Reduction of Molybdenite with Carbon in the Presence of Lime

R. PADILLA, M.C. RUIZ, and H.Y. SOHN

The thermodynamics of the MoS_2-C-CaO system has been studied in order to understand the carbothermic reduction of molybdenite in the presence of CaO. Kinetic studies were also conducted with mixtures of $MoS_2 + C + CaO$ in the temperature range of 900 °C 1200 °C. The reduction of MoS_2 with carbon in the presence of lime proceeds through the direct oxidation of MoS_2 by CaO to form intermediate molybdenum oxidized species, MoO_2 and $CaMoO_4$, which subsequently undergo reduction by CO to yield mixtures of Mo, Mo_2C, and CaS. Complete conversion of MoS_2 can be obtained at 1200 °C in less than 20 minutes for molar concentrations of MoS_2:C:CaO = 1:2:2. The kinetic model $\ln (1 - X) = kt$ was used to determine the rate constants. The activation energy found for the temperature range studied was 218.8 kJ/mol.

I. INTRODUCTION

MOLYBDENITE, MoS_2, is the most abundant molybdenum containing mineral and is thus the main source of metallic molybdenum. The conventional technology for production of molybdenum from molybdenite concentrates consists of various steps which include roasting of the concentrates to produce technical grade molybdenum trioxide, purification of the MoO_3 (a process that usually includes pyro- and hydrometallurgical operations), and finally reduction of the MoO_3 with hydrogen in two or more stages to produce commercial grade molybdenum. Even though this industrial method to produce molybdenum is well established, it has two drawbacks: the overall recovery of molybdenum is low, due to the numerous steps involved; and in the roasting step, there is evolution of SO_2 which contaminates the atmosphere.

To overcome the SO_2 emission problem, the direct reduction of sulfides in the presence of sulfur acceptors such as lime has received much attention. In such a system, one possible reaction for the reduction of molybdenite with carbon in the presence of lime to yield metallic Mo can be represented by the following overall reaction:

$$MoS_2 + (2 - z)C + 2CaO = Mo + 2CaS + 2(1 - z)CO\ (g) + zCO_2\ (g) \quad [1]$$

with z being dependent on the thermodynamics and the relative kinetics of the intermediate reactions. Other reactions may also occur depending on the relative amounts of CaO and C initially present.

The principal advantage of this scheme is that the sulfur contained in the MoS_2 is fixed as a solid (CaS), thus eliminating the emission of SO_2 to the atmosphere.

In the past, various methods to produce molybdenum from molybdenite concentrates have been proposed, such as thermal dissociation of molybdenite at high temperature and under vacuum conditions,[1,2] chlorination of molybdenite,[3] and aluminothermic reduction.[4,5,6] However, none of those methods have been commercially adopted. On the other hand, the direct reduction of molybdenite has received little attention. Habashi and Dugdale[7] reported on a study of molybdenite reduction with hydrogen in the presence of lime. These investigators reported 40 pct reduction at 1073 K using stoichiometric amounts of CaO. Later, Mankand and Prasad[8] indicated for the same reduction system that lime enhances tremendously the reduction rate, and at 1173 K, the optimum results were obtained at three times the theoretical requirements of lime additions. The reduction of molybdenite with carbon in the presence of lime and iron was investigated by Johnston and Pickles[9] at plasma temperatures. They observed molybdenum recoveries over 90 pct for lime additions in excess of the stoichiometric amount. In that system, a matte phase, composed of Cu_2S and FeS, was also formed.

Due to the growing worldwide concern about pollution, there is a renewed interest in the production of metals without the emission of SO_2. Within this framework, we present a thermodynamic and kinetic analysis of the direct reduction of molybdenite with carbon in the presence of CaO.

Thermodynamics of the MoS_2-C-CaO System

Equilibrium relations in a system with many components, such as the carbothermic reduction of molybdenite in the presence of lime (Mo-Ca-S-O-C), are complex due to the various reaction paths encountered among the different phases present in the system. Even in a simpler chemical system, such as the carbothermic reduction of molybdenite (Mo-S-C), a large number of compounds may be present at equilibrium. The following analysis was carried out by using relevant thermodynamic sources.[10,11] For the calculations, the values for the Gibbs energy of formation for some compounds were extrapolated: Mo_2C and MoC over 1400 K; and $CaMoO_4$ over 1000 K.

1. *MoS_2-C system*

It is well known that the carbothermic reduction reactions proceed mainly through gaseous intermediate compounds.[12,13,14] Consequently, it is conceivable that mixtures of MoS_2-C can react at high temperatures forming gaseous

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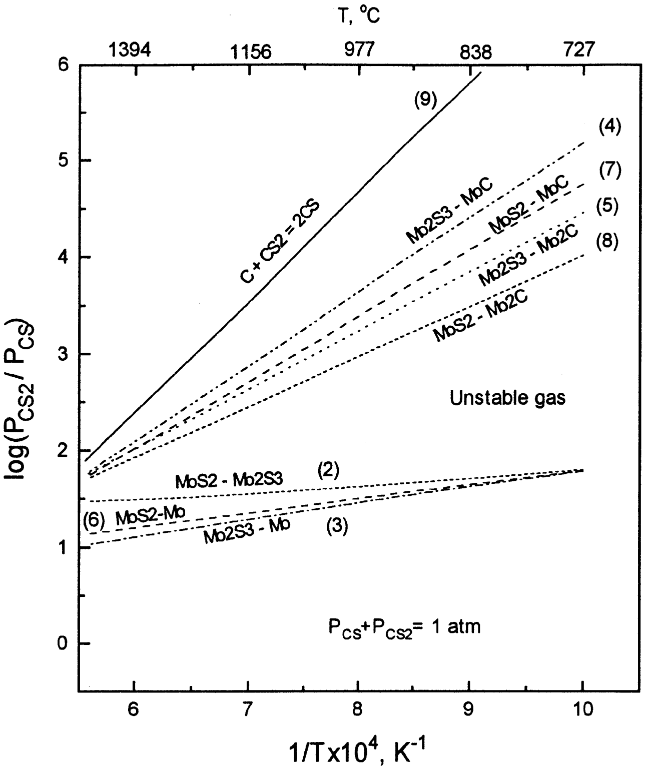

Fig. 1—Equilibrium gas ratio P_{CS_2}/P_{CS} for the direct reduction of MoS_2 with carbon as a function of temperature. The numbers in parentheses correspond to the reactions in the text. The only stable Mo containing phase is MoS_2.

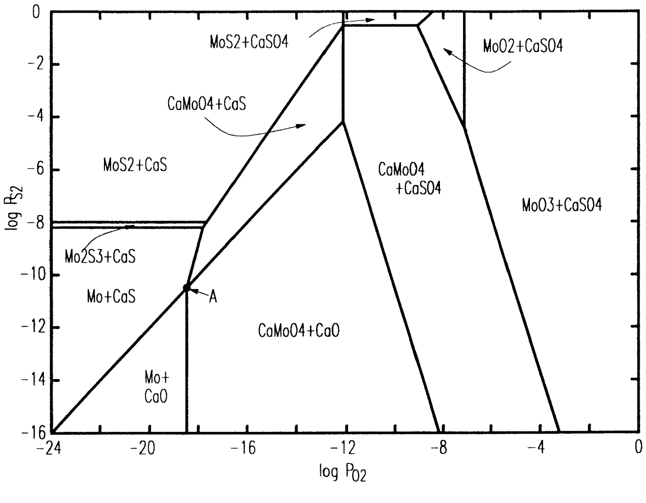

Fig. 2—Stability diagram for the system Mo-Ca-S-O at 900 °C for metallic fraction 0 < Mo/(Mo + Ca) < 0.5. Point A is a stable invariant point where the phases Mo, CaO, CaS, and $CaMoO_4$ coexist in equilibrium with a gas phase. (Data for $CaMoO_4$ were extrapolated from 1000 K.)

species such as CS_2 and CS in equilibrium with condensed phases. In the temperature range of interest, 700 °C to 1400 °C, the stable molybdenum solid phases that can be found are MoS_2, Mo_2S_3, Mo, MoC, and Mo_2C.[15,16] Therefore, the direct reduction of molybdenite by carbon will be governed by the prevailing chemical equilibrium between these phases and the reaction kinetics. Consequently, the following reduction reactions of the molybdenum compounds in terms of the gaseous species can be written:

$$2MoS_2 + CS\ (g) = Mo_2S_3 + CS_2\ (g) \qquad [2]$$

$$Mo_2S_3 + 3CS\ (g) = 2Mo + 3CS_2\ (g) \qquad [3]$$

$$Mo_2S_3 + 7CS\ (g) = 2MoC + 5CS_2\ (g) \qquad [4]$$

$$Mo_2S_3 + 5CS\ (g) = Mo_2C + 4CS_2\ (g) \qquad [5]$$

$$MoS_2 + 2CS\ (g) = Mo + 2CS_2\ (g) \qquad [6]$$

$$MoS_2 + 4CS\ (g) = MoC + 3CS_2\ (g) \qquad [7]$$

$$2MoS_2 + 6CS\ (g) = Mo_2C + 5CS_2\ (g) \qquad [8]$$

and the carbon gasification reaction:

$$C + CS_2\ (g) = 2CS\ (g) \qquad [9]$$

This MoS_2-C system can be conveniently analyzed by plotting the equilibrium ratios P_{CS_2}/P_{CS} for the preceding reactions as a function of temperature. Such a plot is shown in Figure 1. Since the gas ratio for some of the reactions depends on the total pressure, $P_{CS_2} + P_{CS} = 1$ atm was considered. The corresponding equilibrium gas ratio P_{CS_2}/P_{CS} for the carbon gasification Reaction [9] is shown as a continuous line on this figure. This equilibrium during the carbothermic reaction of molybdenite sets the lower limit on the CS_2/CS ratio which can be obtained at any temperature. This means that the area to the right of the carbon gasification line, Reaction [9], represents an unstable condition, *i.e.*, a gas having a tendency to precipitate soot until the equilibrium line is reached. Since all the lines corresponding to the listed reduction Reactions [2] through [8] fall in that area, none of these reactions is thermodynamically feasible between 700 °C to 1400 °C. Consequently, reduction of the MoS_2 by carbon to produce Mo, Mo_2C, or MoC cannot occur in the temperature range considered, which includes the experimental temperature range used in the present work.

2. *MoS_2-CaO and MoS_2-CaO-C systems*

The equilibrium phases present in the systems Mo-Ca-S-O and Mo-Ca-S-O-C can be conveniently visualized in two metal predominance area diagrams. These diagrams can be constructed for metallic fraction of $0 < R < 0.5$ and $0.5 < R < 1$, where R is given as Mo/(Mo + Ca). The range of the atomic fraction, R, is given by the stoichiometry of the two metal species $CaMoO_4$. The pertinent diagrams shown in Figures 2 and 3 were constructed for the range $0 < R < 0.5$, which is the most relevant to our study since it includes the critical fraction of 0.33 for complete desulfidation of MoS_2, as given by Reaction [1]. In these phase diagrams, the activities of all solid phases were considered equal to one and the activities of the gaseous phases equal to their partial pressure. It should also be noted that the total pressure varies over a wide range for the entire equilibrium assemblage of phases to exist. Thus, Figure 2 shows the phase stability diagram for the Mo-Ca-S-O system at 900 °C, where the area of interest for reduction of molybdenite is the lower left portion of the diagram. In this region, it is interesting to observe that mixtures of Mo-$CaMoO_4$-CaO-CaS form a stable invariant point shown in the figure as point A, and mixtures of Mo-$CaMoO_4$-CaO or Mo-$CaMoO_4$-CaS coexist in equilibrium with a gas phase. On the other hand, mixtures of MoS_2-CaO are unstable and will react to give either (Mo + CaS) or ($CaMoO_4$ + CaS) depending upon the prevailing gas composition and the amount of the starting MoS_2 and CaO. It can also be noted that MoO_2 is unstable in the presence of CaO and would react to form $CaMoO_4$.

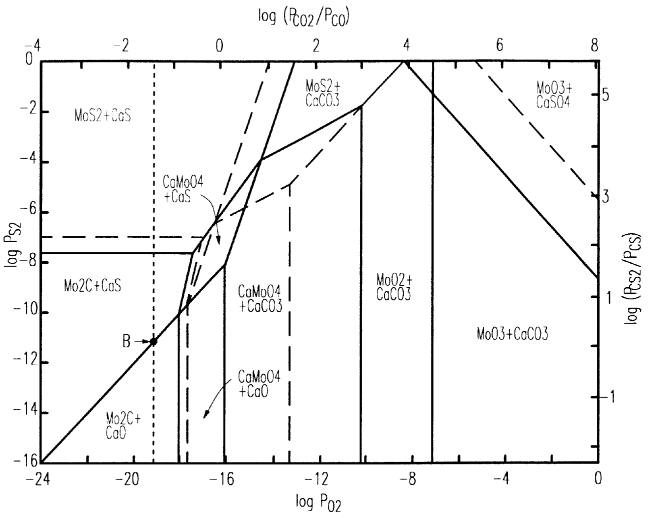

Fig. 3—Stability diagram for the system Mo-Ca-S-O-C at 900 °C for metallic fraction $0 < Mo/(Mo + Ca) < 0.5$ when $(P_{CO})^2/P_{CO_2} = 1$(—) and 34.5 (– –). Point B indicates coexistence of condensed C, CaO, CaS, and Mo_2C when total pressure is 1 atm. Activity of carbon is equal to one in the short-dashed line passing through point B. (Data for $CaMoO_4$ were extrapolated from 1000 K.)

On the other hand, Figure 3 shows the predominance area diagram for the Mo-Ca-S-O-C system at 900 °C. This diagram was constructed for the ratio $(P_{CO})^2/P_{CO_2} = 1$ and 34.5. The ratio $(P_{CO})^2/P_{CO_2} = 34.5$ corresponds to the value of the equilibrium constant of the Boudouard Reaction [10] at a temperature of 900 °C. The equilibrium gas ratio P_{CO_2}/P_{CO} for the Boudouard reaction when $P_{CO} + P_{CO_2} = 1$ atm is also included in the figure as the short-dashed line passing through point B, where the activity of carbon is equal to one. Thus, at 1 atm, the gas compositions to the left of this line are unstable with respect to the sooting of carbon. The first significant point to be noted in Figure 3 is that in the region of reducing conditions, Mo_2C is the stable phase instead of metallic molybdenum. One can observe also that mixtures of MoS_2 and CaO are unstable, and in the presence of carbon, they would react to form Mo_2C + CaS or $CaMoO_4$ + CaS depending on the gas phase composition and the nature of the starting mixture. The gas phase composition of the major species corresponding to the equilibrium of C, CaS, and CaO at a total pressure of 1 atm can be calculated considering the following reactions:

$$C + CS_2 (g) = 2CS (g) \qquad [9]$$

$$C + CO_2 (g) = 2CO (g) \qquad [10]$$

$$CaO + CS (g) = CaS + CO (g) \qquad [11]$$

$$2CO (g) + O_2 (g) = 2CO_2 (g) \qquad [12]$$

$$2CS (g) + S_2 (g) = 2CS_2 (g) \qquad [13]$$

$$2CO (g) + S_2 (g) = 2COS (g) \qquad [14]$$

and the condition that $P_{CO} + P_{CO_2} + P_{CS} + P_{CS_2} + P_{O_2} + P_{S_2} + P_{COS} = 1$ atm.

In the calculations, the activities of C, CaO, and CaS were considered equal to one, and the calculated partial pressures for various temperatures are shown in Table 1.

This table shows that the gaseous phase is composed mainly of CO at temperatures over 900 °C, and the equilibrium partial pressures of COS, CS, CS_2, and S_2 are very small, illustrating the great desulfidation power of CaO. The calculated gas composition at 900 °C is shown as point B in Figure 3. It can be seen that this point is located within the area of stability of molybdenum carbide, Mo_2C. This implies that MoO_2 or $CaMoO_4$ is an unstable compound in the presence of carbon at this temperature and should be reduced to Mo_2C.

The reduction of the oxidized molybdenum species, MoO_2 and $CaMoO_4$, with carbon can be analyzed by using log P_{CO_2}/P_{CO} *vs* $1/T$ plots. Figure 4 shows such a diagram for the reduction of molybdenum dioxide, where the equilibrium gas ratios for the following reactions were plotted:

$$MoO_2 + 2CO (g) = Mo + 2CO_2 (g) \qquad [15]$$

$$2MoO_2 + 6CO (g) = Mo_2C + 5CO_2 (g) \qquad [16]$$

$$MoO_2 + 4CO (g) = MoC + 3CO_2 (g) \qquad [17]$$

$$C + CO_2 (g) = 2CO (g) \qquad [10]$$

$$2Mo + 2CO (g) = Mo_2C + CO_2 (g) \qquad [18]$$

$$Mo_2C + 2CO = 2MoC + CO_2 (g) \qquad [19]$$

Since the gas ratio for the Boudouard Reaction [10] and Reactions [16] through [19] depends on the total pressure, $P_{CO_2} + P_{CO} = 1$ atm was also considered. Figure 4 shows that at 1 atm, simultaneous equilibrium among MoO_2, C, and MoC occurs at 600 °C. This means that MoO_2 can be reduced by carbon over this temperature to MoC in a small and narrow zone. Over 629 °C, the reduction product will be Mo_2C, which is more stable. It can also be observed that Mo could be produced only over 1070 °C under certain CO_2/CO gas ratios.

In Figure 5, a similar plot for the reduction of calcium molybdate is shown. The reactions considered are as follows:

$$CaMoO_4 + 3CO (g) = Mo + CaO + 3CO_2 (g) \qquad [20]$$

$$2CaMoO_4 + 8CO (g) = Mo_2C + 2CaO + 7CO_2 (g) \qquad [21]$$

$$CaMoO_4 + 5CO (g) = MoC + CaO + 4CO_2 \qquad [22]$$

We can observe that at 1 atm, the reduction of $CaMoO_4$ is feasible over 779 °C and Mo_2C definitively is the stable phase with respect to carbon, while MoC is not.

In the present work, experiments using single cylindrical pellets have been carried out to study the reduction of molybdenite by carbon in the presence of lime. The effect of various parameters, including temperature and molar ratios of MoS_2:C:CaO, on the overall reduction rate has been investigated.

II. EXPERIMENTAL PROCEDURE

A. *Materials and Sample Preparation*

The molybdenite concentrate used in this study was obtained from the Andina Mines of CODELCO, Chile. This concentrate was chemically upgraded and subjected to size analysis. The sieve analysis of the purified concentrate indicated that 98.5 pct of the material was finer than 106 μm (150# Tyler, Mentor, Ohio). This material was screened, and only the most abundant size fraction, $-45 + 38$ μm (325/400# Tyler), was used in the reduction experiments. The chemical analysis of this monosized material is shown in Table II.

Table I. Equilibrium Compositions of the Gaseous Phase in the Ca-S-O-C System When the Activities of the Present Condensed Phases C, CaO, and CaS Are Unity

T, °C	P_{CO_2}	P_{CO}	P_{COS}	P_{CS_2}	P_{CS}	P_{S_2}	P_{O_2}
700	0.387	0.613	3.91×10^{-6}	9.23×10^{-12}	1.57×10^{-13}	1.14×10^{-12}	1.02×10^{-21}
800	0.114	0.886	3.44×10^{-6}	2.41×10^{-11}	3.21×10^{-12}	3.34×10^{-12}	6.07×10^{-21}
900	0.027	0.973	2.04×10^{-6}	3.54×10^{-11}	3.18×10^{-11}	5.42×10^{-12}	6.37×10^{-20}
1000	7.39×10^{-3}	0.993	1.19×10^{-6}	4.40×10^{-11}	2.07×10^{-10}	7.35×10^{-12}	4.12×10^{-19}
1100	2.37×10^{-3}	0.998	7.36×10^{-7}	5.23×10^{-11}	1.02×10^{-9}	9.38×10^{-12}	2.01×10^{-18}
1200	8.89×10^{-4}	0.999	4.88×10^{-7}	6.10×10^{-11}	4.01×10^{-9}	1.16×10^{-11}	7.92×10^{-18}

The corresponding molybdenite content of the concentrate was 97.1 pct and the insoluble was essentially quartz. The mineralogical analysis of the monosized fraction showed, in addition to quartz, the presence of trace amounts of chalcopyrite consistent with the analysis shown in Table II.

The reducing agent used was activated carbon (Merck KGa A, Darmstadt, Germany) of particle size −150 + 106 μm (100/150# Tyler) which contained 92.2 pct fixed carbon. The calcium oxide used in this study was prepared by thermal decomposition of calcium carbonate powder of 99.5 pct purity at 1000 °C for 10 hours. The X-ray diffraction analysis of the calcine indicated the presence of CaO only.

Sample mixtures were prepared by thoroughly mixing in a mortar predetermined amounts of molybdenite, carbon, and CaO in order to produce various mixtures of different molar ratios of MoS_2:C:CaO. These mixtures were compressed to the form of cylindrical pellets of 1.2 to 1.8 g, which were used in the reduction experiments.

B. *Reduction Experiments*

Isothermal experiments were carried out in a conventional vertical tube furnace setup which contained a quartz reaction tube. At the beginning of each experiment, the sample pellet was placed in a porcelain crucible in the upper section of the reaction tube under a nitrogen flow. Then the sample was lowered to the equitemperature region of the furnace. A slow flow of a purified nitrogen in the reaction tube was used to ascertain an inert atmosphere. After completion of the predetermined time of reaction, the sample was raised to the upper end of the reaction tube and allowed to cool under the nitrogen flow (for about 40 seconds) before removing it to a desiccator to cool off completely for weighing. The temperature of the sample was measured by means of a chromel/alumel thermocouple located just below the crucible that contained the sample. The extent of reaction was calculated from the sample weight loss due to the overall reduction reactions, and the solid products were identified by X-ray diffraction analysis.

Initial tests carried out at increasing nitrogen flow rates indicated that 0.3 L/min of N_2 was sufficient to avoid the leakage of ambient air into the system. Consequently, the reduction experiments were conducted under such nitrogen flow.

III. RESULTS

A series of experiments were performed to study the main variables, namely, temperature, molar ratios of MoS_2:C:CaO, and reaction time.

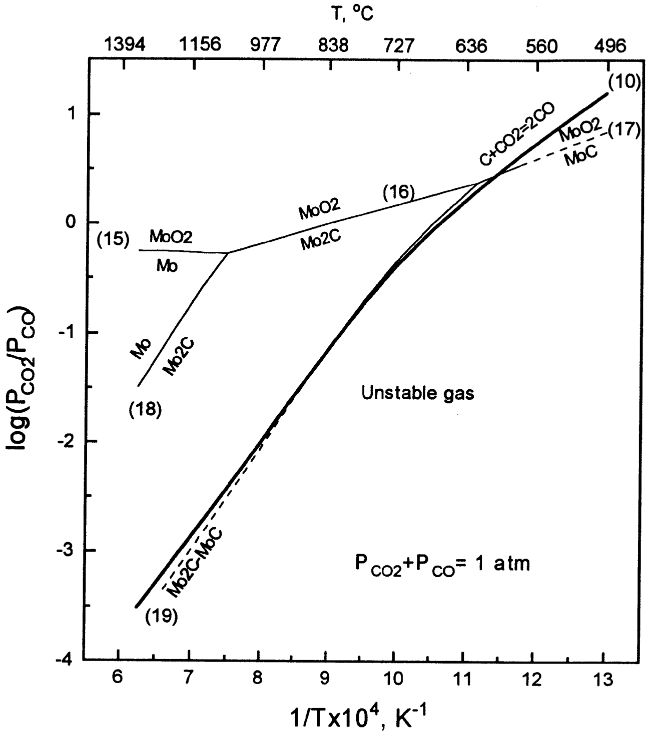

Fig. 4—Equilibrium gas ratio P_{CO_2}/P_{CO} for the reduction of MoO_2 with carbon. The numbers in parentheses correspond to the reactions in the text.

A. *Preliminary Experiments*

A few experiments were conducted by using (1) a powder sample and (2) a pellet sample. The results of these experiments are shown in Figure 6, where ΔW is the weight loss of the sample and W_0 is the initial weight. The experimental conditions for the runs were molar ratios of MoS_2:C:CaO = 1:2:4 and a temperature of 1050 °C. The results obtained in these experiments indicated that the reduction rate was the same for both cases, suggesting negligible back diffusion of nitrogen gas into the interparticle pores of the samples, *i.e.*, the outward flow of product gas is sufficiently large to prevent back diffusion. The fact that both types of samples of substantially different dimensions and thermal conductivities showed an identical reaction behavior indicates also that heat transfer was not an important factor. To confirm this conclusion, an approximate heat transfer calculation was carried out which showed that for the small pellet samples used in this study the possible temperature variation within the sample was very small; therefore, heat transfer can be neglected as a factor, and the sample was essentially isothermal. Since no difference was found in the

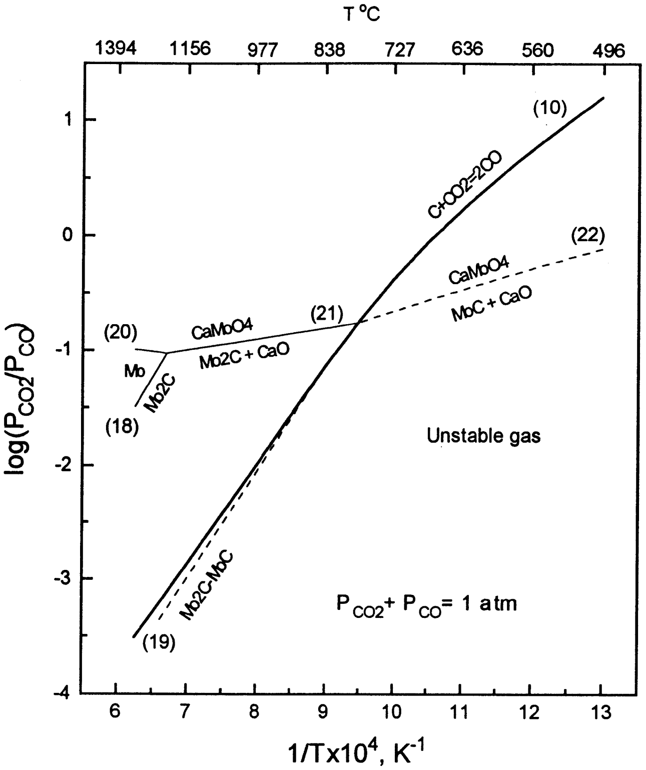

Fig. 5—Equilibrium gas ratio P_{CO_2}/P_{CO} for the reduction of $CaMoO_4$ with carbon as a function of temperature. Numbers in parentheses correspond to the reactions in the text. (Data for $CaMoO_4$ were extrapolated from 1000 K.)

Table II. Chemical Analysis of the −45 + 38 μm Molybdenite Concentrate

Element	Pct
Mo	58.22
Cu	0.005
Fe	0.075
Insoluble (SiO_2)	2.78

reaction rates for both types of samples, in all subsequent experiments, pellet samples were used due to convenience in handling.

In Figure 7, the weight loss of the reacting sample is presented for various temperatures. The experimental conditions were molar ratios MoS_2:C:CaO = 1:2:2 and reaction times of 90 minutes. It can be observed that the temperature has a very significant influence on the reduction of molybdenite, giving a maximum weight loss at 1200 °C. The slight decrease in weight loss at 1300 °C implies a smaller conversion at this temperature, which may be due to mild charge sintering. This effect has also been observed in the hydrogen reduction of molybdenite in the presence of lime.[8] The preceding results demonstrated that the range of temperature of importance in this system was from 900 °C to 1200 °C.

B. *Reaction Products*

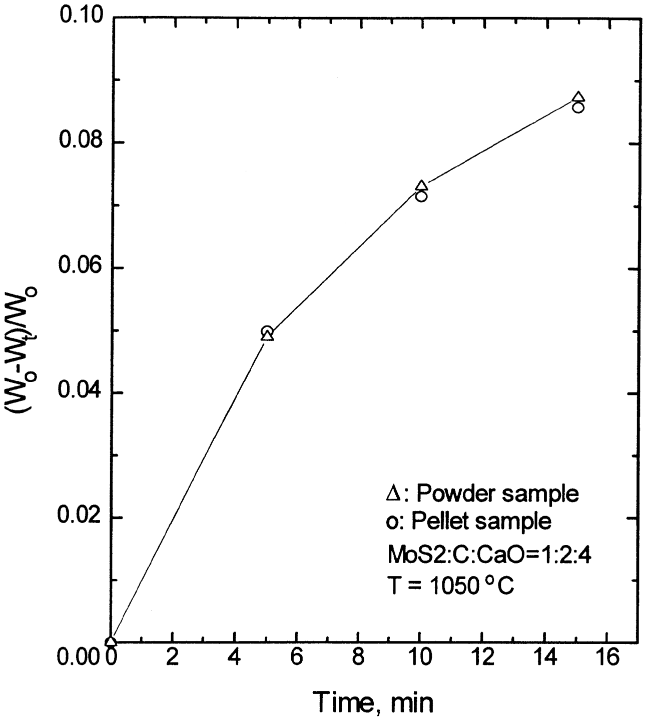

Fig. 6—Reduction of molybdenite with carbon in the presence of lime in powder sample and pellet sample. T = 1050 °C, MoS_2:C:CaO = 1:2:4.

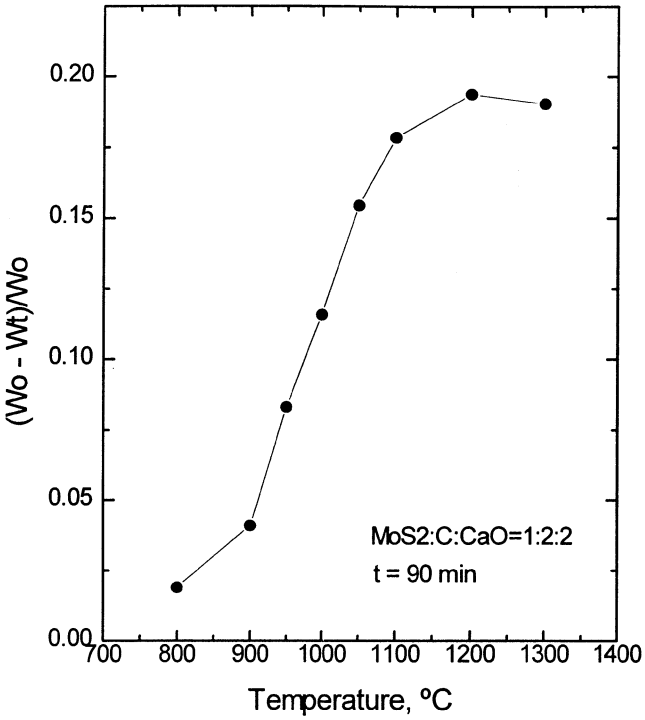

Fig. 7—Reduction of molybdenite with carbon in the presence of lime as a function of temperature.

Experiments were also conducted with MoS_2-CaO mixtures heated in oxygen-free nitrogen at various temperatures. During the reaction, the samples experienced a negligible amount of weight loss, indicating that no gaseous products were evolved. The reacted samples were analyzed by X-ray diffraction techniques, and the diffractograms obtained for samples reacted at 750 °C, 1000 °C, and 1200 °C are shown in Figure 8. This figure shows clearly the presence of MoO_2 at 750 °C as well as 1000 °C. CaS,

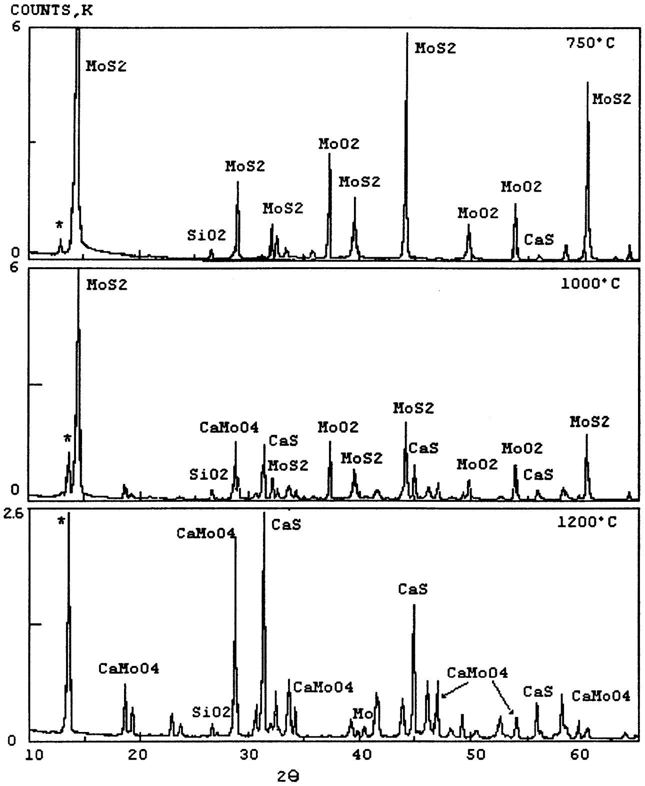

Fig. 8—X-ray diffraction patterns for MoS_2-CaO mixtures (molar ratio MoS_2:CaO = 1:2) reacted at 750 °C, 1000 °C, and 1200 °C for 30 min. (*Unidentified compound present in the molybdenite sample.)

$CaMoO_4$, Mo, and unreacted MoS_2 were also identified in the diffractograms. At the higher temperature of 1200 °C, the X-ray diffractogram showed the absence of MoO_2 peaks and strong peaks for calcium molybdate. These findings indicate the formation of MoO_2 as intermediate species and the subsequent formation of $CaMoO_4$.

Some experiments conducted with mixtures of MoS_2-C-CaO at various temperatures were also subjected to X-ray diffraction analysis. The results of the analysis for mixtures with molar ratios of MoS_2:C:CaO = 1:2:2 are shown in Figure 9. At 900 °C, strong peaks for unreacted MoS_2, $CaMoO_4$, and CaS were identified, whereas at 1000 °C, the strong peaks identified were for CaS, Mo, and $CaMoO_4$. At temperatures higher than 1100 °C, the X-ray diffractogram indicated the presence of CaS, Mo, and Mo_2C as the major species. In this range of temperatures (900 °C to 1200 °C), the presence of MoO_2 was not detected. This is probably due to the fast reduction rate of the MoO_2 with CO to Mo or to Mo_2C. Additional data on X-ray analysis of sample mixtures of MoS_2:C:CaO = 1:4:2 reacted at 1100 °C showed stronger peaks for Mo_2C than for Mo compared to the peaks obtained for sample mixtures of MoS_2:C:CaO = 1:2:2.

C. *Reaction Mechanism*

In the range of 900 °C to 1300 °C, the reduction of molybdenite with carbon in the presence of lime can be represented by the following overall reaction to produce metallic molybdenum:

$$\begin{aligned} MoS_2 + (2 - z)C + 2CaO &= Mo + 2CaS \\ &+ 2(1 - z)CO\ (g) + zCO_2\ (g) \end{aligned} \qquad [1]$$

and in the case of carbide formation, the overall reduction reaction can be represented by

$$\begin{aligned} 2MoS_2 + (5-w)C + 4CaO &= Mo_2C \\ &+ 4CaS + 2(2-w)CO\ (g) + wCO_2\ (g) \end{aligned} \qquad [23]$$

to produce Mo_2C, since the other carbide, MoC, is not stable in this temperature range. In these reactions, z and w are dependent on the thermodynamics and relative kinetics of the intermediate steps.

Based on the preceding thermodynamics analysis and the experimental evidence on the reaction product formation, mixtures of MoS_2-C-CaO in the range 900 °C to 1300 °C are expected to react through the formation of intermediate oxidized molybdenum species according to

$$MoS_2 + 2CaO = MoO_2 + 2CaS \qquad [24]$$

In the presence of a local excess of CaO, MoO_2 becomes unstable and reacts according to

$$3MoO_2 + 2CaO = 2CaMoO_4 + Mo \qquad [25]$$

The oxidized species of molybdenum, MoO_2, and $CaMoO_4$ in the presence of carbon can be reduced to Mo or Mo_2C as follows:

$$MoO_2 + (2-r)C = Mo + 2(1-r)CO\ (g) + rCO_2\ (g) \qquad [26]$$

$$\begin{aligned} 2CaMoO_4 + (6-p)C &= 2CaO + 2Mo + 2(3-p)CO\ (g) \\ &+ pCO_2\ (g) \end{aligned} \qquad [27]$$

$$2MoO_2 + (5-s)C = Mo_2C + 2(2-s)CO\ (g) + sCO_2\ (g) \qquad [28]$$

$$\begin{aligned} 2CaMoO_4 + (7-q)C &= 2CaO + Mo_2C + 2(3-q)CO\ (g) \\ &+ qCO_2\ (g) \end{aligned} \qquad [29]$$

where r, p, s, and q are dependent on the thermodynamics.

The reduction Reactions [26] through [29] may operate at the initial stage of the process; however, after a small amount of Mo or Mo_2C products is formed, these reactions can only proceed by solid-state diffusion of one reacted species to another through the product layer. This type of process is usually very slow, and high conversions are difficult to obtain by this mechanism. Therefore, the reduction of MoO_2 and $CaMoO_4$ should mainly proceed by the following reactions:

$$MoO_2 + 2CO\ (g) = Mo + 2CO_2\ (g) \qquad [15]$$

$$CaMoO_4 + 3CO\ (g) = Mo + CaO + 3CO_2\ (g) \qquad [20]$$

$$2MoO_2 + 6CO\ (g) = Mo_2C + 5CO_2\ (g) \qquad [16]$$

$$2CaMoO_4 + 8CO\ (g) = Mo_2C + 2CaO + 7CO_2\ (g) \qquad [21]$$

$$C + CO_2\ (g) = 2CO\ (g) \qquad [10]$$

Combining Eqs. [24], [15], and [10] or Eqs. [24], [25], [20], and [10], we obtain the overall Reaction [1]. Similarly, combining Eqs. [24], [16], and [10], we obtain the overall Reaction [23].

In the proposed reaction mechanism, the sulfidation of lime occurs by direct oxidation of the molybdenum sulfide with CaO to produce MoO_2 and subsequently $CaMoO_4$ as intermediate oxides which are in turn reduced by carbon initially and then by CO to metallic molybdenum or molybdenum carbide. The oxidation of a metal sulfide by CaO to form the corresponding oxide and CaS has also been

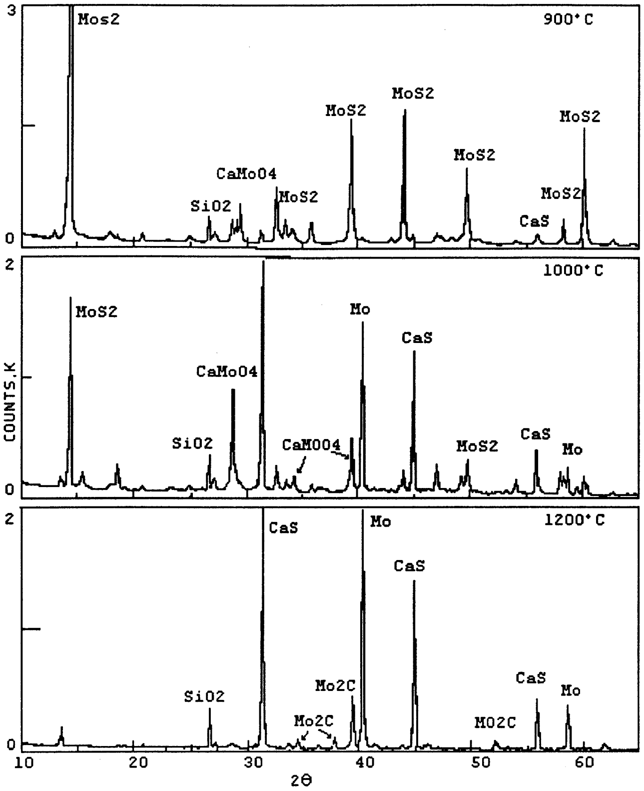

Fig. 9—X-ray diffraction pattern for reacted samples of MoS_2:C:CaO = 1:2:2 mixtures. Samples reacted at 900 °C and 1000 °C for 60 min and at 1200 °C for 30 min.

postulated by other investigators in the carbothermic reduction of metal sulfides in the presence of lime.[17,18,19] However, in those studies, no experimental evidence demonstrated the formation of the intermediate metal oxide; instead, the formation of metal oxysulfide or other complex compounds was reported.

It has been reported before in the reduction of metal oxides and sulfides that the carbon gasification reaction is slower than the oxide reduction reaction.[12–14,20,24] It is expected that the carbon gasification reaction may also be the rate controlling step of the overall reduction process studied here.

D. *Effect of Temperature*

The results of isothermal kinetic studies carried out for mixtures with molar ratios MoS_2:C:CaO = 1:2:2 are shown in Figure 10. In this figure, the rate of conversion of molybdenite is presented in terms of fractional conversion of molybdenite, X. This fractional conversion was defined as $\Delta W/W_{oc}$, where ΔW is the weight loss of the sample at time t and W_{oc} is the weight loss corresponding to complete conversion of molybdenite according to Reaction [1] or [23]. Based on the thermodynamic calculations shown in Table I, it was assumed that the off gas was CO (g) at temperatures over 900 °C with a negligible amount of CO_2 (g). Thus, the weight loss corresponding to CO (g) formation is the same for both Reactions [1] and [23]. The actual CO_2/CO ratio depends on the relative kinetics of intermediate reactions, say, Reactions [15] and [10], but even if Reaction [15] is fast, and thus near equilibrium, the CO_2 content would only be about 30 pct.

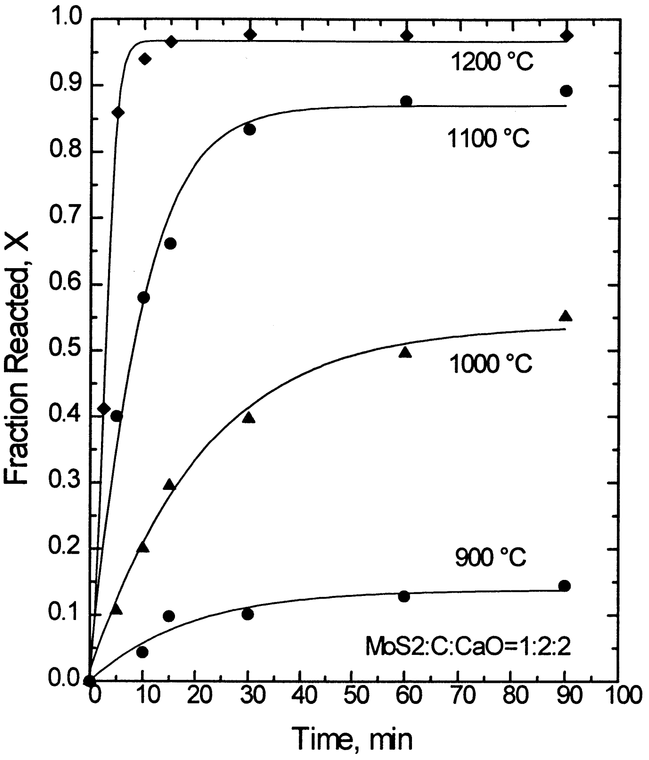

Fig. 10—Effect of temperature on the reduction rate of molybdenite with carbon in the presence of lime. MoS_2:C:CaO = 1:2:2.

Temperature has a pronounced effect on the reduction rate. With increasing temperature from 900 °C to 1100 °C, there is a dramatic increase not only in the reduction rate but also in the fraction converted. At 1200 °C, the reaction proceeds rapidly, reaching essentially complete conversion in less than 20 minutes. The reason why the curve for 1200 °C levels off at somewhat less than unit fraction may be because of the formation of some Mo_2C according to Reaction [23], which consumes more carbon than Reaction [1]. A similar effect was found for a MoS_2:C:CaO ratio of 1:1:2, as shown in Figure 11. In this case, the amount of C added is only one-half of the stoichiometric value indicated by Reaction [1]. These results also confirm the stoichiometry of the reaction as well as the assumption of negligible CO_2 formation.

E. *Effect of the Amount of CaO*

The experimental results concerning the effect of the molar fraction of CaO in the sample on the reduction of molybdenite are shown in Figure 12 for a temperature of 1200 °C. The fractional conversion for the case of mixtures MoS_2:C:CaO = 1:2:0 was based on the reaction

$$MoS_2 + C = Mo + CS_2\ (g) \qquad [30]$$

because CS_2 is the predominant gas product at this temperature. It can be observed in Figure 12 that the fraction of molybdenite reacted in the absence of CaO is very low; however, as expected from the thermodynamic calculations, the addition of a stoichiometric amount of CaO to the reaction mixture produces a large increase in the fraction reacted and the rate of reaction. This illustrates the outstanding capacity of lime to improve the reduction of

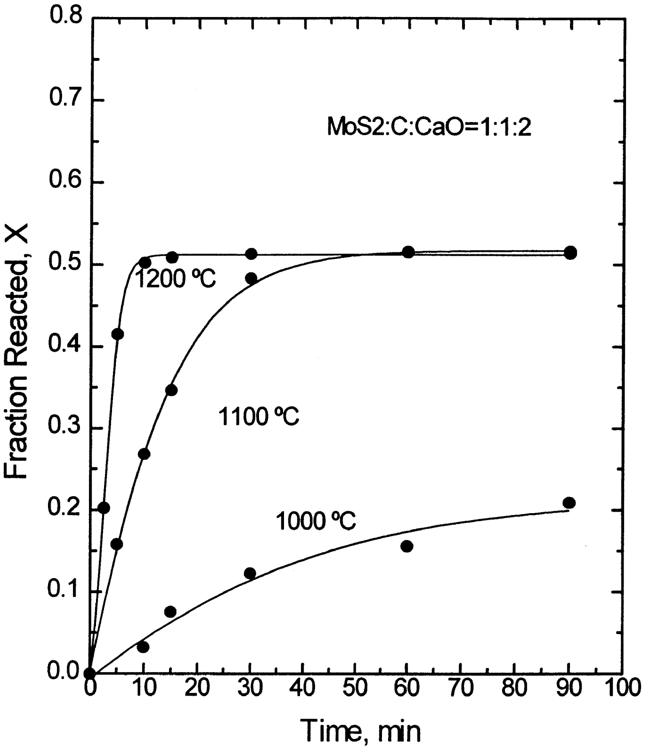

Fig. 11—Effect of temperature on the rate of reduction of molybdenite with carbon in the presence of lime. MoS_2:C:CaO = 1:1:2.

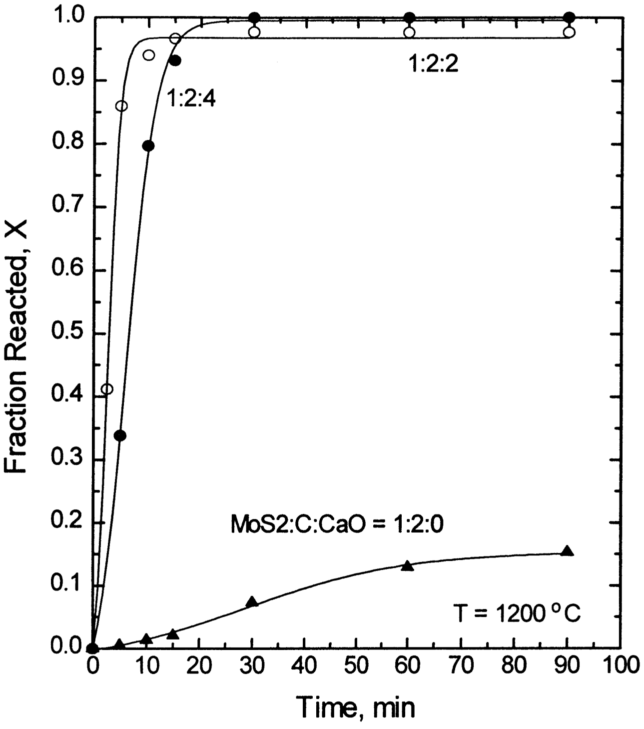

Fig. 12—Effect of the amount of CaO on the rate of reduction of molybdenite with carbon. Reduction temperature = 1200 °C.

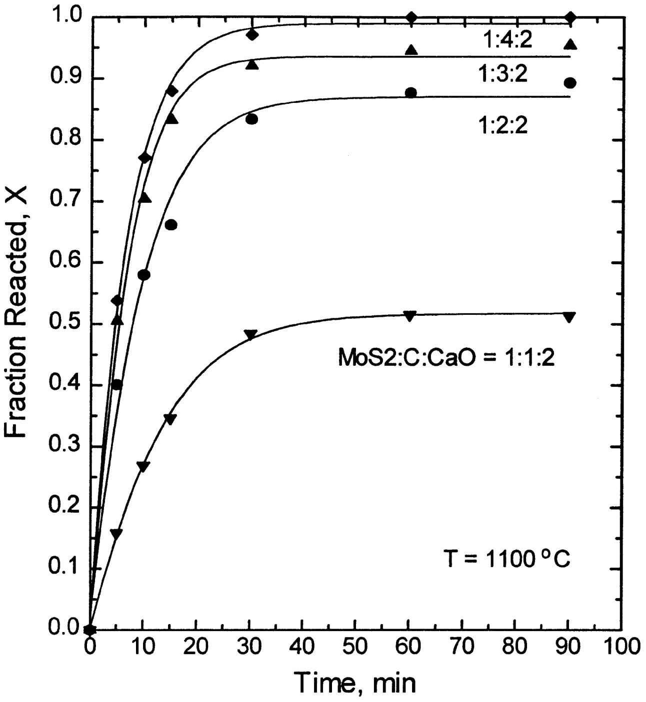

Fig. 13—Effect of the amount of carbon on the rate of reduction of molybdenite. Reduction temperature = 1100 °C.

molybdenite with carbon. An excess of CaO in the sample, 1:2:4 mixture, is not needed, since the effect at this temperature is minor and the excess amount of CaO apparently slows the reduction rate, probably due to an increase in the distance between the molybdenite and carbon particles or to enhanced formation of $CaMoO_4$, which apparently has a slower reduction rate.

F. *Effect of the Amount of Carbon*

The effect of carbon additions on the reduction rate at temperature of 1100 °C is shown in Figure 13. In addition to the obvious stoichiometric effect, the overall rate is seen to increase somewhat with the amount of carbon.

G. *Reaction Kinetics*

During the reaction of MoS_2-C-CaO mixtures, the back diffusion of nitrogen into the pores of the pellet is negligible, as evidenced by the data shown in Figure 6. Therefore, a uniform internal reduction reaction can be assumed to occur in the sample. Under such conditions, the rate of the overall reduction can be represented by a simplified model assuming chemical control. The following pseudo-first-order kinetics with respect to the fractional conversion was found to yield a satisfactory fit:

$$\ln (1-X) = kt \qquad [31]$$

where X is the fraction of MoS_2 reacted at time t and k is the apparent kinetic constant. Equation [31] has also been used rather extensively in studies concerning the reduction of metal oxides, where the carbon gasification with CO_2 was the controlling step of the overall process.[12,21,22] The experimental data were plotted according to Eq. [31] for mixtures with MoS_2:C:CaO = 1:2:2 and 1:1:2 in Figures 14 and 15, respectively. The data for both mixtures fit Eq. [31] well up to conversions corresponding to about 80 pct. For higher conversions, the data deviate from the linear dependence at all temperatures, due probably to the fact that some carbon is consumed for Mo_2C formation which leaves some unreacted MoS_2 in the mixture.

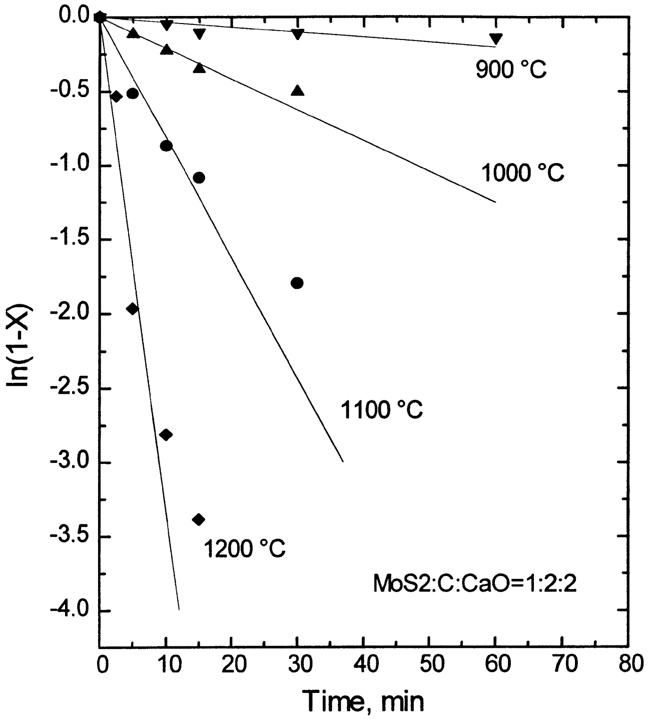

Fig. 14—Rate of reduction of molybdenite with carbon in the presence of lime. MoS_2:C:CaO = 1:2:2.

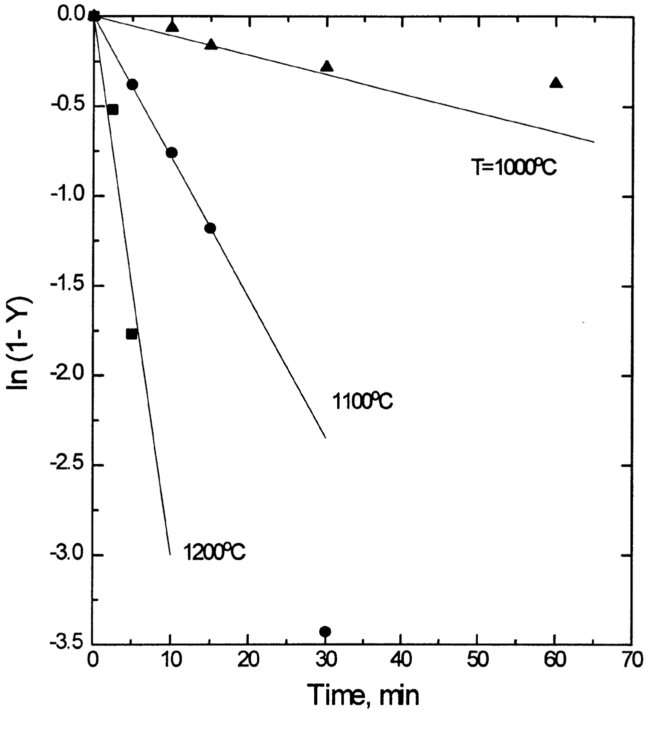

Fig. 15—Rate of reduction of molybdenite with carbon in the presence of lime for MoS_2:C:CaO = 1:1:2. For this mixture, the fractional conversion in the plot is $Y = X/0.5$.

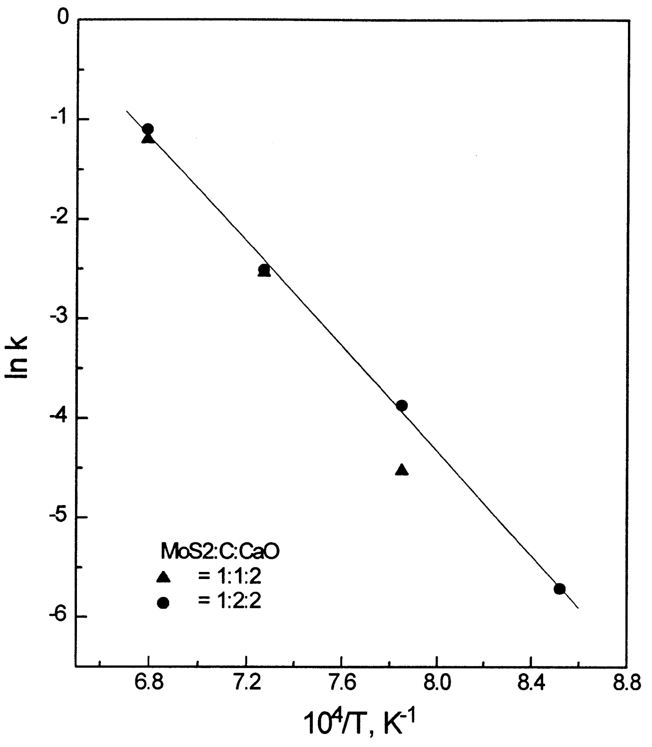

Fig. 16—Arrhenius plot for the reduction of molybdenite with carbon in the presence of lime. MoS_2:C:CaO = 1:1:2 and 1:2:2.

The rate constants obtained from the slopes of this figure were used to draw an Arrhenius-type plot, which is shown in Figure 16. The rate dependence on temperature fits well a straight line in the range of temperatures 900 °C to 1200 °C, not only for the sample mixtures of molar ratios of MoS_2:C:CaO of 1:2:2 but also for the lower carbon content mixtures of 1:1:2. The apparent activation energy was calculated from the slope of the straight line to be 218.8 kJ/mol.

Meaningful comparison of the energy of activation determined in this study with earlier work is difficult, since there are no kinetic data available in the literature concerning the carbothermic reduction of molybdenum disulfide. It is known, however, that the activation energy for the catalyzed oxidation of carbon by CO_2 is less than that for the uncatalyzed reaction. The values reported for the uncatalyzed oxidation range from 251 to 359.8 kJ/mol.[25,26,27] On the other hand, various alkali salts have been found to catalyze the oxidation of carbon by CO_2 in the reduction of metal oxides and metal sulfides.[13,14,22,23] Since in this work alkali salts were not present, it seems that the value of energy of activation found in this study would correspond to calcia or molybdenum catalyzed oxidation of carbon. This type of catalysis has been reported previously for the carbothermic reduction of SnO_2[12] and NiO.[28]

The results of the present study have demonstrated the feasibility of producing molybdenum metal and Mo_2C from sulfide by carbothermic reduction in the presence of lime. In the present study, the postreduction treatment of the products for the separation of Mo and/or Mo_2C from the waste CaS and the unused reactants has not been studied; however, two routes can be envisaged to accomplish the separation: (1) physical separation of the metallic compounds from the waste material, *i.e.*, sieving and/or gravimetric methods; and (2) chemical separation of the waste by dilute acid (HCl) leaching methods.[8]

IV. CONCLUSIONS

A thermodynamic analysis of the MoS_2-C and MoS_2-C-CaO systems was carried out. The results for the MoS_2-C system showed that the direct reduction of MoS_2 by carbon is not thermodynamically feasible in the range of temperatures of 700 °C to 1400 °C. On the other hand, mixtures of MoS_2-CaO are unstable and react mainly to produce $CaMoO_4$ and CaS as final products. Experimental evidence confirmed the formation of $CaMoO_4$ and MoO_2 as intermediate oxides. Based on these findings, it is concluded that the reduction of molybdenite with carbon in the presence of lime probably proceeds through the intermediate molybdenum oxidized compounds, MoO_2 and $CaMoO_4$, and the subsequent reduction of these oxides by gaseous CO to yield mixtures of Mo, Mo_2C, and CaS.

Complete conversions of MoS_2 can be obtained at temperatures of 1200 °C in less than 20 minutes for a molar ratio of MoS_2:C:CaO equal to 1:2:2. The kinetic data follow the equation $\ln (1 - X) = kt$ for conversions up to 80 pct in the temperature range 900 °C to 1200 °C. The activation energy in this temperature range was 218.8 kJ/mol.

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