

Application of a Nonisothermal Thermogravimetric Method to the Kinetic Study of the Reduction of Metallic Oxides: Part I. A General Treatment and Its Application to the Reduction of the Oxides of Molybdenum by Hydrogen

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A theoretical treatment to evaluate activation energies of reactions by means of nonisothermal experiments was developed. The treatment considers the case where either the surface reaction or the intraparticle diffusion could be rate-controlling. Complementary to the theoretical treatment, thermogravimetric experiments have been carried out under both isothermal and nonisothermal conditions. The reduction of MoO_3 to Mo was found to pass through an intermediate MoO_2 phase. The rate of reduction to MoO_2 seems to be controlled by surface reaction, and the activation energy obtained from isothermal studies is 205.7 kJ/mol. This is comparable to the value of 211.6 kJ/mol obtained from nonisothermal reduction studies using the present theoretical treatment. The rate of reduction to Mo appears to be influenced by gas diffusion through voids. The activation energy from isothermal studies is 85.2 kJ/mol.

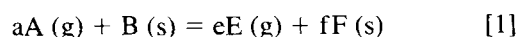
I. INTRODUCTION

AN understanding of the mechanism of a reaction requires a knowledge of the kinetics of the reactions. For example, in the case of gas-solid reactions, high activation energy values are often associated with the chemical reaction at the interface as rate-controlling, whereas lower values could indicate a diffusion-controlled mechanism. Among the various experimental techniques that are used for kinetic studies of gas-solid reactions, thermogravimetry is the most widely used method. During kinetic studies, the reaction is normally conducted at various temperatures and the activation energy is evaluated by an Arrhenius plot. The amount of experimental work can be significantly reduced if the activation energy of a reaction could be reasonably estimated from a single non-isothermal experiment. In the present work, a method for such an estimation is developed and its reliability is examined by applying the same to the reduction of oxides of molybdenum.

While theoretical analyses of isothermal kinetic studies are well developed today, to the present knowledge of the authors, very few attempts have been made to describe nonisothermal experiments in a systematic way. Gentry *et al.*^[1] have derived an expression for the activation energy in the case of temperature-programmed reduction of copper ions in zeolites carried out in a tubular reactor. These authors obtained a relationship between the activation energy of the reaction and the temperature of maximum reaction rate observed experimentally, which had been used in later studies.^[2,3] Arnoldy *et al.*^[4] applied this theory to the temperature-programmed reduction of MoO_3 and MoO_2 . In the present work, the theoretical approach is somewhat different in the sense that it deals with the reaction at a microscopic level between the reactant gas and single particles of the solid reactant.

II. THEORETICAL CONSIDERATIONS OF NONISOTHERMAL REDUCTION

Let us consider the reaction



The reactant solid B can be considered to be made up of a loose compact of small particles and considerably porous. Let us assume that in view of the openness and the "large" diameter of the pores, the resistance to both molecular as well as Knudsen diffusion of the gas is negligible so that the reactant gas A has access to all the small particles and the product gas E can leave the site without any hindrance. In such a case, the "shrinking-core model"^[5] can be applied to the individual particle. The possible rate-controlling step can be the chemical reaction at the interface or the intraparticle diffusion. The latter stands for the inward diffusion of A through the product layer of each particle and outward diffusion of E. In order to simplify the present treatment, it may be assumed that all the particles are spherical and have the same initial radius r_0 . The following theoretical analysis will consider two possible rate-controlling mechanisms, namely,

- (1) surface reaction as the rate-controlling step and
- (2) intraparticle diffusion as the rate-controlling step.

This treatment is based on the assumption that gas-phase diffusion of the reactant and product gas species has no limiting effect on the reaction rate.

A. Surface Reaction as the Rate-Controlling Step

If reaction [1] is controlled by the chemical reaction at the surface, the reaction rate dN_R/dt (moles per unit time) can be expressed as

$$-\frac{dN_R}{dt} = n \left(\frac{\rho_B}{M_B} \right) 4\pi r_c^2 \frac{dr_c}{dt} \quad [2]$$

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where n is the number of particles in the pellet, ρ_B is the density of each B particle, M_B is the molecular weight of B, and r_c is the radius of the unreacted core. At constant temperature, when the surface reaction is rate-controlling, dr_c/dt can be considered to be constant. Hence, Eq. [2] can be rewritten as

$$-\frac{dN_B}{dt} = n \left(\frac{\rho_B}{M_B} \right) 4\pi r_c^2 k \quad [3]$$

The constant k in Eq. [3] is a function of temperature and can be represented by Arrhenius rate law

$$k = k_0 \exp \left(-\frac{Q}{RT} \right) \quad [4]$$

During a nonisothermal reduction experiment, let the rate of temperature scanning be ν (K per unit time). Assuming that the pellet has instantaneously achieved uniform temperature throughout, the temperature of the pellet at time t can be represented by a linear relationship, namely,

$$T = T_0 + \nu t \quad [5]$$

where T_0 denotes the initial temperature at the start of the scanning.

Inserting Eqs. [4] and [5] in [3], the differential dN_B/dT can be expressed as

$$-\frac{dN_B}{dT} = n \left(\frac{\rho_B}{M_B} \right) 4\pi \left(\frac{k_0}{\nu} \right) r_c^2 \exp \left(-\frac{Q}{RT} \right) \quad [6]$$

As the temperature is increased during the experiment, both $(-dN_B/dt)$ and $(-dN_B/dT)$ would show an increase. On the other hand, due to the receding reaction front, the radius of the core would decrease as the reaction proceeds, resulting in a reduction in the surface area. This, in turn, will lead to a retardation of the reaction. A combination of these two effects would naturally lead to a temperature, T_m , at which the reaction rate attains a maximum value. In other words, at the temperature T_m both $(-dN_B/dt)$ as well as $(-dN_B/dT)$ will exhibit a maximum as represented by the relationship

$$\frac{d \left(\frac{dN_B}{dT} \right)}{dT} = 0 \quad \text{when } T = T_m \quad [7]$$

Combining Eqs. [6] and [7], it can be written that

$$-\frac{4\pi n \rho_B k_0}{M_B \nu} \left[2r_c \exp \left(-\frac{Q}{RT} \right) \frac{dr_c}{dT} + r_c^2 \frac{Q}{RT^2} \exp \left(-\frac{Q}{RT} \right) \right] = 0 \quad [8]$$

Equation [8] would lead to the following relationship:

$$\left(\frac{dr_c}{dT} \right)_m = -\frac{Q}{2RT_m^2} (r_c)_m \quad [9]$$

where subscript m stands for the condition $T = T_m$.

Combining Eqs. [2] and [9], it is possible to derive

an expression for $(-dN_B/dT)$ at $T = T_m$. This would be

$$\begin{aligned} \left(-\frac{dN_B}{dT} \right)_{\max} &= 2\pi n \left(\frac{\rho_B}{M_B} \right) \frac{Q}{RT_m^2} (r_c)_m^3 \\ &= \frac{3}{2} (N_B)_m \frac{Q}{RT_m^2} \end{aligned} \quad [10]$$

During a thermogravimetric reduction experiment, the loss of the sample mass is followed as a function of time. Hence, it would be more useful to express the rate in terms of the mass change. The relationship between N_B and mass change ΔW at a given instance can be expressed as

$$N_B = \frac{W_0 \left(1 - \frac{\Delta W}{\Delta W_\infty} \right)}{M_B} \quad [11]$$

where W_0 represents the initial mass of the pellet, ΔW is the dimensionless mass change at that instance, and ΔW_∞ is the total dimensionless mass change at the completion of the reaction.

Combining Eqs. [5], [10], and [11], one can arrive at the relationship

$$\left(\frac{d\Delta W}{dt} \right)_m = \frac{3}{2} \nu (\Delta W_\infty - \Delta W_m) \frac{Q}{RT_m^2} \quad [12]$$

Equation [12] provides a method for determining the activation energy of a reaction from the differential thermogravimetric results at the point of maximum reaction rate.

B. Intraparticle Diffusion as Rate Controlling

If the rate-determining step for Reaction [1] is the diffusion of gas species through the product layer, dr_c/dt can be expected to be proportional to $1/(r_0 - r_c)$. In this case, Eq. [2] may be written as

$$-\frac{dN_B}{dt} = n \left(\frac{\rho_B}{M_B} \right) 4\pi r_c^2 \frac{k'}{(r_0 - r_c)} \quad [13]$$

where k' is the proportionality constant.

A relationship for $(d\Delta W/dt)_m$ can be derived as in the previous case

$$\frac{d\Delta W}{dt} = \frac{3}{2} \nu (\Delta W_\infty - \Delta W_m) \frac{Q'}{RT_m^2} \frac{(1-L)}{\left(1 - \frac{L}{2} \right)} \quad [14]$$

where

$$L = \frac{(r_c)_m}{r_0} = \left[\frac{\Delta W_\infty - \Delta W_m}{\Delta W_\infty} \right]^{1/3} \quad [15]$$

and Q' is the activation energy for the diffusion-controlling reaction.

III. APPLICATION OF THE THEORY TO THE REDUCTION OF MOLYBDENUM OXIDES BY HYDROGEN

Reduction of molybdenum oxides to the metal is of technological importance, especially with reference to the development of molybdenum catalysts. Philips and Chang^[6] observed four oxides in the system, namely, MoO_2 , Mo_4O_{11} , Mo_9O_{26} , and MoO_3 in the temperature range of 873 to 1973 K. While Kay and Langston,^[7] as well as Wassiliev *et al.*,^[8] considered only MoO_2 as the intermediate oxide in the reduction studies of MoO_3 , Bond and Tripathi^[9] from their studies on Pd-catalyzed reduction of MoO_3 suggest the formation of oxides lower than MoO_2 below 873 K. Hawkins and Worrell^[10] studied the H_2 reduction of MoO_3 in the temperature range of 573 to 723 K and confirmed the formation of a suboxide of Mo having a composition between Mo_2O and MoO . On the other hand, Brewer and Lamoreaux^[11] suggest that no well-defined phase exists between MoO_2 and Mo metal.

Extensive studies of reduction of the oxides of molybdenum using hydrogen have been carried out by both isothermal^[10,12-15] and nonisothermal methods.^[4,9] The discrepancy among the different studies can be exemplified by the value for the activation energy for reduction of MoO_3 to MoO_2 , which has been variously reported in the range of 63 to 202 kJ/mol. The differences in the results could be attributed to the various experimental conditions. In the present work, the reduction of MoO_3 by H_2 was carried out by both isothermal and nonisothermal methods in the temperature range of 473 to 1173 K.

A. Materials

MoO_3 powder (Mallinckrodt Chemical Works, 99.5 pct purity, particle size approximately 5 μm) was calcined at 823 K for 20 hours. The oxide was then pressed into cylindrical pellets (6.1 mm in diameter and 2 mm in thickness) at a pressure of about 5×10^6 Pa. One sample (sample 4) was made with a thickness of 2.3 mm. The porosity of the samples was estimated to be 40 pct. In order to study the effect of initial porosity of the sample on the reduction kinetics, some samples were prepared with a porosity of 30 pct by sintering the same at 973 K for 60 hours. The pellets were weighed accurately before reduction studies.

In the case of reduction study of MoO_2 to Mo at 1173 K, the oxide was prepared by reducing MoO_3 to MoO_2 at 973 K using H_2 in the thermogravimetric apparatus and changing the atmosphere from H_2 to Ar.

Argon gas (maximum 2 ppm impurity, AGA Special Gas, Stockholm) was used as the protective gas during the heating of the sample before starting the reduction studies. No detectable extent of reduction of MoO_3 in the Ar gas could be observed in the thermograms. The hydrogen used for the reduction studies was of SR grade and was supplied by AGA Gas, Stockholm.

B. Apparatus and Procedure

The reduction studies were carried out both under isothermal and nonisothermal conditions. For both types of studies, a SETARAM TGA 92 (France) thermogravi-

metric instrument having a detection limit of 1 μg was used. The system was fully controlled by an IBM PC*

*IBM PC is a trademark of International Business Machines Corporation, Armonk, NY.

through a control module. In general, a platinum basket containing a weighed MoO_3 pellet was hung by a Pt suspension wire from the thermobalance. The basket was introduced into the Al_2O_3 reduction tube (16-mm ID), which was positioned in a graphite furnace. A schematic diagram of the assembly is given in Figure 1. Before heating the sample, the reaction tube was evacuated for 15 minutes down to a vacuum of 10 Pa. The chamber was then filled with argon gas through the carrier gas inlet shown in Figure 1. The sample was then heated in a constant argon flow up to the reaction temperature. The argon gas was then stopped, and hydrogen was introduced through the auxiliary gas inlet. In all the experiments, a constant H_2 flow rate of 0.12 l/min was maintained. The gas was led out through the outlet provided at the lower end of the reaction tube.

During the isothermal experiments, the reaction rate was found to be extremely slow below 773 K. Hence, the lower temperature limit for these experiments was kept at 773 K. As MoO_3 would melt above 1073 K,^[16] the upper temperature limit was fixed at 1053 K for the reduction of MoO_3 to MoO_2 . The isothermal reduction of MoO_2 to Mo metal was studied below 1173 K. The nonisothermal reduction studies were carried out between 473 and 1173 K. In these experiments, the gas atmosphere was changed from Ar to H_2 at 473 K. The scanning rates were 5, 15, 18, 20, and 22 K/min.

The weight changes of the samples were registered by the computer at intervals of 2 seconds during the thermogravimetric studies. The calculation of the reduction rate was carried out using the software supplied by SETARAM for the TGA 92 system.

Repetition of some of the experiments showed high reproducibility of the same.

In order to examine the phases formed during reduction, partially reduced samples were subjected to scanning electron microscope studies. For this, some samples were reduced partially to obtain a desired degree of

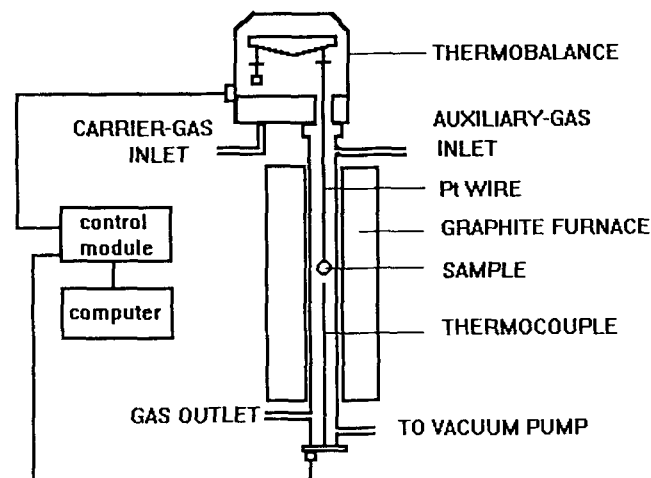


Fig. 1—The experimental assembly.

reduction, after which the atmosphere was changed from H₂ to Ar. The partially reduced samples were studied using a scanning electron microscope, model JEOL JSM-840. An energy-dispersive spectroscopy detector AN10000 Link system attached to the scanning electron microscope enabled the determination of the composition of the phases present.

IV. RESULTS

A. Isothermal Reduction

The isothermal reduction curves are presented in Figure 2. The raw data which are abundant have not been included for the sake of brevity but can be supplied on request. The ratio of the mass loss to the initial mass, the dimensionless mass change, is represented by ΔW . At 773 and 823 K, the reduction is seen to be very slow. At 873 K and above, it is seen that the reduction proceeds with a discontinuity occurring around $\Delta W = 0.11$. This would correspond to the complete reduction of MoO₃ to MoO₂, thereby implying that all MoO₃ is reduced to MoO₂ before the reduction to Mo takes place. This could be confirmed by scanning electron microscope studies of a specimen reduced at 973 K. The reduction was stopped when ΔW was 0.11. The photomicrograph of the specimen is given in Figure 3. The specimen consisted of a single phase. Energy-dispersive spectroscopy analysis showed that the composition of the phase corresponded to MoO₂. This was further confirmed by scanning electron microscope studies of the specimen partially reduced at 873 K.

The effect of the initial porosity of the sample on the reduction rate is shown in Figure 4. It is seen that the reduction curves at 973 K for the sintered as well as the nonsintered pellets show total overlap up to $\Delta W =$

0.11, implying thereby that neither the transfer of H₂ to the particle surface nor that of H₂O away from the surface through the voids is likely to be the rate-controlling factor in the reduction of MoO₃ to MoO₂. On the other hand, further reduction seems to be affected by initial porosity of the sample. This would mean that the transfer of H₂ and/or H₂O has definite influence on the reduction rate of MoO₂ to Mo and that the reaction mechanism may be different.

B. Nonisothermal Reduction

The results of the nonisothermal reduction studies at different scanning rates are presented in Figures 5(a) and (b). It is seen that all the reduction curves show a similar pattern. Even in the case of nonisothermal reduction, the curves indicate a discontinuity at $\Delta W = 0.11$, showing that MoO₃ is first reduced to MoO₂ before the reduction to Mo starts. Below 823 K, the reduction appears to be very slow irrespective of the scanning rate. The reduction to MoO₂ proceeds at a very fast rate above 873 K. These trends are quite in agreement with the observations during the isothermal reductions. The reduction rate for sample no. 4 with higher thickness was the same as the other samples up to $\Delta W = 0.11$, while beyond this value, there was a marked slowdown in the reduction process. Both the reduction to MoO₂ as well as the reduction to Mo were dependent on the scanning rate in the respect that it took higher temperatures at higher scanning rates before reduction was complete.

V. DISCUSSION

The sharp discontinuity exhibited by the reduction curves at $\Delta W = 0.11$ shows that the reduction proceeds mainly in two steps, namely,

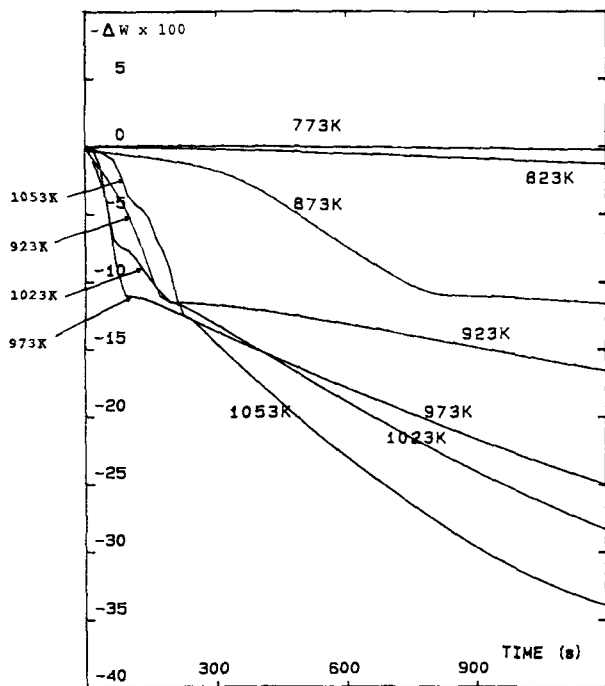
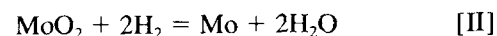
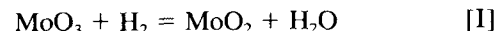


Fig. 2—The isothermal reduction curves.

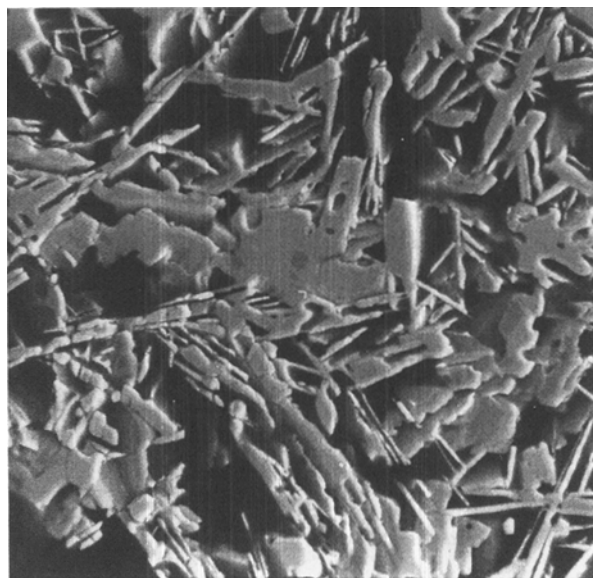


Fig. 3—The photomicrograph of the partially reduced sample with $\Delta W = 0.11$; Magnification 1000 times.

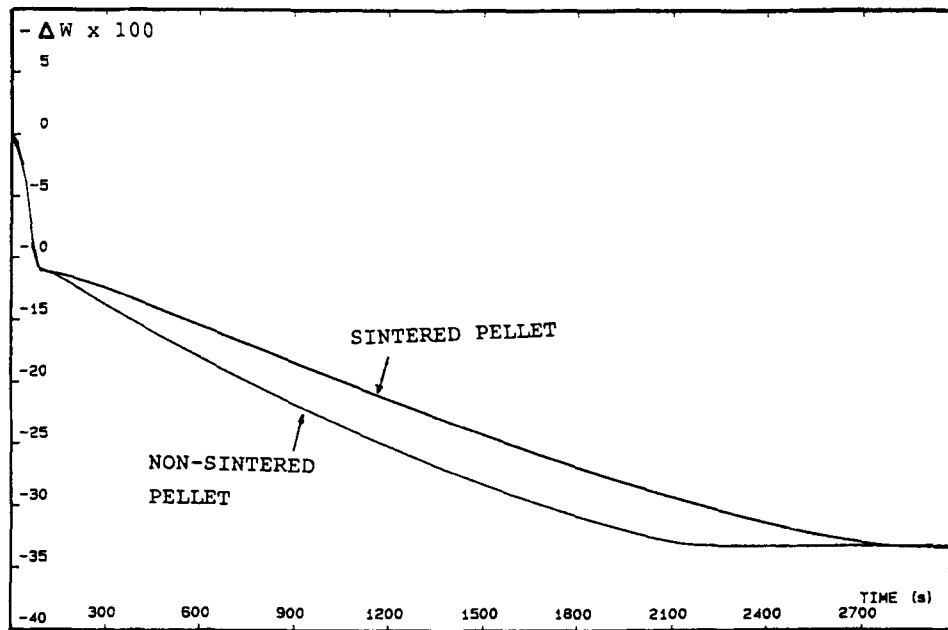
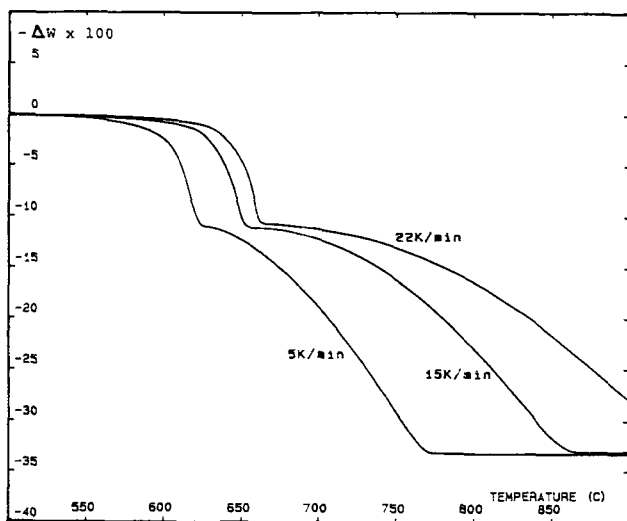
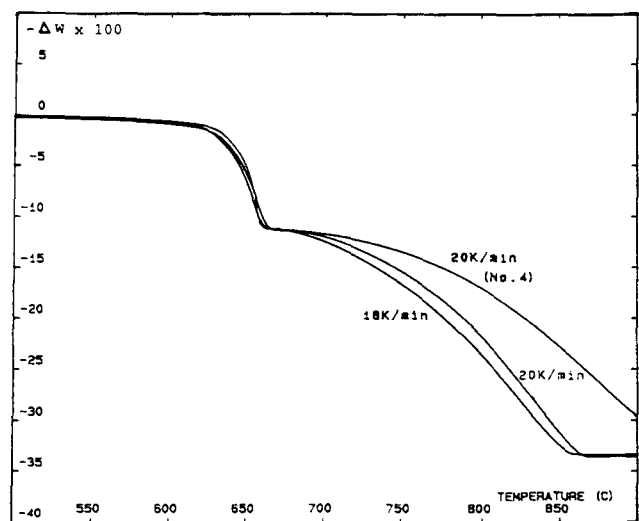


Fig. 4—The effect of the initial porosity of the sample on the reduction rate at 973 K.



(a)



(b)

Fig. 5—The nonisothermal reduction curves (a) for heating rates 5, 15, and 22 K/min and (b) for heating rates 18 and 20 K/min; sample no. 4 had a higher thickness (2.3 mm).

The reaction steps corresponding to the other oxide phases reported in literature are not conspicuous in the present study and, hence, have not been considered.

A. Reduction of MoO_3 to MoO_2

The rate of Reaction [I] corresponds to the rate of the reduction when $\Delta W < 0.1112$. As can be seen in Figure 2, the overall rate of Reaction [I] increases with increasing temperature up to 973 K, beyond which there is an actual decrease in the reduction rate.

As mentioned earlier, the transfer of H_2 to the reaction site and the removal of H_2O from there do not seem to have any influence on the rate of Reaction [I]. Hence,

it is logical to assume that the rate-controlling mechanism could be the chemical reaction at the surface. This rate may have a maximum value at the early stages of the reaction and may start decreasing with diminishing surface area as the reaction proceeds. By taking the maximum reaction rate values at the early stages of the reaction at various temperatures, it should be possible to derive a value for the activation energy of this reaction. Such a plot has been represented in Figure 6. As can be seen in the figure, the points corresponding to temperatures 1023 and 1053 K lie below the Arrhenius plot. This tendency is seen already for the point corresponding to 973 K. It should be pointed out that the initial reaction rates at and above 973 K are quite high even though the

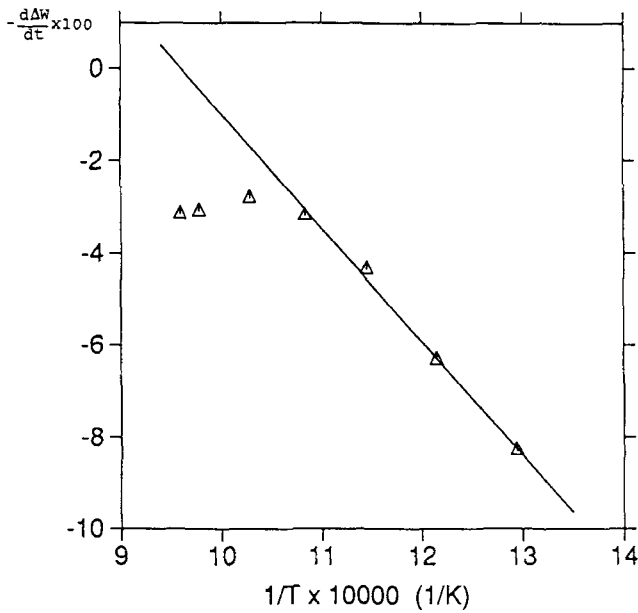


Fig. 6—Arrhenius plot for the reduction of MoO_3 to MoO_2 .

overall rate for Reaction [I] shows a decrease, as can be seen in Figure 2. This high initial reaction rate would lead to sharp diminution in the surface area. Further, the time lag in the reaction due to the change in the gas atmosphere would be considerable at these extremely high rates. These two factors would result in low maximum reaction rate values at the early stages, thereby leading to great uncertainties. In view of these considerations, the points corresponding to 973, 1023, and 1073 K were left out in the calculation of the activation energy for Reaction [I]. The value of the activation energy obtained from the slope of the line in Figure 6 was 205.7 kJ/mol. This high value for the activation energy indicates that the rate-controlling mechanism is the surface reaction.

From the nonisothermal experimental results presented in Figures 5(a) and (b), it is possible to calculate the activation energy for Reaction [I] corresponding to $\Delta W < 0.1112$ using Eq. [12]. It is to be noted that Eq. [12] is applicable in those cases where the surface reaction is rate-limiting, and the underlying assumptions have already been mentioned in the theoretical part (Section II) of this article. The values of Q calculated for various scanning rates are in agreement with each other except in the case of experiment 1, with a scanning rate of 5 K/min. The high activation energy in this

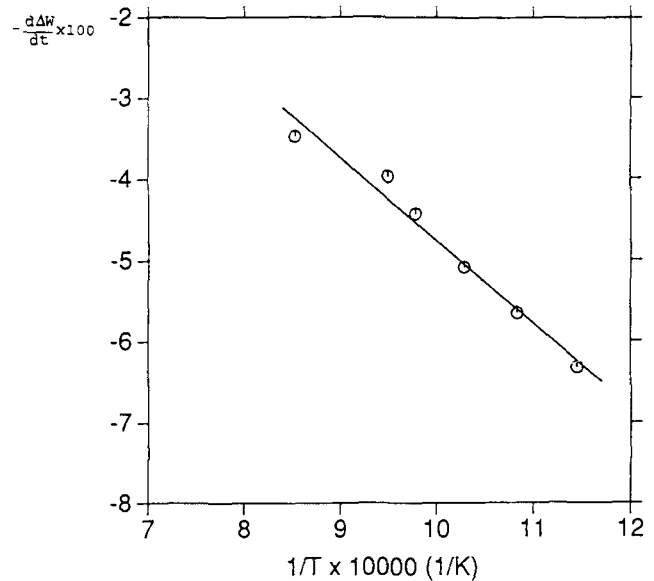


Fig. 7—Arrhenius plot for the reduction of MoO_2 to Mo .

particular case could probably be due to the low scanning rate. As the reaction rate is quite high around T_m , at low scanning rate, ΔW as well as $d\Delta W/dt$ can be expected to vary considerably within a very small temperature range. This would result in considerable experimental uncertainty. Omitting this, an average value for the activation energy for the reduction of MoO_3 to MoO_2 could be calculated from the values in Table I as 211.6 kJ/mol. This value is in good agreement with the value of 205.7 kJ/mol obtained from isothermal experiments. This is a further confirmation of the fact that the rate-controlling step is the surface reaction.

In view of the good agreement between the isothermal and nonisothermal studies, the assumption underlying the derivation of Eq. [12], namely, the gas-phase diffusion of reactant and product gas species having no limiting effect on the reaction rate, appears to be valid as well. This suggests that the gas flow used in the present study was above the starvation rate.

Arnoldy *et al.*,^[4] in their nonisothermal studies of the reduction of MoO_3 by hydrogen, observed high activation energies for the reaction at temperatures around 1073 K. These authors maintain that the reduction rate depends on experimental factors such as sample size, precalcination temperature, as well as heating rate. In the present study, the particle size and precalcination

Table I. The Calculated Activation Energy of Reaction [I]

Number	ν (K/min)	$\left[\frac{d(\Delta W)}{dt} \right]_{\max}$	ΔW_m	Q (kJ/mol) Eq. [12]	Q' (kJ/mol) Eq. [14]	T_m (K)	T_0 (K)
1	5	0.0220	0.0600	373.9	1007.6	886	473
2	15	0.0435	0.0512	223.3	712.3	913	473
3	18	0.0459	0.0550	212.4	628.2	919	473
4	20	0.0516	0.0512	202.6	646.2	922	473
5	20	0.0472	0.0565	203.3	584.3	922	473
6	22	0.0504	0.0608	216.5	575.1	927	473

Table II. The Calculated Q and Q' Values for Reaction [II]

Number	ν (K/min)	$\left[\frac{d(\Delta W)}{dt}\right]_{\max}$	ΔW_m	Q (kJ/mol) Eq. [12]	Q' (kJ/mol) Eq. [14]	T_m (K)	T_0 (K)
3	18	0.032	0.271	188.7	314.5	1094	473
4	20	0.0214	0.274	139.8	229.8	1149	473
5	20	0.0375	0.270	118.7	199.1	1103	473
6	22	0.0300	0.268	153.8	260.2	1154	473

temperature of 823 K were kept constant. Results of the experiments 2 through 5 presented in Table I show clearly that the heating rate does not affect the reaction rate. Arnoldy *et al.* suggest that the surface reaction could be catalyzed by H_2 dissociation on traces of low-valent (<4+) Mo or even Mo atom formed. The experimental techniques used in the present study are not sensitive enough to detect these species at extremely low concentration levels, thus leaving this aspect unanswered.

B. Reduction of Mo_2O to Mo

The rate of Reaction [II] corresponding to $\Delta W > 0.1112$ increases with increasing temperature, as seen in Figure 2. In contrast to Reaction [I], this reaction rate is affected by the initial porosity of the sample, as shown in Figure 4. The sample with low porosity is reduced at a lower rate. This would indicate that the transport of H_2 and/or H_2O has a significant role in the reduction mechanism. The reaction rate is also strongly affected by sample thickness, as can be seen in the case of sample 4 in Figure 5(b), further confirming the above conclusion.

An Arrhenius plot for this reaction is presented in Figure 7. The activation energy obtained from the slope of the straight line corresponds to a value of 85.2 kJ/mol for Reaction [II] under the conditions of the present experiments. This value is in reasonable agreement with the value of 74.5 kJ/mol reported by Orchotsky and Kaczynski.^[15]

It is to be admitted that no attempt has been made in the present work to estimate the pore volume or the nature of the pores in the specimens. It would be interesting to know the nature of the pores at the completion of Reaction [I] and how it is affected by the higher initial sintering temperatures. However, it is hoped that such an investigation could be carried out in the near future.

In order to arrive at the reaction mechanism from the results of the nonisothermal experiments, Eqs. [12] and [15] need be applied to calculate the activation energy. Such an attempt was made in the present work, and the results are presented in Table II. The values of Q and Q' evaluated are shown in columns 5 and 6. It is seen that there is a wide variation in the values, indicating that the reaction mechanism is somewhat more complicated, probably due to mixed control. The present treatment may be inadequate to explain the results. In this respect, it should be mentioned that the present treatment does not take into account temperature inhomogeneities in the sample due to heat transfer from the furnace as well as the enthalpy of the reaction. Further attempts are in progress to improve the theoretical treatment in this regard.

VI. SUMMARY

In the present work, a theoretical model for using nonisothermal reaction rate data to estimate the activation energy of a process controlled by either surface reaction or intraparticle diffusion has been developed. The equations were applied to the nonisothermal reduction of molybdenum oxides carried out as part of this work in the temperature range of 473 to 1173 K. The nonisothermal reduction studies were complemented by isothermal reduction experiments in the temperature range of 773 to 1053 K. Both the studies were carried out by the thermogravimetric method.

The reaction appears to take place in two stages, namely, $MoO_3 \rightarrow MoO_2 \rightarrow Mo$. The activation energy for the first stage calculated from the results of the isothermal studies was found to be 205.7 kJ/mol. The value is in agreement with the value of 211.6 kJ/mol calculated from the nonisothermal reduction experiments using the theoretical treatment developed in the present work assuming surface reaction as rate-controlling.

The reduction of MoO_2 to Mo appears to be influenced by the transport of H_2 and/or H_2O through the voids of the sample. The activation energy for this reaction was calculated to be 85.2 kJ/mol from isothermal studies. The calculation of the activation energy for this reaction by the nonisothermal method assuming either surface reaction or intraparticle diffusion control leads to a wide variation of the activation energy values, indicating the need for improvement of the theoretical treatment.

NOMENCLATURE

A, B	reacting species
C	subscript, stands for core
E, F	product species
k	constant denoting dr_c/dt , $cm \cdot s^{-1}$
k'	proportionality constant, $cm^2 \cdot s^{-1}$
L	dimensionless radius
M_i	molecular weight of species i , $g \cdot mol^{-1}$
N_i	number of moles of species i
Q	activation energy for the rate-controlling chemical reaction, $J \cdot mol^{-1}$
Q'	activation energy for the rate-controlling diffusion reaction, $J \cdot mol^{-1}$
r_c	radius of the core, cm
r_0	initial radius of the particle, cm
R	gas constant
t	time, s
T	temperature of the pellet, K
T_0	initial temperature of the pellet, K
T_m	temperature at which the reaction rate shows a maximum

W	mass of the sample, g
W_0	initial mass of the sample, g
ΔW	dimensionless mass change
ΔW_x	total dimensionless mass change at the completion of the reaction
ρ_i	density of species i , $\text{g} \cdot \text{cm}^{-3}$
ν	scanning rate, $\text{K} \cdot \text{s}^{-1}$

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REFERENCES

1. S.J. Gentry, N.W. Hurst, and A. Jones: *Chem. Soc., Faraday Trans. 1*, 1979, vol. 65, pp. 1688-99.
2. O.J. Wimmers, P. Arnoldy, and A.J. Moulijn: *J. Phys. Chem.*, 1986, vol. 90, pp. 1331-37.
3. P. Arnoldy, O.S.L. Bruinsma, and J.A. Moulijn: *J. Mol. Catal.*, 1985, vol. 30, pp. 111-23.
4. P. Arnoldy, J.C.M. de Jonge, and J.A. Moulijn: *J. Phys. Chem.*, 1985, vol. 89, pp. 4517-26.
5. J. Szekeley, J.W. Evans, and H.Y. Sohn: *Gas-Solid Reaction*, Academic Press, New York, NY, 1976, pp. 642-45.
6. B. Phillips and L.L.Y. Chang: *Trans. TMS-AIME*, 1965, vol. 233, pp. 1433-36.
7. H. Kay and B.G. Langston: *J. Met.*, 1964, pp. 877-81.
8. C. Wassiliev, R. Nicolov, and M. Tschimbulev: *Ann. Ecole Sup. Chim. Techn.*, 1967, vol. 13, p. 125.
9. G.C. Bond and J.B.P. Tripathi: *J. Less-Common Met.*, 1974, vol. 36, pp. 31-40.
10. Donald T. Hawkins and Wayne L. Worrell: *Metall. Trans.*, 1970, vol. 1, pp. 271-73.
11. L. Brewer and L.H. Lamoreaux: *Atomic Energy Review Special Issue, No. 7, Molybdenum: Physico-chemical Properties of Its Compounds and Alloys*, International Atomic Agency, Vienna, 1980, pp. 30 and 285.
12. O. Bertrand and L.C. Dufour: *C. R. Acad. Sci. Paris*, 1974, vol. 278, pp. 315-18.
13. J.M. Zabala, P. Grange, and B. Delmon: *C. R. Acad. Sci. Paris*, 1974, vol. 279, pp. 725-28.
14. D.M. Chizhikov, Yu. E. Ratner, and Yu. V. Tsvetkov: *Russ. Metall.*, (Engl. Transl.), 1970, vol. 6, pp. 5-9.
15. J. Orchotsky and M. Kaczinski: *Mater. Sci. Eng.*, 1979, vol. 40, pp. 245-50.
16. *Binary Alloy Phase Diagrams*, 1st ed., T.B. Massalski, ed., ASM, Metals Park, OH, 1986, p. 1613.