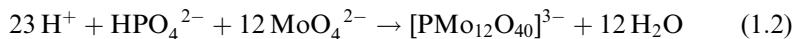
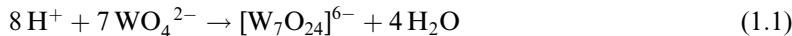

1 Introduction

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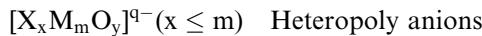
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1.1 SCOPE AND DEFINITIONS

Polyoxometalates belong to a large class of nanosized metal–oxygen cluster anions.^[1,2] These form by a self-assembly process, typically in an acidic aqueous solution as illustrated by equations 1.1 and 1.2 and can be isolated as solids with an appropriate counterion, for example, H⁺, alkali metal cation, NH₄⁺, etc.



Generally, two types of polyoxometalates are distinguished as based on their chemical composition – isopoly anions and heteropoly anions. These anions may be represented by the general formulas:^[1,2]



where M is the addenda atom and X is the heteroatom also called the central atom when located in the centre of the polyanion. The distinction between the two groups is frequently artificial, especially in the case of mixed-addenda polyoxometalates.^[2] Heteropoly compounds are by far more important for catalysis as well as for other applications; hence this book is mainly focused on them. Heteropoly acids – strong acids composed of heteropoly anions and protons as the counterions – constitute a special case of heteropoly compounds that is particularly important for catalytic applications.

The most common addenda atoms are molybdenum or tungsten, less frequently vanadium or niobium, or mixtures of these elements in their highest oxidation states (d^0 , d^1). Much broader range of elements act as the heteroatoms; as such, almost all elements of the Periodic Table can be incorporated in heteropoly anions, most typical ones being P^{5+} , As^{5+} , Si^{4+} , Ge^{4+} , B^{3+} , etc. Molybdenum(VI) and tungsten(VI) are the best polyoxometalate formers as the result of a favourable combination of ionic radius and charge and of accessibility of empty d orbitals for metal–oxygen π bonding.^[2]

1.2 NOMENCLATURE

A systematic nomenclature of polyoxometalates has been developed.^[2,3] It uses a labelling system for the metal atoms and, in some cases, for the oxygen atoms to avoid ambiguity. The resulting names, however, are too long and complicated; these are practically never used for routine purposes.

In catalytic applications, only a relatively small number of well-known types of polyoxometalates have been involved so far, largely limited to the Keggin compounds and their derivatives. Usually, simplified conventional nomenclature, sometimes even trivial names, are sufficient for reporting and retrieving information in the field. Here we adopt the current nomenclature that treats polyoxometalates (also referred to as heteropoly anions, polyoxoanions, or polyanions) as quasi coordination complexes.^[2] The heteroatom, if present, is considered as the central atom of a complex, and the addenda as the ligands. In the formulas of heteropoly anions, the heteroatoms are placed before the addenda, and the countercations before the heteroatoms; the heteropoly anion is placed in square brackets and thus separated from the countercations, as illustrated by the following examples:

$[SiW_{12}O_{40}]^{4-}$	12-tungstosilicate or dodecatungstosilicate
$H_3[PMo_{12}O_{40}]$	12-molybdophosphoric acid
$Na_5[PMo_{10}V_2O_{40}]$	sodium decamolybdodivananophosphate

For simplicity, the countercations and the charge of polyanion and even the oxygen atoms may be omitted; for example, $Na_6[P_2Mo_{18}O_{62}]$ may be abbreviated to $\{P_2Mo_{18}O_{62}\}$ or P_2Mo_{18} .

1.3 HISTORICAL BACKGROUND

The history of polyoxometalates dates back to 1826 when Berzelius^[4] discovered the first heteropoly salt, ammonium 12-molybdophosphate. Later on in 1848, Svanberg and Struve^[5] introduced this compound in analytical chemistry as the

basis for the determination of phosphorus that has been widely used since. By 1908, approximately 750 heteropoly compounds had been reported. However, the structure of polyoxometalates had remained a mystery for more than a century since their discovery. Werner,^[6] Miolati,^[7] Rosenheim,^[8] and Pauling^[9] proposed structures based on sharing metal–oxygen polyhedra. It was Keggins who in 1933 solved the structure of the most important 12:1 type of heteropoly anions by a powder X-ray diffraction study of $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$.^[10] This structure, now named after its discoverer, contained 12 WO_6 octahedra linked by edge and corner sharing, with the heteroatom occupying a tetrahedral hole in the centre. In 1948, Evans^[11] determined the structure of another widespread type – the Anderson's heteropoly anion (6:1 series) – by single-crystal X-ray analysis of $[\text{Te}^{6+}\text{Mo}_6\text{O}_{24}]^{6-}$ salts; this structure is now often referred to as the Anderson–Evans structure. In 1953, Dawson^[12] reported the next new structure (now frequently referred to as the Wells–Dawson's) of a 18:2 heteropoly anion $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$. This structure was shown to be closely related to the Keggins structure. In 1968, Dexter and Silverton^[13] reported the X-ray structure of $[\text{Ce}^{4+}\text{Mo}_{12}\text{O}_{42}]^{8-}$ and showed the large Ce heteroatom to be in a CeO_{12} central icosahedron. By the early 1970s, the chemistry of polyoxometalates had been greatly expanded. This period is associated with extensive work of many groups and especially those of Souchay (France), Ripan (Rumania), Spitsyn (USSR) and Baker (USA). In the 1980–90s, the number of groups involved in the field increased enormously in parallel with expanding applications of polyoxometalates. Recently Baker and Glick^[14] reviewed the history of polyoxometalate chemistry and contributions of various groups to date. By 1995, the X-ray structures of approximately 180 polyoxometalates had been reported.^[15] Among them, salts of giant heteropoly anions such as $[\text{La}_{16}\text{As}_{12}\text{W}_{148}\text{O}_{524}]^{76-}$ (ion mass ca. 40000, diameter 40 Å) and others were prepared and characterised by Müller *et al.*^[16] The application of modern characterisation techniques had led to much better understanding of the structural principles of polyoxometalates and their properties. However, there is still plenty of scope for further work in this field, as many fundamental questions regarding the structural principles, mechanisms of synthesis and reactivity of polyoxometalates remain unanswered.

The chemistry of polyoxometalates has been reviewed extensively. This includes classical monographs by Souchay^[1,17] and Pope^[2] and also by Nikitina^[18] and a large number of review articles, for example Ref.^[15,19–26] Much useful information about the chemistry and various applications of polyoxometalates, including the nomenclature, synthesis of organic and organometallic derivatives of polyoxometalates, electron-transfer reactions, very large polyoxometalate clusters, solution equilibria, polyoxometalate-based molecular materials, scanning probe microscopy of polyoxometalate surfaces, photo- and electrochromism, and application of polyoxometalates in medicine, can be found in the recent collections.^[27,28]

1.4 INTRODUCTION TO CATALYSIS BY POLYOXOMETALATES

Among numerous applications of heteropoly compounds, catalysis is by far the most important. Presently, over 80 % of the patent applications concerning with polyoxometalates is related to catalysis.^[29] First attempts to use polyoxometalates as catalysts can be traced back to the beginning of the twentieth century. Compilations of early works up to 1973 are available.^[30]

Systematic investigation of catalysis by polyoxometalates began in the early 1970s when the great potential of these compounds for catalytic applications became apparent. Most of pioneering work at that time was carried out in Japan (Izumi, Misono, Ono, Otake, Yoneda and co-workers) and Russia (Matveev and co-workers). The string of successful industrial applications of polyoxometalate catalysts in the 1970–80s triggered an explosion of innovative research in this field; the rapid development has continued to date and is bound to move on in the future.

Heteropoly compounds have several advantages as catalysts, the most important being their *multifunctionality* and *structural mobility*. On the one hand, they (heteropoly acids) have a very strong Brønsted acidity; on the other, they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under mild conditions. Their acid–base and redox properties can be varied over a wide range by changing the chemical composition. Solid heteropoly compounds possess a discrete ionic structure, comprising fairly mobile structural units – heteropoly anions and counter-cations – unlike the network structure of, e.g., zeolites and metal oxides. The structure is frequently preserved upon substitution or oxidation/reduction and manifests itself to exhibit extremely high proton mobility and a ‘pseudoliquid phase’ (Chapter 2). On top of that, many heteropoly compounds have a very high solubility in polar solvents and fairly high thermal stability in the solid state.

Because of their unique properties heteropoly compounds are promising acid, redox, and bifunctional (acid and redox) catalysts. The catalytic reactions can be performed in homogeneous as well as in heterogeneous (gas–solid, liquid–solid or biphasic liquid–liquid) systems. Heteropoly compounds are frequently used as model systems for fundamental research, providing unique opportunities for mechanistic studies on the molecular level. At the same time, they have become increasingly important for applied catalysis.

In the 1970–80s, several new industrial chemical processes utilising polyoxometalate catalysis were developed and commercialised in Japan.^[31,32] The first commercial process was the liquid-phase hydration of propene to 2-propanol launched in 1972. It followed by the vapour-phase oxidation of methacrolein to methacrylic acid in 1982, the liquid-phase hydration of isobutene for its separation from the butane–butene fraction in 1984, the biphasic polymerisation of tetrahydrofuran to polymeric diol in 1985, the hydration of n-butenes to 2-butanol in 1989 and other processes. More recently, in 1997, the direct oxidation of ethylene to acetic acid was industrialised by Showa Denko and, in 2001,

the production of ethyl acetate using a heteropoly acid catalyst was launched by BP Amoco (Chapter 7).

Many reviews on catalysis by polyoxometalates have been published. Otake and Onoda^[33] (1976) reviewed early works on heterogeneous catalysis; Matveev^[34] (1977), Matveev and Kozhevnikov^[35-37] (1980, 1982, 1983), Kozhevnikov^[38,39] (1987, 1998), and Jansen *et al.*^[40] (1994) discussed the acid and oxidation catalysis in liquid phase; Izumi *et al.*^[32] (1992) and Ono^[41] (1992) gave comprehensive survey of polyoxometalate catalysis to that date; Kozhevnikov^[42,43] (1993, 1995) described catalysis for fine chemicals synthesis; Misono^[44,45] (1987, 1988, 1993), Moffat^[46] (1987, 1989), Corma^[47] (1995), Mizuno and Misono^[48] (1998), and Misono (2001)^[49] reviewed heterogeneous acid and oxidation catalysis by polyoxometalates; Misono and Nojiri^[31] (1990) described industrial applications of polyoxometalate catalysts; Mizuno and Misono^[50] (1998) described light alkane functionalisation by polyoxometalate catalysis; Okuhara, Mizuno, and Misono^[51] (1996) published the most comprehensive review of the field to that date; Papaconstantinou^[52] (1989, 2001) and Yamase^[53] (1998) addressed photocatalysis; Ishii and Ogawa^[54] (1990) described catalysis for hydroperoxide oxidations; Hill and Prosser-McCartha^[55] (1995) and Neumann^[56] (1998) discussed transition metal substituted polyoxometalates as catalysts for liquid-phase oxidation; Cavani^[57] (1998) described catalysis for vapour-phase oxidation of hydrocarbons; Kuznetsova *et al.*^[59] (1999) addressed the use of polyoxometalates for studies of catalyst active sites; and Misono^[58] (2000) reviewed 'green' aspects of heteropoly acid catalysis. The recent monograph by Moffat^[60] describes the surface properties of polyoxometalates and their use for heterogeneous catalysis. Centi, Cavani, and Trifirò^[61] reviewed the heterogeneous catalysis by polyoxometalates for selective oxidation in their recent book.

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