3.06	3.97	-
5a	1.031	9.32	-	0.138	-	3.93	5.27	-
6a	1.021	13.48	-	0.136	-	4.18	9.21	-
7a	1.010	11.59?	-	0.133	-	4.26	10.40	-
112	1.024	2.58	0.100	0.018	0.186	0.88	1.68	0.85
3	1.015	3.76	0.206	0.080	0.258	1.42	2.32	1.18
4	1.009	7.61	0.198	0.114	0.242	2.98	4.60	-
5a	0.990	9.76	-	0.138	-	3.99	5.81	-
6a	0.988	12.06	-	0.133	-	4.10	8.10	-
7a	0.985	14.80	-	0.130	-	4.14	10.73	-
8a	0.985	16.00	-	0.127	-	4.15	11.92	-
9a	0.985	18.76	-	0.124	-	4.17	14.66	-

a - Too much interference was observed probably due to the appearance of protonated species, and α_3 and $\bar{A}_2^{315}$ could not be obtained. Therefore $\bar{n}$ was calculated by using α_4 and S_T with successive approximation. But the values obtained for $\bar{n}$ were rather doubtful since α_4 might also contain the interference stated above.

TABLE A-1-2

Calculation of the Conversion Factor

1. N_T vs. 10^{pH} plot, Figure 6a

Temperature °C.	$[NH_3]/[NH_4^+]$ M./M.	No.	pH	N_T M.	10^{pH} $\times 10^{-9}$	$[NH_3]$ M.	$[NH_4^+]$ M.
150	1/1	8-h	9.61	1.557	4.07	0.746	0.811
		8-c	9.62	1.581	4.17	0.770	0.811
	0.5/1	9-h	9.38	1.256	2.40	0.445	0.811
		9-c	9.39	1.270	2.46	0.459	0.811
	0.1/1	10-h	8.82	0.946	0.66	0.135	0.811
		11-h	8.89	0.938	0.78	0.125	0.811
120	1/1	5-h	9.46	1.363	-	0.542	0.821
		5-c	9.43	1.375	-	0.524	0.851
		6-h	9.62	1.525	-	0.745	0.780
		6-c	9.66	1.640	-	0.840	0.800
		12-h	9.70	1.65	-	0.88	0.77

pH was measured at room temperature.

'h' and 'c' in column 3 mean the sample taken from experimental temperatures and the sample taken after systems were cooled to room temperature, respectively.

2. $[NH_4^+]/[NH_3]$ vs. $[S]_f [NH_4^+]/[NH_3]$ plot, Figure 6b.

$\bar{n}$	$[NH_3]/[NH_4^+]$ (nominal) M./M.	$[S]_f$ M. $\times 10^3$	$[NH_3]$ M.	$[NH_4^+]$ M.	$[NH_4^+]/[NH_3]$	$[S]_f [NH_4^+]/[NH_3]$ M. $\times 10^3$
1.42	1/1	9.2	0.746	0.811	1.09	10.0
	0.5/1	5.3	0.445	0.811	1.82	9.6
	0.1/1	2.8	0.135	0.811	6.0	16.3
0.85	1/1	5.5	0.746	0.811	1.09	6.0
	0.5/1	3.3	0.445	0.811	1.82	6.0
	0.1/1	1.6	0.135	0.811	6.0	9.4

3. Conversion Equation

$$[\text{H}_2\text{S}]_{\text{aq}} = [\text{S}]_{\text{f}} / (1 + m [\text{NH}_4^+]),$$

From the plots (1) and (2), $m = 5.8$, and consequently:

A: Nominal $[\text{NH}_3]/[\text{NH}_4^+] = 1/1$; $[\text{H}_2\text{S}]_{\text{aq}} = 0.15_8 [\text{S}]_{\text{f}}$

B: Nominal $[\text{NH}_3]/[\text{NH}_4^+] = 0.5/1$; $[\text{H}_2\text{S}]_{\text{aq}} = 0.23_9 [\text{S}]_{\text{f}}$

D: Nominal $[\text{NH}_3]/[\text{NH}_4^+] = 0.1/1$; $[\text{H}_2\text{S}]_{\text{aq}} = 0.50_8 [\text{S}]_{\text{f}}$

TABLE A-2

Precipitation Under Nitrogen Atmosphere

Temperature 158.8°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $(\text{NH}_4)_2\text{SO}_4 = 0.5 \text{ M.}$ Sulphide was added as a $(\text{NH}_4)_2\text{S}$ solution.

			Run 49	Run 47	Run 46
$[\text{Mo}]_T$	X_i	$\text{M.} \times 10^3$	11.2	19.1	19.4
	X_e	$\text{M.} \times 10^3$	8.6	16.0	14.5
	k	$\text{min.}^{-1} \times 10^3$	3.2	11.3	8.9
$[\text{S}]_T$	X_i	$\text{M.} \times 10^3$	27.5	51.5	53.5
	X_e	$\text{M.} \times 10^3$	20.4	42.6	38.5
	k	$\text{min.}^{-1} \times 10^3$	5.8	10.7	8.8
C_4	X_i	$\text{M.} \times 10^3$	1.11	2.97	3.27
	X_e	$\text{M.} \times 10^3$	0.68	1.28	1.27
	k	$\text{min.}^{-1} \times 10^3$	15.4	18.0	22.2
C_3	X_i	$\text{M.} \times 10^3$	2.93	4.55	3.78
	X_e	$\text{M.} \times 10^3$	1.63	2.34	3.35
	k	$\text{min.}^{-1} \times 10^3$	10.0	12.9	19.9
-----			-----	-----	-----
k/X_e for	$[\text{S}]_T$	$\text{M.}^{-1} \text{min.}^{-1}$	0.28	0.25	0.23
	C_4	$\text{M.}^{-1} \text{min.}^{-1}$	22.	14.	18.
	C_3	$\text{M.}^{-1} \text{min.}^{-1}$	6.1	5.5	5.9
$k_{\text{Mo}}/[\text{Mo}]_e$	$[\text{S}]_e$	$(\text{M.}^{-2} \text{min.}^{-1} \times 10^{-5})$	1.8	1.7	1.6
-----			-----	-----	-----
Composition of precipitates (%)					
Mo			40.1	45.0	44.9
S			41.4	39.9	39.8
difference			18.5	15.1	15.3
			<u>100.0</u>	<u>100.0</u>	<u>100.0</u>
Molar ratio $\text{S/Mo} = r_S$					
Observed			3.10	2.65	2.65
Calculated			4.20	3.08	2.83

TABLE A-3

A-3-1 Analysis of Precipitates, r_S and r_{H_2}

Series A Mo variation

151.6°C., $NH_3 = 0.86$ M., $NH_4^+ = 0.98$ M.,Initial conditions: $S_T = 0.211$ M., $P_{H_2} = 860$ psi.

No.	Mo _T M.	S/Mo	r_S	r_{H_2}	
101	0.049	4.28	2.14	1.29	
102	0.099	2.14	1.93	1.22	
103	0.148	1.42	1.45	1.20	
104	0.198	1.07	1.11	1.16	
105	0.247	0.85	0.91	1.15	

Series B S variation

158.8°C., $NH_3 = 0.84$ M., $NH_4^+ = 0.97$ M.,Initial conditions: Mo_T = 0.097 M., $P_{H_2} = 600$ psi.

No.	S _T M.	S/Mo	r_S	r_{H_2}	
79	0.646	7.0	2.30	1.35	
72	0.616	6.6	n.d.	1.24	
80	0.327	3.41	2.08	1.23	
86	0.235	2.42	2.10	1.41	
81	0.154	1.59	1.53	1.29	
85	0.116	1.18	1.23	1.39	
83	0.079	0.81	0.80	1.23	

Series C Constant (Mo + S), 167.7°C, $NH_3 = 0.86$ M., $NH_4^+ = 0.98$ M.
 $P_{H_2} = 530$ psi

No.	Mo _T M.	S _T M.	S/Mo	r_S	r_{H_2}
94	0.002	0.014	7.0	2.45	2.5?
95	0.004	0.012	3.0	2.16	1.6
96	0.006	0.010	1.67	1.62	1.6
97	0.008	0.008	1.00	1.02	1.2
98	0.010	0.006	0.60	0.61	1.2
99	0.012	0.004	0.33	0.32	1.3
100	0.014	0.002	0.17	0.15	1.1

Series D P variation

158.8°C., $\text{NH}_3 = 0.84 \text{ M.}$, $\text{NH}_4^+ = 0.96 \text{ M.}$,Initial concentrations: $\text{Mo}_T = 0.097 \text{ M.}$, $\text{S}_T = 0.194 \text{ M.}$

No.	P_{H_2} initial psi.	P_{H_2} final psi.	r_{S}	r_{H_2}
86	602	420	2.10	1.41
87	441	220	1.83	1.51
88	310	95	1.96	1.47
89	228	16	1.96	1.45

158.8°C., $\text{NH}_3 = 1.00 \text{ M.}$, $\text{NH}_4^+ = 0.99 \text{ M.}$,Initial concentrations: $\text{Mo}_T = 0.020 \text{ M.}$, $\text{S}_T = 0.054 \text{ M.}$

titanium autoclave, pressure maintained constant.

No.	P_{H_2} psi.	r_{S}	r_{H_2}	
44	100	2.33	n.d.	
43	200	2.09	n.d.	
42	300	2.16	n.d.	
41	400	2.06	n.d.	
40	500	2.04	n.d.	

Series E pH variation

151.6°C., no NH_3 ,Initial concentrations: $\text{Na}_2\text{MoO}_4 = 0.097 \text{ M.}$, $\text{Na}_2\text{S} = 0.211 \text{ M.}$,

Initial pressure 880 psi.

No.	$(\text{NH}_4)_2\text{SO}_4$ M.	r_{S}	r_{H_2}	Mo_T in final solutions, M.
106	0.490	1.96	1.28	nil.
109	0.392	1.93	1.26	nil.
107	0.294	1.85	1.26	nil.
110	0.245	1.66	1.35	0.014
108	0.191	1.65	1.48	0.039

TABLE A-3-2
Analysis of Precipitates
T.G.A. Results

No.	r_S	Weight Loss in g./mole Mo		
		ΔW_1	ΔW_2	ΔW_3
83	0.80	13.4	25.6	-5.2
85	1.23	11.7	23.3	3.4
81	1.53	9.8	17.6	9.3
86	2.10	7.1	25.9	17.2
80	2.08	7.4	26.8	18.5
79	2.30	9.2	29.3	31.3
87	1.83	5.3	21.6	13.1
88	1.96	7.8	21.9	16.2
89	1.96	7.3	14.3	17.3
90	1.64	11.1	16.9	12.4
91	1.98	7.9	18.3	17.7
92	1.99	11.6	28.0	18.5

r_S : molar ratio of sulphur to molybdenum in precipitates

ΔW_1 : weight loss in Ar at 200°C.

ΔW_2 : weight loss in Ar at 650°C.

ΔW_3 : weight loss in air at 550°C. after T.G.A. in Ar.

TABLE A-3-3

Kinetic Study

3-1 P Dependence -- Series D

1. Constant Pressure
 158.8°C., $\text{NH}_3 = 1.00 \text{ M.}$, $\text{NH}_4^+ = 0.99 \text{ M.}$,
 Initial Concentrations: $\text{Mo}_T = 0.020 \text{ M.}$, $S_T = 0.054 \text{ M.}$
 Titanium Autoclave,

No.	P_{H_2} psi.	slope ₁ min.	intercept $\text{M.} \times 10^3$
44	100	-0.0057	2.57
43	200	-0.0140	1.34
42	300	-0.0214	1.25
41	400	-0.0301	0.90
40	500	-0.0321	0.32

Slope and intercept were obtained by plotting the equation:

$$\log (\text{Mo}_0 - \text{Mo}) = -St + \log I$$

2. Constant Volume
 158.8°C., $\text{NH}_3 = 0.84 \text{ M.}$, $\text{NH}_4^+ = 0.96 \text{ M.}$,
 Initial Concentrations: $\text{Mo}_T = 0.097 \text{ M.}$, $S_T = 0.194 \text{ M.}$

No.	P_{H_2} initial psi.	slope min. ⁻¹	
86	602	0.086	
87	441	0.061	
88	310	0.053	
89	228	0.029	

Slope was obtained by plotting the equation:

$$\ln (P/(\underline{a} + P_0 - P)) = -St + \ln P_0/\underline{a}$$

where $\underline{a}$ was taken as 10 psi.

3-2 Effect of Solution Conditions
151.6°C.

No.	Slope psi.-lmin. ⁻¹ x10 ⁵	Fractional Distribution					$\frac{(\text{NH}_4^+)}{(\text{NH}_3)}$
		α_0	α_1	α_2	α_3	α_4	
101	8.3	0.020	0.019	0.123	0.400	0.439	0.515
102	7.3	0.246	0.093	0.235	0.298	0.128	0.460
103	5.7	0.438	0.117	0.206	0.184	0.055	0.455
104	4.8	0.532	0.120	0.179	0.135	0.034	0.450
105	3.5	0.606	0.118	0.153	0.100	0.022	0.448
106	3.9?	0.208	0.086	0.233	0.323	0.150	1.444
109	4.6?	0.220	0.088	0.234	0.315	0.142	0.975
107	7.0	0.243	0.093	0.234	0.300	0.129	0.466
110	6.2	0.277	0.099	0.233	0.279	0.112	0.266
108	3.2	0.389	0.113	0.217	0.211	0.069	0.110

158.8°C.

No.	Slope atm.-lmin. ⁻¹ x10 ³	Fractional Distribution					$\frac{(\text{NH}_4^+)}{(\text{NH}_3)}$
		α_0	α_1	α_2	α_3	α_4	
79	1.56	0.134	0.067	0.221	0.370	0.208	0.030
72	1.70	0.106	0.058	0.211	0.387	0.239	0.037
80	2.48	0.085	0.051	0.199	0.398	0.267	0.250
86	2.07	0.183	0.080	0.231	0.339	0.167	0.408
81	1.74	0.364	0.111	0.222	0.226	0.077	0.590
85	1.74	0.478	0.119	0.195	0.163	0.046	0.696
83	1.73	0.694	0.112	0.119	0.064	0.012	0.815

Slopes were obtained by plotting reduced rate, $(-d \ln P/dt)$, against hydrogen consumption, $(P_0 - P)$.

α 's were calculated by using stability constants at 150°C. obtained in Part 1.

TABLE A-4

Precipitation Under Carbon Monoxide Atmosphere

Table A-4-1 Effect of Pressure

Series A 158.8°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.5 \text{ M.}$,
Initial Concentrations: $[\text{Mo}]_T = 0.020 \text{ M.}$, $[\text{S}]_T$
 $= 0.056 \text{ M.}$

No.	Pressure (atm.)	Induction period(min.)	Growth rate (M.min. ⁻¹) $\times 10^4$
39	6.8	6.1	2.33
38	13.6	4.2	4.13
37	20.4	4.3	5.85
35	27.2	5.5	7.46
30	34.0	5.3	8.65

Series B 158.8°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.5 \text{ M.}$,
Initial Concentrations: $[\text{Mo}]_T = 0.001 \text{ M.}$, $[\text{S}]_T = 0.022 \text{ M.}$

No.	Pressure (atm.)	Induction period(min.)	Growth rate (initial slope (M.min. ⁻¹) $\times 10^5$
56	6.8	(short)	0.98
54	13.6	(short)	1.63
53	20.4	(short)	2.54
52	27.2	(short)	3.12
51	34.0	(short)	3.21
57	40.8	(short)	3.63

Series C 151.6°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $[(\text{NH}_4^+)_2\text{SO}_4] = 0.5 \text{ M.}$,
Initial Concentrations: $[\text{Mo}]_T = 0.001 \text{ M.}$,
 $[\text{S}]_T = 0.022 \text{ M.}$

No.	Pressure (atm.)	Induction period(min.)	Growth rate (initial slope) (M.min. ⁻¹) $\times 10^5$
63	13.6	(short)	1.34
62 ^a	20.4	(short)	1.44
60	27.2	(short)	2.26
59	34.0	(short)	2.36
58	40.8	(short)	2.85
61	47.6	(short)	5.06

a: $[\text{Mo}]_T = 0.0008 \text{ M.}$

TABLE A-4-1
Effect of Pressure
(continued)

Series D 139.1°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $[\text{NH}_4\text{Cl}] = 1.0 \text{ M.}$,
Initial Concentrations: $[\text{Mo}]_T = 0.010 \text{ M.}$,
 $[\text{S}]_T = 1.0 \text{ M.}$

No.	Pressure (atm.)	Induction period(min.)	Growth rate ($\text{M} \cdot \text{min}^{-1}$) $\times 10^4$
12	6.3	20?	0.73
13	10.9	16?	1.24
11	17.5	7	1.37
14	23.3	10	2.45

TABLE A-4-2
Effect of Sulphide Concentration

Series E 158.8°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.5 \text{ M.}$,
 $P_{\text{CO}} = 34.0 \text{ atm.}$
Initial Concentrations: $[\text{Mo}]_T = 0.020 \text{ M.}$

No.	$[\text{S}]_T$ (M.)	Growth rate ($\text{M} \cdot \text{min}^{-1}$) $\times 10^4$	Induction period(min.)	Induction rate constant(min^{-1})
34	0.011	1.3	10.9	7.1
33	0.023	3.2	9.0	11.7
31	0.033	4.3	8.2	14.7
32a	0.033	5.5	8.7	13.2
30	0.056	8.3	5.3	24.4
29	0.089	14.4	3.2	40.6

a: The surfaces of autoclave were not treated with nitric acid.

Series F 139.1°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.5 \text{ M.}$,
 $P_{\text{CO}} = 34.0 \text{ atm.}$
Initial Concentrations: $[\text{Mo}]_T = 0.020 \text{ M.}$

No.	$[\text{S}]_T$	Growth rate ($\text{M} \cdot \text{min}^{-1}$) $\times 10^4$	Induction period(min.)	Induction rate constant(min^{-1})
23	0.011	0.30	n.d.	0.9
24	0.023	0.52	n.d.	2.6
25	0.033	1.26	40	3.3
22	0.056	2.87	13.2	8.9
26	0.089	5.39	7.5	15.9

TABLE A-4-2

Effect of Sulphide Concentration
(continued)

Series G 120°C., $[\text{NH}_3] = 1.0 \text{ M.}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.5 \text{ M.}$,
 $P_{\text{CO}} = 3.4 \text{ atm.}$

Initial Concentrations: $[\text{Mo}]_{\text{T}} = 0.020 \text{ M.}$

No.	$[\text{S}]_{\text{T}}$	Growth rate ($\text{M} \cdot \text{min}^{-1}$) $\times 10^4$	Induction period (min.)	Induction rate constant (min^{-1})
27	0.056	0.22?	n.d.	1.3
28	0.089	1.28	42.	3.3

Appendix B Spectrogram of the Solution

Spectrograms of the solution were taken using the transmission scale and some of them are reproduced here without alteration.

In Figure 1, 2, 5 and 6, the 0 and 100% transmission of the solutions were adjusted to the scale at 600 mμ (using a tungsten lamp) and the spectrum was taken to 315 mμ. Then the light source was changed to the hydrogen lamp and the 0% and 100% readings were adjusted in such a way that the transmission values agreed with the ones obtained with the tungsten lamp at around 350 mμ. Finally a further spectrum was taken to 260 mμ.

In Figures 3 and 4, the 0% and 100% transmissions were adjusted at 700 mμ with the tungsten lamp light source and the scan was performed to 300 mμ. A linear drift of the 100% line was observed and the necessary correction was made for the calculation of the concentrations of complex species.

The use of the wavelength at 600 mμ and 700 mμ for calibration was justified by the fact that the transmission was maximum at around 700 mμ and also close to the value observed for distilled water.

The following table shows the conditions of the solutions whose spectrum were taken.

Figure 1 Part 1, The study of the equilibrium

150.0°C., $[\text{Mo}]_T = 1 \times 10^{-3}$ M., $[\text{S}]_T = 2 - 20 \times 10^{-3}$ M.,
nominal compositions $[\text{NH}_3] = 1$ M., $[\text{NH}_4^+] = 1$ M.

(See Appendix A, Table A-1-1, Series A, No. 8, 2-9).

Figure 2 Part 1, The study of the equilibrium

150.0°C., $[\text{Mo}]_T = 1 \times 10^{-3}$ M., $[\text{S}]_T = 2 - 20 \times 10^{-3}$ M.,
nominal compositions $[\text{NH}_3] = 0.1$ M., $[\text{NH}_4^+] = 1$ M.

(See Appendix A, Table A-1-1, Series D, No. 11, 2-9).

Figure 3 Part 2, Precipitation under a nitrogen atmosphere

158.8° C., $[\text{Mo}]_{Ti} = 19 \times 10^{-3}$ M., $[\text{S}]_T = 52 \times 10^{-3}$ M.,
 $[\text{NH}_3]_i = 1$ M., $[\text{NH}_4^+] = 1$ M.

(See Figure 13).

Figure 4 Part 2, Precipitation under carbon monoxide

158.8° C., $[\text{Mo}]_{Ti} = 20 \times 10^{-3}$ M., $[\text{S}]_{Ti} = 54 \times 10^{-3}$ M.,
 $[\text{NH}_3]_i = 1$ M., $[\text{NH}_4^+]_i = 1$ M., $P_{\text{CO}} = 6.4$ atm.

Figure 5 Part 2, Precipitation under hydrogen

150.0° C., $[\text{Mo}]_{Ti} = 1 \times 10^{-3}$ M., $[\text{S}]_{Ti} = 14 \times 10^{-3}$ M.,
 $[\text{NH}_3] = 0.7$ M., $[\text{NH}_4^+] = 1.0$ M., $P_{\text{H}_2} = 8.3$ atm.

Figure 6 Appendix B, The study of the equilibration
reaction, room temperature,

$[\text{Mo}]_T = 1 \times 10^{-4}$ M., $[\text{S}]_T = 19 \times 10^{-3}$ M.,
 $[\text{NH}_3] = 1$ M., $[\text{NH}_4^+] = 1$ M.

Fig. B1 EQUILIBRIUM

Fig.B2. EQUILIBRIUM, LOW NH_3

Fig.B3 RUN UNDER N₂

Fig.B4. RUN UNDER CO

Fig. B5 RUN UNDER H₂

Fig. B6 EQUILIBRATION

Appendix C Rate of Equilibration

The rate of equilibration between various species in the Mo-S-H₂O system was studied for two reasons: 1) for comparison with the rate of molybdenum reduction to check the rate controlling step 2) to check the validity of the quenching method used for the study of equilibrium between thio-molybdenum complexes.

An experiment at high temperature was attempted using the high temperature spectrocell developed in this department, but difficulty in the injection of the solution made the operation impossible. Thus the results of room temperature experiments are presented here.

Experimental

Solutions of Mo and S were made fresh in buffer solutions. Suitable portions were taken in a beaker and buffer solution was added to make a constant volume [10 ml.]. The mixed solution was poured into a spectrocell, a lid was placed on top to avoid evaporation and oxidation, and the cell was placed in the light-path. Distilled water was used as the reference. In a run (Figure B6 in Appendix B), wave length scan was made repeatedly with a Beckman DK-2 Spectrometer at approximately 10 minute intervals. The peaks at 465, 395, 315 and 290 mμ were read and plotted against the time when they were recorded. The instantaneous values of the absorbancy at each wavelength were read from the smooth fitting curves at the time desired and the con-

centrations were calculated. In the other runs readings were made with a Beckman Model B Spectrometer at the wavelengths of 395 and 465 mμ. Time was measured from the moment when sulphide and molybdenum solutions were mixed. The mixing was expected to be perfect within half a minute. Temperature of the cell was not controlled, but it stayed between 26° and 32° C. during the whole experiment in most cases. When the DK-2 was used, the temperature went up as high as 36° C. towards the end of the experiment.

Results

Figure B-6 in Appendix B shows the time variation of the spectrogram of a mixture. Steady increase of the peaks at 465 and 395 mμ and decrease of the peak at 290 mμ clearly points to the stepwise shift of composition from MoO_4^{2-} to MoS_4^{2-} . The existence of equilibrium is more clearly seen in Figure C-1, where calculated concentrations of MoS_4^{2-} , MoOS_3^{2-} and $\text{MoO}_2\text{S}_2^{2-}$ are plotted against time. [See Part 1 for calculation methods.] The rapid reaction to $\text{MoO}_2\text{S}_2^{2-}$ and subsequent relatively slower shift to MoOS_3^{2-} and MoS_4^{2-} is observed.

Figure C-2 shows variation of the concentration of species MoOS_3^{2-} , C_3 , against time where $[\text{Mo}]_T$ was kept constant and $[\text{S}]_T$ was varied. These series were measured with the Beckman Model B, thus A_2^{315} was not measured. It was found that the concentration of species MoS_4^{2-} was less than 5% of the concentration of MoOS_3^{2-} . In addition, this range

Fig. C.I. VARIATION OF COMPLEX CONCENTRATIONS

Fig. C2. C_3 vs. TIME, S_T VARIED

of time corresponds to the initial rapid increase seen in Figure C-1. Therefore the effect of MoS_4^{2-} was considered insignificant.

When the initial maximum slope [corresponds to approximately 3 to 7 minute range], and the average slope between 20 and 30 minutes were plotted against the total sulphide concentration $[\text{S}]_T$, a good linearity was observed in both cases and their slopes, in turn showed a good linearity against the total molybdenum concentration $[\text{Mo}]_T$. Thus the same mechanism was suspected for both the initial rapid part and subsequent slower part of the curves.

When values of C_3 were normalized by the products of $[\text{Mo}]_T$ and $[\text{S}]_T$, i.e., $C_3/[\text{Mo}]_T[\text{S}]_T$, and plotted against time, the data fell into two groups. In the runs which had a ratio of $[\text{S}]_T$ to $[\text{Mo}]_T$ greater than 26, the plots were almost identical [within $\pm 0.1 \text{ M.}^{-1}$ in the scale] for the whole experimental time range. For the cases where the ratio was smaller than 26, the plots were of the same shape but their magnitudes decreased as the ratio decreased. Figure C-3 shows the results, in which the first group are represented by averaged values.

Figure C-4 shows the plot of the instantaneous rates, $d(C_3/[\text{Mo}]_T[\text{S}]_T)/dt$, against $C_3/[\text{Mo}]_T[\text{S}]_T$. The rate was calculated by approximating the plots to quadratic equations around the point in question.

Fig. C3. $C_3 / Mo_T S_T$ vs. TIME

Fig.C4 PLOT OF RATE v.s. CONCENTRATION

Good linearity was found with approximately the same slope as shown in Table C-1 in column 3, except for the region where $C_3/[Mo]_T[S]_T$ was small corresponding to the initial regions.

TABLE C-1

No.	Intercept $M.^{-1} \min.^{-1}$	Slope $\min.^{-1}$	S/Mo	S_T $M.X 10^3$	k_{-3} $\min.^{-1}$	$k_3 \alpha \gamma S_f$ $\min.^{-1}$
7,8,9,10	0.67 ₂	-0.075 ₄	26	13.0	0.066 ₆	0.0087
11	0.56 ₄	-0.072 ₀	17.3	8.7	0.067 ₁	0.0049
12	0.43 ₃	-0.078 ₁	8,7	4.3	0.076 ₂	0.0019
13	0.38 ₇	-0.079 ₃	4.3	4.3	0.077 ₆	0.0017
14	0.32 ₄	-0.081 ₀	2.2	4.3	0.079 ₆	0.0014

Thus the empirical rate equation can be written as equation (C-1).

$$-dX/dt = I - SX \quad (C-1)$$

where I and S are the intercept and negative of the slope of the above plot respectively and $X = C_3/[Mo]_T[S]_T$.

Integration of equation (C-1) gives equation (C-2).

$$X = [I/S] - B \exp[-St] \quad (C-2)$$

Where B is the integration constant.

B was calculated for the averaged data of the case where $([S]_T/[Mo]_T) > 26$ and the differences of calculated X from the observed values are shown in Figure C-5. Agreement was very good [less than 1% difference] except at the initial and final parts, where the effect of species MoS_4^{2-} is expected to raise the observed value larger than the calculated.

Discussion

The results obtained above are consistent with a model in which a rapid equilibrium is established to form species $MoO_2S_2^{2-}$ which further reacts to form $MoOS_3^{2-}$.

rapid equilibrium

$$\text{then } dC_3/dt = k_3 C_2 [H_2S] - k_{-3} C_3 \quad (C-3)$$

$$C_2 = \alpha ([Mo]_T - C_3), \quad \alpha = \frac{\beta_2 [H_2S]}{1 + \beta_1 [H_2S] + \beta_2 [H_2S]^2}$$

where β_1 are stability constants. $[H_2S]$ is the concentration of aqueous hydrogen sulphide and, at constant temperature

Fig. C5 TEST OF
INTEGRAL EQUATION,

$$\Delta Y = Y_{obs} - Y_{calc}$$

$$Y = C_3 / Mo_T S_T$$

Fig. C6 PLOT FOR
 C_4 , EQUATION C-5

$$Mo_T = 1 \times 10^{-4} \text{ M.}$$

$$S_T = 196 \text{ "}$$

$$NH_3 = NH_4^+ = 1.0 \text{ M.}$$

and pH, it is related to the total concentration of free sulphide species, S_f , by the equation:

$$[H_2S] = \gamma S_f, \quad \gamma = 1/[(1 + (K_{S1}/[H^+]) + (K_{S1}K_{S2}/[H^+]^2))]$$

where K_{S1} , K_{S2} are the first and second dissociation constant of aqueous hydrogen sulphide.

The equation (C-3) becomes equation (C-4) by substitution.

$$\frac{dC_3}{dt} = [k_3\alpha\gamma [Mo]_T S_f] - [k_3\alpha\gamma S_f + k_{-3}] C_3 \quad (C-4)$$

Dividing by $[Mo]_T[S]_T$ yields

$$d(C_3/[Mo]_T[S]_T)/dt = [k_3\alpha\gamma S_f/[S]_T] - [k_3\alpha\gamma S_f + k_{-3}] (C_3/[Mo]_T[S]_T)$$

At high sulphide concentrations

$$S_f \approx [S]_T$$

and $\alpha \approx 1$

Thus the first term will be independent of the sulphide concentration which agrees with the observation. The coefficient will also be independent of the sulphide concentration if $k_3\alpha\gamma[S]_f$ is insignificant compared with k_{-3} .

k_{-3} and $k_3\alpha\gamma[S]_f$ were calculated from the observed values of the intercept I , slope S and $[S]_T$, by the following equation and the results are seen in columns 6 and 7 of Table C-1.

$$[k_3\alpha\gamma S_f] = I \cdot [S]_T$$

$$k_{-3} = S - I \cdot [S]_T$$

The magnitude found justifies the above argument.

The second order rate constant, k_3 , was estimated for the first group by putting $\alpha = 1$, $[S]_f = [S]_T$ and by the literature values of dissociation constants for NH_3 and H_2S . The value found was $2.3 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$ (Note)

Similar calculation was performed for the variation of the concentration of species MoS_4^{2-} and the equilibration reaction mechanism also seemed to apply:

$$dC_4/dt = k_4[\text{H}_2\text{S}] C_3 - k_{-4}C_4$$

(Note) - The following values were used for calculation:

ref. 37

Division by C_3 gives

$$(dC_4/dt)/C_3 = k_4[H_2S] - k_{-4}(C_4/C_3) \quad \dots (C-5)$$

The plot of $(dC_4/dt)/C_3$ against $[C_4/C_3]$ is shown in Figure C-6. The linearity seems to hold and the rate constants were calculated although the accuracy was relatively poor.

$$k_{-4} = 0.03 \text{ min.}^{-1}, \quad k_4 = 70 \text{ M.}^{-1} \text{ min.}^{-1}$$

For most of the study of the equilibrium in Part 1, $[NH_4^+] = [NH_3] = 1 \text{ M.}$ $[S]_T = 2 \sim 20 \times 10^{-3} \text{ M.}$, $C_4/C_3 = 0.1 \sim 1$, $C_2/C_3 = 1 \sim 10$.

The error by the shift of equilibrium was estimated by using the rate equation obtained above, i.e.,

$$\Delta C_3/C_3 = [k_3[H_2S]C_2/C_3 - k_{-3} - k_4[H_2S] + k_{-4}C_4/C_3] \Delta t \approx 0.05\Delta t$$

$$\Delta C_4/C_4 = [k_4[H_2S]C_3/C_4 - k_{-4}] \Delta t \approx 0.02\Delta t$$

The estimated error in 10 min. amounts to maximum 50%. The rate of the disappearance of molybdenum at high temperature was in general of the order of $10^{-2} \text{ min.}^{-1}$. In view of the fact that the rate of equilibration was of the same order at room temperature, the equilibration reaction at 150°C. would not interfere in the reduction reaction.