

THERMAL ANALYSIS AND X-RAY DIFFRACTION OF ROASTING OF EGYPTIAN MOLYBDENITE*

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Abstract

Molybdenite is the main ore mineral for the molybdenum industry and the production of molybdenum. The industrial processing of molybdenite is based on its oxidized roasting to technical grade molybdenum oxide, followed by its purification by distillation or its ammonia leaching.

The present work reports a thermal analysis study of the oxidized roasting of Egyptian molybdenite, using a derivatograph. The reaction products were identified microscopically and by using a Siemens Crystalloflex diffractometer.

The DTA curves of the roasting of molybdenite show that its oxidation begins at 360–370°C, as indicated by the small exothermic peak at such temperatures. This is followed immediately by a large, wide exothermic peak with maximum at 510–520°C, representing the intensive oxidation of molybdenite. The medium endothermic peak at 795–800°C reflects the melting and sublimation of molybdenum oxide. The vigorous vaporization of molybdenum oxide and its boiling are associated with the large, sharp endothermic peak at 1150°C. This is accompanied by a large loss in mass (TG).

The study includes calculation of the thermodynamic constants and the kinetics of the reaction of oxidation of molybdenite.

The oxidized roasting of molybdenite results in the production of molybdenum oxide, which is the essential starting material of the molybdenum industry. The molybdenum oxide produced has the molybdite structure and crystallizes in the orthorhombic system in the form of elongated, thin, light-green crystals.

Keywords: DTA, roasting of molybdenite, XRD

Introduction

Molybdenite (MoS_2) is the essential ore mineral of the molybdenum industry for the production of molybdenum, ferromolybdenum and pure chemical molybdenum compounds, mainly molybdenum trioxide, ammonium paramolybdate, and sodium and calcium molybdate.

Different methods are available for the processing of molybdenite for the production of molybdenum and its compounds [1, 3–12]. These include the oxidized roasting of molybdenite to the oxide, acid leaching, alkaline leaching in an autoclave at 170–200°C under oxygen at 50 atm, chlorination at 250–400°C in the presence or absence of oxygen, followed by hydrolysis of the resulting molybdenum chlorides

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and oxychlorides, bacterial leaching and sintering with sodium sulphate in the presence of coal.

The main industrial method of processing molybdenite is its oxidized roasting in air atmosphere [4–12]. This is based on the oxidation of molybdenite to technical grade molybdic oxide, which is the essential starting material for most molybdenum products. The roasting of molybdenite is carried out in a multiple hearth furnace and fluidized bed furnaces. The roasting is followed by the purification of molybdic oxide by distillation or its leaching by ammonia.

Molybdenite has been reported [3, 7, 8, 10, 14–17] to display variable thermal behaviour, depending on the heating conditions. In vacuum, a marked dissociation of molybdenite is observed at 1100–1300°C, with the formation of Mo_2S_3 . At high-temperature, it dissociates in an electric arc furnace with the formation of molybdenum metal. Other data [7, 8] indicate that molybdenite melts with decomposition at 1650–1700°C, probably with the formation of Mo_2S_3 , and boils at 2102°C.

In an air atmosphere, the thermal behaviour of molybdenite includes a small exothermic peak at 345–380°C, followed by a large exothermic peak at 500–570°C, reflecting its oxidation, with the formation of molybdenum oxide. Molybdenum oxide melts at 770–795°C and boils at 1150–1280°C. Its marked sublimation is observed at 600–650°C. At higher temperatures, molybdic oxide vaporizes in the form of $(\text{MoO}_3)_3$ or Mo_3O_9 [1–3, 7, 8, 10, 21].

The present work relates to a thermal analysis and X-ray diffraction study of the oxidized roasting of Egyptian molybdenite, using a derivatograph.

Experimental techniques

This research was carried out with molybdenite separated from the Gattar mineralization, Eastern Desert, Egypt. The molybdenite mineralization at Gebel Gattar occurs in quartz veins and as disseminated grains in the host granitic rocks.

Mineralogy

Molybdenite is dark-grey in hand specimens, having a grey streak with a greenish tint, a metallic lustre, a greasy feel, very low hardness and perfect basal cleavage. Its crystals occur mostly as thin rough hexagonal plates and scales in quartz veins and disseminated grains in granite.

In polished sections, it is white, with moderate reflectivity, extremely high birefractance, strong anisotropism and no internal reflection. It crystallizes in the hexagonal system and is optically negative.

The X-ray diffraction pattern of the studied molybdenite sample (Fig. 1) shows the characteristic peaks of molybdenite; no mineral impurity was detected. The X-ray peaks of molybdenite are well-defined, narrow and intense, suggesting good crystallinity, and their data are consistent with those given in the ASTM index.

Chemical composition

The chemical composition of the studied molybdenite sample is given in Table 1.

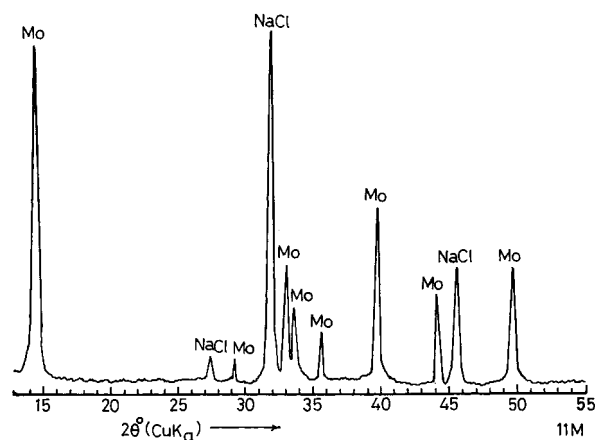


Fig. 1 X-ray diffraction pattern of molybdenite; Mo – molybdenite

Table 1 Chemical composition of Gattar molybdenite

Chemical component	Content/%
Mo	56.78
S	38.85
Fe ₂ O ₃	0.52
SiO ₂	2.84
Sn	0.10
+ H ₂ O	0.40

Procedure

Molybdenite was processed by repeated grinding in an automated agate mortar, followed by sieving until all the powder passed through 115 and 200 mesh sieves. The powder was then ground with a pestle and mortar for 1 h to achieve homogeneity.

Apparatus

Experiments were carried out using ceramic crucibles, heated in an electrical furnace in an air current with the removal of sulphur dioxide gas, which resulted from the oxidation of molybdenite. The temperature was regulated automatically with an accuracy of $\pm 5^\circ\text{C}$.

The thermal analysis study of the oxidized roasting of molybdenite was carried out with a MOM derivatograph [18]. This apparatus simultaneously records four curves: the change in temperature (T), differential thermal analysis (DTA), thermogravimetric analysis (TG), quantitatively in mg, and the derivative thermogravimetric curve (DTG) on a single sample under controlled conditions.

The parameters during the test were as follows: ceramic crucible; inert material aluminium oxide. Mass of sample 200 mg; temperature range from ambient up to 1200°C; in air atmosphere; mass used for TG curve, 20–50 mg; heating rate, 10°C min⁻¹, and sensitivities of DTA and DTG circuits, 1/5. The DTA and temperature measuring thermocouples were made of Pt–Pt/Rh wire. The atmosphere was air and sulphur dioxide was removed as formed.

Phase identification

The phases of the products of molybdenite roasting were identified microscopically and by X-ray diffraction analysis, using a Siemens Crystalloflex diffractometer. The finely ground product of roasting was mixed with sodium chloride as a standard. Its peaks occurring at $2\theta=31.38$ and 45.44° were used for corrections. Nickel-filtered copper radiation was used. The exposure time was 1 h. Intensities were collected to a maximum $2\theta=65^\circ$. The sensitivity of the experiment was $4 \cdot 10^4$ impl/min and the statistical error was 1.5%.

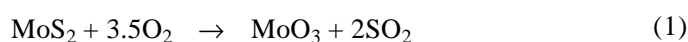
Determination of thermodynamic constants

Before the thermal analysis study of molybdenite roasting, an attempt was made to calculate the thermodynamic constants. The thermodynamic data given in Table 2 were used in the calculations.

Table 2 Thermodynamic data used

Thermodynamic function	Value/kcal mol ⁻¹	Reference
ΔF° molybdenite	-71.086	[20]
ΔF° MoO ₃ (c)	-159.06	[7, 19, 20]
ΔF° SO ₂ (g)	-71.79	[19, 20]

The reaction of the oxidized roasting of molybdenite may be represented as



The standard free energy of the reaction at 298 K is

$$\begin{aligned} \Delta F_{\text{reaction}}^\circ &= \Delta F_{\text{MoO}_3}^\circ + 2\Delta F_{\text{SO}_2}^\circ - \Delta F_{\text{MoS}_2}^\circ - 3.5\Delta F_{\text{O}_2}^\circ = \\ &= -159.6 - 2 \cdot 71.79 + 71.086 = -232.094 \text{ kcal mol}^{-1} \end{aligned} \quad (2)$$

The relation between the change in the standard free energy of the reaction (ΔF°) and temperature for the oxidized roasting of molybdenite is given by the following equation [7]:

$$\Delta F_T^\circ = -256870 + 14.67T \log T - 5.4 \cdot 10^{-3}T^2 + 0.62 \cdot 10^{-6}T^3 + 13.80T \quad (3)$$

The equilibrium constant K of the reaction at temperature T may be calculated from Eq. (4):

$$\log K_T = \frac{-\Delta F_T^0}{2.303RT} \quad (4)$$

The calculated values of the standard free energy (ΔF^0) and equilibrium constant (K) of the reaction of the oxidized roasting of molybdenite at different temperatures are given in Table 3. The plot of the obtained standard free energy (ΔF^0) data vs. temperature (Fig. 2) shows the linear proportionality between them, as there are no phase changes in either the reactants or the products.

Table 3 Standard free energy (ΔF^0) and equilibrium constant (K) of the reaction of oxidized roasting of molybdenite

Temperature/ $^{\circ}$ C	$-\Delta F^0/\text{kcal mol}^{-1}$	K
300	227.43	$5.73 \cdot 10^{86}$
350	224.68	$6.74 \cdot 10^{78}$
400	221.92	$1.19 \cdot 10^{72}$
450	219.16	$1.80 \cdot 10^{66}$
500	216.39	$1.54 \cdot 10^{61}$
550	213.63	$5.45 \cdot 10^{56}$
600	210.86	$5.23 \cdot 10^{52}$
650	208.10	$1.90 \cdot 10^{49}$
700	205.33	$1.34 \cdot 10^{46}$
750	202.57	$1.91 \cdot 10^{43}$
800	199.81	$5.05 \cdot 10^{40}$

It is observed that the equilibrium constant is very large and the reaction of the oxidized roasting of molybdenite is considered in practice to be an irreversible one. The oxidation of molybdenite should preferably be carried out at low-concentration of oxygen in the gaseous phase. The plot of $\log K$ vs. $1/T$ (Fig. 3) yields a straight line, from which the calculated heat of the reaction is $265.4 \text{ kcal mol}^{-1}$. This value is in good agreement with the previously reported literature value of $266.2 \text{ kcal mol}^{-1}$ [7, 8]. The high exothermic heat released in molybdenite oxidation satisfies the possibility of carrying out oxidized roasting via the resulting heat.

Results and discussion

DTA of roasting of molybdenite with a particle size of 0.075 mm

The thermal analysis data on the oxidized roasting of molybdenite with a particle size of 0.075 mm (Fig. 4) demonstrate that molybdenite oxidation begins at 360°C , as indicated by the small exothermic peak at such temperature. This is followed di-

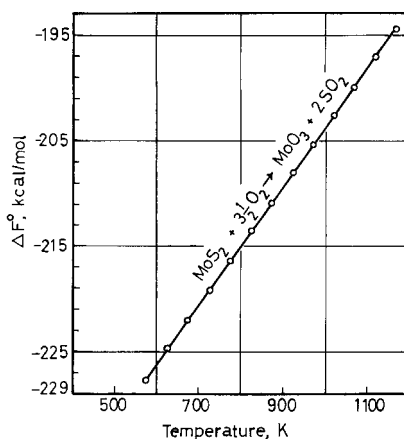


Fig. 2 Free energy diagram for oxidized roasting of molybdenite

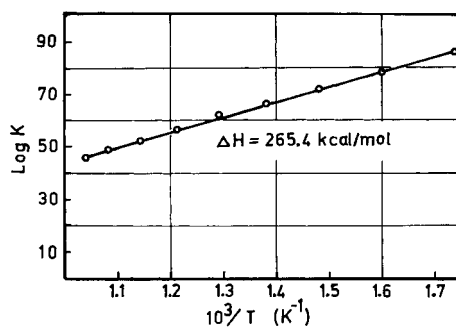


Fig. 3 Plot of $\log K$ vs. $10^3/T$ (K^{-1})

rectly by a large wide exothermic peak with maximum at 510°C, representing the intensive oxidation of molybdenite. The endothermic peak at 795°C reflects the melting of the produced molybdenum trioxide or molybdite and its vaporization. The process of oxidation involves a marked, sharp decrease in mass (TG curve), due to the liberation of sulphur dioxide, resulting from the oxidation of molybdenite. This is followed by a gradual decrease in mass, due to the vaporization of molybdenum trioxide.

The results obtained are consistent with the literature data [1–3, 5, 7, 8, 14–16], as the oxidation of molybdenite and its conversion to molybdite is accompanied by an initial small exothermic peak near 345–380°C, followed by a major exotherm beginning at about 400°C, reaching a maximum near 500–570°C. The reaction decreases gradually at higher temperatures, up to the sublimation temperature near 800°C.

The vigorous vaporization of molybdenum oxide begins at a temperature higher than 800°C and continues up to its boiling point, where it reaches its maximum

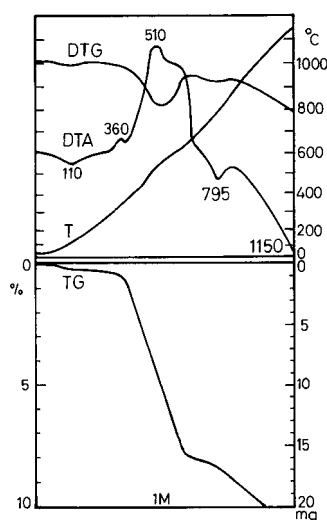


Fig. 4 DTA curve of oxidized roasting of molybdenite with a particle size of 0.075 mm. Mass of sample 200 mg; heating rate $10^{\circ}\text{C min}^{-1}$

value. This is revealed by the wide, sharp, endothermic peak at 1150°C . According to the literature data [7, 8, 21], molybdenum oxide vaporizes at higher temperatures in the form of $(\text{MoO}_3)_3$ or Mo_3O_9 .

Microscopic and X-ray diffraction study

The products of the runs at 360 , 400 and 510°C during 1 h were identified microscopically and by using X-ray diffraction.

At 360 – 400°C , molybdenite constitutes the main component of the polished sections and its particles are covered by a thick compact oxide layer. This layer resists the diffusion of gases, and the degree of oxidation of molybdenite is low. All particles are partially desulphurized and oxidized. The particles exhibit a homogeneous white core, which is composed of molybdenite, surrounded by a dark layer of molybdic oxide. At 450 and 510°C , the surface oxide layer around the molybdenite grains is a friable one and a porous structure is formed. The core of the particles is altered and the surface of the particles is cracked due to the strong reaction of oxidation of molybdenite at 510°C , accompanied by some fragmentation of the particles.

The X-ray diffraction patterns of these products are shown in Fig. 5 (A, B and C, at 360 , 450 and 510°C , respectively). At 360°C , the product of roasting consists mainly of molybdenite with some molybdite. This indicates a low rate of oxidation of molybdenite. At 450°C , the major phase of the product is molybdite, with some unreacted molybdenite. At 510°C , molybdite is seen to be the main constituent of the product, with a small amount of molybdenite. The X-ray peaks of molybdite are well-defined, sharp and intense, suggesting good crystallinity.

It is observed that at low-temperature the mineral is quite inert, undergoing only low oxidation and desulphurization until the ignition temperature is achieved. Be-

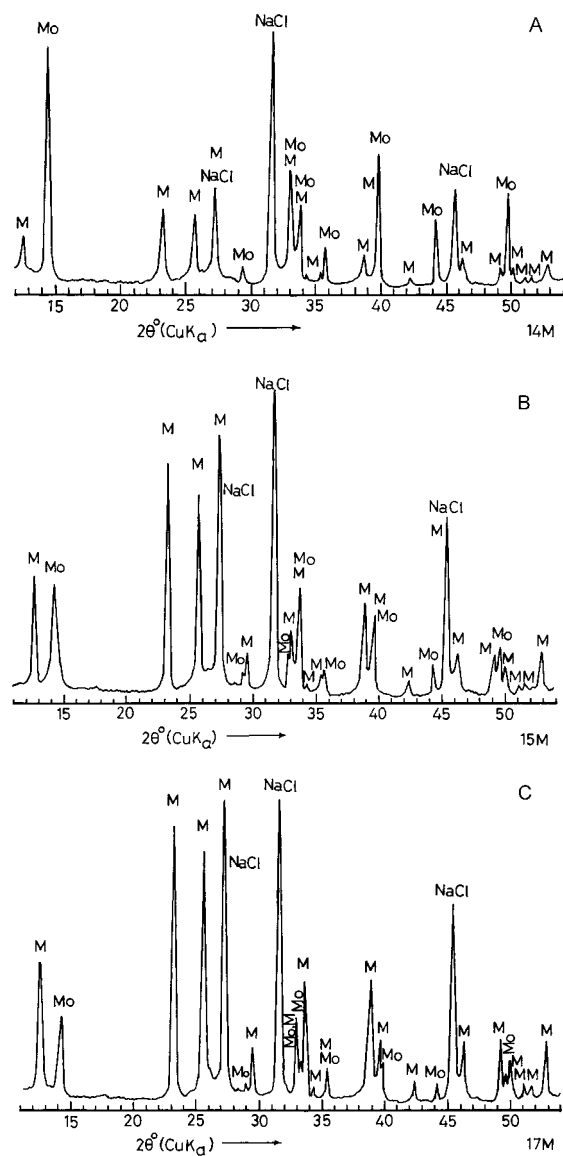


Fig. 5 X-ray diffraction patterns of the products of oxidized roasting of molybdenite. (A, B and C at 360, 450 and 510°C); Mo – molybdenite and M – molybdenite

yond this limit, the rate of oxidation of molybdenite is maximum, the reaction takes place spontaneously, and the oxidation and removal of sulphur is vigorous. Molybdenite has a comparatively low ignition temperature (365°C for fine molybdenite particles measuring less than 0.063 mm, and 490°C for coarser grains measuring 0.09–0.127 mm) [7, 8, 12].

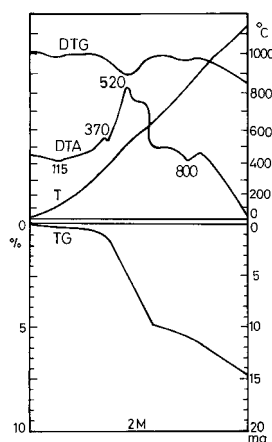


Fig. 6 DTA curve of oxidized roasting of molybdenite with a particle size of 0.125 mm

DTA of roasting of molybdenite with a particle size of 0.125 mm

The thermal analysis data on the oxidized roasting of molybdenite with a particle size of 0.125 mm (Fig. 6) reveal similar peaks at slightly higher temperature than for the finer molybdenite sample with a particle size of 0.075 mm. Here, the intensive oxidation of molybdenite is reflected by the wide, large exothermic peak with maximum at 520°C, and the melting of molybdic oxide by the endothermic peak at 800°C. At temperatures higher than 800°C, intensive vaporization of molybdenum oxide is observed up to the boiling point.

Differential thermal analysis of molybdite

The thermal analysis data on the produced molybdite (molybdic oxide) (Fig. 7) show a small, wide endothermic peak at 650°C, which may represent the beginning of sublimation of molybdite. The vapour pressure of molybdic oxide at 650°C is 0.05 mm Hg [7]. The sharp, medium endothermic peak at 795°C indicates its melting. This is accompanied by a gradual decrease in mass (TG curve) due to the vaporization of molybdic oxide. The vapour pressure of molybdic oxide at 800°C is 10.1 mm Hg. The large, sharp endothermic peak at 1150°C denotes the intensive vaporization and boiling of molybdite. The TG curve reveals a sharp, large decrease in mass due to such vaporization of molybdic oxide. At 800–1000°C, molybdic oxide vaporizes in the form of polymerized molecules, $(\text{MoO}_3)_3$ or Mo_3O_9 [7, 21].

The thermal data obtained on the produced molybdite or molybdic oxide are consistent with the literature data [1, 7, 8, 21], as molybdic oxide melts at 770–795°C and boils at 1155°C with appreciable vaporization. Its marked sublimation begins at 625–650°C. The vaporization of molybdic oxide takes place with high rate at temperatures higher than 900°C. That is why the purification of molybdic oxide by distillation is performed industrially at 900–1000°C, at which its vapour pressure ranges from 53.9 to 198.8 mm Hg.

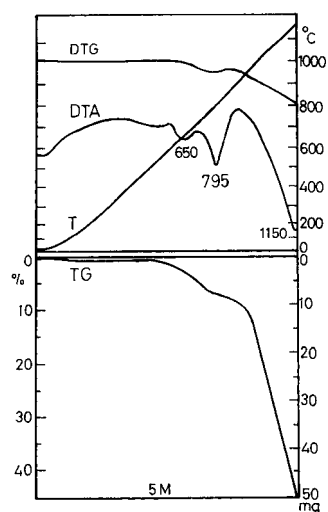


Fig. 7 DTA curve of the produced molybdenite

Kinetics of oxidized roasting of molybdenite

The kinetics of the oxidized roasting of molybdenite was studied over the temperature range 360–650°C during different times. The experimental data obtained (Figs 8 and 9) permit the following conclusions:

1. In general, as the temperature increases, the degree of oxidation of molybdenite increases with time. This increase is large and sharp up to 510°C, especially during a long time; there is then a slow increase in the oxidation.

2. At 360–400°C, the oxidation of molybdenite is low, even during 120 min, reaching only 43.7% at 400°C. This is due to the formation of a compact thick layer of molybdic oxide around the molybdenite particles. This layer resists the diffusion of oxygen and sulphur dioxide and the reaction velocity is low.

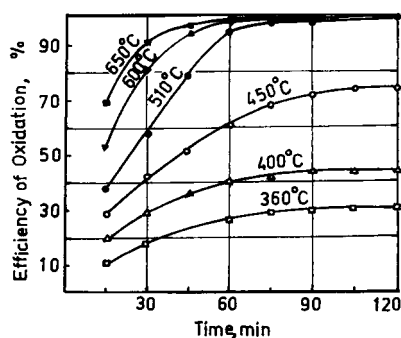


Fig. 8 Relation between the efficiency of oxidation of molybdenite and time at different temperatures

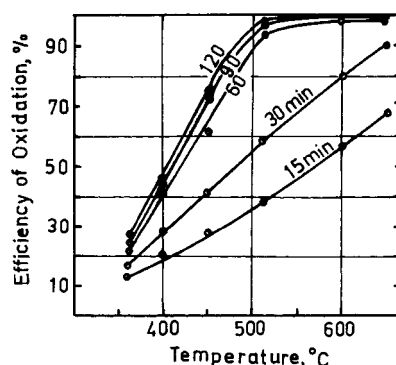


Fig. 9 Relation between the efficiency of oxidation of molybdenite and temperature during different time

3. At 450°C, there is a gradual increase in the oxidation of molybdenite with time. At 510–650°C, intensive oxidation of molybdenite takes place. A sharp, large increase in the degree of oxidation is observed during time up to 60 min at 510 and 600°C, and up to 45 min at 650°C, after which it increases slowly. Nearly complete oxidation of molybdenite (98.8%) is reached at 510°C during 1.5 h.

The high oxidation of molybdenite at 510°C and higher temperatures is due to the oxide layer formed around the mineral particles being friable and porous, which does not prevent further oxidation from taking place. Also, this temperature is higher than the ignition temperature of molybdenite [7, 8, 10].

The kinetics of the oxidized roasting of molybdenite is governed by the structure and condition of the surface oxide coating, whether it is porous or nonporous. The rate of the reaction of oxidation was studied for two models controlled by (a) chemical reaction, or (b) diffusion through the oxide layer.

Rate controlled by chemical reaction

At 450–650°C, the molybdic oxide layer formed around the particles of molybdenite during its oxidation is friable and porous. In this condition, there will be no resistance to the flow of air reaching the interface, and the rate is not affected by the coating. The process of oxidation is therefore controlled by the chemical reaction at the interface and the following equation is applied:

$$kt = [1 - (1 - \alpha)^{1/3}] \quad (5)$$

where k – rate constant of the reaction, and α – fraction of molybdenite oxidized by time t .

The experimental data in Fig. 8 were plotted as a function of $[1 - (1 - \alpha)^{1/3}]$ vs. time t (Eq. (5)) for the temperature range 450–650°C, as shown in Fig. 10. It is observed that the data display a linear relation with respect to the chemical model. The slopes of such straight lines determine the rate of the reaction (k). The rate of the reaction

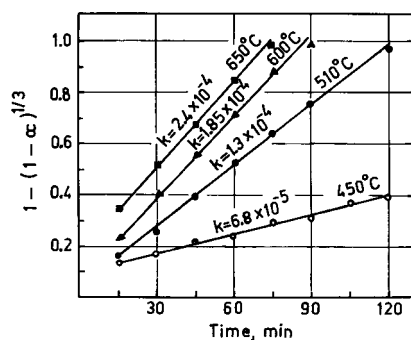


Fig. 10 Plot of $[1-(1-\alpha)^{1/3}]$ vs. time t

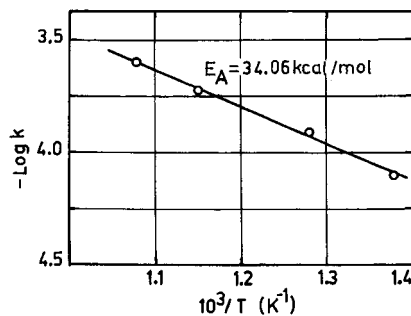


Fig. 11 Arrhenius plot of molybdenite oxidation as a function of $\log k$ vs. $10^3/T(K^{-1})$

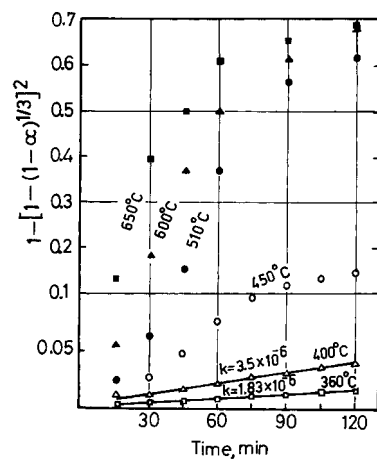


Fig. 12 Plot of $[1-(1-\alpha)^{1/3}]^2$ vs. time t

of molybdenite oxidation increases as the temperature increases and reaches its maximum, $2.4 \cdot 10^4 \text{ s}^{-1}$, at 650°C and low value, $6.8 \cdot 10^5 \text{ s}^{-1}$, at 450°C . At 510°C ,

which represents the maximum of the exotherm of the DTA curve of molybdenite oxidation, the rate of the reaction reaches a quite high value, $1.3 \cdot 10^4 \text{ s}^{-1}$.

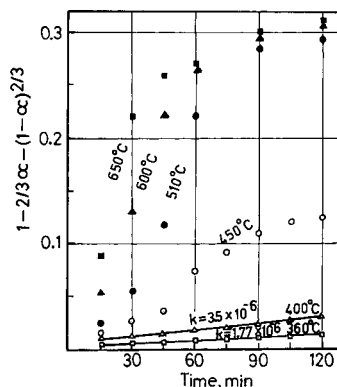


Fig. 13 Plot of $[1 - 2/3\alpha - (1 - \alpha)^{2/3}]$ vs. time t

From the Arrhenius plot (Fig. 11), the calculated apparent activation energy (E) of the reaction is $34.06 \text{ kcal mol}^{-1}$. The high value of the activation energy and the observations in Fig. 10 confirm that the oxidized roasting of molybdenite at 450°C and higher temperatures is controlled by the chemical reaction occurring at the surface of the molybdenite particles.

Rate controlled by diffusion through the oxide layer

At 360 and 400°C , the oxidation of molybdenite leads to the formation of a dense, thick, compact layer of molybdic oxide surrounding the reacted molybdenite core. Here, the reaction product is nonporous and consequently the rate of reaction of molybdenite oxidation is controlled by diffusion through this oxide layer. In this case, the rate of the reaction may be determined by the following equations [12, 17]:

$$kt = [1 - (1 - \alpha)^{1/3}]^2 \tag{6}$$

$$kt = 1 - 2/3\alpha - (1 - \alpha)^{2/3} \tag{7}$$

where α – fraction of molybdenite reacted by time t , and k – rate constant of the reaction.

If the oxidation of molybdenite is controlled by diffusion through the oxide layer, the experimental data in Fig. 8 must give a linear relation when the right-hand side of Eqs (6) and (7) are plotted vs. time t . As shown in Figs 12 and 13, the data give straight lines at 360 and 400°C , indicating a diffusion-controlled model, where the slopes of the straight lines give the rate constant of the reaction (k). The calculated values of the reaction rates at 360 and 400°C for Fig. 12 are in good agreement with those for Fig. 13, $1.8 \cdot 10^6$ and $3.5 \cdot 10^6 \text{ s}^{-1}$, respectively.

At 360 and 400°C , this diffusion-controlled process depends on the rate of flow of air and the velocity of diffusion of gases through the oxide layer. The rate of the

Table 4 X-ray powder diffraction data on molybdenite

d/Å		I/I ₀ /%		h k l
ASTM	observed	ASTM	observed	
6.93	6.936	34	45	0 2 0
3.81	3.805	82	85	1 1 0
3.463	3.452	90	95	0 4 0
3.260	3.253	100	100	0 2 1
3.006	3.018	13	10	1 3 0
2.702	2.701	19	15	1 0 1
2.655	2.653	35	30	1 1 1
2.607	2.609	6	4	1 4 0
2.527	2.529	12	9	0 4 1
2.331	2.322	12	9	1 3 1
2.309	2.310	31	40	0 6 0
2.271	2.271	18	15	1 5 0
2.131	2.129	9	7	1 4 1
1.996	1.994	4	3	1 6 0
1.982	1.982	13	11	2 0 0
1.960	1.956	17	16	0 6 1
1.849	1.846	21	19	0 0 2
1.821	1.819	11	10	2 3 0
1.771	1.769	5	5	1 7 0
1.756	1.754	5	5	1 6 1
1.733	1.731	17	15	0 8 0
1.693	1.695	8	8	2 2 1
1.663	1.662	13	11	1 1 2
1.631	1.628	13	11	0 4 2
1.597	1.597	15	14	1 7 1
1.587	1.586	6	5	1 8 0
1.569	1.567	16	15	0 8 1
1.504	1.504	5	5	2 6 0
1.477	1.477	10	8	2 5 1
1.443	1.443	12	10	0 6 2
1.435	1.436	12	10	1 9 0
1.400	1.406	5	5	2 7 0
1.380	1.385	5	5	0 10 0
1.352	1.349	6	6	2 0 2

reaction of molybdenite oxidation becomes limited by the diffusion of oxygen to (and of sulphur dioxide away from) the mineral surface.

General characteristics of the synthesized molybdite

The produced molybdite is white with a greenish tint and has an adamantine lustre. In thin sections, the molybdite crystals are colourless and elongated, striated parallel to the *c*-axis, flattened on the (010) surface and with a strong birefringence. Cleavage is not observed. Molybdite crystallizes in the orthorhombic system and is optically positive.

The X-ray diffraction pattern of the product of the run at 510°C during 1.5 h (Fig. 14) shows that molybdite is the only constituent of the product. The molybdenite peaks have completely disappeared, indicating the completeness of oxidation of molybdenite. The X-ray peaks of molybdite are well-defined, sharp and intense, suggesting good crystallinity. The X-ray diffraction data on the produced molybdite are consistent with the corresponding values for standard molybdite (Table 4).

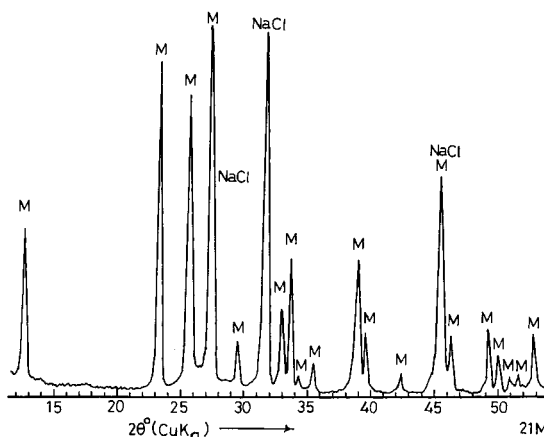


Fig. 14 X-ray diffraction pattern of the produced molybdite; M – molybdite

The unit cell dimensions and constants of the produced molybdite are given in Table 5. It is observed that the calculated cell dimensions, constants and optic axial angles of the produced molybdite are consistent with the corresponding data for the natural mineral.

Table 5 Unit cell dimensions and axial angles of orthorhombic molybdite

Mineral	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	α_{\min}	β_{\min}	γ_{\min}	<i>V</i> /Å ³
Synthetic	3.9468	13.7945	3.6878	90.00	90.00	90.00	200.779
	±0.0209	±0.0232	±0.0145	00.00	00.00	00.00	±0.01
Standard	3.954	13.808	3.690	90.00	90.00	90.00	201.462

Conclusions

This thermal analysis study of the oxidized roasting of molybdenite has demonstrated that its oxidation begins at 360–370°C, as indicated by the small exothermic peak at such temperatures. This is followed immediately by a large, wide exothermic peak with maximum at 510–520°C, representing the intensive oxidation of molybdenite. The medium endothermic peak at 795–800°C reflects the melting and sublimation of molybdenum oxide. The vigorous vaporization of molybdenum oxide and its boiling are associated with the large, sharp endothermic peak at 1150°C.

The standard free energy (ΔF°) equilibrium constant (K) of the reaction of oxidation of molybdenite at 500°C are $-216.4 \text{ kcal mol}^{-1}$ and $1.54 \cdot 10^{61}$, respectively. These values reflect the irreversibility of the reaction.

The kinetic study of the oxidized roasting of molybdenite is governed by the structure and condition of the molybdenum oxide surface coating. The experimental data reveal that the rate of the reaction of molybdenite oxidation is controlled by diffusion at 360 and 400°C. At 450°C and higher temperatures, it is chemically rate-controlled, as confirmed by the high value of the calculated apparent activation energy ($34.06 \text{ kcal mol}^{-1}$) and other observations. The rate of oxidation of molybdenite is therefore a function of temperature, time and the solid–gas contact. Nearly complete oxidation of molybdenite (98.8%) is achieved at 510°C during 1.5 h.

The oxidation of molybdenite results in the production of molybdenum oxide, which is the essential starting material of the molybdenum industry. The molybdenum oxide produced has the molybdite structure and crystallizes in the orthorhombic system in the form of elongated thin crystals with a light-greenish colour.

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