| Impact Factor: | | | | | |
|---|---|---|---|---|---|
| | ISRA (India) = 6.317 | SIS (USA) = 0.912 | ICV (Poland) = 6.630 |
| | ISI (Dubai, UAE) = 1.582 | РИНЦ (Russia) = 0.191 | PIF (India) = 1.940 |
| | GIF (Australia) = 0.564 | ESJI (KZ) = 8.100 | IBI (India) = 4.260 |
| | JIF = 1.500 | SJIF (Morocco) = 7.184 | OAJI (USA) = 0.350 |

SOI: 1.1/TAS DOI: 10.15863/TAS

International Scientific Journal

**Theoretical & Applied Science**

**p-ISSN:** 2308-4944 (print) **e-ISSN:** 2409-0085 (online)

**Year:** 2025 **Issue:** 12 **Volume:** 152

**Received:** 26.12.2025
**Accepted/Published:** 30.12.2025 https://T-Science.org

Issue Article

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# FEATURES OF THE CONDITIONS FOR THE REDUCTION OF MOLYBDENUM TRIOXIDE WITH HYDROGEN

***Abstract***: *The reduction of molybdenum trioxide ($MoO_3$) to metallic molybdenum is a critical technological stage in the production of high-purity molybdenum and its alloys, widely used in mechanical engineering, metallurgy, and high-temperature applications. This study investigates the fundamental features of the conditions governing the reduction of molybdenum trioxide using hydrogen as a reducing agent. Particular attention is paid to the thermodynamic feasibility, reaction mechanisms, and kinetic regularities of the hydrogen reduction process under controlled temperature and gas-phase conditions. The work analyzes existing reduction methods employing various reducing agents and provides a comparative assessment emphasizing the advantages of hydrogen in terms of selectivity, environmental compatibility, and product purity. The chemical transformations occurring during the stepwise reduction of $MoO_3$ to intermediate oxides ($MoO_2$) and subsequently to metallic molybdenum are examined from the standpoint of atomistic and molecular interactions between solid oxide phases and gaseous hydrogen. The influence of temperature, hydrogen flow rate, particle size, and phase composition on reaction kinetics is systematically evaluated. Kinetic studies reveal that the reduction process is governed by both chemical reaction control and diffusion limitations, depending on the operating conditions. Recovery curves obtained experimentally illustrate the characteristic stages of oxide transformation and highlight the critical temperature ranges in which phase transitions and rate changes occur. The role of hydrogen dissociation, gas–solid interface reactions, and the formation of porous structures in the reduced product are discussed in detail. The results contribute to a deeper understanding of the physicochemical principles underlying hydrogen reduction of molybdenum trioxide and provide a scientific basis for optimizing industrial reduction regimes. The findings can be applied to improve energy efficiency, enhance reduction completeness, and ensure consistent quality of molybdenum powders produced for advanced engineering applications.*

***Key words***: *Anchor, rock mass, stress, tensile force, reinforcing structure, elastic and dynamic force, static force, failure.*

***Language***: *English*

***Citation***: Asatov, S.N., Ashurov, Kh.Kh., & Ulugov, G.D. (2025). Features of the conditions for the reduction of molybdenum trioxide with hydrogen. *ISJ Theoretical & Applied Science, 12 (152),* 101-105.

***Soi***: https://s-o-i.org/1.1/TAS-12-152-17 ***Doi***: https://dx.doi.org/10.15863/TAS.2025.12.152.17

**Introduction**

The production of metal powders through oxide reduction represents one of the most widely applied technological routes in modern powder metallurgy. This approach is based on the chemical transformation of metal oxides into the corresponding metallic state or into oxides with a lower oxidation degree by removing oxygen from the crystal lattice. The oxygen removal is achieved by means of a reducing agent capable of forming a more thermodynamically stable compound with oxygen under the given reaction conditions. Consequently, effective reduction is only possible when the reducing agent exhibits a higher chemical affinity for oxygen than the metal contained in the oxide phase. Among various reducing agents, hydrogen is of particular interest due to its high reducing potential, absence of solid reaction by-products, and the ability to obtain metals of high chemical purity.

In the case of molybdenum trioxide, hydrogen reduction is a technologically significant process that ensures controlled transformation of $MoO_3$ into metallic molybdenum via intermediate oxide phases. Understanding the physicochemical principles governing this process is essential for optimizing reaction conditions and improving product quality.

From a thermodynamic standpoint, any chemical system tends to evolve toward a state of minimum potential energy, which corresponds to the most stable configuration of its constituent molecules. When chemical reactions occur, the initial molecular arrangement is transformed into a new set of molecules that also represents a stable energy minimum. However, the transition between these two equilibrium states cannot occur spontaneously without overcoming an intermediate energetic barrier. In this transitional state, the potential energy of the system reaches a maximum, corresponding to a highly activated configuration of atoms or molecules.

The amount of energy required for reacting species to reach this activated state is defined as the activation energy of the reaction. This parameter plays a decisive role in determining the rate of oxide reduction. The reaction rate constant is directly related to the number of atoms or molecules that successfully overcome the activation energy barrier per unit time. As a result, the overall reaction rate is proportional to the concentration of energetically activated species capable of participating in effective collisions.

In gas–solid reduction systems, such as the hydrogen reduction of molybdenum trioxide, the reaction kinetics are influenced not only by chemical reaction rates but also by mass transfer processes. These include hydrogen diffusion to the oxide surface, adsorption and dissociation of hydrogen molecules, oxygen removal from the oxide lattice, and diffusion of gaseous reaction products away from the reaction interface. Depending on temperature and structural characteristics of the oxide particles, the reduction process may proceed under chemical reaction control or be limited by diffusion phenomena.

To illustrate the fundamental kinetic principles, one may consider the simplest reduction reaction, in which a metal oxide interacts with hydrogen to form the corresponding metal and water vapor. This elementary scheme provides a basis for analyzing more complex multistage reduction mechanisms characteristic of molybdenum trioxide.

$$MeO + X = Me + XO \quad (1)$$

where Me is any metal giving oxide MeO;

X is the substance used as a reducing agent.

As is known, the affinity for oxygen is determined by the change in the isobaric thermodynamic potential (Δz) during the formation of an oxide from an element, in accordance with which, during reduction, the values of Δz for two reactions should be compared:

$$2Me + O_2 = 2MeO \quad (2)$$

$$2X + O_2 = 2XO \quad (3)$$

The higher the affinity of a substance for oxygen, the greater the decrease in the isobaric potential of its oxide is formed, that is, the more negative the value is

$$\Delta Z = - A_p = - RT\ln K_p \quad (4)$$

where Ap is the maximum work of the reaction at constant pressure;

P - gas constant;

T is the absolute temperature;

Kp is the equilibrium constant of the reaction.

Therefore, the condition for reaction (1) to proceed in the direction of metal oxide reduction is determined by the inequality, according to which Δ Z according to reaction (3) should be less (in absolute value) than according to reaction (2).

If the energy used is denoted by ΔU, then some of the atoms with such energy can be expressed through $l^{-\Delta U/RT}$, and the reaction rate is $K = Al^{-\Delta U/R}$, where A is a constant,

T - thermodynamic temperature,

P is the gas constant.

This can be written in the vice Arrhenius equation

$$\ln K = \ln A - \Delta U / RT$$

Graphic dependence K - I / T should be straight. If a noticeable deviation from the straight line is observed, it can be stated with full confidence that the observed reaction is complex and consists of two or more simultaneous reactions, which are affected by temperature in different ways.

As a rule, gases (hydrogen, carbon monoxide and gases containing CO and $H_2$, as well as various

dissociated gases, for example, ammonia) serve as reducing agents.

In industrial practice, hydrogen is used as a reducing agent to obtain powdered molybdenum.

In the reduction of molybdenum trioxide with hydrogen, two reduction steps are clearly identified, corresponding to reactions 2.

$$MoO_3 + H_2 = MoO_{2,78} + H_2O$$
$$MoO_{2,78} + nH_2 = MoO_{2,72} + H_2O$$
$$MoO_{2,72} + nH_2 = MoO_{2,27} + H_2O$$
$$MoO_{2,27} + H_2 = MoO_{2,22} + H_2O$$
$$MoO_{2,22} + H_2 = MoO_2 + H_2O$$
$$MoO_2 + H_2 = Mo + H_2O$$

The process can be carried out in one or two stages. In a single-stage reduction, coarse-grained powders are obtained due to the fact that hydrogen, containing water vapor, in this case is in long-term contact with the reduced molybdenum oxides. This favors grain growth. Therefore, preference is given to two-stage reduction, which makes it possible to obtain finely dispersed powders of a certain grain size, intended for the production of compact metal by powder metallurgy.

Research by Hegedyush and co-workers found that on thermogravimetric curves expressing the dependence of mass change on temperature, a stop is observed corresponding to the composition of $MoO_2$, and the area is larger, the more moisture is present in hydrogen (Fig. 1.).

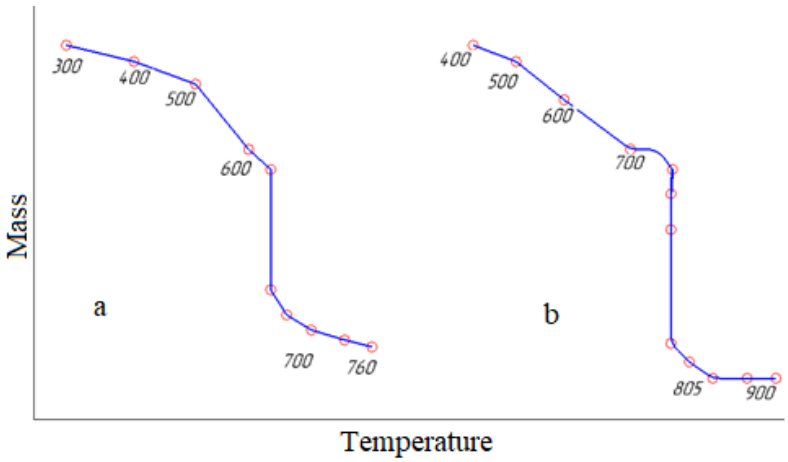


**Fig.1 Mass-temperature curves for MoO3 reduction:**
**(a) in a dry hydrogen flow; (b) in a hydrogen flow with 3% water vapor.**

The rate of temperature rise is 150°C per hour (numbers on the curves indicate temperature, °C).

Table 1 presents the data of a thermogravimetric study of $MoO_3$ reduction. From Table 1. It can be seen that the temperatures of the beginning of $MoO_3$ reduction and the temperatures corresponding to the completion of the first stage of reduction and complete reduction in a dry hydrogen flow are approximately 120°C lower than in wet hydrogen.

In the products of incomplete reduction, the composition of which lies in the range $MoO_3$ - $MoO_2$, X-ray analysis did not detect intermediate oxides such as $Mo_4O_{11}$, $Mo_9O_{26}$ and others.

These oxides, predominantly $Mo_4O_{11}$ (γ-phase), appear in small amounts in the reduction products only after almost all of the trioxide of molybdenum has been reduced to dioxide. The intermediate oxide γ - $Mo_4O_{11}$ is formed as a result of the secondary interaction between $MoO_2$ and $MoO_3$:

$$3MoO_3 + MoO_2 = MoO_4O_{11}$$

**Table 1.**

| Composition of the gas | Recovery start temperature °C | Composition of the first stage product | Temperature, °C | |
|---|---|---|---|---|
| | | | first stage | full recovery |
| Dry Hydrogen | 300 | $MoO_{0,87}$ | 495 | 610 |
| | 310 | MoO | 512 | 615 |
| | 320 | $MoO_{1,1}$ | 524 | 620 |
| | 330 | $MoO_{1,2}$ | 533 | 630 |
| | 340 | $MoO_{1,37}$ | 542 | 635 |
| | 350 | $MoO_{1,48}$ | 557 | 645 |
| | 360 | $MoO_{1,6}$ | 561 | 650 |
| | 370 | $MoO_{1,7}$ | 572 | 655 |

| | | | | |
|---|---|---|---|---|
| | 380 | $MoO_{1,87}$ | 580 | 660 |
| | 390 | $MoO_{1,96}$ | 590 | 670 |
| Hydrogen with 3% water vapor | 400 | $MoO_{1,15}$ | 590 | 700 |
| | 410 | $MoO_{1,25}$ | 600 | 710 |
| | 420 | $MoO_{1,35}$ | 610 | 720 |
| | 430 | $MoO_{1,45}$ | 620 | 725 |
| | 440 | $MoO_{1,55}$ | 635 | 735 |
| | 450 | $MoO_{1,7}$ | 640 | 745 |
| | 460 | $MoO_{1,8}$ | 655 | 750 |
| | 470 | $MoO_{1,85}$ | 660 | 760 |
| | 480 | $MoO_{1,9}$ | 680 | 775 |
| | 490 | $MoO_{1,95}$ | 690 | 780 |
| | 510 | $MoO_{2,05}$ | 710 | 795 |

This reaction proceeds rapidly with an endothermic effect at a temperature of 610–640°C [4]. No intermediate phases were found between $MoO_2$ and Mo. Rode and Lysanova, who studied the reduction of molybdenum trioxide with hydrogen by thermographic, thermogravimetric, and X-ray phase methods, confirmed the main conclusions of the work of Hegedyush and co-workers. They found only two stages of reduction, corresponding to the formation of $MoO_2$ and Mo. At temperatures below 500°C, the reduction products are mixtures of $MoO_3$ with $MoO_2$, and above 500°C, mixtures of $MoO_2$ and Mo.

The inhibition of the process near the completion of the first stage of $MoO_3$ - $MoO_2$ reduction (Fig. 1.) is probably due to the endothermicity of the second stage of $MoO_2$ reduction to Mo. The reaction of the first stage of reduction is accompanied by the release of heat.

An accurate assessment of the thermal effects of the reactions of the first and second stages is hampered by discrepancies in the values of the heat of formation of $MoO_2$ and the lack of data on the heat capacity of molybdenum dioxide.

**Table 2**

| Temperature, °C | ΔZ, kcal/mol $MoO_3$ | K = PH O / P $H_2$ |
|---|---|---|
| 25 | - 21279 | $3,98 * 10^{-15}$ |
| 100 | -21823 | $4,52 * 10^{-7}$ |
| 200 | -22568 | $1,7 * 10^{-1}$ |
| 300 | -23095 | 2,2* 10 |
| 400 | - 23730 | $5,0 * 10^{7}$ |
| 500 | -24023 | $3,3 * 10^{7}$ |
| 600 | - 24305 | $1,7 * 10^{6}$ |
| 700 | -24985 | $1,62 * 10^{6}$ |
| 800 | - 25564 | $1,58 * 10^{5}$ |

The first stage of recovery is accompanied by a large decrease in the isobaric potential. The values of the equilibrium constants are so high (Table 2.) that the reaction is practically irreversible and can proceed at very low hydrogen contents in the $H_2$ + $H_2O$ mixture. Approximate values of isobaric potentials and equilibrium constants of the reaction:

$MoO_{3\ sol} + H_2 = MoO_{2\ gas} + H_2O_{gas}$

In the calculation, the equations Δz for $MoO_2$ = -140100-4.67 lg T + 55.8T were used

for $MoO_3$: $- \Delta z_T = -178900 - 4,6TlgT + 75,3T$

for $H_2O$: $\Delta z = - 58900 + 13,1\ T$.

The reaction of the second reduction stage is endothermic. For this reaction, depending on the accepted value of Δ H298 for $MoO_2$, the standard thermal effect of the reaction varies from + 16.1 to + 25.2 kcal. At 815°C, in the second stage of reduction, 21.0 kcal per 1 mol of $MoO_2$, or 164.5 kcal per 1 kg of $MoO_2$, is absorbed.

**Conclusion.**

The thermodynamic reduction of $MoO_2$ to Mo is possible in the temperature range of 665-900°C if the content of water vapor in the gas mixture does not exceed 18 and 30%, respectively. In practice, to ensure a high reduction rate, it is necessary to use well-dried hydrogen and carry out the process in a gas flow, continuously removing the released water vapor.

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