

Thermal Investigation and Characterization of Molybdic Acid

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Abstract: Thermal behaviour of molybdic acid, H_2MoO_4 has been investigated by DSC and thermogravimetry. The results obtained from the study demonstrated that it decomposes at the temperature range of 373 to 973 K in two steps. In the 1st step the peak was obtained at 604 K (Range 547.7-641 K) which is associated with 8.4 mass losses and in the 2nd step the peak was obtained at 688 K where decomposition started at 657 K and was completed at 710.3 K is associated with 2.2 mass losses.

The different phases of H_2MoO_4 have been characterized by IR spectroscopy and Magnetic susceptibility. Magnetic susceptibility, after the diamagnetic corrections suggests that all the samples are diamagnetic. This is because of the fact that the Mo^{+6} ions, present in these samples, contain no unpaired electron. The kinetic studies suggest that the kinetic data in the first transition follow the Ginstling-Brounshtein mechanism, while the second transition obeys the Mampel's unimolecular law of random nucleation.

Keywords: DSC, IR spectroscopy, Kinetic parameters, Magnetic susceptibility, Molybdic acid, TG, Thermal analysis.

I. INTRODUCTION

Formation of molybdenum oxides has got attention from number of workers. Starting from different materials under different experimental conditions, numerous phases with a range of composition, crystal structure and physical behaviour have also been reported in the literature [1-6]. One of the important oxides of Mo is considered as molybdenum trioxide which on hydration forms H_2MoO_4 , an acid. The Molybdic acid is a yellow diamagnetic salt that exists as the hydrated form of MnO_3 (mono- or dihydrate).

Molybdic acid exists as a coordination polymer in its solid state (Fig. 1 (A)). Wells *et al.* in 1984 showed that Mo is present in the octahedral geometry where 4 corners of octahedron are occupied by O-atoms by single bond, 5th corner by doubly bonded O-atom and sixth corner by water molecule [7]. The four O-atoms that are singly bonded to central Mo are further bonded to four different Mo molecules from other side resulting

into a cluster polymer with bridging Oxygens. Kerbs *et al.* have shown that in dehydrated form of MoO_3 the extra H_2O is intercalated between the layers of the structure shown for $MoO_3 \cdot H_2O$ [8]. Oyeyemi *et al.* have performed DFT studies to elucidate the structure of molybdic acid in solution state using B3LYP functional and 6-311+G(2df, p) basis set. They found that the best agreement between the computational and experimental data was obtained for $MoO_3(H_2O)_3$ in octahedral geometry (Fig. 1 (B)). Therefore, it was concluded that structure of molybdic acid is octahedral with Mo at center of octahedron and three corners occupied by H_2O and three by oxo ligands [9].

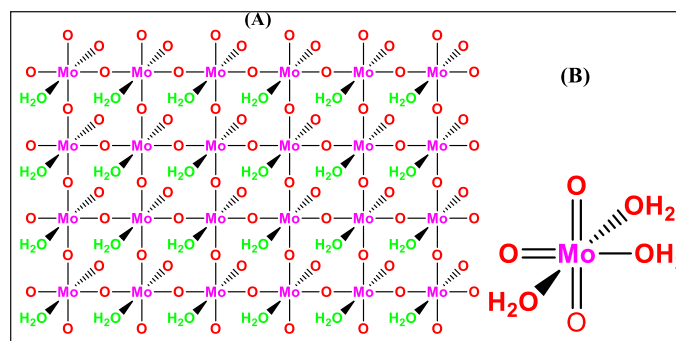


Fig. 1: Structure of H_2MoO_4 Acid in (A) Solid and (B) Aqueous Phase

Molybdic acid has found a lot of applications in developing science. It has been used in the heterogenous catalysis mostly in oxidation reaction such as oxidation of alkenes. Furthermore, it is used in froehde reagent which is used in identification of alkaloids, especially opioids. It is also been found that molybdic acid show different types of biological activities [10-12].

In this article we have investigated the thermal behaviour of H_2MoO_4 by DSC and thermo-gravimetric studies and identified various stable phases formed. The DSC data obtained under isothermal as well as dynamic conditions was used to compute kinetics parameters of the different transitions. Different phases, so formed have been analysed for molybdenum to determine their composition. IR spectra and magnetic susceptibility of all the phases have also been recorded.

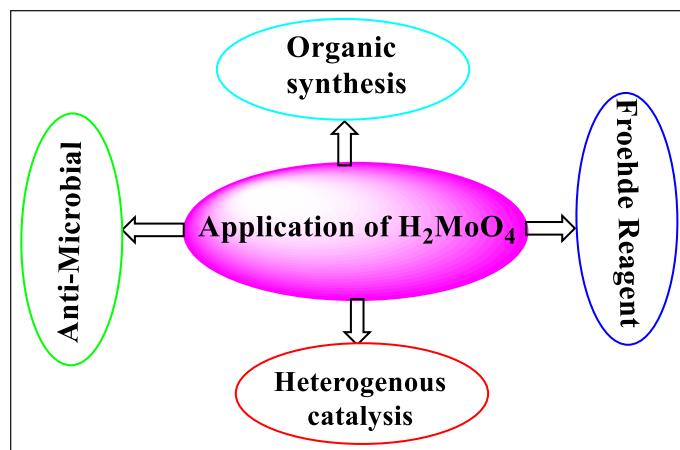


Fig. 2: Applications of Molybdic Acid

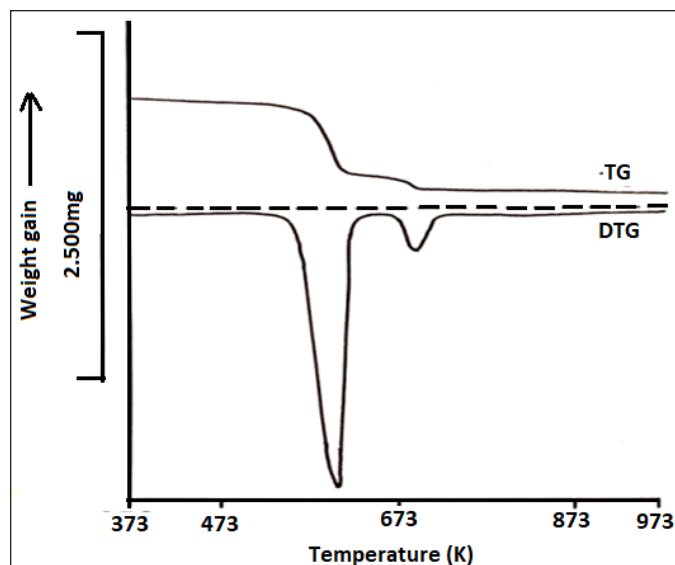
II. EXPERIMENTAL

AR grade Molybdic acid (Sarabhai Chemicals) was used as such. The provided chemical was analysed for Mo metal by a reported method [13]. The study depicted the stoichiometry of the given chemical that suggested the molecular formula for molybdic acid is H_2MoO_4 . DSC and thermo-gravimetric analyses were performed using Mettler thermal analysis system (TA 3000). The investigations were performed in system with the microprocessor TC 10, in the presence of oxygen flowing continuously at the rate of 25 ml/minute. The plots were obtained with the aid of programme available in the microprocessor TC 10. The IR spectra (Data: Table III) for the different phases of the molybdic acid obtained from thermogravimetric analyser after heating from 641 and 710.3 K was recorded on Pye Unicam spectrophotometer SP 2000, utilizing the KBr pellets. Gouy balance was used to record the molar magnetic susceptibility data for the different samples of molybdic acid obtained after the heat-treatment up to 641-710.3 K. During the measurement of magnetic susceptibility magnetic field for the Gouy's balance was kept constant at 2000 gauss and $HgCo(CNS)_4$ was used as celebrant.

III. RESULTS AND DISCUSSION

A. Thermal Analysis

The TG-DTG curves (Fig. 3 and Table I) exhibit two mass loss regions in the temperature region 547.7-641 K and 657-710 K, with peak temperatures of 604 and 688 K respectively. The mass loss associated with these steps is 8.4 and 2.2% respectively. The DSC curves (Fig. 4, Table II) exhibits an endothermic peak in the temperature region 513-633 K with peak temperature 596.9 K. The curve further exhibits an exothermic transition in the temperature region 643-713 K with peak temperature at 680.9 K.

Fig. 3: TG-DTG Plots for H_2MoO_4 at the Heating Rate of 10 deg/minuteTABLE I: THERMOGRAVIMETRIC, DATA FOR TRANSITIONS OF H_2MoO_4

Sr. No.	Steps/ Transitions	Start Temperature	Peak Temperature	End Temperature
1.	First Transition	547.7 K	604 K	641 K
2.	Second Transition	657 K	688 K	710.3 K

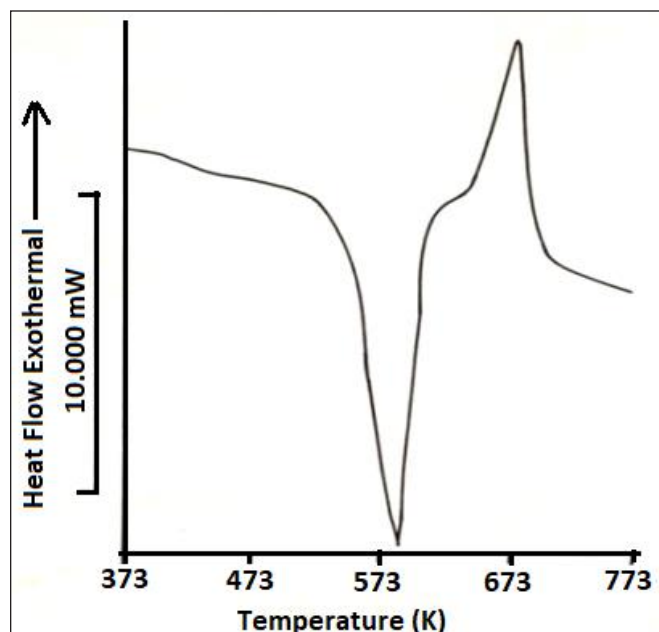
Fig. 4: DSC Curves (dH/dt versus T) for H_2MoO_4 at the Heating Rate of 10 deg/minute in Oxygen

TABLE II: DIFFERENTIAL SCANNING CALORIMETRIC DATA FOR THE TRANSITIONS OF H₂MoO₄

Sr. No.	Steps/Transitions	Start Temperature	Peak Temperature	End Temperature
1.	First Transition	513 K	596.9 K	633 K
2.	Second Transition	643 K	680.9 K	K

B. IR Spectra

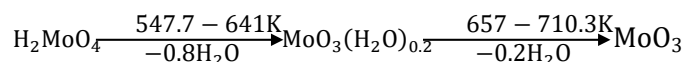
The IR spectra data (Table III) for the different samples show that H₂MoO₄ as such and the samples drawn after the first step have a broad band in the region 3800-2500 cm⁻¹, shows the stretching vibration of O-H bond in water molecules [14], while

the peak at 425 cm⁻¹ is also due to the vibrational mode of water molecules [15]. The peaks observed at 960, 900, 860, 760, 630 and 325 cm⁻¹ in spectra of all the samples are attributed to the molybdenum – oxygen (Mo-O) bond.

TABLE III: SPECTROSCOPIC AND MAGNETIC SUSCEPTIBILITY DATA OF THE DIFFERENT PHASES DRAWN FROM THE TG CELL

Sr. No.	Temperature at Which Phase is Drawn (K)	IR Frequency cm ⁻¹	Molar Magnetic Susceptibility $\chi_m \times 10^6$ cgs units
1.	H ₂ MoO ₄	3700-2400, 1420, 950, 910, 870, 760, 635, 425 and 325	-15
2.	641.1	3725-2450, 1430, 970, 920, 860, 750, 640, 425 and 310	-14
3.	710.3	1400, 950, 900, 860, 750, 635 and 320	-10

The mass loss data from TG analysis, DSC, magnetic susceptibility and infra-red spectra data suggest that molybdc acid decomposes in the following sequence:



The DSC data show that the first transition in the temperature region 513-633 K is endothermic which is in accordance with the general behavior of such decomposition processes [16]. However, the transition in the temperature region 643-713 K, which is attributed to the loss of H₂O, is exothermic. This shows that the product of first transition MoO₃(H₂O)_{0.2} is meta stable and is associated with high energy content. The meta-stable phase decomposes further during this process to more stable MoO₃, having low energy content.

Magnetic susceptibility, after the diamagnetic corrections (Table III) suggests that all the samples are diamagnetic. This is because of the fact that the Mo⁺⁶ ions, present in these samples, contain no unpaired electron.

C. Kinetic Analysis

Kinetic parameters from DSC data under dynamic conditions have been calculated from the relationship [17-18].

$$\frac{d\alpha}{dt} = A e^{\frac{-E}{RT}} \cdot (1 - \alpha)^n$$

Where α is the fraction of the reaction completed at any time t , E is the energy of activation, A is the pre-exponential factor and n is the order of the reaction. Assuming that the fraction of reaction completed is proportional to the heat taken up or consumed at any instant, the above equation in the logarithmic form is transferred to the following relationship.

$$\ln \frac{dH}{dt} = \ln A + n \ln \frac{H_r}{H_t} - \frac{E}{RT}$$

In the analysis using the above given equation it is considered that the fraction of the completed reaction is directly proportional to the DSC signal of the given compound.

Where, $\frac{dH}{dT}$ → Heat flow (mW)

H_t → Reaction's total enthalpy given by the area under DSC peak

H_r → Remaining peak area

Knowing the values of dH/dT , H_t, H_r and T from the DSC data, the rest of the parameters can be calculated with the help of the microprocessor TC 10. Table IV shows the values of $\ln A$, H and E for the two transitions of H₂MoO₄.

TABLE IV: KINETIC DATA FOR THE THERMAL DECOMPOSITION OF H_2MoO_4 IN THE PRESENCE OF THE CONTINUOUSLY FLOWING OXYGEN

Transition Temperature (K) DSC/TG	Peak Temperature (K) DSC/TG	E kJ/mole	$\ln A$	ΔH kJ/mole	Mass Loss %
513-633/547.7-641	596.9/604	168	29	54	8.4
643-713/657-710.3	680.9/688	280	45	10(exo)	2.2

The values of activation energy (E) for both the transitions are comparatively low. The low value suggests that water molecule is loosely bound and may not be structurally coordinated. We have applied various kinetic equations to isothermal data obtained from DSC (Fig. 5 and Fig. 6) of the solid-state reactions [19] to understand the mechanism of the different steps of the thermal decomposition of molybdic acid.

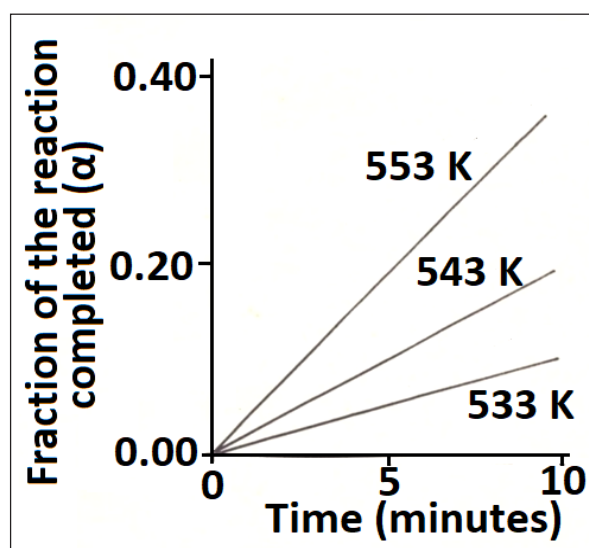


Fig. 5: Plot Showing α (y-axis) versus t (min) for the First Transition

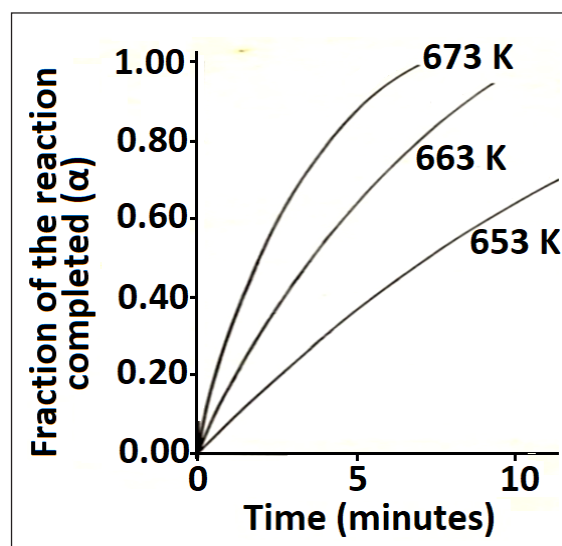


Fig. 6: Plot of α (y-axis) versus t (min) for the Second Transition

Results suggested that the data for the first transition (Fig. 5) follow the Ginstling-Brounshtein equation for the diffusion-controlled reaction [20]. Plots of $[1-2/3\alpha-(1-\alpha)^{2/3}]$ versus time are found to be linear. For the data in the second transition (Fig. 6) it is observed that Mampel's unimolecular law of random nucleation, $kt = -\ln(1-\alpha)$ is applicable to this transition [21]. The applicability of the equation suggests that the random nucleation of the product phase controls the reaction rate in the exothermic process.

IV. CONCLUSIONS

Thermal decomposition of molybdic acid, H_2MoO_4 has been investigated by DSC and TG analysis. The studies suggest that the material decomposes to MoO_3 in two steps in the temperature range 373-973 K. The phases have been characterized by Magnetic susceptibility as well as IR spectroscopy. Magnetic susceptibility, after the diamagnetic corrections suggests that all the samples are diamagnetic. This is because of the fact that the Mo^{6+} ions, present in these samples, contain no unpaired electron. The kinetic studies suggest that the kinetic data in the first transition follow the Ginstling-Brounshtein mechanism, while the second transition obeys the Mampel's unimolecular law of random nucleation.

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REFERENCES

- [1] P. G. Dickens, A. C. Halliwell, D. J. Murphy, and M. S. Whittingham, "Preparation and characterization of a hexagonal ammonium tungsten bronze phase $(NH_4)_xWO_3$," *Trans Faraday Soc.*, vol. 67, pp. 794-800, 1971.
- [2] D. Hunyadi, I. Sajó, and I. M. Szilágyi, "Structure and thermal decomposition of ammonium metatungstate," *J. of Thermal Analysis and Calorimetry*, vol. 116, no. 1, pp. 329-333, 2014.
- [3] T. N. Kovács, D. Hunyadi, A. L. Lucena, and I. M. Szilágyi, "Thermal decomposition of ammonium molybdates," *Journal of Thermal Analysis and Calorimetry*, vol. 124, pp. 1013-1021, 2016.

- [4] N. G. Chernorukov, A. V. Knyazev, N. Y. Kuznetsova, and I. V. Ladenkov, "Investigation of phase transitions and thermal expansion of some complex tungsten-containing oxides," *Phys. Solid State*, vol. 53, p. 292-298, 2011.
- [5] E. Shima, "Structure of the $\text{Mo}_7\text{O}^{6-}_{24}$ ion in a crystal of ammonium heptamolybdate tetrahydrate," *Nature*, vol. 214, pp. 170-171, 1967.
- [6] M. Taniguchi, and T. R. Ingraham, "Mechanism of thermal decomposition of ammonium metavanadate," *Canad. J. of Chemistry*, vol. 42, p. 2467, 1964.
- [7] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed. Oxford Science Publications, 1984.
- [8] B. Krebs, "Die kristallstruktur von $\text{MoO}_3(\text{H}_2\text{O})_2$," *Acta Crystallographica B.*, vol. 28, no. 7, pp. 2222-2231, 1972.
- [9] O. F. Oyerindea, C. L. Week, A. D. Anbarb, and T. G. Spiro, "Solution structure of molybdic acid from Raman spectroscopy and DFT analysis," *Inorganica Chimica Acta*, vol. 361, no. 4, pp. 1000-1007, 2008.
- [10] M. Rana, P. Bhandana, X. C. Sun, M. Imran, M. Shaaban, M. Moussa, and M. Hamzah Saleem, "Molybdenum as an essential element for crops: An overview," *Int. J. Sci. Res. Growth*, vol. 24, p. 18535, 2020.
- [11] U. G. Centa, P. Kocbek, A. Belcarz, S. D. Škapin, and M. Remškar, "Polymer blend containing MoO_3 nanowires with antibacterial activity against staphylococcus epidermidis ATCC 12228," *Journal of Nanomaterials*, vol. 2020, 2020.
- [12] S. Viesca, Francisco, and R. Gómez, "On the mechanism of the Froehde reaction," *World J. Org. Chem*, vol. 7, no. 1, pp. 1-4, 2019.
- [13] A. I. Vogel, *Quantitative Inorganic Chemistry*. London: Longman, 1961.
- [14] I. B. Sharma, and S. Batra, "Characterization and thermal investigations of ammonium heptamolybdate," *J. Thermal Anal.*, vol. 34, p. 1273, 1988.
- [15] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*. New York: Wiley, 1963.
- [16] G. Sartori, C. Furlani, and A. Damiani, "On the problem of the vibrational frequencies of water in complexes," *Journal of Inorganic and Nuclear Chemistry*, vol. 8, pp. 119-125, 1958.
- [17] R. S. Porter, and J. F. Johnson, *DSC Kinetics Methods*. New York: Plenum, 1974, p. 537.
- [18] W. W. Wendlandt, *Thermal Methods of Analysis*. New York: Wiley, 1974.
- [19] K. J. Laidler, *Chemical Kinetics*. New Delhi: Tata-McGrawHill, 1983, p. 747.
- [20] A. M. Ginstling, and B. I. Brounshtein, "Concerning the diffusion kinetics of reaction in spherical particles," *J. Appl. Chem. USSR (Engl. Trans.)*, vol. 23, p. 1327, 1950.
- [21] K. L. Mampel, *Z. Phys. Chem. A*, vol. 187, p. 235, 1940.
- [22] D. A. Young, *Decomposition of Solids*. Oxford: Pergamon, 1966, p. 28.