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Advances in the synthesis of polyoxometalates and in the study of heteropolyacids

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Contents

I. Introduction 445
II. Polyoxometalates with known structures 446
III. Polyoxometalates known in the form of protic acids 447

Abstract. The review surveys data on the known structures of polyoxometalates. The changes in this field which have occurred in the last ten years are traced. Heteropolyacids are considered in detail as a special case of polyoxometalates: their composition and structure, methods of synthesis, stability, and acidity. The bibliography includes 309 references.

I. Introduction

Polyoxometalates are an extensive class of polyoxoanions formed by Group V and VI metals.[1-3] They can be represented by the general formulae $(M_mO_y)^{x-}$ [isopolyanions (IPA)] and $(X_nM_mO_y)^{x-}$ [heteropolyanions (HPA)], where M = Mo, W, and V and, more rarely, Nb, Ta, or a mixture of these elements in the highest oxidation states, while X is a heteroatom. Iso- and hetero-polyanions are historic terms assigned at the time to families of typical representatives of these classes. As the chemistry of these compounds developed (particularly vigorously during the last 25 years), the boundary between IPA and HPA began to blur, which led to a more general name — polyoxometalates.[1] It has recently been suggested[2] that a still more general name be employed — metal–oxygen clusters. However, careful examination shows that IPA and HPA constitute merely an island (although a substantial one) in the vast sea of metal–oxygen clusters. We shall therefore employ for the time being the term polyoxometalates or polyoxoanions. The term heteropolyanions has been firmly retained for the special case involving the presence of one or several heteroatoms X within the ligand sphere of a polyoxometalate with X–O bonds. This applies also to the free protic acids corresponding to the HPA — they are unambiguously referred to as heteropolyacids (HPAC).

The set of elements M incorporated in polyoxometalates is restricted to atoms having a suitable combination of ionic radius and charge and capable of forming element — oxygen $d\pi-p\pi$ bonds. For the heteroatoms X, there is no such limitation. Bearing in mind that the heteroatoms can exist not only within but also outside the polyoxometalate sphere, it is clear that virtually all the elements of the Periodic System can serve as the heteroatoms X with the exception of the noble gas subgroup. The diversity of the X and M atoms and of their proportions is responsible for the existence of an enormous number of polyoxometalates.

The range of applications of these compounds is fairly wide and includes fields such as catalysis, analytical chemistry, medicine, electronics, protective coatings, and many others. The continuously growing interest of investigators in HPA and IPA is indicated by the extensive review literature. During the 10 years which have elapsed since the publication of Pope's monograph in 1983,[1] about 100 reviews have been published in English, German, Russian, Japanese, Chinese, Polish, Czech, and Spanish on the synthesis, structure, properties, and applications of HPA and IPA. We shall mention some of the most complete and interesting reviews. Thus the structures of polyoxometalates have been examined in Refs 2 and 4–7, and their spectra in Refs 8 and 9. The application of polyoxometalates in catalysis,[10-14] in analytical chemistry,[15-19] for the preparation of photochromic coatings,[20] and in pharmacology[17] has been described in fair detail. There are reviews on the use of polyoxometalates in electrocatalysis[21] and photocatalysis.[22] More than half of all the reviews are devoted to the use of polyoxometalates in catalysis, which indicates their effectiveness as catalysts. One may say that to a large extent the studies on IPA and HPA (especially HPA and HPAC) have been associated with their use in catalysis. The frequency of the publication of reviews concerning the structure, chemistry, and applications of polyoxometalates in catalysis and analytical chemistry is sufficient to trace the rapid changes in these branches of knowledge. At the same time, for a long time (20 years) there have been no reviews on the chemistry of defective HPA and their complexes, whilst a detailed review on the chemistry of HPAC[3] was published more than 30 years ago.

The elaborate chemistry of IPA and HPA has led to the existence of an enormous amount of spectroscopic data, the reviews and catalogues of which are extremely useful but their number is small. A review on nontraditional applications of IPA and HPA, including nontraditional catalytic reactions, has also been useful.

The question of the industrial application of polyoxometalates has been dealt with to a very slight extent indeed. Apart from the wide scale general application of HPA for analytical purposes on an industrial scale and in research laboratories, only the employment of HPA and HPAC as catalysts has been described.[11,20,23-25]

The aims of the present review are as follows: to trace the changes in the structural chemistry of polyoxometalates which have taken place after the publication of Pope's monograph[1] and to represent their entire diversity. Particular emphasis is laid on

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the study of the present state of the chemistry of HPAC in connection with properties which are important for their employment in acid catalysis.

II. Polyoxometalates with known structures

After the publication of Pope's classical work,[1] an enormous number of communications concerning the determination of the structures of polyoxometalates by X-ray diffraction (XRD) appeared. In the course of only ten years, the number of new structures trebled. The extensive introduction of high-resolution NMR spectroscopy into practical research made it possible also to obtain in many instances data the information content of which was close to that of XRD results. This contributed significantly to progress in the chemistry of polyoxometalates. It is nowadays impossible to make any kind of reliable judgments about the structure of a new polyoxoanion without resorting to XRD or NMR spectroscopic data.

The principles governing the construction of polyoxometalates have been examined in detail[1,2,4,5] and we shall therefore not deal with this question. The empirical formulae of all the known IPA and HPA, which exist in solution in the form of discrete anions, polymeric anions, and anions detected only in the solid state and whose structures have been established,[26-93] are presented below. Their common feature is their synthesis in solution or from solution. The structures, differing in the construction of the inorganic framework of the anion, are indicated for organic IPA and HPA derivatives. The inorganic framework is understood as a three-dimensional lattice consisting mainly of Mo, W, V, and Nb (sometimes Ta and Cr) atoms to which the atoms of any elements other than C, N, and H are attached. The criteria for the differentiation of the structures are as follows: the number of atoms in the inorganic framework, the disposition of the atoms relative to one another without taking into account the type of atoms, the way in which the atoms are joined together, and isomerism. The structural distortions associated with changes in the type of atoms (for example, when W is replaced by Mo, P by As, etc.) are not taken into account and the fine details in the secondary structure (the disposition of the anions and countercations in the crystal lattice) are also disregarded, apart from the instances where the cations are linked directly to the framework of the anion (for example, in lanthanum decavanadate). When a homologous series exists, the general structural formula is indicated (R is the organic residue). If a single representative of the given structure is known, the complete composition of its anion is indicated.

For each structure, the literature references are given to one source (for an homologous series, as a rule the first source) in which the structure has been adequately described or to the only source available (so far as possible, references are given to reviews in which the structures are described). The IPA and HPA whose structures have been determined by X-ray diffraction are listed.

$M_5O_{12}(NO)_2R_4^{2-}$ [26]
$M_7O_{24}^{6-}$ [1]
$M_{10}O_{28}^{x-}$ (possibly with R) [1]
$(V_3O_8^-)_n$ [1]
$V_4O_8XR_4^{2-}$ [6]
$H_6As_6V_4O_{30}^{4-}$ [1]
$V_5O_{14}^{3-}$ [6]
$V_5O_{22}R_2(PR)_5^-$ [28]
$V_6O_{10}(AsR)_6^{2-}$ [29]
$(RX)_4V_6O_{19}$ [31]
$V_{10}O_{26}^{4-}$ [1]
$V_{10}O_{24}(ASR)_3^{4-}$ [29]
$H_4V_{10}O_{14}(PO_4)_7^{5-}$ [34]
$H_3V_{12}As_4O_{43}^{7-}$ [2]
$H_3Mn_3V_{12}O_{40}^{3-}$ [35]
$XV_{13}O_{38}^{7-}$ [1]
$V_{14}As_8O_{42}X^{x-}$ [2]
$M_6O_{19}^{x-}$ (possibly with R)[1,6]
$M_{10}O_{32}^{4-}$ (possibly with R)[1,6]
$Nb_8O_{10}R_{20}$ [27]
$V_4O_{12}^{3-}$ [1]
$V_4O_8R_4^{4-}$ [6]
$(V_5O_{14}^{3-})_n$ [1]
$V_5O_9XR_4^{2-}$ [6]
$V_6O_{10}R_9$ [6]
$V_6O_8R_6^{2-}$ [30]
$V_9O_{16}R_4^{7-}$ [6]
$La_2V_{10}O_{28}$ [32]
$Se_4V_{10}O_{37}^{8-}$ [33]
$V_{12}O_{32}R^{4-}$ [6]
$XV_{12}As_8O_{40}^{x-}$ [2]
$V_{13}O_{34}^{3-}$ [36]
$XV_{14}O_{40}^{9-}$ [1]
$H_4V_{14}O_{50}(PR)_8^{6-}$ [37]
$XV_{15}O_{36}^{6-}$ [6]
$XV_{18}O_{42}^{x-}$ [1]
$HV_{19}O_{49}^{8-}$ [1]
$Mn_2V_{22}O_{64}^{10-}$ [35]
$(Se_2MoO_8^{2-})_n$ [41]
$Mo_4O_{11}R'NOR^{2-}$ [26]
$HXMo_4O_{15}R^{x-}$ [1]
$H_2As_6Mo_4O_{22}^{4-}$ [42]
$Mo_5O_{10}(O_2)_8^{6-}$ [44]
$Mo_5O_{17}R_4NO^{3-}$ [26]
$Mo_5O_{17}R'_4NO(RhR)_2$ [26]
$Mo_6O_{10}R_{12}$ [6]
$RAsMo_6O_{21}^{2-}$ [1]
$AsCoMo_6O_{30}^{4-}$ [46]
$(H_9NaP_4Mo_6O_{31}^{2-})_n$ [48]
$Mo_8O_yR_n^{x-}$ (7 isomers) [1,6]
$(Cu_2Mo_8O_{28}^{4-})_n$ [50]
$(Mo_8P_6O_{36})_n$ [52]
$M_{10}O_{34}^{8-}$ [1]
$Na_2Mo_{10}N_2O_{28}R_5^{4-}$ [53]
$Mo_{10}O_{29}R_9(NO)_3^{2-}$ [26]
$Te_6Mo_{12}O_{60}^{12-}$ [55]
$(H_{14}Fe_2Mo_{12}P_8O_{62}^{4-})_n$ [57]
$NaMo_{12}O_{54}(PR)_4^{9-}$ [59]
$Mo_{13}O_{40}(XR)_8^{2+}$ [60]
$H_6As_{10}Mo_{24}O_{90}^{8-}$ [62]
$Ce_4Mo_{29}O_{100}^{14-}$ [64]
$Mo_{36}O_{110}(NO)_4$ [65]
$X_8Mo_{58}O_{200}^{28-}$ [67]
$H_3W_6O_{22}^{5-}$ [68]
$H_2W_{12}O_{42}^{10-}$ (paratungstate)[1]
$Mn(Nb_6O_{19})_2^{12-}$ [1]
$(RX)_2(Nb_2W_4O_{19})_2^{x-}$ (2 isomers)[31]
$RX(M_6O_{19})_2^{5-}$ [31]
$V_5Mo_8O_{40}^{7-}$ [1]
$XM_4O_{24}^{3-}$ [71]
$XM_6O_{24}^{x-}$ (Anderson)[1]
$HS_2W_8O_{31}^{7-}$ [73]
β-A – $XM_9O_{34}^{x-}$ [1]
$Mg_8SiW_9O_{37}^{*}$ (2 isomers) [75]
$XW_{10}O_{36}^{x-}$ [1]
β-$XM_{11}O_{39}^{x-}$ [76]
α-$XM_{12}O_{40}^{x-}$ (Keggin, possibly with R) [1]
$PV_{14}O_{42}^{9-}$ [1]
$Cu_2Si_2Mo_{18}O_{66}^{12-}$ [1]
$P_4W_{14}O_{58}^{12-}$ [80]
$P_6W_{18}O_{79}^{20-}$ [80]
$KP_2W_{20}O_{72}^{13-}$ [82]
$As_2W_{21}O_{69}^{6-}$ [1]
$P_8W_{48}O_{184}^{40-}$ [85]
$XH_4NaW_{17}O_{56}F_6^{x-}$ [87]
$H_2SbW_{18}O_{60}^{7-}$ [74]
α_2-$P_2W_{18}O_{62}^{6-}$ [88]
α-A – $Ge_2Ti_6W_{18}O_{77}^{14-}$ [89]
$X_4X'_2W_{18}O_{64}^{x-}$ [1]
$H_2Sb_2W_{22}O_{76}^{12-}$ [74]
$H_5P_5Co_9W_{27}O_{116}^{16-}$ [91]
cis-$X(X'_2W_{17}O_{61})_2^{x-}$ [1]
$Na_2Sb_8W_{36}O_{132}^{22-}$ [74]
$XAs_4Co_2W_{40}O_{140}^{23-}$ [1]
$X_2X'Mo_{12}O_{42}^{x-}$ [1]
$(XX'Mo_{12}O_{42}^{x-})_n$ [1]
$H_2V_{15}As_6O_{42}^{6-}$ [2]
$V_{18}O_{44}R^{x-}$ [38]
$V_{22}O_{54}X^{x-}$ [39]
$V_{34}O_{82}^{10-}$ [40]
$(Mo_3O_{10}^{2-})_n$ (2 isomers) [1]
$Mo_4O_yR_n^{x-}$ (10 isomers) [6]
$H_4As_4Mo_4O_{26}^{4-}$ [1]
$(Mo_4P_2O_{16}^{2-})_n$ [43]
$Mo_5O_{16}R^{3-}$ [6]
$Mo_5O_{17}R'_4NORhR^-$ [26]
$(HMo_5O_{16}^-)_n$ [1]
$(RX)_2Mo_6O_{24}^{4-}$) (2 isomers)[1]
$SeS_3Mo_6O_{33}^{8-}$ [45]
$(Nd_2TeMo_6O_{24})_n$ [47]
$Mo_6O_{17}(P_2R)_2^{6-}$ [49]
$Mg_2Mo_8O_{22}R_{10}^{2-}$ [6]
$H_2TeMo_8O_{31}^{4-}$ [51]
$Mo_{10}O_{28}R_4^{4-}$ [6]
$H_4Co_2Mo_{10}O_{38}^{6-}$ [1]
$NiMo_{10}P_4O_{46}^{8-}$ [54]
$Mo_{12}O_{36}R_4^{4-}$ [6]
$As_2Mo_{12}O_{42}^{6-}$ [56]
$H_4As_4Mo_{12}O_{50}^{4-}$ [1]
$(H_{14}X_3P_8Mo_{12}O_{62}^{4-})_n$ [58]
$Mo_{14}O_{46}^{10-}$ [61]
$H_{31}Na_{14}Mo_{24}P_{17}O_{128}^{6-}$ [63]
$Mo_{36}O_{112}^{8-}$ [1]
$NaH_{15}Mo_{42}O_{109}R_7^{7-}$ [66]
$W_4O_{16}^{4-}$ [1]
$H_4W_{11}O_{38}^{6-}$ [69]
$RXM_6O_{19}^{x-}$ [31]
$(RU)_2(TiW_5O_{19})_2^{4-}$ [31]
$(RX)_5(Nb_2W_4O_{19})_2^{3-}$ [31]
$V_8Mo_4O_{36}^{8-}$ [1]
$X_6Mo_{57}O_{183}(NO)_6^{6-}$ [70]
$X_2M_5O_{21-23}^{x-}$ [1]
$H_2S_2W_6O_{31}^{4-}$ [72]
α-A – $XM_9O_{34}^{x-}$ [1]
α-B – $XW_9O_{33}^{9-}$ [74]
$XM_9O_{32}^{6-}$ [1]
α-$ZM_{11}O_{39}^{x-}$ [1]
$PW_{10}Ni_3O_{39}^{7-}$ [77]
β-$XM_{12}O_{40}^{x-}$ [1]
γ-$PV_2W_{10}O_{40}^{5-}$ [78]
$PMo_4V_9O_{41}^{8-}$ [79]
$P_4W_8O_{40}^{12-}$ [1]
$H_3P_5W_{18}O_{78}^{20-}$ [80]
$P_2W_{19}O_{69}^{14-}$ [81]
$X_2W_{21}O_{71}^{6-}$ [83]
$XP_5W_{30}O_{110}^{x-}$ [84]
α-$P_2W_{17}O_{61}^{10-}$ [86]
$H_2XW_{18}O_{60}^{7-}$ [1]
α-$X_2M_{18}O_{62}^{6-}$ (Dawson) [1]
β_2-$As_2W_{18}O_{62}^{6-}$ [88]
β-A – $Si_2X_6W_{18}O_{77}^{x-}$ [90]
$XSb_9W_{21}O_{86}^{18-}$ [1]
$X(\alpha$-$X'M_{11}O_{39})_2^{x-}$ [1]
$X_4P_4W_{30}O_{112}^{x-}$ [1]
$(RuClP_2W_{17}O_{61})_2O^{16-}$ [92]
$XMo_{12}O_{42}^{8-}$ (Dexter – Silverton) [1]
$XCr_4O_{16}^{3-}$ [93]

Compounds whose structures are postulated on the basis of spectroscopic data:

$H_7W_{11}O_{40}^{7-}$ [94]
$HMo_8V_2O_{32}^{5-}$ [95]
$(RX)_3(Nb_2W_4O_{19})_2^{5-}$ [31]
$Mo_4V_5O_{27}^{5-}$ [95]
$(Nb_2W_4O_{18})_2O^{6-}$ [96]
$P_2W_{12}O_{47}^{12-}$ [1]

β-B$-XW_9O_{34}^{x-}$ [97]
$X(HSiW_9O_{34})_2^{15-}$ [98]
$X(\alpha\text{-}X'W_{11}O_{39})_2^{x-}$ [99]
$X(\beta_i\text{-}SiW_{11}O_{39})_{62}^{x-}$ [101]
$XW_{11}X'(RX'')O_{39}^{x-}$ [1]
$\alpha_1\text{-}P_2W_{17}O_{61}^{10-}$ [1]
$\beta_1\text{-}As_2W_{18}O_{62}^{6-}$ (γ-[1]) [102]
$X_2W_{15}O_{56}^{12-}$ [1,103]
$X_2W_{16}O_{59}^{12-}$ [1,103]
$As_2W_{20}O_{68}^{10-}$ [1]
$X_4P_2W_{18}O_{64}^{x-}$ [105]
$X(\alpha_1\text{-}P_2W_{17}O_{61})_2^{17-}$ [106]
$NaSb_9W_{21}X_6O_y^{x-}$ [1]
$XAs_4W_{40}O_{140}^{x-}$ [1]
$RXP_2W_{15}Nb_3O_{62}^{x-}$ [109]
β-$XM_{11}O_{39}^{x-}$ (2 isomers) [1]
$(XX'W_{11}O_{39})_2O^{x-}$ [1]
$X(\alpha,\beta_2\text{-}SiW_{11}O_{39})_2^{x-}$ [100]
$SiW_{11}(Si_2R_2O)O_{39}^{4-}$ [1]
$[(XW_{11}X'O_{39})_2X'']_n^{x-}$ [1]
$\beta\text{-}P_2W_{17}O_{61}^{10-}$ [1]
$(\alpha,\beta)_1\text{-}X_2W_{18}O_{62}^{6-}$ (β-[1]) [102]
$As_2W_{19}O_{67}^{14-}$ [1]
$X_2W_{20}O_{70}^{10-}$ [104]
trans-$X(\alpha_2\text{-}X_2'W_{17}O_{61})_2^{x-}$ [1]
$NaSb_9W_{21}X_3O_{86}^{x-}$ [107]
$X_2X_2'As_4W_{40}O_y^{x-}$ [1]
$P_4W_{30}Nb_6O_{123}^{16-}$ [109]
$RXX'W_9Nb_3O_{40}^{x-}$ [108]

The $Mg_8SiW_9O_{37}$ isomers have been described insufficiently clearly[75] which gives rise to doubts concerning their genuine existence.

Polyoxometalates with a degree of condensation of the atoms M in the polyanion not less than 4 are listed above. One cannot fail to recognise that such subdivision appears somewhat artificial because species with degrees of condensation of 2 and 3 actually belong to the class of polyoxoanions. Pope[1] began his consideration of polyoxometalates with the lowest polyoxoanions (with a degree of condensation of 2 but without organic derivatives), while Chen and Zubieta [6] considered polyoxoanions with a degree of condensation of 3. The remaining reviews on IPA and HPA are frequently restricted to the description of the structures of polyoxoanions beginning with degrees of condensation of 5 or 6 without an explanation of such restriction. Thus by the time the present review was written, the structures of 176 polyoxometalates had been determined by X-ray diffraction. The existence of a further 36 structures has been postulated on the basis of some kind of spectroscopic data. In addition, there exist polyoxometalates (several tens) the structural formulas of which are based solely on the results of elemental analysis.

III. Polyoxometalates known in the form of protic acids

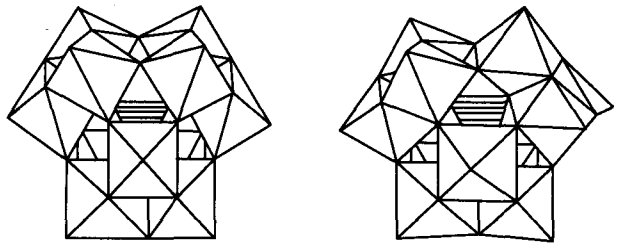
As already mentioned above, the interest in HPAC and their salts has been induced to a large extent by their use in catalysis and in the first place in acid catalysis. A large number of a wide variety of HPAC are known, but only some of them are used in laboratory practice, such as $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and, much more rarely, $H_6P_2Mo_{18}O_{62}$ and $H_6P_2W_{18}O_{62}$. In our view, this is a consequence of the insufficient amount of information as to which HPAC exist. Experience gained in the use of HPAC in acid catalysis has shown that the effect of the HPAC does not always reduce solely to their action as strong acids. The properties of HPAC (including catalytic properties) differ significantly and sometimes also fundamentally depending on their structure and composition. In this sense, there still remains much to be done by investigators. In contrast to polyoxometalates as a whole, the number of new HPAC obtained during the last ten years has changed little. Only a few new HPAC with the Keggin structure and one HPAC of a new structural type have been synthesised. Apparently, the main types of HPAC have already been dis-covered, but the possibilities for the variation of the composition within the structural types are still great.

This section presents data on HPAC which exist in the solid state or at least in the form of a concentrated (not less than 0.1 M) solution. The properties of HPAC important for their employment in acid catalysis are listed briefly below: composition and structure, stability, acidity, and availability.

For the sake of brevity, henceforth abbreviated designations of HPAC will be used in the text (without H and O atoms), indicating the composition of the inorganic framework.

1. Heteropolyacids with the Keggin structure

In terms of a number of known compounds, HPAC with the Keggin structure constitute the most extensive and important class of polyoxometalates. It has been named after Keggin, the English investigator who first determined accurately the structure of the HPA anion of this class (Fig. 1).[1] Table 1 presents the compositions and temperatures of the onset of decomposition of the known HPAC with the Keggin structure, the existence of which is not open to doubt.



a *b*

Figure 1. The structures of the α- (*a*) and β-isomers (*b*) of Keggin HPAC: 12 MO_6 octahedra surround the XO_4 tetrahedron.

There is no doubt about the existence of the following HPAC with the Keggin structure:

$\alpha\text{-}H_3PW_{12}O_{40-n}(O_2)_n$, $n=1-4$ (not isolated in the solid state) [113]
$\beta\text{-}H_4SiW_{12}O_{40}$ [114]
$\beta\text{-}H_4GeW_{12}O_{40}$ [114]
$\alpha\text{-}H_6CoW_{12}O_{40}$ [3,123–125]
$\alpha\text{-}H_{6-n}H_2W_{12}F_nO_{40-n}$, $n=1-3$ [126]
$\beta\text{-}H_3PMo_{12}O_{40}$ [127]
$\beta\text{-}H_4SiMo_{12}O_{40}$ [110,129]
$\alpha\text{-}H_4GeMo_{12}O_{40}$ [3,129]
$\beta\text{-}H_4GeMo_{12}O_{40}$ [129]
$\alpha\text{-}H_4TiMo_{12}O_{40}$ [3,130,131]
$\alpha\text{-}H_3AsMo_{12}O_{40}$ [1,132]
$\beta\text{-}H_8AsMo_{12}O_{40}$ [1]
$H_7PV_{12}O_{36}$ [133]
$H_{3+n}PV_nW_{3-n}Mo_9O_{40}$, $n=1-3$ [136]
$H_5PV_2W_{10-n}Mo_nO_{40}$ [3]
$H_5PNb_2W_nMo_{10-n}O_{40}$ [137,138]
$\alpha\text{-}H_4PW_{11}NbO_{40}$ [141,142]
$H_4VW_{11}VO_{40}$ [144]
$H_5PW_{10}Nb_2O_{40}$ [142]
$H_5VW_{10}V_2O_{40}$ (not isolated in the solid state) [144]
$H_6SiW_{10}Nb_2O_{40}$ [147]
$H_7BW_{10}V_2O_{40}$ [3,148]
$H_{4+n}SiW_{12-n}V_nO_{40}$ ($n=2\pm4$) [3,146]
$H_4SiMo_nW_{12-n}O_{40}$ [3,145]
$H_6GeW_{10}V_2O_{40}$ [3]
$H_5BW_6Mo_6O_{40}$ [148]
$H_5GeW_{11}VO_{40}$ [150]
$H_4PMo_{11}NbO_{40}$ [152,153]
$H_5PMo_{10}Nb_2O_{40}$ [110]
$H_5SiMo_{11}NbO_{40}$ [157]
$H_6GeMo_{10}V_2O_{40}$ [3]
$H_7H_2W_{11}CrO_{39}$ (not isolated in the solid state) [158,159]

The existence of the following HPAC requires further confirmation (the temperatures of the onset of decomposition in the solid state in °C are given in brackets):

$H_6H_2W_{11}MnO_{39}$ [159]
$H_6CuW_{12}O_{40}$ [160]
$H_5AsW_{10}V_2O_{40}$ [161]
$H_5AsMo_{10}V_2O_{40}$ [161]
$H_6AsMo_9V_3O_{40}$ [161]
$H_7AsMo_8V_4O_{40}$ [162]
$H_3SbMo_{12}O_{40}$ [163]
$H_4CW_{12}O_{33}(O_2)_7$ [164]
$H_6H_2W_{12}O_{33}(O_2)_7$ [164]
$H_4SiW_{11}CrO_{40}$ (~300) [165]
$H_4SiW_{11}AlO_{39}$ [166]
$H_5GeW_{11}SnCo(CO)_3^-$
$P(C_6H_5)_3O_{39}$ [167]

The following are the heteropolyanions the existence of which is not open to doubt:

$H_4ZrW_{12}O_{40}$ [168]
$H_4TeW_{12}O_{40}$ (200) [169,170]
$H_4SeW_{12}O_{40}$ (47) [168,171]
$H_8SeW_8V_4O_{40}$ (187) [171]
$H_6SeW_{10}V_2O_{40}$ [172]
$H_7TeW_9V_3O_{40}$ [173]
$H_8TeW_8V_4O_{40}$ (~300) [173,174]
$H_8SiMo_{10}Sn_2O_{40}$ [177]
$H_{3+n}PMo_{12-n}V_nO_{40}$, $n=4-7$ [175,176]

Table 1. The known HPAC with the Keggin structure.

HPAC	T/°C[a]	Ref.
α-$H_3PW_{12}O_{40}$	400	3, 110–112
α-$H_4SiW_{12}O_{40}$	370	3, 110, 112
α-$H_4SiW_{12}O_{40}$	370	3, 110, 112
α-$H_6H_2W_{12}O_{40}$	20	3, 110
α-$H_5BW_{12}O_{40}$	240	3, 110, 112
α-$H_4GeW_{12}O_{40}$	~453	3, 115
α-$H_5GaW_{12}O_{40}$	380	116, 117
α-$H_4CW_{12}O_{40}$	280	118, 119
α-$H_5AlW_{12}O_{40}$	~400	120–122
α-$H_6ZnW_{12}O_{40}$	320	3, 112, 121, 123
α$H_5FeW_{12}O_{40}$	~390	122, 123
α-$H_5CoW_{12}O_{40}$	~370	3, 123, 124
α-$H_3PMo_{12}O_{40}$	300	3, 110, 112
α-$H_4SiMo_{12}O_{40}$	200	3, 110
	300	112
	370[b]	128
α-$H_6SiMo_{12}O_{40}$	390[b]	128
α-$H_8SiMo_{12}O_{40}$	445[b]	128
$H_3PW_{12-n}Mo_nO_{40}$, $n = 1-11$	~490 for $n = 6$	3, 110, 134, 135
$H_{3+n}PV_nW_{12-n}O_{40}$ $n = 1-4$	~300 for $n = 1$	110, 139, 140
α-$H_5PW_{11}TiO_{40}$	450	143
α-$H_5PW_{11}ZrO_{40}$	450	143
α-$H_5PW_{11}CeO_{40}$	150	143
$H_6ZnW_6Mo_6O_{40}$	~300	149
$H_4PMo_{11}VO_{40}$	442	110, 151
	400	140
$H_5PMo_{10}V_2O_{40}$	~412	110, 151
$H_6PMo_9V_3O_{40}$	~396	110, 151
$H_5SiMo_{11}VO_{40}$	110	154, 155
$H_6SiMo_{10}V_2O_{40}$	200	3, 155, 156

[a] The temperature of the onset of decomposition in the solid state.
[b] At a heating rate of 300 K per hour.

The diversity of the HPAC is due to the variation of the central heteroatom X and of the composition of the ligand sphere. The available information about certain HPC, listed above (mainly with different X), has not been confirmed by reliable spectroscopic data and is based solely on the results of chemical analysis. The existence of these compounds requires further confirmation. For example, As^{5+} tends to form HPA of the type As_2W_{21} and As_2Mo_{18}, while HPA of the Keggin type are not characteristic of this anion. However, the introduction of vanadium into the ligand sphere sometimes stabilises the particular HPA structure (instances of stabilisation for $X = V^{5+}$ or S^{6+} have been accurately established) and the formation of stable HPAC having the composition $H_{3+n}As.(W, Mo)_{12-n}V_nO_{40}$ is therefore possible.

The existence of zirconium-containing HPAC is doubtful because Zr^{4+} is too large to be accommodated in the central cavity of the Keggin HPA. Furthermore, it does not form compounds with a coordination number of 4. ZrW_{12} was synthesised from the fluoride complex. Bearing in mind that fluorine forms a very stable complex with Zr^{4+},[168] one can postulate that this compound is in fact a fluorine-containing HPAC with an unknown structure.

As stated correctly by Pope,[1] in the study of HPAC with $X = Se^{4+}$, Te^{4+}, or As^{3+} 'one cannot ignore the influence of the lone pair of the heteroatom'. The compounds $PMo_{12-n}V_n$ are stable for $n = 1-3$.[179] In the synthesis of compounds with $n > 3$ by known methods, the latter undergo partial decomposition with loss of vanadium, the loss being greater the higher the value of n. HPAC with $n > 3$ can be scarcely obtained in a pure form.[142,146,179] It has been shown by spectroscopic methods that, on decomposition of $PMo_{12-n}V_n$, a certain amount of vanadium passes to the cationic component with simultaneous ejection of the excess phosphorus in the form of H_3PO_4.[179,180] The chemical composition of the mixture does not then change, or the change is much less than the extent of the synthesis of HPAC. For this reason, the postulated HPAC with $n = 4-7$ are most probably a mixture of HPAC with $n = 1-3$, H_3PO_4, and VO_2^+.

HPAC known not to exist (the corresponding HPA are stable in nearly neutral media) are sometimes mentioned in patents devoted to the application of HPAC in catalysis. Such non-existent HPAC include $H_nPW_9X_{3-n}Z_xO_{37}$ ($n = 6-7$; $x = 0, 1$; $X^{3+} = Fe^{3+}$, Cr^{3+}, $Z^{2+} = Co^{2+}$, Mn^{2+}, Zn^{2+}, Ni^{2+}),[181] $H_6P_2Mo_5O_{23}$, $H_9CoW_6O_{24}$, $H_7AsMo_{11}O_{39}$, $H_9PMo_9O_{34}$,[182] etc. In such cases, it is more correct to speak of catalysts having the corresponding composition and not of the individual HPAC. This also applies to $SiMo_{10}Sn_2$.

A whole series of HPAC with the Keggin structure have been obtained by cation exchange—for example, $H_2W_{11}Mo$,[183] $TlMo_{12}$,[184] $InMo_{12}$,[185] and the complex HPAC having the composition $X(Mo \text{ or } W)_{11}Z$.[1,186–193] They exist in the form of dilute solutions. Virtually nothing is known about the possibility of their existence in the solid state or in the form of concentrated solutions.

The replacement of W or Mo in the ligand sphere of the HPAC by V has an unambiguous effect on the stability of the HPAC. In terms of their stability in aqueous solutions, HPAC can be arranged in the following sequences:

$$PMo_{11}V > PMo_{12} > PMo_{10}V_2 > PMo_9V_3$$ [194]

$$SiMo_{12} > SiMo_{11}V > SiMo_{10}V_2$$ [195]

$$PW_{12},\ PW_{11}V,\ PW_{10}V_2 > PW_9V_3 > PW_9V_4$$ [139]

$$VW_{10}V_2 > VW_{11}V > VW_{12} \text{ (hypothetical)}.$$[144]

All the vanadium-containing HPAC are in fact mixtures of HPAC with different values of n.[139,144,179,195] Only $PMo_{11}V$ and $PW_{11}V$ have been synthesised relatively easily.

$PMo_{12-n}W_n$,[179] $PW_{12-n}Nb_n$,[142] and apparently all the remaining mixed-ligand HPAC with $n > 1$ are also mixtures.

The stabilities of various HPAC in aqueous solution have been investigated by ^{17}O NMR methods (based on the rate of isotope exchange with $H_2^{17}O$) and by observing the formation of deposits in concentrated solutions (Table 2). The following HPAC stability series have been constructed on the basis of these data:

$$SiW_{12} > PW_{12} \gg PMo_{12} > SiMo_{12} > GeMo_{12}\ .$$

Hence it is seen that the composition of the ligand sphere has a greater influence on the stability of HPAC than X: HPAC with W are much more stable than those with Mo. The products of the hydrolysis of these HPAC have also been investigated. On hydrolysis of $SiMo_{12}$ and $GeMo_{12}$, deposits of MoO_3, SiO_2, and GeO_2 were precipitated from the solutions. $MoO_3(H_2MoO_4)$ was also precipitated from the PMo_{12} solution, the compound P_2Mo_{18} accumulating in the solution in accordance with the postulated reaction

$$PMo_{12} \longrightarrow PMo_9 \longrightarrow P_2Mo_{18}\ .$$

PW_{12} is apparently hydrolysed via a different mechanism:

$$PW_{12} \longrightarrow PW_{11} + WO_4^{2-}\ .$$

The hydrolysis of PW_{11} does not proceed any further.[196] A series of various tungsten-containing HPAC in terms of their resistance to acid hydrolysis in concentrated aqueous solutions has been

Table 2. Hydrolytic properties of HPAC in aqueous solutions.

HPAC	Temperature/ °C				
	70	110	200	250	270
$SiMo_{12}$	x	x	–	–	–
PMo_{12}	o	x	–	–	–
PW_{12}	o	o	o	+	+
P_2W_{18}	o	o	o	o	o
SiW_{12}	o	o	o	o	o
P_2Mo_{18}	o	o	x	–	–

Note. The solutions were kept in sealed tubes for 24 h (c_{HPAC} = 0.45 M (Keggin) and 0.225 M (Dawson).[196] Here and henceforth the following designations have been adopted: o—compound stable (no deposit); +—compound partly stable (solution turbid but a deposit is not precipitated); x—compound unstable (appreciable deposit); *compound almost stable.

constructed on the basis of experiments on ether extraction in the presence of inorganic acids:

$$PW_{12},\ P_2W_{21},\ P_2W_{18} > PW_{11}Ti > (PW_{11})_2Ce^{4+} > PW_{11}Ce^{4+},\ PW_{11}Cr^{3+} > PW_{11}Zr,\ PW_{11}Bi.$$

In these experiments, the compound $PW_{11}Cr^{3+}$ was obtained as a relatively unstable component in a mixture with PW_{12} and P_2W_{21}.[143] In organic and aqueous organic media, the HPAC are most stable than in water.[110]

The hydrolytic transformations in dilute solutions have been investigated only in relation to PMo_{12}. At a concentration of 0.01 M and below, PMo_{12} decomposes in water, affording unsaturated HPA of the type PMo_{11} and PMo_9 apparently via a mechanism involving alkaline hydrolysis as a result of the decrease in the acidity of the solution. At a concentration of 0.001 M, there is virtually no initial HPAC in the solution.[197] On the basis of general data indicating a decrease in the degree of polymerisation of tungsten and molybdenum following dilution of solutions,[198] it is reasonable to suggest that all the HPAC should hydrolyse in dilute solutions although to different extents and at different rates. One should apparently treat with extreme caution all data concerning dilute (less than 0.01 M) solutions of the HPAC.

Numerous published data on the thermal stabilities of HPAC (see above) should also be treated with care. The assignment of the position of the exothermic peak on the differential thermal analysis curve to the HPAC decomposition temperature is a source of numerous errors.[110] Under these conditions, factors such as the dependence of the rate of decomposition of the HPAC on the heating rate and the possibility of structural changes initiated by the supply of heat are frequently ignored. Thus, decomposition temperatures which are clearly too high have been indicated for HPAC such as (the decomposition temperatures are indicated in brackets in °C) PW_{12} (620), SiW_{12} (530), BW_{12} (420), etc.[199] In this connection, the study[112] where the measurements were accompanied by monitoring involving the ^1H NMR method appears accurate. It was stated in the corresponding communication that not all the HPAC can be obtained in the anhydrous state. Thus H_2W_{12}, BW_{12}, $SiMo_{12}$, and $GeMo_{12}$ decompose during dehydration.

Tsigdinos[110] suggested that the thermal stability be estimated by the method involving a check of the solubility of the HPAC after heat treatment under isothermal conditions. This method demonstrated that the HPAC with molybdenum decompose slowly even at room temperature, the decomposition accelerating above a certain temperature (350 °C for PMo_{12} and 200 °C for $SiMo_{12}$). This method was applied also to other HPAC (Table 3). A HPAC thermal stability series was constructed:

$$PW_{12} > PMo_{12} \gg SiW_{12} > GeMo_{12} > SiMo_{12}.$$

Table 3. Thermal stabilities of HPAC estimated by the Tsigdinos method (2 g of the HPAC was heated for 3 h in air and then stirred in 50 ml of water for 30 min).[196]

HPAC	Isothermal heat-treatment temperature/°C						
	180	250	300	350	370	390	400
$SiMo_{12}$	+	x	x	–	–	–	–
$GeMo_{12}$	o	o	+	–	–	–	x
SiW_{12}	o	o	*	*	*	+	x
PMo_{12}	o	o	o	o	o	+	x
PW_{12}	o	o	o	o	o	o	o

It did not agree with the hydrolytic stability series.[196] The Tsigdinos method makes it possible to estimate to some extent the thermal stability of the HPAC but does not take into account the possibility of solid-phase transformations.

The thermal transformations have been investigated in detail in relation to the following compounds: $SiMo_{12-n}V_n$, $PMo_{12-n}V_n$, PW_{12}, $PW_{11}Z$, and PMo_{12}. It has been shown with the aid of the NMR method that a mixture of $SiMo_{11}V$ and $SiMo_{10}V_2$ decomposes smoothly in the temperature range between 110 and 400 °C.[155] $SiMo_{11}V$ decomposes fully at 300 °C,[200] while $SiMo_{10}V_2$ is relatively stable up to 200 °C and its complete decomposition takes place in the temperature range 300 to 400 °C.[156] No structural rearrangements occur under these conditions.

The heteropolyacids $PMo_{12-n}V_n$, (n = 1 – 3) become insoluble after heat treatment at 200–400 °C,[201] their thermal stability diminishing with increase in n. The data on the decomposition temperatures, determined with the aid of derivatographic measurements and vibrational spectroscopy, are different in the studies of different authors (Table 4). The observed tendency[151,203] appears correct, but, bearing in mind the decrease in solubility,[201] the values obtained appear too high. Complete dehydration takes place in the temperature range between 380 and 410 °C.[202] The mechanism of the thermal decomposition of the vanadium-containing HPAC has been investigated. It was found that during heat treatment vanadium and phosphorus are ejected, compounds with a smaller vanadium content being stabilised under these conditions.[204]

After heat treatment for 2–5 h at 110–400 °C, the acid PW_{12} fully retains its solubility and the ^{31}P NMR spectrum also remains unchanged under these conditions (–15.0 ppm). After heat treatment at 500 °C, the HPAC becomes partly soluble and new lines appear in the ^{31}P NMR spectrum at –12.5 and –13 ppm. Above 600 °C, the PW_{12} is fully insoluble.[205] It has been established by X-ray diffraction that the HPAC begins to change at 400 °C.[111] Salt-forming protons begin to be removed at 420 °C without the formation of the WO_3 phase.[206,207] Different investigators apply the same term (anhydride) to the phase formed at 420 °C, but they attribute different structures to it: $PW_{12}O_{38.5}$[208] or $PW_{12}-O-PW_{12}$.[207] The problem of the real structure of PW_{12} in the temperature range 400–500 °C remains obscure.

Table 4. Decomposition temperatures of HPAC of the type $PMo_{12-n}V_n$.

HPAC	n	T_{decomp}/°C	Ref.
PMo_{12}	0	433	203
$PMo_{11}V$	1	442	151
$PMo_{10}V_2$	2	412	151
PMo_9V_3	3	396	151
PMo_8V_4	4	293	203
$PMo_{12-n}V_n$	0–3	460	202

The thermal stability of complex HPAC of the type $PW_{11}Z$ (Z = Ti, Zr, Bi, Ce) has been investigated by IR and ^{31}P NMR spectroscopy after heat treatment under isothermal conditions. It was found that $PW_{11}Ti$ and $PW_{11}Zr$ are stable up to 450 °C (the decomposition to oxide phases takes place in the temperature range 450–500 °C), while $PW_{11}Bi$ decomposes partially at temperatures above 150 °C and fully at temperatures above 300 °C with formation of the bismuth salt of PW_{12}. The complex $PW_{11}Ce^{4+}$ begins to be converted into $(PW_{11})_2Ce^{4+}$ even at 150 °C and disappears from the thermolysis products in the temperature range 300–400 °C depending on the heat treatment time. After heat treatment, the specimens dissolve incompletely owing to the formation of Ce^{3+} salts. Owing to the subsequent decomposition of $(PW_{11})_2Ce^{4+}$, PW_{12}, H_3PO_4, and $PW_{11}Ce^{3+}$ appear in the thermolysis products. In terms of their thermal stabilities, cerium-containing HPAC can be arranged in the following sequence:[143]

$$PW_{11}Ce^{3+} > (PW_{11})_2Ce^{4+} > PW_{11}Ce^{4+}.$$

Numerous studies have been devoted to the problem of the thermal stability of PMo_{12}. Most information has been obtained by means of a combination of the methods of thermal analysis, X-ray diffraction, and ^{31}P NMR spectroscopy.[197,209] The PMo_{12} specimens retain their complete solubility after heating to 350 °C. At 385 °C, the specimens still dissolve almost completely but more slowly. After heat treatment at 400 °C and above, the specimens dissolve only partially, the Mo : P ratio in the solutions differing from 12 : 1.[197] The following scheme has been proposed for the thermal transformation on the basis of the results:[209]

$$H_3PMo_{12}O_{40}\cdot n\,H_2O \underset{n\,H_2O}{\overset{200-350\,^\circ C}{\rightleftharpoons}} H_3PMo_{12}O_{40} \underset{\sim 1.5\,H_2O}{\overset{385\,^\circ C}{\rightleftharpoons}}$$

$$\rightleftharpoons H_xPMo_{12}O_{38.5+0.5x} \xrightarrow{> 400\,^\circ C}$$

$$\longrightarrow (PMo_{12}O_{38.5})_n + MoO_3 + (MoO_2)_2P_2O_7 \xrightarrow[50\%]{450\,^\circ C}$$

$$\longrightarrow MoO_3 + (MoO_2)_2P_2O_7$$

$x \sim 0.1$

The phase with $x = 0.1 - 1.0$ is readily soluble in air with a humidity of 80%–90% and is converted into PMo_{12} in 2–4 days. It has been suggested[197] that the $(PMo_{12}O_{38.5})_n$ phase is the cationic-anionic complex $[PMo_{12}O_{39}^{-}][PMo_{12}O_{38}]^{+}$. The anionic part of the complex readily interacts with water, while the cationic component reacts with difficulty but also with regeneration of the initial HPAC.

The formation of the anhydride (or anhydride phases) is apparently a common feature of those HPAC which can exist in the anhydrous state. A partial loss (5%–10%) of protons occurs even on simple dehydration of the HPAC.[112] A gradual loss of protons in the temperature range 300–450 °C has also been noted for ZnW_6Mo_6.[149]

The decomposition temperatures of the mixed HPAC $SiMo_{12-n}W_n$ depend directly on n and have intermediate values between those for $SiMo_{12}$ and SiW_{12}.[210]

The Keggin heteropolyanions are capable of combining with electrons reversibly.[1] The corresponding HPAC also retain this property. Thus it has been possible to reduce PW_{12},[1] SiW_{12}, BW_{12}, H_2W_{12} [211] (by the addition of 6 $\bar{e}$), $SiMo_{12}$,[128] and PMo_{12} [212] (by the addition of 4 $\bar{e}$), fluorine-containing metatungstic acids[213] (by the addition of 6–24 $\bar{e}$), and many other HPAC (by the addition of 1–2 $\bar{e}$). The reduction has different effects on the properties of the HPAC. Thus the compound $AsMo_{10}V_2$ (provided that it exists) loses vanadium after the addition of two electrons.[161] The tungsten-containing compounds do not undergo a change in composition and structure on reduction (at least after the addition of 6 $\bar{e}$). The molybdenum-containing HPAC frequently undergo the isomerisation $\alpha \rightarrow \beta$.[1,110,212] For example, the following reactions take place on reduction in solution:

$$\alpha\text{-}PMo_{12} \xrightarrow{2^-} \alpha\text{-}PMo_{12}(2^-) \longrightarrow$$

$$\longrightarrow \beta\text{-}PMo_{12}(2^-) \longrightarrow \beta\text{-}PMo_{12}(4^-) + \beta\text{-}PMo_{12}$$

$$\downarrow 2^-$$

$$\beta\text{-}PMo_{12}(4^-)$$

The stable form β-PMo_{12} (4 $\bar{e}$) is rapidly reconverted into α-PMo_{12} on oxidation in water. In aqueous dioxane, this process is slower.[212] It is believed that α-$SiMo_{12}$ behaves similarly.[1,110] However, it has been found by X-ray diffraction that the reduced $SiMo_{12}$ (4 $\bar{e}$) has the structure of the α-isomer.[214]

The thermal stability of the reduced HPAC has been investigated in relation to $SiMo_{12}$. It was found that the specimens of the reduced HPAC are more stable than the initial $SiMo_{12}$. The reduced HPAC β-PMo_{12} (4 $\bar{e}$) is stable in aqueous solution up to 180 °C and is much superior in this respect to α-PMo_{12}.[215]

A high acidity is a most important property of the HPAC, which makes it possible to devise effective acid catalysts based on

Table 5. Acid dissociation constants of the HPAC in various solvents at 25 °C.[217]

HPAC	Acetone			Ethanol			Acetic acid
	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1
H_3PW_{12}	1.6	3.0	3.98	1.6	3.0	4.1	4.77
$H_4PW_{11}V$	1.8	3.2	4.37	–	–	–	4.74
$H_5PW_{10}V_2$	–	–	–	–	–	–	4.78
H_4SiW_{12}	2.0	3.61	5.3	2.0	3.96	6.3	4.97
H_3PMo_{12}	2.0	3.62	5.3	1.8	3.41	5.1	4.70
H_4PMo_{12} (1 $\bar{e}$)	2.1	3.69	5.5	1.9	3.77	5.9	
$H_4PMo_{11}V$	2.1	3.73	5.6	1.9	3.74	5.8	4.68
H_4SiMo_{12}	2.1	3.90	5.9	–	–	–	4.78
H_4GeW_{12}	–	–	–	–	–	–	4.25
$H_5GeW_{11}V$	–	–	–	–	–	–	4.65
$H_6GeW_{10}V_2$	–	–	–	–	–	–	4.60
$HClO_4$	–	–	–	–	–	–	4.87
HBr	–	–	–	–	–	–	5.6
H_2SO_4	–	–	–	–	–	–	7.0
HCl	4.0	–	–	–	–	–	8.4
HNO_3	–	–	–	3.57	–	–	10.1

them. A lot of space is always devoted to this property in reviews concerning the applications of the HPAC. The acidity of the Keggin HPAC has been investigated by various methods, which include the indicator method, the measurement of the diffusion coefficients and ionic conductivities, ion exchange, thermal desorption of bases, ^1H NMR spectroscopy,[20] kinetic methods,[10,13,125,216] and measurement of dissociation constants in solutions (Table 5).

It has been shown that all the HPAC investigated are strong multibasic Brønsted acids. In solutions, they are stronger than inorganic acids such as H_2SO_4, HBr, HCl, HNO_3, and even $HClO_4$. This is due to the large size of the HPA (diameter 10–12 Å) combined with a relatively low charge. In water, the Keggin HPAC are fully dissociated and it is impossible to determine the first three dissociation constants. However, this can be done in polar organic solvents (see Table 5). The weak dependence of the strength of the HPAC on their composition is striking, although here too one can differentiate certain characteristic features: (1) the tungsten-containing HPAC are stronger than the molybdenum-containing HPAC; (2) with increase in the basicity of the HPAC, their acidity diminishes; (3) the acidity of the HPAC diminishes after reduction.

Some doubts about the measurements of the dissociation constants arise from the fact that they were made for highly dilute solutions ($\sim 10^{-5}$ M) and the individuality of the HPAC in them had not been confirmed. However, there are grounds for the assumption that the correction for the hydrolysis of the HPA may influence at the same time the dissociation constants of the HPAC without affecting the general trends observed.

After the introduction of vanadium atoms into the HPAC, their basicity increases whilst their acidity falls. At the same time, HPAC such as PMo_9V_3 and PW_9V_3 are protonated even in their solutions.[218,219] Not all the protons are equivalent in the pentabasic GaW_{12}.[220] The reduced PMo_{12} and $SiMo_{12}$ (4 $\bar{e}$) contain protons bound to the heteropolyanion, but they are all equally strong acids as regards the first 3–4 protons.[221,222] Even the highly reduced $H_2W_{12}F$ (12 $\bar{e}$) affords an amorphous brown powder, having the general composition $H_{19}W_{12}O_{39}F$, which retains its acid character.[213]

The acidity of concentrated solutions of HPAC in water is greater than the acidity of solutions of sulfuric and perchloric acids at the same concentration by 1–1.5 units of the Hammett acidity function H_0.[13,217] The acidity of concentrated solutions of HPAC diminishes in the sequence

$$SiMo_{12} > PMo_{12} > SiW_{12} \sim PW_{12} .$$

This sequence does not agree with that of the dissociation constants possibly owing to the salt effects or the influence of hydrolysis.

The acidities of HPAC in nitrobenzene have been estimated from the formation constants of complexes with chloral hydrate. The following series was obtained:[13]

$$PW_{12} > PMo_{12} > SiW_{12} \approx GeW_{12} > SiMo_{12} > GeMo_{12} .$$

It follows from the data presented that the acidities of different HPAC in solutions vary in different ways with concentration and the solvent.

The mixed HPAC of the type $XMo_{12-n}W_n$ also exhibit a high acidity in solution, the latter increasing with increase in n.[135,223] A high acidity is apparently a common feature of all the Keggin type HPAC.

It has been shown by conductimetric, IR spectroscopic, and thermal desorption methods that the HPAC retain a high acidity also in the solid state (higher than that of aluminosilicate). In anhydrous HPAC, the protons are localised, but their mobility increases at temperatures above 150 °C for PW_{12} and SiW_{12} and above 250 °C for PMo_{12} and $SiMo_{12}$. The catalytic activities of the solid HPAC in acid-catalysed reactions usually decrease in the sequence

$$PW_{12} > SiW_{12} \approx PMo_{12} > SiMo_{12} ,$$

which agrees fully with the acidity series in solutions.[13]

According to adsorption calorimetric data, the proton centres of PW_{12} are fairly uniform and have strengths similar to those in H-mordenite; PW_{12}, which is believed to be the strongest acid among the HPAC, has acid centres with $H_0 < -8.2$.[20] Superacids with $H_0 = -14.52$ and even less can be obtained by combining the HPAC with $SbCl_5$.[224]

The distribution of the acid centres of PW_{12} and SiW_{12} in terms of strength has been investigated in detail by the indicator method combined with titration by n-butylamine (Fig. 2). The largest number of strong acid centres with $H_0 \leqslant -5.6$ have been observed in the HPAC after heat treatment in the temperature range 300–400 °C, their number diminishing sharply above 400 °C. The compound PW_{12} has a larger number of acid centres than SiW_{12}.[225] Such behaviour of the HPAC agrees well with their thermal stability data.

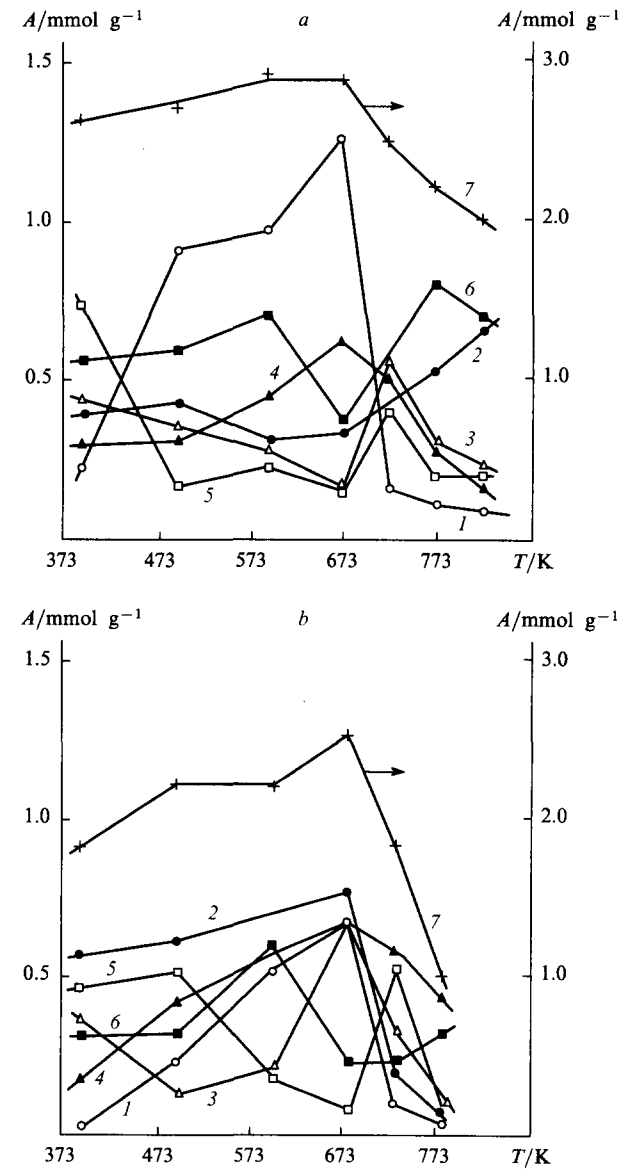


Figure 2. Distribution of the acid centres (A) in PW_{12} (a) and SiW_{12} (b) as a function of temperature.[225] Theoretical numbers of proton centres: 1.04 for PW_{12} and 1.39 for SiW_{12}. Hammett acidity functions: (*1*) $H_0 \leqslant -5.6$; (*2*) $-5.6 < H_0 < -3.0$; (*3*) $-3.0 < H_0 < 1.5$; (*4*) $1.5 < H_0 < 3.3$; (*5*) $3.3 < H_0 < 5.0$; (*6*) $5.0 < H_0 < 6.8$; (*7*) $H_0 \leqslant 6.8$.

The acidity of the HPAC $PMo_{12-n}V_n$ ($n = 0 - 3$) has been investigated by the method involving the thermal desorption of bases. After the introduction of vanadium into the PMo_{12} molecule, the acid centres become nonuniform and their strength and number decrease with increase in n.[226] After evacuation at 350 °C, such HPAC acquire the Mo^{5+} and V^{4+} centres and the Lewis acidity associated with them.[227]

HPAC with $X = P^{5+}$, in particular PW_{12}, PMo_{12}, and $PMo_{12-n}V_n$, are most important in practice because of their relatively high stability and availability. It is not fortuitous that all the examples of the industrial use of HPAC as catalysts known hitherto are based on the application of precisely these HPAC. The HPAC PW_{12} became exceptionally important for acid catalysis, since it has the highest thermal stability and acidity and the methods for its synthesis have been developed in fair detail. In Russia, PMo_{12} is cheaper but has poorer technological properties (lower resistance to hydrolysis and to the reduction of the anion by the organic medium).

2. Heteropolyacids with the Dawson structure

The structure of compounds of this type was first determined by Dawson in 1953 (Fig. 3). The compositions of the known HPAC with the Dawson structure are presented below (the temperatures of the onset of decomposition in the solid state are indicated in brackets):

α-$H_6P_2W_{18}O_{62}$ (210) [1,3,110,228]	α-$H_6As_2W_{18}O_{62}$ [1,3,110]
α-$H_6P_2Mo_{18}O_{62}$ (>120) [1,3,110,229]	α-$H_6As_2Mo_{18}O_{62}$ [1,3,110]
α-$H_6P_2W_{13}Mo_5O_{62}$ [3]	α-$H_6P_2W_{14}Mo_4O_{62}$ [3]
α_1-$H_6P_2W_{17}MoO_{62}$ [230]	α_2-$H_6P_2W_{17}MoO_{62}$ [230]

The existence of certain HPAC with the Dawson structure requires confirmation. These include $H_6PAsW_{18}O_{62}$[231] and $H_{6+n}P_2Mo_{18-n}V_nO_{62}$.[232] There are comparatively few compounds of this type. There is also little information about them.

Investigators have not been very active in the synthesis and study of the HPAC with the Dawson structure. Apart from those indicated above, $X_2W_{17}Z$, where $X = As^{5+}$ or P^{5+} and $Z = Sn^{4+}$, Ge^{4+}, Mn^{3+}, Co^{3+}, Fe^{3+}, or Cr^{3+}, have been obtained by cation exchange in the form of dilute aqueous solutions.[190,233-235] Nothing is known about the possibility of their existence in the solid state or in the form of concentrated solutions. The heteropolyacid $P_2W_{17}Ce^{4+}$ has not been obtained, while $P_2W_{17}Ti$ exists in a concentrated solution (with a content of 43%) only in a mixture with other HPAC.[142] Dawson β-heteropolyacids have not been obtained. The synthesis of β-P_2W_{18} in a concentrated solution has been reported,[231] but it was subsequently found that, when the solution of the salt is acidified, the HPAC decomposes to PW_{12} and α-P_2W_{18}.[142]

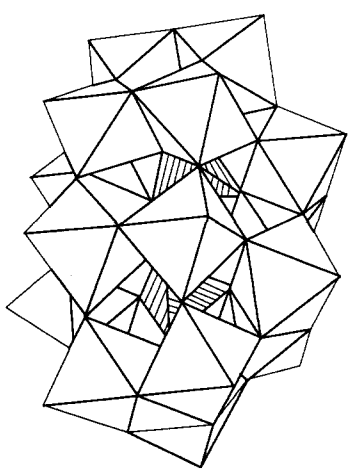


Figure 3. The structure of the Dawson HPAC (α-isomer). The two XM_9 fragments of the Keggin HPA are joined together to form a dimer.

In highly acid solutions, the HPAC α-P_2W_{18}, α-As_2W_{18}, and α-P_2Mo_{18} are entirely stable and are actually more stable than the corresponding Keggin HPAC (α-P_2W_{18} is very stable on hydrolysis in water, although α-P_2Mo_{18} is less stable) (Table 2). In contrast to these compounds, α-As_2Mo_{18} decomposes slowly in the presence of strong acids.[110]

The thermal stability of α-P_2W_{18} has been studied in relative detail. It has been found by differential thermal analysis at a heating rate of 2.5 K min^{-1} that α-P_2W_{18} is dehydrated at 350 °C. Although the DTA curve did not show a distinct exothermic peak, which is usually identified as the HPAC decomposition point, it was concluded that α-P_2W_{18} decomposes at 640 °C.[236] Other workers[207] noted that the behaviour of α-P_2W_{18} on heating is different from that of PW_{12}. They did not detect the anhydride and postulated (without any evidence) that this HPAC decomposes immediately to WO_3, but it was not clear what was the decomposition temperature. It was noted that, after heat treatment at 400 °C for 2 h, the HPAC ceased to dissolve. Subsequently, the same workers[237] recorded the ^{31}P NMR spectra of the heat-treated specimen but these did not throw light on the situation either.

In the most thorough investigation,[228] the thermal transformations of α-P_2W_{18} were investigated by a set of methods: differential thermal analysis (DTA) (heating rate 2.5 K min^{-1}), ^1H NMR, and IR spectroscopy. It was shown that the anhydrous HPAC cannot be obtained and that the last phase retaining the structure of the initial HPAC is $H_6P_2W_{18}O_{62}.2.6H_2O$ and all the protons in this phase are nonhydrated. The phase is formed in the temperature range from 225 to 250 °C and on further increase of temperature the protons are gradually eliminated. The crystallisation of $18WO_3.P_2O_5$ begins at a temperature of about 610 °C (at the selected heating rate), but the deformation of the structure of the initial HPAC was already noted at 210 °C. It remained obscure which phases exist in the temperature range 210-610 °C.

The thermal transformations of α-P_2Mo_{18} were also investigated combining the DTA and IR and ^1H NMR spectroscopic methods. Four endothermic effects due to the dehydration and partial decomposition of the HPAC were observed in the temperature range 120-300 °C. It was discovered that the phase $H_6P_2Mo_{18}O_{62}.3H_2O$ with non-hydrated protons was formed at 270 °C. On further heating, a change in the HPAC structure was observed and the oxide phase crystallised at 530 °C.[229] On thermolysis, α-P_2W_{18} and α-P_2Mo_{18} behave similarly.

The Dawson heteropolyacids can also be reduced without change in structure, at least on addition of 6 $\bar{e}$,[238] the reduction occurring more readily than that of the corresponding Keggin HPAC.[110] It has been found[238] that stable Dawson HPAC have been reduced by the addition of an odd number of electrons.

The direct determination of the acid salts of Dawson HPAC by the indicator method is difficult owing to their colour. It has only been possible to demonstrate[239] that H_0 for P_2W_{18} is less than −3.0. However, according to certain indirect data, it is possible to infer a high acidity of the Dawson HPAC. Thus all the protons of P_2Mo_{18} (2 $\bar{e}$) and P_2Mo_{18} (4 $\bar{e}$) are titrated (8 and 10 respectively), and only in P_2Mo_{18} (6 $\bar{e}$) the last two protons are not titrated.[238] The reduced P_2W_{18} (2 $\bar{e}$) is also a strong acid, all eight of its protons being titrated.[240] It has been noted that the reduced tungsten HPAC are stronger acids than the reduced molybdenum HPAC.[238] In the acid-catalysed conversion of methanol, P_2W_{18} is almost as active as PW_{12} even after preliminary reduction with hydrogen.[239] On the other hand, in the synthesis of *tert*-butyl methyl ether, the Dawson HPAC proved actually more active than the Keggin acids,[13] which indicates not only their very high acidity but also the specificity of their catalytic action. In the decomposition of isobutyl

propionate, P_2W_{18} is less active than the Keggin HPAC,[125] but these data require confirmation, since the question of the thermal stability of α-P_2W_{18} is not clear — the HPAC may change with the conditions of their preparation (evacuation for 8 h at 150 °C).[125]

The methods of synthesis of the Dawson HPAC have been less thoroughly developed and are more difficult than for the Keggin HPAC. This in fact accounts also for the small number of studies in which the HPAC were used as catalysts. Conditions for the synthesis of α-P_2W_{18} and α-P_2Mo_{18} by electrodialysis in almost quantitative yields have been discovered recently.[142] Only the ammonium salt of P_2W_{18} is manufactured in Russia, whilst other Dawson HPAC or their salts are not.

No examples of the practical use of the Dawson HPAC are known. One may mention only a Japanese patent[241] in which it is stated that P_2Mo_{18} may be employed in the industrial hydration of isobutene instead of the unstable PMo_{12}.

3. Other heteropolyacids and isopolyacids

The compositions of other isopolyacids and heteropolyacids, different from the Keggin and Dawson HPAC, the existence of which has been reliably established are presented below (the temperatures of the onset of decomposition in the solid state are indicated in brackets in °C):

$H_6As_2W_{21}O_{69}$ [1,142]
$H_8TeMo_6O_{24}$ (Anderson) [243]
$H_9CrMo_6O_{24}$ [3,110,142,245]
$H_5IMo_6O_{24}$ [3,110]
$H_8ThMo_{12}O_{42}$ (125) [110,246]
$H_8UMo_{12}O_{42}$ (120) [110,247]
$H_2Ln_2XMo_{12}O_{42}$ [249]
$H_9NaF_6W_{18}O_{56}$ [251]
β-$H_4Mo_8O_{26}$ [252]
$H_6P_2W_{21}O_{71}$ (150) [242]
$H_9FeMo_6O_{24}$ [3,110,244,245]
$H_9CoMo_6O_{24}$ [3,110,142,245]
$H_8CeMo_{12}O_{42}$ (Dexter–Silverston) [3,110]
$H_8NpMo_{12}O_{42}$ [248]
$H_6MnMo_9O_{32}$ [110,250]
$H_{10}(PW_{11}O_{39})_2Ce$ (300) [143]
$H_8Mo_{36}O_{112}$ [253].

The existence of certain HPAC requires confirmation:

$H_9AlMo_6O_{24}$ (270) [110,254]
$H_{11}(SiW_{11}SnO_{39})_2Co(CO)_3$ [167]
$H_9GaMo_6V_6O_{24}$ (270) [110,254]
$H_9(PW_{11}SnO_{39})_2PdC_3H_5$ [167].

The structures of many HPAC are unknown:

h-$H_5BW_{12}O_{40}$ [1]
$H_{16}S_2W_{16}V_4O_{72}$ [144]
$H_8VMo_6O_{24}$ [257]
$H_2W_{10}VO_{33}$ [259]
$H_4SW_8V_2O_{34}$ (225–300) [260]
$H_6As_2Mo_2O_{12}$ [3]
$V_2O_5 \cdot I_2O_5$ [3]
$WO_3 \cdot n H_2O_2$ ($n = 0.4-0.7$) [262]
$Te^{4+}W_{18}$ [263]
$Te^{4+}W_8V_4$ (300) [173,174]
$Se^{4+}W_{12}$ (47) [168,171]
$Se^{4+}W_8V_4$ (187) [171]
$Se^{4+}W_7V_3$ [265]
$Sb^{3+}-W$ [266]
M–F–W (M = Nb, V, Fe, Al) [267]
$As^{3+}-W$ [268]
$H_{10}NiW_{17}F_4O_{55}$ [255]
$H_6V_2Mo_{12}O_{44}$ [256]
$H_4V_2W_8O_{31}$ [258]
$H_{18}W_{24}VO_{83}$ [259]
$10\,WO_3 \cdot V_2O_5$ [261]
$H_3AsMo_3O_{13}$ [3]
BeW_9 [110]
$Te^{4+}W_{12}$ (200) [169,170]
$Te^{4+}W_9V_3$ [173]
$W:Te^{6+} = 4-18$ [264]
$Se^{4+}W_{10}V_2$ [172]
$Se^{4+}W_8V_3$ [265]
$Se^{4+}W_6V_3$ [265]
$As^{5+}-W$ [266]
M–F–Mo (M = V, Ti) [267]

Heteropolyacids the existence of which is open to doubt:

$H_8CeMo_{10}O_{36}$ [269]
$H_8CeW_{12}O_{42}$ [270]
$H_4CeW_8O_{28}$ [270,271]
$H_6ThUW_{18}O_{61}$ [272]
$H_8CeMo_8O_{30}$ [269]
$H_6CeW_{10}O_{35}$ [270]
$H_5CeW_8O_{28}$ [271]
$H_8SiW_{11}O_{39}$ [273]

The heteropolyacids β-$H_4Mo_8O_{26}$, $H_8Mo_{26}O_{112}$, BeW_9, $H_{10}NiW_{17}F_4O_{55}$, $H_8CeMo_{10}O_{36}$, $H_8CeMo_8O_{30}$, $H_5CeW_8O_{28}$, and $H_6ThUW_{18}O_{61}$ have not been isolated in the solid state. The HPAC belonging to the series with the Anderson structure are most numerous (Fig. 4). Dilute solutions of GaW_6[274] and $NiMo_{6-n}W_n$ ($n = 0-6$)[275] have been obtained by cation exchange, but nothing is known about the stability of these HPAC.

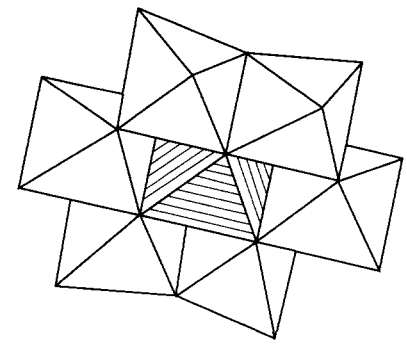


Figure 4. The structure of the Anderson HPAC. Six MO_6 octahedra surround the central XO_6 octahedron.

As a rule, the Anderson HPAC (except the HPAC with $X = I^{7+}$) are tribasic–tetrabasic, whereas the remaining protons are rigidly bound to the HPA. The stability of such HPAC is low. Thus $FeMo_6$ and $CoMo_6$ are stable in aqueous solutions for several weeks,[245] but in the solid state all the Anderson HPAC can be isolated only by evaporation at a low temperature. The strength of their acid centres is unknown. One can only postulate that the titratable protons are fairly weakly bound to the HPA. Examples of the use of such HPAC are also unknown.

The structure of the molybdenum HPAC with heteroatoms having high coordination numbers was first described correctly by Dexter and Silverton in 1968 (Fig. 5).[1] The stability of such HPAC is low. In aqueous solutions, they decompose gradually, but their hydrates can be stored for some time.[246,247] On heating, UMo_{12} loses part of the water of crystallisation in the temperature range from 40 to 120 °C and subsequently the compound begins to decompose. Its analogues behave similarly.[247] The minimum degree of hydration of $ThMo_{12}$ corresponds to ten water molecules. The compound $ThO_2 \cdot 12MoO_3 \cdot 4H_2O$ undergoes rapid dehydration on heating to 200 °C. It dissolves in water, but is not the initial HPAC. Slow heating to 125 °C leads to the same compound, but it has now lost its solubility. In aqueous solutions, these HPAC decompose slowly to complexes of the type X_nMo_{12} ($n = 2-3$).[246] As a result, it becomes possible to obtain HPAC with a ratio $Mo:X < 12$, which are in fact mixtures of the initial HPAC and their complexes. The structure of one of these complexes, namely $H_2Nd_2(H_2O)_{12}UMo_{12}O_{42} \cdot 12H_2O$, has been determined (Fig. 6). This compound is not a salt of a HPAC, since the neodymium atom is bound covalently to the HPA. This is a dibasic

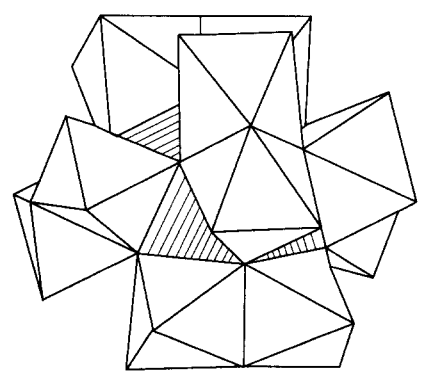


Figure 5. The structure of the Dexter–Silverton HPAC: 12 MoO_6 octahedra surround the central XO_{12} icosahedron.

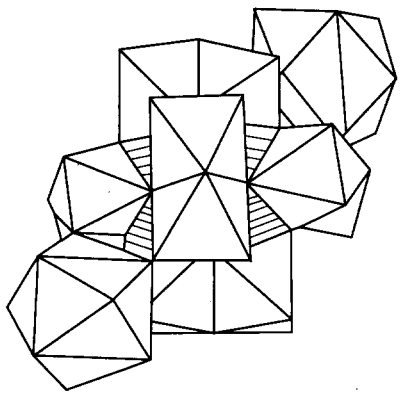


Figure 6. The structure of the HPAC $H_2Ln_2XMoO_{12}O_{42}$: two tri-capped trigonal Ln^{3+} prisms are joined to the Dexter–Silverton anion.

complex HPAC — a strong acid with respect to both protons. It is almost insoluble in water (7×10^{-4} M)[249,276] and is therefore of interest for heterogeneous acid catalysis as the only example of an insoluble HPAC.

Among other similar complex HPAC, dilute aqueous solutions of acids having the compositions $CeMo_{12}Nb$ and $CeMo_{12}Nb_2$ have been obtained. Their structures have not so far been established.[269]

The Dexter–Silverton heteropolyacids are strong acids. Thus five of the eight protons in $NpMo_{12}$ form H_3O^+ ions,[248] while $CeMo_{12}$ is also active in the acid-catalysed synthesis of *tert*-butyl methyl ether, like PMo_{12}.[277] The synthesis of the ether is the only known attempt to employ HPAC of a similar type as a catalyst, probably in view of their low availability and low stability.

The HPAC of the type P_2W_{21} has been investigated in relatively high detail (Fig. 7). It is entirely stable on storage in solution and in the solid state. In their study of the thermal stability of P_2W_{21} by the DTA method alone, French investigators[207] concluded that P_2W_{21} is also stable, like PW_{12}. Later they found[237] that nevertheless P_2W_{21} and PW_{12} behave differently on heating. It was found with the aid of IR and ^{31}P NMR spectroscopy that, on heating in the temperature range 150–300 °C, P_2W_{21} is converted into PW_{12} both in solution and in the solid state. Measurements of the Hammett acidity functions H_0 of concentrated aqueous solutions showed that,

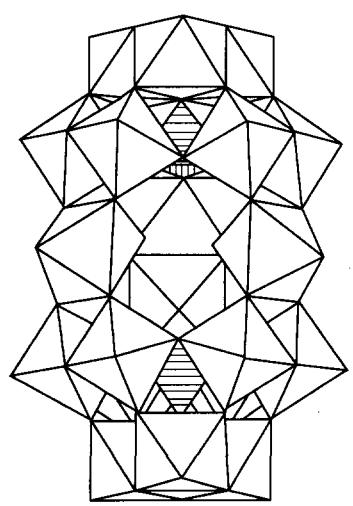


Figure 7. The structure of the HPAC $H_6P_2W_{21}O_{71}$: three $WO_5(H_2O)$ octahedra connect two PW_9 fragments of the Keggin HPA.

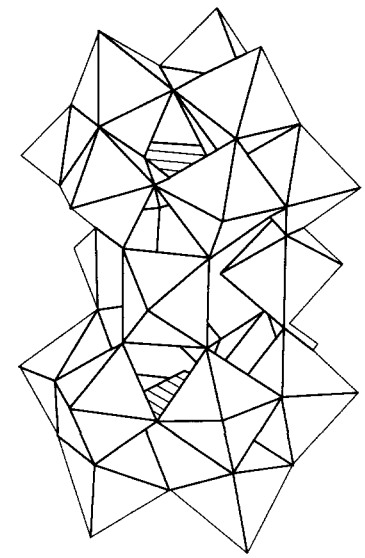


Figure 8. The structure of the HPAC $H_6As_2W_{21}O_{69}$: the $WO_5(H_2O)$ octahedron and two WO_5 pyramids connect two AsW_9 fragments in which the WO_6 octahedra surround the AsO_3 pyramids.

at equal concentrations, P_2W_{21} is actually a stronger acid than PW_{12}, although their acidities are approximately the same when calculated per proton.[242] Examples of the use of P_2W_{21} are unknown. It has been suggested that the HPAC $As_2^{5+}W_{21}$ exists, but it has not been isolated. The HPAC $As_2^{3+}W_{21}$ has a similar structure (Fig. 8) but its properties have not been studied.

NaF_6W_{18} is extremely resistant to the action of acids and alkalis (Fig. 9).[251,278] Apparently complex HPAC based on it exist.[251,255] The properties of similar HPAC have also not been investigated; their study is probably held back by the inconvenient methods of synthesis.

The heteropolyacid $(PW_{11})_2Ce^{4+}$ (Fig. 10) is entirely stable in the solid state at moderate temperatures. Above 300 °C, the following transformations take place:

$$(PW_{11})_2Ce^{4+} \longrightarrow PW_{12} + PW_{11}Ce^{3+} + H_3PO_4.$$

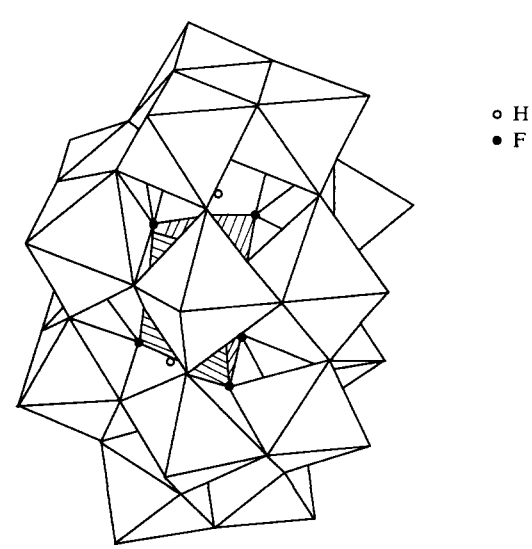


Figure 9. The structure of the HPAC $H_7H_2NaF_6W_{18}O_{56}$: the trigonal Na^+ prism and two protons occupy the central cavity of the HPA having a structure close to that of the Dawson HPA.

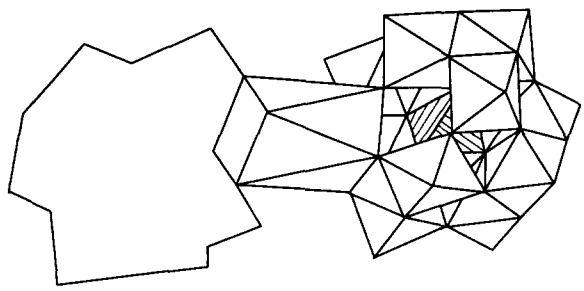


Figure 10. The structure of the HPAC $H_{10}(PW_{11}O_{39})_2Ce$: the square CeO_8 antiprism connects two PW_{11} fragments of the Keggin HPA.

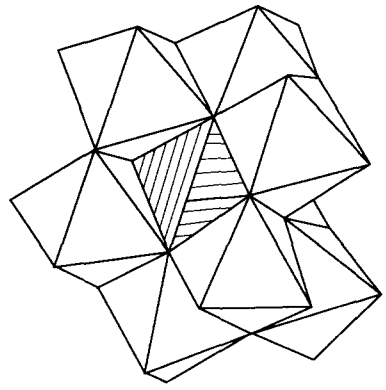


Figure 11. The structure of the HPAC $H_6XMo_9O_{32}$: nine MoO_6 octahedra surround the central XO_6 octahedron.

The mixtures of thermolysis products always contain also the initial HPAC. The decomposition to oxide phases is observed in the temperature range 450–500 °C.[143] Probably other complex HPAC with lanthanide and actinide ions exist.

The heteropolyacid $Mn^{4+}Mo_9$ (Fig. 11) can be obtained in the solid state, but its solutions are relatively unstable.[110,250] The stability of the acid $H_8As_4Mo_{12}O_{50}$, obtained by cation exchange in the form of a dilute aqueous solution, is also low. It is a strong acid: the first four hydrogen atoms dissociate fully and a further four dissociate partially.[279]

Electrodialysis of a solution containing $NaAsO_2$ and Na_2WO_4 in molar proportions of 1:11 afforded a concentrated solution in which 50% of the tungsten was in the form of $H_7AsH_2W_{18}O_{60}$. However, this HPAC was not isolated in the solid state and its properties were not investigated.[142]

The heteropolyanions $XP_5W_{30}O_{110}^{x-}$ are stable in strongly acid (6 M HCl) aqueous solutions,[280] which suggests the existence of the corresponding HPAC. However, such HPAC were not specially isolated and investigated.

As already mentioned above, there are a series of HPAC about which it is only known that they exist. As regards the type of their behaviour, one may postulate that these mixed Mo–V and W–V HPAC have the Keggin structure. However, another structure of these acids is also possible. It has been suggested (but not demonstrated) that the S–W–V HPAC has a structure analogous to that of P_2W_{20}.[144] According to ^1H NMR data, all its protons are hydrated,[260] i.e. it is a fairly strong acid.

Heteropolyacids containing an X heteroatom with a lone pair (Se^{4+}, Te^{4+}, Sb^{3+}, As^{3+}) cannot have the Keggin structure (attributed to them previously) by virtue of the coordination structure of the XO_n polyhedron (usually a trigonal pyramid). HPA with the following structures are known for them: $X_2W_{21}O_{69}^{6-}$, $H_2XW_{18}O_{60}^{7-}$, $X_4W_{40}O_{140}^{29-}$, and $X_9W_{21}O_{86}^{19-}$. Probably the HPAC synthesised with such heteroatoms have one of the structures presented above or they are mixtures of HPAC with similar structures. All these HPAC are strong acids[173,263,281] with moderate thermal stability (up to 200 °C), but some of their protons are retained up to 500 °C.[170]

HPAC containing Te^{6+} are strong acids.[264]

The structures of the corresponding Keggin HPAC have been attributed to the acids synthesised in the presence of HF.[267] However, experience gained in a number of investigations[126,251,255] has shown that it is impossible to ignore the influence of F^- on the structure of the HPA and to reduce the effect of HF to the simple effect of an acid. Two versions of the synthesis of such HPAC are known: from the metatungstate[126] or from NaF_6W_{18}.[251] In terms of the conditions in their synthesis,[267] the second version is more probable, but this naturally requires confirmation.

The existence of certain HPAC, indicated in the literature, may be questioned. Thus the HPAC with a Mo : Ce ratio less than 12 were already mentioned. It is known that the Ce^{4+} ion does not form with tungsten HPA having the Dexter–Silverton structure,[1] so that there is also no corresponding CeW_{12} HPAC. The HPAC containing W^{6+} and Ce^{3+} or Ce^{4+} do not exist in a strongly acid medium.[1,142] This can also be said about the HPAC $UThW_{18}$. The heteropolyanion SiW_{11} is a precursor of the acid SiW_{12} and does not exist in the form of a free acid.[1]

Among the isopolyacids, only the Mo^{6+} acids are known in solutions. When the solutions are acidified, cation exchange or electrodialysis affords solutions which are stable for 24 h.[142] It has been suggested that molybdenum is present in these acids in the form of β-Mo_8[252] or Mo_{36}.[253] Such solutions are suitable for the synthesis of MoO_3 or deposited MoO_3/SiO_2 catalysts.[252]

4. Methods of synthesis of heteropolyacids

Several methods of synthesis of HPAC are known. The most general of these involves the acidification of a solution of a mixture of the initial reactants.[1,3,110,139,250]

$$Na_2WO_4 + H_3PO_4 \xrightarrow{H^+} H_3PW_{12}O_{40}$$

$$Na_2WO_4 \xrightarrow{HF} H_{6-n}H_2W_{12}O_{40-n}F_n$$

$$Na_2MoO_4 + Cr(NO_3)_3 \xrightarrow{H^+} H_9CrMo_6O_{24}$$

$$Na_2MoO_4 + NaVO_3 + H_3PO_4 \xrightarrow{H^+} H_{3+n}PMo_{12-n}V_nO_{40}$$

The reaction by no means takes place smoothly in all cases and in conformity with the stoichiometry. Sometimes an excess of the heteroatom is needed (for example, $X = B^{3+}$ or Si^{4+} in the synthesis of XW_{12} or $X = P^{5+}$ or As^{5+} in the synthesis of X_2W_{18}), or the appropriate temperature must be maintained (low for relatively unstable HPAC or actual refluxing for X_2W_{18}), or a definite order of mixing of the reactants is required. If the component containing X is sparingly soluble, special measures must be adopted to transfer it to the solution.[267]

Acidification can be achieved in several ways. The commonest way involves the use of an inorganic acid (usually HCl or H_2SO_4), after which the HPAC is isolated from the solution of the salts by extraction with ether.[1,3,110,250] However, this method of isolation has numerous disadvantages: a narrow range of extractable HPAC (Keggin and Dawson HPAC and HPAC of the type X_2W_{21} and NaF_6W_{18}), among which compounds with low stabilities may decompose during extraction as a result of the very high acidity of the solution, the nonquantitative yield of the HPAC (for example, not more than 80% for PW_{12}[282] and in reality the yield is even less), fire risk, the need to employ an extraneous reagent, a large amount of waste water produced, corrosion of the equipment, and contamination of the products by the inorganic acid. There is also an advantage: the possibility of removing from the HPAC the impurities which are not

extractable by ether (for example unsaturated HPAC) or of separating mixtures of HPAC extractable under the conditions of different acidities. Despite the disadvantages, the method has been used hitherto in industry to synthesise PW_{12} and SiW_{12} and also in laboratory practice.

In another procedure, acidification is carried out by cation-exchange resins.[3,110,250] Almost all the known HPAC can be obtained with its aid. This method can be regarded as the most universal among all those known. It also has its disadvantages and advantages. The former include the need to regenerate the resins, which leads to waste water, and the need to concentrate dilute solutions of the HPAC; the latter include the absence of corrosion, a very high yield of the HPAC (100% with respect to W or Mo), universality, the 'softness' of the acidification, and a high degree of purification as regards cations. The Dexter–Silverton heteropolyacids can be obtained only in this way, since ion exchange makes it possible to remove the cations even from sparingly soluble HPAC salts. After the cation exchange, dilute solutions of the HPAC are obtained, from which the product is isolated either by evaporation or by salting out with an acid.[283] A combination of two methods is also possible — acidification by an acid and ion-exchange resins.[284,285]

The third acidification procedure, the most progressive one, is electrochemical acidification. It consists in the electrochemical removal of the cations from the initial solution and compensating for them with protons. The process is carried out in flow-type electrodialysers (when all the components are in solution) or dialysers of the nonflow type (solutions with precipitates, as in the synthesis of SiW_{12}).[286] The anodic compartment contains a solution of the initial components, while the cathodic compartment contains a solution of alkali. The compartments are separated by a membrane based on a cation-exchange resin. When a current is passed through the apparatus, the cations pass through the membrane into the cathodic compartment and the anolyte is acidified.

Compounds containing tungsten, molybdenum, and heteroanions are incapable of passing through the membrane. On acidification of the anolyte, they interact, forming the HPAC. The alkali accumulates in the catholyte and can be used again to prepare the initial solution. The only side products of the synthesis are gaseous H_2 and O_2, formed as a result of the decomposition of water at the electrodes. The advantages of this method include a high yield of the HPAC (100% with respect to W and Mo), the absence of solid and liquid waste, and the possibility of doing without extraneous reagents. The disadvantages are the use of special equipment, including dangerous equipment (powerful current sources), the need for the additional removal of impurities from the HPAC (for example the excess of X or impurity HPAC), and the need to follow the concentration of the cation in the anolyte. However, the principal advantages of the method — the high yield of the HPAC and the absence of waste — make up for the above disadvantages and therefore the method is being developed actively at the present time.

Almost all the known most important HPAC such as SiW_{12},[286,287] BW_{12} (with additional purification by extraction with ether),[288] PW_{12},[282,289] P_2W_{21},[242] P_2Mo_{18}, α-P_2W_{18}, PMo_6W_6, $CoMo_6$, $PMo_{12-n}V_n$, $PW_{12-n}V_n$, and $PW_{12-n}Nb_n$ ($n = 1, 2$),[142] as well as new HPAC such as $PW_{11}Ti$, $PW_{11}Zr$, $PW_{11}Bi$, $PW_{11}Ce$, and $(PW_{11})_2Ce$[143] have been obtained by the electrodialysis method. A mixture of HPAC, 90% of which comprised $As_2^{3+}W_{21}$ and $H_2As^{3+}W_{18}$, has been obtained in a system containing As^{3+} and W^{6+}. Assessment of the possibilities of electrodialysis led to the conclusion that this method is suitable for the synthesis of HPAC stable in the form of concentrated aqueous solutions. On the basis of this principle, it proved impossible to obtain HPAC of the type β-P_2W_{18}, NaP_5W_{30}, and many others. The limitations of the methods have also been noted. Thus, owing to the chemical processes on slow electrochemical acidification, it is impossible to obtain PMo_{12}. Solutions of certain HPAC (for example, those containing Cr^{3+}) have a high electrical resistance, which prevents cation exchange through the membrane.[142]

Apart from the synthesis of HPAC, electrodialysis is used to obtain H_2WO_4 with an increased purity[290] and metatungstate salts.[291–295] The creation of an industrial electrodialyser with an output of 50–70 tonnes of tungsten per year and an overall membrane area of 2.5 m^2 has been reported.[297]

We may mention yet another (obsolete) acidification method — the method involving the decomposition of salts,[3,110] for example in accordance with the reactions[3]

$$Ba_3H_2W_{12}O_{40} + 3\,H_2SO_4 \longrightarrow 3\,BaSO_4 + H_6H_2W_{12}O_{40},$$

$$Hg_5BW_{12}O_{40} + 5\,HCl \longrightarrow 5\,HgCl + H_5BW_{12}O_{40}.$$

The initial HPAC salts were obtained in their turn with the aid of inorganic acids. Thus this procedure is a modification of the method involving the acidification of the initial solutions by inorganic acids. Previously this method has a preparative value, but nowadays it has lost it.

The method of synthesis of HPAC next in importance involves the interaction of simple oxides (oxides or acids). Thus phosphomolybdic acids can be obtained from H_3PO_4 and $MoO_3(H_2MoO_4)$.

$$MoO_3 + H_3PO_4 \longrightarrow PMo_{12}\ (\text{or } P_2Mo_{18})$$

The composition of the product depends on the reaction conditions: reactant ratio, temperature, and reaction time. For the molar ratio Mo : P = 12, approximately 70% of the molybdenum dissolves in the form of PMo_{12} after refluxing for 3–5 h. After evaporation, the product is isolated in the solid state, but it has to be recrystallised in order to remove the excess H_3PO_4. The best version of the synthesis of PMo_{12} involves the use of a fourfold excess of molybdenum. In this case, the pure acid PMo_{12} is formed immediately, while the excess molybdenum is used for the succeeding cycles of the synthesis. After refluxing with an excess of H_3PO_4 (the optimum ratio is Mo : P = 3) and allowing the mixture to stand for 15–17 days at 20 °C, P_2Mo_{18} is formed. It is best to use MoO_3, since H_2MoO_4 is usually contaminated by ammonia.[3] For the ratio Mo : P = 12, it is possible to attain the complete dissolution of MoO_3 with formation of pure PMo_{12}, provided that one adds to the solution an organic solvent (for example *tert*-butyl alcohol) or a reductant until the attainment of the degree of reduction corresponding to PMo_{12} (4 $\bar{e}$) with subsequent reoxidation.[296] For the ratio Mo : P < 12, mixtures of the HPAC P_2Mo_{18}, PMo_{12}, PMo_{11}, and PMo_9 are obtained[3,197] and the attempt to increase the yield of PMo_{12} by employing an excess of H_3PO_4 (75%–100%) in the synthesis[297] must therefore be recognised as unsuccessful. If the MoO_3 is subjected to preliminary mechanochemical activation, the time required for its dissolution is shortened to several minutes even without using an excess of H_3PO_4 (as happens, for example, in the synthesis of P_2Mo_{18}).[298]

For catalytic purposes it is not always important which of the P–Mo HPAC is present in the solution, since they are all strong acids. Simple dissolution of MoO_3 in a solution with H_3PO_4 (this is achieved using the ratio Mo : Po $\approx$ 6) is sometimes sufficient to obtain an active catalyst.[293,300]

Certain vanadium-containing HPAC can be obtained in the same way. Thus $PMo_{11}V$ is synthesised in a quantitative yield by refluxing a suspension of MoO_3 and V_2O_5 in H_3PO_4 solution with stoichiometric reactant ratios for 5–6 h.[301,302] The heteropolyacid $PMo_{10}V_2$ is more difficult to synthesise: an excess of V_2O_5 and a time of the order of 20 days are required. If hydrothermal conditions are employed, the process is accelerated and in this case it is actually possible to introduce

tungsten into the HPAC.[302] The duration of the synthesis of $PMo_{12-n}V_n$ ($n = 1-6$) is reduced to 1–2 days if V_2O_5 is dissolved beforehand in a dilute solution of H_2O_2 at a low temperature and with the molar ratio $H_2O_2 : V_2O_5 = 1.5-40$.[303]

After a suspension of MoO_3 has been refluxed in a Na_3AsO_4 solution, a solution of the sodium salt of As_2Mo_{18} is formed, from which the HPAC can be isolated by extraction with ether or by cation exchange.[3,250] The heteropolyacids $H_3AsMo_3O_{13}$ and $V_2O_5.I_2O_5$ with hitherto unknown structures have been synthesised by interaction in solutions of oxides or acids.[3]

In the synthesis of tungsten-containing HPAC, the method considered involves considerable difficulties. The reactivities of the initial reactants H_2WO_4 and WO_3 are very low and these compounds hardly dissolve in acid solutions. Only H_2WO_4 freshly precipitated at a temperature below 50 °C reacts with H_3PO_4, affording a yield of the HPAC up to 92%.[3] Apart from PW_{12}, other P–W HPAC are formed under these conditions. These as well as other impurities have to be removed by extraction with ether.[304] The method of synthesis via molybdenum or tungsten halides is a variety of this method. The halides hydrolyse rapidly with formation of molybdenum and tungsten oxy-acids, which immediately react with the heteroatom.[268]

Thus the method of synthesis of HPAC from the initial acids and oxides has limitations associated with the low solubilities or reactivities of the initial compounds. Realistically, one can obtain with its aid only certain HPAC containing molybdenum and vanadium, whereas for the purposes of acid catalysis tungsten-containing HPAC are of greatest interest. In order to facilitate the synthesis or reduce the amount of waste, it is possible to use a combination of methods. For example, WO_3, MoO_3, and V_2O_5 may be dissolved in solutions of Na_2WO_4, Na_2MoO_4, or $NaVO_3$ and the latter can then be acidified by some method.[142] Another application of this procedure involves the synthesis of HPAC/carrier catalysts by forming the HPAC directly on the surface of the carrier.[305,306]

The third method of synthesis of the HPAC, which can be regarded as general, involves their preparation via other HPA or IPA.[1] This method is almost always used in the synthesis of complex HPAC, where the starting materials are unsaturated HPA.[1,142,143]

$$SiW_{11} + Z^{x+} \xrightarrow{H^+} SiW_{11}Z$$

$$PW_{11} + Z^{x+} \xrightarrow{H^+} (PW_{11})_2Z$$

$$P_2W_{17} + Z^{x+} \xrightarrow{H^+} P_2W_{17}Z$$

Bearing in mind the enormous diversity of the ions Z, the unsaturated HPA, and their combinations, there is no doubt that a multiplicity of new HPAC can be obtained by this procedure.

The unsaturated heteropolyanion PW_{11} serves as a source for the synthesis of the acid P_2W_{21}.[242,289] Vanadium-containing HPAC can be conveniently obtained from a simpler HPAC.[307]

$$PMo_{12} + V_2O_5 + H_3PO_4 \longrightarrow H_{3+n}PMo_{12-n}V_nO_{40}$$

$n = 1-3$

Keggin β-heteropolyacids can be readily obtained by reducing (4 $\bar{e}$) Keggin α-HPAC in solutions.[1,110,130,212] HPAC with a definite composition and definite positions of other atoms in the structure can be conveniently constructed from polyunsaturated HPA of the type of PMo_9.[136]

Various HPAC are frequently synthesised from tungsten, molybdenum, and niobium isopolyanions. Almost all the HPAC with Anderson, Dexter–Silverton, and Keggin structures, in which a transition metal ion serves as the heteroatom, have been obtained in this way. In the synthesis, this ion must be retained in solution and, in order to achieve this, the latter must be acid. In such cases, the IPA is the most suitable source of ligands.

$$Mo_4O_{24}^{6-} + Cr^{3+} \xrightarrow{H^+} H_9CrMo_6O_{24}$$

$$H_2W_{12}O_{42}^{10-} + Zn^{2+} \xrightarrow{H^+} H_6ZnW_{12}O_{40}$$

$$H_2W_{12}O_{40}^{6-} + Ga^{3+} \xrightarrow{H^+} H_5GaW_{12}O_{40}$$

Under these conditions, it is also possible to employ isopolyacids as such.[266] In some cases, the use of IPA is particularly preferable. Thus, in order to avoid the formation of P_2W_{21} in the synthesis of PW_{12} by electrodialysis, the PO_4^{3-} anion should be added to the acidified solution only after the complete conversion of the WO_4^{2-} ion into the IPA.[289] The compound $K_7HNb_6O_{19}$ is the only convenient source of niobium in the synthesis of niobium-containing HPAC. The acids $H_2Ln_2XMo_{12}O_{42}$ are obtained from Dexter–Silverton HPAC as such.[249]

Finally, mention should be made of a specific method of synthesis of the HPAC CW_{12} and of its peroxo-analogue by dissolving WC_2 in H_2O_2.[118,119,164]

A method of synthesis of HPAC by the heat treatment of their ammonium or tetraalkylammonium salts may be encountered in certain patents.[181,308,309] However, on thermal elimination of the ammonium cations, the structure of the HPA is disrupted. Such methods may be regarded as methods of synthesis of catalysts whose compositions correspond to those of the initial HPA salts but not the HPAC.

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