ISOPOLYMOLYBDATES AND ISOPOLYTUNGSTATES

KARL-HEINZ TYTKO and OSKAR GLEMSER

Anorganisch-Chemisches Institut der Universität Göttingen, Göttingen, West Germany

I. Introduction

The chemistry of isopolymolybdates and isopolytungstates has been an area of intense activity for several decades. Yet, even today we cannot claim that all the important processes occuring on acidification of a molybdate or tungstate solution have been elucidated. Numerous contradictory reports appearing in the literature right up to the present have repeatedly done more to confuse than to clarify the subject. Thus it is hardly surprising that not a single textbook correctly describes the situation in acidified molybdate and tungstate solutions.

The number of proposals for polyions occurring in such solutions is legion. With little exaggeration it may be said that there is no conceivable species that has not been proposed at some time or other.

Much of the effort involved in this field consists in scrutinizing the experimental conditions, the evaluation of measurements, and the interpretations given in past and present publications. The large number of methods already used in these studies presents a further difficulty. Many of the contradictions abounding in the literature arise from attempts to establish the existence of a given species from very small, often rather doubtful changes in the difference quotient of a physical quantity and the amount of H^+ added with the initial ratio H^+/MO_4^{2-} (M = Mo, W). Yet even the interpretation of obvious breaks or jumps in experimental plots can often cause considerable difficulty, as will be shown later.

This review aims to provide a critical account of the present state of research in the field of isopolymolybdates and isopolytungstates. Such an aim requires that we also take a detailed look at the methods of investigation. Several contradictions in the literature have arisen because the state of the systems was inaccurately defined. Earlier studies will be considered only in so far as the results are still valid or, even if incorrect, have played a significant role in the development of this field. Access to the earlier literature is facilitated by previous reviews or articles with lengthy introductory surveys, particularly those by Lindqvist (*1*), Kepert (*2–4*), Aveston *et al.* (*5*, *6*), Glemser *et al.* (*7*), Jahr and Fuchs (*8*), and Sasaki and Sillén (*9*), as well as the monographs by Souchay (*10*, *11*). Compounds prepared by thermal routes (e.g., from melts) that do not contain discrete anions and, therefore, do not strictly belong to the isopolyanions will not be considered here.

II. Characterization of the Species

A. QUANTITIES P, Z, AND Z^+

The overall equation for formation of isopolymolybdate and isopolytungstate ions in aqueous solution reads

$$pH^+ + qMO_4^{2-} \rightleftharpoons [H_{p-2r}M_qO_{4q-r}]^{(2q-p)-} + r\,H_2O \tag{1}$$

In dealing with H^+/MO_4^{2-} systems it has proved expedient to introduce the following three quantities.

a. The degree of acidification P of *a solution*. This is the molar ratio of H^+ ions *initially* present to MO_4^{2-} ions *initially* present:

$$P \equiv C_{H^+}/C_{MO_4^{2-}} \tag{2}$$

where C is the initial concentration of the species denoted by the subscript. The utility of quantity P in practical work is obvious: its value is obtainable directly from the quantities used (molar numbers, masses, volumes) and can thus also be directly adjusted.

b. The acidity Z of *a solution*. This is defined as the molar ratio of *reacted* H^+ ions to *initially* present $MO_4{}^{2-}$ ions, so that

$$Z = \frac{C_{H^+} - c_{H^+} + K_W/c_{H^+}}{C_{MO_4{}^{2-}}} \tag{3a}$$

In this expression c is the equilibrium concentration of the species denoted by the subscript, and K_W is the ionic product of water. The degree of acidification P and the acidity Z are related by the expression

$$Z = P - \frac{c_{H^+} - K_W/c_{H^+}}{C_{MO_4{}^{2-}}} \tag{3b}$$

It should be noted that Eqs. (3a and b) contain the equilibrium *concentration* of H^+. This necessitates corresponding calibration of the potentiometric measuring technique (glass or quinhydrone electrode).

Quantity Z is required if the experimental results are evaluated with the aid of the law of mass action, in which case measurements have to be performed in a medium of constant high ionic strength, or if

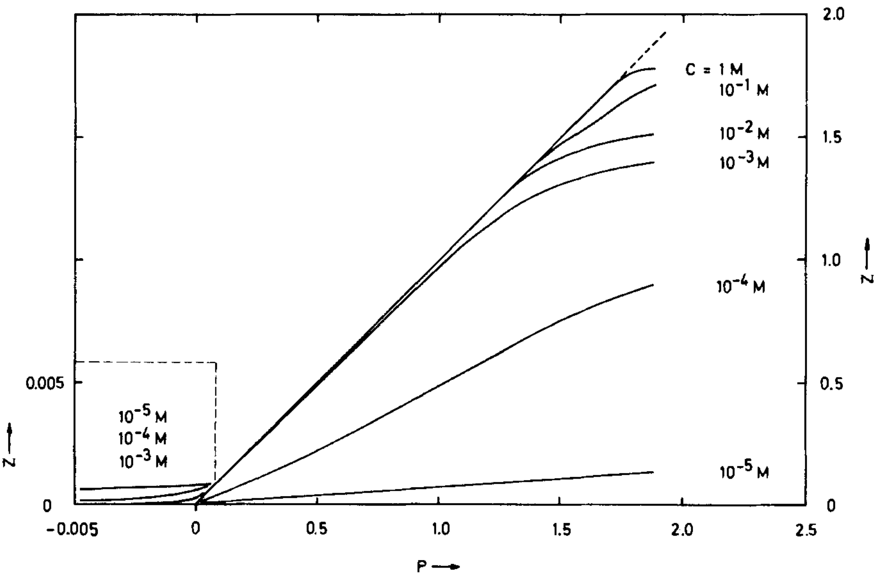

FIG. 1. Relation between Z and P illustrated for the $H^+/MoO_4{}^{2-}$ system [3 M $Na(ClO_4)$ as ionic medium, 25°C].

the equilibrium constant for a reaction indicates that $P \approx Z$ will not apply for the initial ratio $P = p_i/q_i$ (subscript i denotes the polymetalate species under consideration or its formation reaction). The relation between Z and P is shown for the example of the molybdate system in Fig. 1.

c. The Z^+ value of *a polymetalate species* or its *overall formation reaction.* We define this quantity as the ratio of the stoichiometric coefficients of H^+ and MO_4^{2-} in the overall formation reaction (1):

$$Z_i^+ \equiv p_i/q_i \tag{4}$$

To a first approximation, this value, written as a decimal, provides information about the conditions (Z value) for the occurrence of the species i. Expressed as an uncanceled rational fraction, it serves rather to characterize a given species in the absence of a better system of nomenclature (cf. Section II, C).

Regrettably, many authors fail to distinguish between the quantities P and Z, on the one hand, and Z and Z^+, on the other, regarding both symbolism (e.g., using the same symbol for Z and Z^+) and meaning. This is underlined by statements such as "the acidification x denotes the ratio H^+/MO_4^{2-}." The reason for equating these three quantities is that P, Z, and Z^+ do indeed assume identical numerical values in specific cases. Let us assume that we are investigating the formation of the so-called paratungstate A ion,

$$7H^+ + 6WO_4^{2-} \longrightarrow (H^+)_7(WO_4^{2-})_6 \tag{5}$$

(cf. Sections II, C; III, B, 1; and especially V, B, 3, a concerning this formulation of this polyion). Then, assuming complete reaction [large formation constant(s)] of both H^+ and WO_4^{2-} ions, we conclude from the titration result, $P \approx 1.17$ (initial ratio H^+/WO_4^{2-} at "end point") that $Z \approx 1.17$ and, hence, assuming the occurrence of a single reaction, that $Z^+ = 1.17$. Equating P and Z, and Z and Z^+, in this way is permissible only when the system under investigation has a simple structure, i.e., sufficiently large differences in the Z^+ values of the species involved or equilibrium constants favoring the species studied but not favoring species having close Z^+ values. This problem is considered in detail further on (cf. Sections III, A, 3, a; III, A, 4, a; and III, A, 7).

B. CONCENTRATION DATA FOR POLYMETALATE IONS

Concentration data for mono- and polymetalate species usually refer to 1 M atom. For example, a solution of a species $Mo_7O_{24}^{6-}$ whose concentration is given as 1 molar contains 1/7 mole of $Mo_7O_{24}^{6-}$/liter.

Only three reasons will be given for justification of this procedure: (a) the value of q is still unknown for some polymetalate species so that there is no other choice; (b) for several species of various degrees of aggregation coexisting in equilibrium, there is likewise no alternative choice; and (c) quantities such as extinction or intensity coefficients are similar in magnitude for all mono- and polymetalate anions when referred to 1 M atom. If they were not based on the concentration as defined above, then the spectrum of, e.g., the 36-molybdate ion would appear about 36 times more intense than that of the monomolybdate ion plotted on the same scale. (Logarithmic representation of the intensity is undesirable since the spectra are mainly evaluated with respect to their intensity.)

In order to distinguish the concentrations referring to 1 M atom or quantities involving concentration (e.g., extinction or intensity coefficients) from the others, special labels should be used, e.g., c', ε'. In cases complying with condition b, the symbol for the initial (total) concentration (C) is always used.

If the law of mass action is applied, then the equilibrium concentration referring to q M atoms must of course be used.

Assessment of the relative significance acquired by the various species under a set of given conditions [degree of acidification, Z value or pH value; (initial) concentration; time; temperature] makes use of the species fraction F_i, i.e., that fraction of M present as the species under discussion.

C. Nomenclature

A further source of frequent misunderstanding is the nomenclature employed. For instance, we take the term tetrametalate (4-metalate) to mean a salt whose discrete (oxo-)anion contains 4 M atoms. However, the designation is also used for salts having an analytically determined base/acid ratio $A^{I}_{2}O/MO_3$ of 1:4 [the correct and unequivocal designation is A (1:4)-metalate or (1:4)-metalate] whether or not a discrete anion is present. Consequently, three different "tetrametalates" have been reported in the literature: a tetratungstate ion $[W_4O_{12}(OH)_4]^{4-}$ (discrete ion) (*12*, *13*); a "tetramolybdate" $(NH_4)_2O \cdot 4MoO_3 \cdot 2.5H_2O$ (*14*, *15*), that contains the discrete anion $Mo_8O_{26}^{4-}$ (*15*, *16*) and is correctly denoted as octamolybdate; and a "tetramolybdate" $K_2Mo_4O_{13}$ (*17*, *18*) that does not contain a discrete polyanion and, according to its structure (*17*, *18*), can be regarded as polymeric octamolybdate containing the ion $[Mo_8O_{26}^{4-}]_n$. Salts in which discrete polyanions of hitherto unknown size occur and salts without discrete polyanions, of yet unknown structure, should only be represented in the notation $aA_2O \cdot bMO_3 \cdot cH_2O$ to avoid confusion. For nondiscrete polyanions of known structure, the formula should always give an indication that no discrete polyanions are present, e.g., in the case of potassium (1:10)-molybdate ("decamolybdate") by bracketing and addition of subscript ∞, i.e., $[KHMo_5O_{16}(H_2O) \cdot H_2O]_\infty$.

Frequently, the only fact known about a polymetalate species whose existence has been recognized is its Z^+ value. If known as an uncanceled rational fraction this quantity, as already mentioned, provides a good method of nomenclature or abbreviation, e.g., p,q-metalate ion (if only one number is given, it is the value of q), species p,q or (p,q), metalate species ($Z^+ = p/q$). If it is only known as a decimal (e.g., for the salts $aA_2O \cdot bMO_3 \cdot cH_2O$), then only the last approach leads to a useful designation. (Quantities Z^+, a, and b are related according to $Z^+ = 2 - 2a/b$.) Thus the 6-tungstate ion (paratungstate A ion) formed according to Eq. (5) is a 7,6-tungstate ion.

Quantity q in the formula of a polymetalate ion is termed the degree of *aggregation* of the pertinent species. We avoid the designation degree of condensation because studies on the mechanisms of formation (*13*, *19–24*) have revealed the operation of various kinds of aggregation mechanisms, including pure addition mechanisms (*13*, *21*). The degree of aggregation q (number of M atoms in the species) and the "degree of condensation" r (number of condensed H_2O molecules) do not, therefore, agree; nor do they exhibit any obvious mutual relationship (e.g., $r = q - 1$, as is normal for linear condensation reactions). We, therefore, generally speak of aggregation to give a polymetalate ion.

The degree of condensation in the sense of r is frequently unknown, and it has therefore become common practice to give the formula of a polymetalate with as few hydrogen atoms as possible, i.e., $p - 2r = 0$ or 1. For example, the paratungstate A ion is usually formulated as $HW_6O_{21}^{5-}$ or $[W_6O_{20}(OH)]^{5-}$. Formulas $H_3W_6O_{22}^{5-}$ or $[W_6O_{19}(OH)_3]^{5-}$ ($= HW_6O_{21}^{5-} \cdot H_2O$), $H_5W_6O_{23}^{5-}$ or $[W_6O_{18}(OH)_5]^{5-}$ ($= H\,W_6O_{21}^{5-} \cdot 2H_2O$), and $H_7W_6O_{24}^{5-}$ or $[W_6O_{17}(OH)_7]^{5-}$ ($= HW_6O_{21}^{5-} \cdot 3H_2O$) could, however, also apply. This procedure will be criticized later (Section III, B, 1). In the interest of unambiguous characterization, the formulation $(H^+)_p(MO_4^{2-})_q$ should be adopted for polymetalate species of unknown r, as has been done for the paratungstate A ion in Eq. (5).

It is frequently the case that the existence of a (new) species has been definitely recognized [nowadays generally as a fingerprint, preferably a characteristic spectral band (cf. Section III, A, 1)], but neither Z^+ nor even p and q, nor any other data can initially be determined. In such cases it has become customary during the past few decades to append an upper-case letter to the word polymetalate or, if a species formerly regarded as homogeneous proves to be a mixture of two species, to an established trivial name (polytungstate Y, X; paratungstate A, B). No objection can be raised to this practice. However, it seems expedient to avoid using the same letter for several levels of Z^+ in order to rule out any danger of confusion.

III. Experimental Methods for Characterizing Species

The number of methods employed in elucidating the chemistry of polymolybdates and -tungstates is very large. However, this variety of methods is not manifested in a correspondingly extensive knowledge of polymolybdate and polytungstate chemistry, but rather reflects the relatively modest amount of information a single method generally affords and the complexity of the systems.

For our purposes it is appropriate to classify the methods of study according to the information they yield about the formation reaction of polymetalate ions and about the polymetalate ions themselves. Critical literature studies repeatedly show that statements about reactions and species are derived from investigations that are simply incapable of yielding such information with the methods used. It often also happens that a new experimental or evaluation technique has to be used in conjunction with results obtained by other methods, and these results (e.g., taken from the literature) were inadequate or even incorrect, or were merely incorrectly interpreted.

If separate studies show that a solution and the solid crystallizing therefrom contain the same polymetalate species (which is by no means self-evident), then the experimental results obtained for the solid can be applied to the species in solution, and vice versa. By applying the above classification, we can consider the experimental methods for solutions and solids together.

The experimental methods generally require that the species being identified or characterized should predominate (species fraction $\geqslant 0.9$–0.95) in a given range of experimental conditions, or that the species being formed (or undergoing reaction) is accompanied only by the starting species (or the reaction product). Methods suitable for detecting or even identifying several coexisting species are comparatively rare (cf. Sections III, A, 1; III, A, 3, b; and III, A, 5, b).

We shall first consider the most important static methods (Sections III, A and B) and then go on to discuss techniques for fast reactions (Section III, C).

A. METHODS PROVIDING INFORMATION ABOUT THE EXISTENCE AND RANGE OF EXISTENCE OF POLYMETALATE SPECIES

The existence (i.e., occurrence in significant concentration) of a polymetalate species in aqueous medium at a given acidification and a given initial concentration of MO_4^{2-} at a given time after acidification is decided at a given temperature by the p,q values, overall formation constants, and kinetic parameters of all polymetalate species occurring in significant concentration at any acidification and any initial concentration of MO_4^{2-} at any time. With the aid of these quantities the contribution of each species to the aggregation products (species fraction) can be calculated, at least in principle, for any concentration, at any acidification, and at any time. By contrast, solids may also contain species not occurring in significant concentration in aqueous media because their formation constants are unfavorable in comparison with those of the other species. On the other hand, some polymetalate ions occurring as principal components in aqueous media have not yet proved isolable as solid salts.

1. Methods Yielding a Fingerprint of a Species

A fingerprint is a directly measurable complex quantity (e.g., a spectrum) that can be used without further processing to recognize a particular species in different circumstances. Apart from the qualitative component (e.g., the band *frequency* of a spectrum), permitting the actual identification, in solutions the quantitative component, i.e., the component proportional to the concentration (e.g., the band *intensity* of a spectrum) may also be employed, for instance, in establishing a uniform reaction course or determining Z^+ (cf. Sections III, A, 3, a and b, and III, A, 4, a). Further information can also be deduced from the qualitative component (cf. Sections III, B, 2, c; III, B, 3, a; and III, A, 1, e). Assignment of a fingerprint to a species is sometimes problematical.

Closely related to the task of obtaining a spectrum as a fingerprint of a species, or of assigning one to a species, is the question of the homogeneity of a species in a solution or solid. Solution of this problem requires observation of the spectra recorded with a certain degree of variation of the conditions of preparing the solid or, in the case of a solution, with a certain degree of variation of the Z value, the time, or, where applicable, the temperature, as well as also varying the concentration in each case. It is, therefore, expedient to combine work on this problem with questions concerning the uniformity of reaction (especially by the method of extinction difference and intensity difference diagrams) and the identity of a species in the solid and in the corresponding solution (spectroscopic methods).

a. Ultraviolet Spectra of Solutions. Frequency and shape serve for identification (*7*, *25*) and the intensity for determing the concentration of a species.

b. Raman Spectra of Solutions and Solids. Here too the band frequency (and the intensity ratio) serve for identification (*5*, *6*, *26*, *27*), and the intensity (with solutions, suitable calibration of the method being assumed) for determining the concentration (*5*, *26*, *27*) of a species. Furthermore, the spectra also provide information about structural questions (cf. Section III, B, 2, c).

c. Infrared Spectra of Solids. As for Raman spectra, the frequency and relative intensity can be used for identification of species (*7*) and, possibly, for checking product purity. In addition, structural information can also be gleaned from the spectra (cf. Sections III, B, 2, c and III, B, 3, a).

d. Paper Chromatography of Solutions. Polymetalate species are identified by their R_f values (*28*). The amount of substance (content of M) in the spot of the chromatogram affords the concentration; it can be readily determined with the aid of a counter tube using isotopically labeled metalate (*28*).

It should be noted that methods based on separation of a polymetalate mixture—this applies both to paper chromatography and electromigration analysis—can only be applied to systems in which re-equilibration after perturbation of the original equilibrium requires considerably longer than migration.

e. Isomatrix Electromigration Analysis of Solutions. With this technique, species identification is based on the path traveled under standard conditions. The amount of substance at the point concerned affords the concentration. Once again it can easily be determined with a counter, using labeled metalate (*29*, *30*). This technique can also only be applied to systems in which re-equilibration after disturbance of the original equilibrium takes considerably longer than the migration.

The paths traveled by the polymetalate ions depend on their charge, mass, and size (or compactness), with the result that the paths, in turn, provide some estimate of *relative* charge, mass, and size provided that two of the three quantities remain constant or are known (*29*).

Paper chromatography and electromigration analysis are the only methods providing a direct indication of the number of species coexisting in a solution. However, their use should be preceded by a critical assessment of whether interference can arise due to fast equilibrations during the separation.

f. Polarography of Solutions. The half-wave potential is used for identification, and the diffusion current for quantitative determination of the polymetalate species (*31*).

g. Powder Diagrams of Solids. The positions and relative intensities of the lines are used for identification or purity control of a substance (*1*, *8*, *9*).

h. Chemical Reactions in Solution. This method is based on the following principle (*31*): A compound is added to the polymetalate solution to be studied (the published investigations deal with the tungstate system), which is able to form a complex—apparently with the monometalate ions present in equilibrium—whose concentration is determined by a physicochemical method [polarography (*31*), UV spectrophotometry (*32*), etc.]. It then depends on the thermodynamic and kinetic stability of the polymetalate ions whether (and if so to what extent) and how fast the complex is formed at the expense of the polymetalate ions.

It has proved possible, by skillful combination of variously acidified and aged metalate solutions and by use of various complexing agents capable of reacting with the monometalate ions, to identify various polymetalate species and to determine their contribution. Particular use has been made of 11-tungstatosilicic acid (formation of the 12-tungstatosilicate ion) (*31*), the vanadatophosphate ion (formation of the vanadatotungstatophosphate ion) (*33*), and pyrocatechol (formation of the 1:1 complex) (*32*) as complexing agents.

2. *Methods for Establishing the Identity of a Species in a Solid and in Solution*

a. Spectroscopic Methods. Comparison of solution with solid-state spectra (*34*, *5*, *6*, *26*, *27*) is presently the most reliable method for establishing the identity of a species in solution and in the solid state since two fingerprints are being compared. Only Raman measurements have so far been used in the molybdate and tungstate system. Good agreement of the spectra [e.g., in the case of the hepta- and 36-molybdate ion (*27*)] constitutes proof of identity. If they show reasonable overall agreement [as in the case of the paratungstate B ion (*27*)] and a plausible explanation is available for poorer agreement at certain positions (e.g., unresolved bands due to experimental line broadening in the dissolved state, and splitting of bands that are degenerate in solution when spectra are recorded for a crystal lattice), then identity can be assumed in this case too (*6*, *27*).

A variant of this method is employed when identity in solution and the solid state is proved for one of a series of similar compounds and the similarity of all the species of the series in solution has been demonstrated by the similarity of their spectra [in such cases UV studies have also been performed (*7*)]. For example, the metatungstate ion could be shown to have the same structure in solution as the dodecatungstatosilicate ion in the solid state (cf. Sections V, B, 3, b and III, A, 2, b).

b. Direct Comparison of the X-Ray Structure Analysis of a Solid with That of a Solution. Recently, the first comparison of this kind for an isopolymetalate ion became available (*35*). Hitherto, only examples from heteropolyanion chemistry were known (*36*, *37*); however, the structural identity of the above-mentioned dodecatungstatosilicate ion (*36*) in solution and in the solid state has just been demonstrated in this way.

c. Comparison of Stoichiometric Coefficients. A further technique that can provide in certain cases strong evidence for identity, if not conclusive proof, is available. If the accurately known (!) stoichiometric coefficients p and q of the overall formation reaction for a solid and a species in solution are equal, then there is some justification for assuming the same species to be present. Although the probability of the same p,q pair occurring coincidentally for solids and dissolved species is statistically relatively low, mechanistic studies, nevertheless, show that for geometrical reasons several structures can be given for certain pairs of p,q values (e.g., 12,8) (*23*) and are apparently realized (*27*), whereas for other pairs [e.g., 7,6 (*19*) and 8,7 (*23*)] only one or possibly two very closely related structures can indeed be given.

The Z^+ values of solids and species in solution can also be compared in place of p,q values. However, the uncertainty is then greater because the ranges of all integral multiples of $q_{\min}$ (determined from the Z^+ value as the denominator of the rational fraction with the lowest divisor) must be taken into consideration.

Both variants are frequently employed, especially in cases where q and p or Z^+ are accurately known for a solid from structural analysis

(*1*). In general, however, the experimenter's main interest (often unexpressed) was to work backward in order to decide between several possible values of p,q pairs or Z^+ values all of which lie within the limits of experimental accuracy (cf. Sections IV, B, 3, a and V, B, 3, a).

d. Criterion for Determining Time Required for Crystallization (*27*). An additional criterion for establishing identity is provided by the time required for crystallization of the solid. If a species occurs as the main component in solution, then its salt should crystallize rapidly (provided that the solubility product permits crystallization). Very protracted crystallization usually indicates prior formation of a new species. For example, this is assumed to be the case for the octamolybdate $(NH_4)_4Mo_8O_{26}\cdot 5H_2O$, having the structure determined by Lindqvist (cf. Sections IV, A, 1 and IV, B, 3, b), and has been definitely established for the polymetalates $(NH_4)_{4n}[Mo_4O_{14}]_n$, $(NH_4)_{6n}[Mo_8O_{27}]_n\cdot 4nH_2O$, $A_2O\cdot 3MoO_3\cdot yH_2O$, $(NH_4)_2O\cdot 4MoO_3$, $Na_2O\cdot 4MoO_3\cdot 6H_2O$, $(NR_4)_2Mo_6O_{19}$, and $[AHMo_5O_{16}(H_2O)\cdot H_2O]_\infty$ (*27*).

3. Methods for Proving Uniform Course of Formation and Further Reaction of a Polymetalate Species

There are several methods for demonstrating the uniformity of a reaction for a given acidification range. The most reliable results are probably available nowadays from extinction and intensity, or extinction difference and intensity difference diagrams (*27*, *26*, *38*). They have the added advantage of being applicable also to time-dependent reactions (*39–41*). In general, use of these methods simultaneously yields additional quantities such as Z^+ (cf. Section III, A, 4, a) or p and q and the overall formation constants β (cf. Sections III, A, 5, b and III, A, 6).

a. Concentration-Proportional Titrations. This method is based on measurements of a physical quantity X, which is proportional to the concentration of one or more reactants j, at constant initial concentration of the reactant MO_4^{2-} as a function of the "acidification" x:

$$X(x) = \sum_j \chi_j c_j \qquad (C_{MO_4^{2-}} = \text{const.}) \tag{6}$$

[χ_j = proportionality constant valid for the species j (polymetalate and other species)]. A straight line is obtained for a uniform reaction course. If the first uniform reaction is followed by a second one, then another straight line results. Since the second reaction usually starts before the first one has gone to completion, the two straight lines are joined together by a curved line. If several parallel reactions occur or if the consecutive reactions show pronounced overlapping then curves are obtained. After completion of all reactions, a final straight line results.

This method affords a curved line in spite of a uniform reaction course if the formation constant of the polymetalate species is small and the quantity chosen as variable x is proportional to the *initial* concentration of H^+, e.g., P. A plot versus a quantity proportional to the *reacted* concentration, e.g., Z, still gives a straight line for unfavorable formation constants (cf. also the discussion in Section II, A).

Apart from the methods suitable for investigating solutions listed in Section III, A, 1, in which the quantitative component of a complex quantity provides a measure for the concentration, it is of course possible to employ methods in which noncomplex quantities (lacking the qualitative component) are measured. Conductivity titrations (*42*–*47*), as illustrated in Fig. 2, represent the commonest variant of this method, which is generally used for determining the Z^+ value of a polymetalate species. Grave errors are often committed in practical application of this method (see Section III, A, 4, a, where further quantities that have been followed during titration are also given).

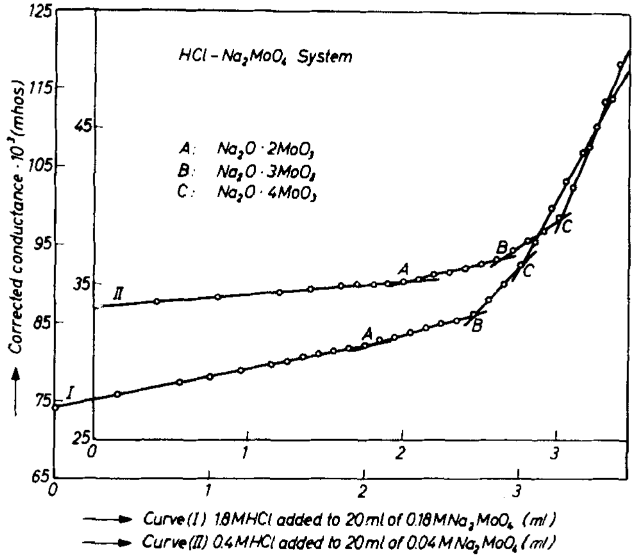

FIG. 2. Example of a conductivity titration (*47*).

b. Extinction Difference and Intensity Difference Diagrams as well as Extinction and Intensity Diagrams. Extinction difference (ED) and intensity difference (ID) diagrams are obtained by calculating the differences in extinction and intensity, respectively, of a series of spectra with increasing conversion on addition of a reactant (*27*, *26*, *38*, *48*) or for a time-dependent reaction (*39–41*) relative to a reference spectrum (appropriately the spectrum of the initial state) at two different wavelengths or wave numbers, and plotting the differences against each other (Fig. 3). Extinction (E) and intensity (I) diagrams result when the extinctions and intensities, respectively, themselves are plotted against each other for two different wavelengths. The validity of Beer's law is assumed for the absorption spectra; suitable measures have to be adopted to ensure linearity between the concentration of a species and the intensity of its spectrum in the case of intensity spectra (e.g., Raman spectra). If a reaction proceeds in a uniform manner,* then a

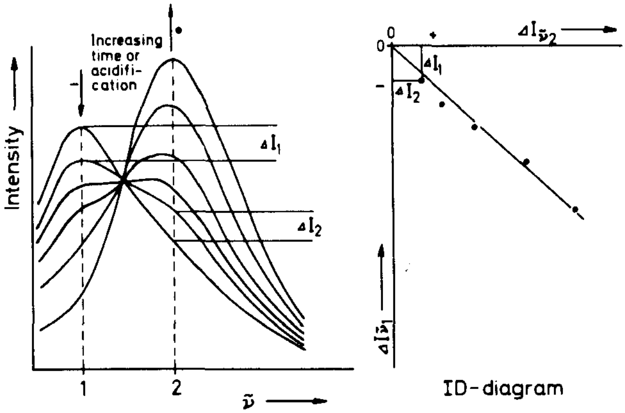

FIG. 3. Construction of an intensity difference (ID) diagram.

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* The concept of a (spectroscopically) uniform reaction should not be taken as meaning that only a single reaction takes place. Several intermediates can, of course, occur (mechanism) if the requirements of a quasi-steady state are fulfilled. Moreover, the term also embraces the case of two (or even more) parallel reactions provided that the reaction products are always formed together in the same ratio regardless of the concentration. For time-dependent reactions this will require the same order of reaction; and equal stoichiometric coefficients will be required for p and q in the reaction equation in the case of equilibrium reactions (titrations). In practice these requirements mean that only reactions having the same kind of mechanism can occur as parallel reactions, such as the formation of planar and compact hexatungstate (para A) ion (*19*) (cf. Fig. 16).

straight line is obtained in the ED (E) or ID (I) diagram, whereas curved lines appear if several parallel reactions take place. Depending on the p,q values and the pertinent equilibrium constants of reactions occurring on successive acidification or the magnitude of the rate constants of reactions occurring with increasing time, one or several regions in which a single reaction predominates can be recognized in a system (*38*, *41*).

The occurrence of two (and only two) linear independent reactions parallel to each other can be ascertained with the aid of extinction (intensity) difference quotient diagrams (EDQ and IDQ diagrams, respectively) which then yield a straight line (*41*). These diagrams are obtained by calculating the extinction (intensity) differences at three different wavelengths and plotting $\Delta E_{\lambda_2}/\Delta E_{\lambda_1}$ versus $\Delta E_{\lambda_3}/\Delta E_{\lambda_1}$ (or the quotients of intensity differences, respectively).

Diagrams ED, ID, E, I, EDQ, and IDQ have two particular advantages over all other methods (*38*).

1. For each reaction taking place and each species appearing in a system, suitable choice of pairs of wavelengths permits construction of a diagram having optimal information content for the pertinent reaction or species.
2. When merely employed to check uniformity of reaction(s), the diagrams are completely insensitive to errors in the Z value.

c. The (Z, log c_{H^+}, $C_{MO_4{}^{2-}}$) *Equilibrium Curves* (*49*). An indication of a possibly uniform reaction course is obtained from (Z, log c_{H^+},

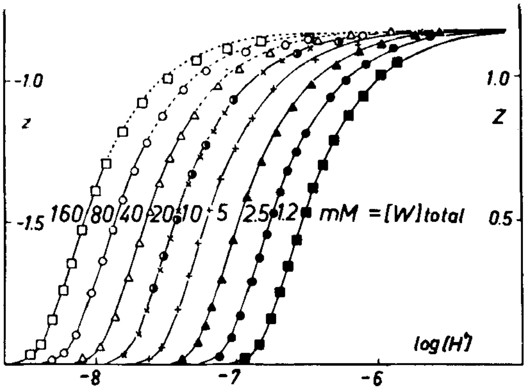

FIG. 4. The (Z, log c_{H^+}, $C_{WO_4{}^{2-}}$) equilibrium curves for the $H^+/WO_4{}^{2-}$ system in 3 *M* Na(ClO$_4$) at 25°C within a short time of acidification. Occurrence of just a single polytungstate ion, 7,6-(paratungstate A) ion, and its formation constant were deduced from the curves (*50*).

$C_{MO_4^{2-}}$) equilibrium curves if the (Z, $\log c_{H^+}$) curves for the various MO_4^{2-} (initial) concentrations lie parallel to one another within a given range of Z. If the curves are parallel, then only so-called core + links complexes can be present. In order to establish whether a single core + links complex is formed, all the curves are superposed by an appropriate coordinate transformation and the new curve analyzed either by comparison with calculated theoretical curves or directly. As an example, the (Z, $\log c_{H^+}$, $C_{MO_4^{2-}}$) diagram for the tungstate system in the range $0 < Z \leqslant 1.17$ shortly after acidification is depicted in Fig. 4 (*50*).

4. *Methods for Determining the Value of Z^+ (As a Decimal)*

a. Concentration-Proportional Titrations ("Break" Titrations). The Z value of the intersection of the extrapolated straight lines obtained by the method described in Section III, A, 3, a (and Section III, A, 3, b) affords the Z^+ value of the species formed (see Fig. 2). The P value may only be used if it is numerically equal to the Z value.

Apart from electrical conductivity, the following quantities have also been measured in the course of titrations: UV absorption (*51–53*); intensity of Raman bands (*27*); Rayleigh scattering (*54*); the refractive index (*55, 56*); the volume dilation of the solution (*57–59*); the increase in temperature (*43, 60, 61*); the cryoscopic depression (*42, 31, 8*); the radioactivity of labeled tungsten in individual fractions after separation of the reaction mixture by paper chromatography (*28*); and the diffusion current on polarographic reduction of the polymetalate species (*62*).

This method is one of the most commonly employed techniques for investigations in isopolymetalate chemistry, although its accuracy is not particularly high. The most frequent errors committed in its application are plots versus P (or analogous parameters) instead of Z; errors in extrapolation on determining the intersection of straight lines, especially when only short sections of a line are available (which in most cases are not really and simply cannot be straight lines at all) (cf. Section III, A, 7); overestimation of the accuracy of the method with regard to determination of $p_{\min}$ and $q_{\min}$ (see Section III, A, 5, a).

b. Potentiometric Titrations. These differ from break titrations in that (a) only one species is responsible for the effect measured, and (b) the measured effect is not proportional to the concentration itself but to its logarithm. For experimental reasons, measurements have so far been limited to the potential due to the H^+ concentration (or H^+

activity) (glass or quinhydrone electrode) (*7*, *47*, *52*, *63*, *64*; see Refs. *2* and *9* for additional references).

The occurrence of one of the reactions describable by Eq. (1) is apparent from the specific shape of the (log c_{H^+}, P) curve from which the (log c_{H^+}, Z) curve may be calculated. The most striking feature of these curves is the potential jump observed at $Z \approx Z^+$. Basically, however, the entire curve is characteristic of the reaction concerned. Thus valuable additional information is lost if the curves are evaluated only with respect to the Z value (or even merely the P value) at which the potential jump occurs. If several reactions take place, then several potential jumps are found, provided that the reactions are not extensively superposed. This requires that the Z^+ values of the species occurring should be sufficiently different and that the overall formation constants should have favorable values. In principle, however, even in those cases where no further (resolved) potential jumps appear the maximum possible information is still present in the overall curve. Mere determination of Z^+ values from the potential jumps cannot, therefore, be regarded as a fitting application of the method.

With additional titration curves for other initial concentrations of MO_4^{2-}, mathematical analysis of the curves (see Sections III, A, 5, b and III, A, 6) affords, in principle, the p,q values and overall formation constants of all species occurring in significant concentration in the range under study.

c. *Analysis of Solids.* If analysis of a substance indicates a formula $aA_2O \cdot bMO_3 \cdot cH_2O$, its Z^+ value* follows from

$$Z^+ = 2 - (2a/b) \tag{7}$$

Here, too, the accuracy with regard to determination of $p_{\min}$ and $q_{\min}$ is grossly overestimated. For the maximum error in Z^+ not to exceed about 0.5% (cf. Section III, A, 5, a), the sum of the relative errors in the analytical values for A_2O and MO_3 should not exceed 0.5%. Salts containing much water of crystallization pose the additional sampling problem of using samples with the same water of crystallization content in the individual analyses because the water is easily given up. This problem led to protracted discussions whether the paramolybdates and paratungstates are (3:7)- or (5:12)-metalates (*65*, *66*, *31*, *67*, *68*).

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* This formula requires that only A^+ may be present as cation in the substance $aA_2O \cdot bMO_3 \cdot cH_2O$. If H^+ (in hydrated form) also occurs as cation (which cannot be established by chemical analysis), then spurious (too high) Z^+ values will be obtained. For example, the substance $A_2O \cdot 10MO_3 \cdot 5H_2O$ might be the polymetalate $A_2M_{10}O_{31} \cdot 5H_2O$ ($Z^+ = 1.80$), $A_2M_{10}O_{30}(OH)_2 \cdot 4H_2O$ ($Z^+ = 1.80$) or $A_2(H_3O)_2M_{10}O_{32} \cdot 2H_2O$ ($Z^+ = 1.60$).

d. Ion Exchange Processes. The amount of metalate removed from a polymetalate solution on contact with an ion exchanger and the amount of anion released by the latter, which is equivalent to the amount of charge of the metalate ions, can be determined by chemical analysis of the solution. Hence, assuming a single polymetalate species to be present, the ratio of charge to degree of aggregation of the polymetalate ion $1/R \equiv (2q - p)/q = 2 - p/q = 2 - Z^+$ can be established. If several species are present and the exchange process is nonselective, then an average value for all the species in the solution is obtained. In cases where selection does occur the average value applies to the adsorbed species. In order to decide whether just one or several species are taken up by the ion exchanger, the method would have to be combined with another one (presence of a single species could be deduced from the occurrence of a plateau in R curves [e.g., R(pH)] in appropriate cases). However, even when this additional method has been found, the problems have by no means been solved. Concentration changes resulting from adsorption (general drop in concentrations, selection, etc.) drastically modify the equilibria so that fast re-equilibration (during the exchange process) further confuses the situation (*69*, *70*). Moreover, it is also possible that the pore size and charge distribution in the matrix of the exchanger may favor formation and adsorption of species occurring only in minimal concentrations, if at all, in solution (*69*, *70*). Thus the results obtained for the molybdate system by the ion exchange process (*71*, *72*) fail to agree with those determined by other methods.

5. *Methods for Determining Degree of Aggregation*

a. Determination of Molar Mass of Dissolved Ions with the Ultracentrifuge. Three different methods are available: the sedimentation equilibrium technique (*5*, *6*, *26*, *73–75*); the sedimentation velocity technique (*7*, *52*, *75*); and the Archibald technique (measurement in transition state) (*7*). All three methods have actually been used. Since the effect of ionic charge cannot be established with certainty and since numerous possibilities exist for formulating the M—O skeletons of the polyions without introducing further assumptions (for instance, the formulation of the 36-molybdate ion can range between $Mo_{36}O_{112}$ and $Mo_{36}O_{144}$ if no restrictive assumptions are made), and a broad range must consequently be considered for the "theoretical" or "calculated" molar mass, errors of 5 to 10% generally have to be expected in the resulting degree of aggregation.

Ultracentrifuge studies can be used to great advantage in combination with X-ray studies on crystals when a polymetalate occurs both in solution and as a crystalline solid. The molar mass of possible formula units can be calculated from the volume of the unit cell, the density, and the various possible values of z (number of formula units in the unit cell) for the space group and compared with that obtained from analysis and studies with the ultracentrifuge. Thus, ultracentrifuge studies indicate the order of magnitude, and X-ray analysis the precise value (*26*). In a similar manner, although with less accuracy, the Z^+ value can also be combined with ultracentrifuge studies. Conversion of Z^+ into the rational fraction with lowest divisor yields p_{min} and q_{min}. p and q are then equal to p_{min} and q_{min} or integral multiples thereof. The order of magnitude of q is again obtained from ultracentrifuge studies and the precise value from Z^+ (*7, 52, 76*). This combination is employed frequently. It is limited to low degrees of aggregation: even 7,6- ($Z^+ = 1.167$) and 8,7-metalate ions ($Z^+ = 1.143$) ($\Delta Z^+ = 0.024 \mathrel{\hat{=}} 2.1\%$) can, if at all (cf. Section III, A, 7), only be distinguished by very careful measurements (maximum error in Z^+ about 0.5%). Diffusion (*43, 77–79*) and dialysis methods (*80*) fail to give accurate values for the molar mass of dissolved ions (*81, 82*). Salt cryoscopy (*42, 31*) has a similar reputation (*83*).

b. Mathematical Analysis of (Z, $\log c_{\mathrm{H}^+}$, $C_{\mathrm{MO}_4^{2-}}$) *Equilibrium Curves* (*84–86*). In principle, this is a very elegant method for identification of species present in solution by means of their p and q values and provides the opportunity of observing several species coexisting in equilibrium and of calculating their formation constants too. However, unequivocal results are obtained only on very accurate measurement of the triple set of values ($\log c_{\mathrm{H}^+}$, Z, $C_{\mathrm{MO}_4^{2-}}$). Evaluation rests solely on application of the law of mass action and observation of mass and charge balance, and requires that measurements are conducted at constant, high ionic strength. The calculations are extremely involved. The solution of the problem is the set of p,q values and the corresponding overall formation constants that give the best fit between experimental and calculated Z values. The standard deviation σ_Z is, therefore, the criterion for assessment. As an example, Fig. 5 shows the (Z, $\log c_{\mathrm{H}^+}$, $C_{\mathrm{MO}_4^{2-}}$) diagram for the molybdate system from which the occurrence of the species (1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (34,19), and (5,2) [alongside (0,1)] was deduced. The points indicate experimental values and the solid lines were calculated assuming occurrence of the above species. The limitations of the technique are reached when several sets of species with their corresponding

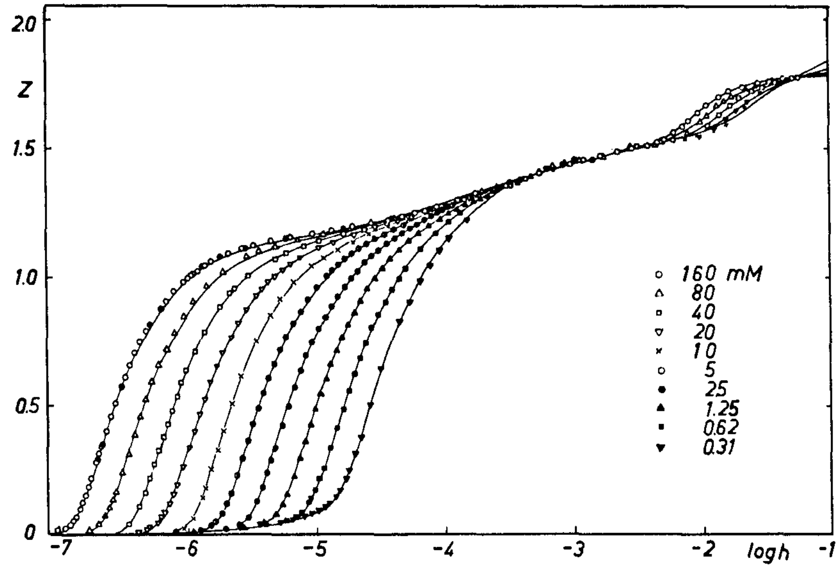


FIG. 5. The (Z, log c_{H^+}, $C_{MoO_4{}^{2-}}$) equilibrium curves for the $H^+/MoO_4{}^{2-}$ system in 3 M $Na(ClO_4)$ at 25°C. Occurrence of the species (1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (34,19), and (5,2) was deduced and the overall formation constants of the species determined from the curves (*9*, *87*). Abscissa: log h = log[H^+].

formation constants lead to similarly small standard deviations (cf. the discussion in Sections IV, B, 3, a–c and V, B, 3, a and b).

An additional method, developed especially for evaluation of measurements at small Z values, permits recognition and elimination of certain systematic errors that play an increasingly significant role with decreasing Z value (*88*, *89*).

c. X-Ray Structure Analysis of Salts and of Species in Solution. The most reliable results are obtained by X-ray structure analysis of crystalline polymetalates (*90–95*, *15*, *16*, *96–106*). The findings are transferable to the situation in solution provided that separate investigations have established the presence of the same species in solution and in the solid state. In certain cases, X-ray structure analysis can also be performed on solutions.

6. *Determination of Overall Formation Constants of Polymetalate Ions*

Mathematical analysis of (Z, log c_{H^+}, $C_{MO_4{}^{2-}}$) equilibrium curves (*84–86*, *88*, *89*) furnishes the stoichiometric coefficients p and q and, at the same time, the overall formation constants of polymetalate ions. The relevant data are listed in Tables I and II (see Sections IV, B, 1 and V, B, 1, respectively).

7. *Computational Methods for Assessing Possible Existence of Isopolymetalate Ions*

We have found a very useful aid in assessing the possible existence of species proposed in the literature and in studying the structure of H^+/MO_4^{2-} systems to be a computer program (*107*) permitting calculation of the Z value and the distribution of the species (species fraction) for a given set of species and their overall formation constants as a function of the initial concentration $C_{MO_4^{2-}}$ and of log c_{H^+}. The most important conclusion (*108*) drawn from such calculations is that use of the method in Sections III, A, 3, and A, 4, a does not permit detection of any number of successive species with increasing Z value, as would appear to be the case on considering the species and reactions proposed in the literature. For a section of a plot to be identifiable as a straight line, it is essential that the Z^+ values of successive species differ by about 0.2 units. Apart from the errors already mentioned, failure to observe this fact is one of the most frequent sources of error in the method of Section III, A, 4, a.

8. *Determination of Kinetic Data*

The methods given in Sections III, A, 1; III, A, 3, a and b; and III, A, 4, a, which are based on measurement of quantities or, in the case of spectra, functions proportional to concentration, may be employed not only for determining the Z or pH dependence but also, as mentioned on various occasions, for investigating the time dependence of reactions. Standard methods of evaluating kinetic data then permit the derivation of rate laws and rate constants, and, where appropriate, activation energies. Special methods are available for fast reactions (see Section III, C).

B. METHODS FOR DETAILED CHARACTERIZATION OF POLYMETALATE SPECIES

1. *Methods for Determining the (Empirical) Formula of a Polymetalate Ion*

The methods described so far furnish the degree of aggregation (q) and the charge number ($2q - p$) of a polyion. Formulation of the M—O skeleton (number of O atoms) also requires knowledge of r, the stoichiometric coefficient of the condensed water. At the same time the number of H atoms in the ion (which are bonded to oxygen) is established. Experimental determination of r can be performed only by examining a solid.

For species known only in solution and also for solids when r could not be determined, it has become common practice, as already mentioned, to give the formula of a polymetalate species with as few H atoms as possible, i.e., $p - 2r = 0$ or 1. Regrettably, the same approach is often adopted when r is known. Experimental findings provide hardly any basis for rules governing the number of H atoms (OH groups) present in a polymetalate ion (e.g., as a function of the degree of aggregation or Z^+ value). Attention has already been drawn to the numerous possible formulations of the paratungstate A ion, and to the resulting difficulties encountered in the interpretation of molar mass determinations (cf. Section III, A, 5 a). Theoretical approaches to the formation mechanisms and structures of polymetalate ions merely indicate that the number of OH groups in stable polymetalate ions can never be large (*23*). In order to distinguish whether a formula is the true (empirical) formula or that having the lowest possible number of H atoms, the latter should always be given. It is most expedient to adopt the proposed notation $(H^+)_p(MO_4^{2-})_q$ when r is unknown and a formula is desired.

a. X-Ray Structure Analysis of Solids. If we know the structure of a polymetalate ion, then we also know the formula of its M—O skeleton (*90–95, 15, 16, 96–106*), from which r and, knowing p, the number of H atoms in the polyion can be determined.

b. Analysis of the Solid. Analysis indicates the formula as $aA_2O \cdot bMO_3 \cdot cH_2O$, where a, b, and c are only *proportional* numbers. In the cases $c = 0$ and $b = 2q$ for $c = 1$, the formula of the M—O skeleton is unequivocally known: The M/O ratio in the M—O skeleton is $b/(3b + a + c)$.

Attempts have also been made to prepare crystalline polymetalates by controlled hydrolysis of tungstic and molybdic tetraesters in organic solvents, expecting the products to contain no water of crystallization and all the hydrogen present to be in the form of OH groups (*8, 109–112*). In this way the formula $W_5O_{16}^{2-}$, or a multiple thereof, has been established for the polytungstate Y ion (*112*), and the number of possibilities (cf. Section II, C) for the paratungstate A ion reduced to two, namely $HW_6O_{21}^{5-}$ {or $[W_6O_{20}(OH)]^{5-}$} and $H_3W_6O_{22}^{5-}$ {or $[W_6O_{19}(OH)_3]^{5-}$} (*109*) (see Section V, B, 3, a).

c. Thermal Degradation of Polymetalates. Assuming that the water of crystallization of polymetalates is released more readily than the so-called water of constitution participating as OH groups in the structure of the M—O skeleton, and that no fundamental changes in the polymetalate ion skeleton occur, various polymetalates have been subjected to stepwise thermal degradation. The individual degradation steps were examined for intactness of the M—O skeletons by means of differential thermal analysis, X-ray analysis, IR spectra, etc. The formula $[H_2W_{12}O_{40}]^{6-}$ for the metatungstate ion was confirmed (*113, 114*) in this way, and strong evidence obtained in favor of the formula $[H_2W_{12}O_{42}]^{10-}$ for the paratungstate B ion (*8, 115–117*). However, it should always be borne in mind that there are OH groups that are eliminated as H_2O more readily than the water of crystallization is released. Location of the OH group within the W—O framework rules out this complication in the case of metatungstate and paratungstate B ions (*2, 118, 119, 98, 99, 21*).

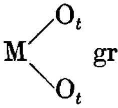
2. *Methods for Structural Elucidation of Polymetalate Ions*

a. X-Ray Structure Analysis of Solids. Nowadays X-ray structural analysis of crystalline solids permits a comprehensive structure determination [geometry of the M—O skeleton; positions of cations and water of crystallization; structure of the hydrogen bond system (*94, 95, 98–100, 103, 104, 106*)]. Within limits, the positions of H atoms (present as OH groups) can also be established by indirect ways (*98, 99, 106*).

The structure of the metatungstate ion could also be determined from its isomorphism with the dodecatungstatophosphate ion (*120*), whose structure had been elucidated by X-ray analysis (*121*) (cf. Section V, A, 1).

Figures 6 and 9 (see Sections IV, A, 1 and V, A, 1, respectively) show the structures found so far for isopolymolybdate and isopolytungstate ions (*90–95, 15, 16, 96–106*).

b. X-Ray Structure Analysis of Solutions. In certain cases, X-ray structure analysis can also be performed on solutions. Up to now, the positions of the M atoms in the M—O skeletons of one isopolymetalate ion, i.e., the heptamolybdate ion (*35*), and of two heteropolymetalate ions, i.e., the dodecatungstatosilicate (*36*) and pentamolybdatodiphosphate ion (*37, 35*), have been determined. However, the dodecatungstatosilicate ion is of significance in the structural elucidation of the metatungstate ion (cf. Sections III, A, 2, a and b).

c. Vibrational Spectroscopy. Assignment of the vibrational spectra of polymetalate ions is rather difficult owing to the large number of atoms participating in the structure and the low symmetries usually encountered in these species. Unequivocal assignment of all the bands of a polymetalate structural type has only been accomplished very recently by normal coordinate analysis of the highly symmetric M_6O_{19} ions (*122*). However, for the present it appears possible to prove the presence of certain groups of atoms, e.g., $M—O_b—M$ bridges and terminal $M—O_t$ and  $M\begin{smallmatrix}\diagup O_t \\ \diagdown O_t\end{smallmatrix}$ groups, (*123–126*), where subscript *b* signifies a bridging O atom, and *t* terminal O atoms.

d. Exchange Reactions with $^*MO_4^{2-}$ *and* $H_2{}^{18}O$. These exchange reactions relate to the M—O skeleton of the polymetalates. The data obtainable are primarily mechanistic in nature and can, therefore, provide structural information.

Exchange between $^*WO_4^{2-}$ and the paratungstate B ion (relatively slow exchange) (*127*, *128*) and between (acidified) $^*WO_4^{2-}$ and the metatungstate ion (no exchange) (*129*, *2*) have been studied.

Measurements on the paratungstate B ion performed with $H_2{}^{18}O$ (*127*, *130*) are too limited to permit any conclusion.

3. *Methods of Determining Kind of Bonding and Positions of* H *Atoms*

a. Infrared Spectra. Attempts were made to determine the kind of bonding of H atoms from IR spectra (*116*, *117*, *131*, *132*). Overlapping with the bands due to water of crystallization precluded detection by this method of OH groups in various polytungstates (*7*). It could, however, be shown (*7*) that H_3O^+ ions are not present, as proposed (*131*, *132*), in paratungstates B.

Experimentally, it should be mentioned that care must be exercised when pressing with KBr samples of the salts having high water of crystallization contents. Even grinding with an embedding agent is sometimes not permissible.

b. ^1H *Nuclear Magnetic Resonance.* It could be established with the aid of ^1H NMR spectra that the H atoms of various polymetalate ions are present in the form of OH groups (*7*). In individual cases, e.g., for the paratungstate B (*119*) and metatungstate ion (*118*), the positions of the H atoms could even be determined.

c. Exchange Reactions with D_2O. Hydrogen atoms lying in the interior of a polyion skeleton should undergo only relatively slow exchange. However, studies performed with paratungstate B and metatungstate ions, which were based on this reasoning, failed to yield conclusive results (*127*, *133*).

4. *Determination of Thermodynamic Data*

a. Determination of Heats and Entropies of Reaction for Formation of Polymetalate Ions. Mathematical analysis of enthalpy titration curves has afforded $\Delta H_r{}^0$ and $\Delta S_r{}^0$ values for the overall formation reactions of those polymolybdate and polytungstate ions that were identified by mathematical analysis of (Z, log c_{H^+}, $C_{MO_4{}^{2-}}$) equilibrium curves (*134*, *135*). The data are listed in Tables I and II.

Methods of determining overall formation constants have already been considered (see Section III, A, 6).

5. *Reducibility of Polymetalate Ions*

According to Pope (*136*) the ease of reduction of hetero- and isopolyanions to "molybdenum blue" and "tungsten blue" depends on the types of octahedra present in the structure: Only those polyanions that possess octahedra with monooxo terminal groups (octahedra with one free corner) are reducible. Thus the presence of octahedra with one free corner can be deduced for polyanions of unknown structure if they are reducible.

Numerous other publications on reduced polymetalates also exist (e.g., Refs. *137–141*; see also footnote on p. 292.

C. METHODS FOR STUDYING FAST REACTIONS

The methods discussed so far belong to the so-called static methods. Those applicable to solutions can be used for reactions having half-reaction times down to 1 min, depending on the nature of the method. For faster reactions, flow (rapid-mixing) and relaxation methods are available. Application of these methods has hitherto only yielded quantities indicating the existence and range of existence. However, the continuous flow method should also permit studies leading to detailed characterization of polymetalate species.

1. *Flow* (*Rapid-Mixing*) *Methods*

Flow methods permit (at least in principle) the techniques described so far to be used within 10^{-3} sec to 1 min after acidification, wherever this is compatible with their nature. With the continuous-flow method, a physical quantity X (a single quantity, e.g., pH value, or a function, e.g., a spectrum) can be measured at certain selected times after mixing of the reactants. In this way X can be investigated as a function of the acidification P and the time, and the information given in Sections III, A and B can be obtained for all applicable methods. By contrast, the stopped-flow method permits continuous measurement of a single quantity as a function of time for the mixture of reactants having a certain P value. The information obtained corresponds to that of methods in Section III, A, 8, i.e., kinetic data. A serious difficulty of this technique often lies in the assignment of the information obtained to a particular reaction or species (see, e.g., Section IV, B, 3, b and Ref. *142*).

With the continuous-flow method, it has become possible to study the simple protonation reactions (duration $\approx 10^{-8}$ sec) of the monometalate ions (formation of the species HMO_4^- and H_2MO_4) in isolation from the subsequent aggregation reactions. However, it was also necessary to delay the aggregation reactions by use of very low initial concentrations of MO_4^{2-} (*143*, *144*). This method has so far afforded the following information: the stoichiometric coefficients p and q of special species [(1,1) and (2,1) for both the molybdate and tungstate system] and their formation constants by mathematical analysis of rapid-titration curves; the Z^+ value ($= 1.25$) of a short lived (primary) aggregation product in the tungstate system that was viewed as 5,4-tungstate ion; the order of magnitude of the protonation constants of various polytungstate ions [paratungstate A and B ions (cf. Section V, B, 3, a), metatungstate ion]; and the order of magnitude of the rate constants for primary aggregation steps (*143*, *144*). Use of the stopped-flow method furnished rate laws and rate constants for hydrolytic disaggregation of various polymetalate ions (cf. Section IV, B, 4).

2. *Relaxation Methods*

The process of relaxation to a new equilibrium state following a very brief perturbation of a chemical system at equilibirum can be studied as a function of chemical parameters, e.g., of the initial concentration $C_{MO_4^{2-}}$ and the Z value, and subjected to mathematical analysis. In the studies performed so far (*145–149*), perturbation was effected by a temperature jump, and the relaxation process was followed by spectrophotometry of a coupled pH indicator equilibrium. Apart from rate constants, the stoichiometric coefficients p and q of several, generally primary aggregation reactions were obtained (cf. Sections IV, B, 2 and V, B, 2).

Very fast reactions (with rates approaching the limits set by diffusion processes) can be studied by ultrasonic methods based on continuous perturbations of equilibria. Protonation reactions of mono- and polymetalate ions have been investigated in this way (*150*) (cf. Sections IV, B, 1 and IV, B, 3, b).

IV. Isopolymolybdates

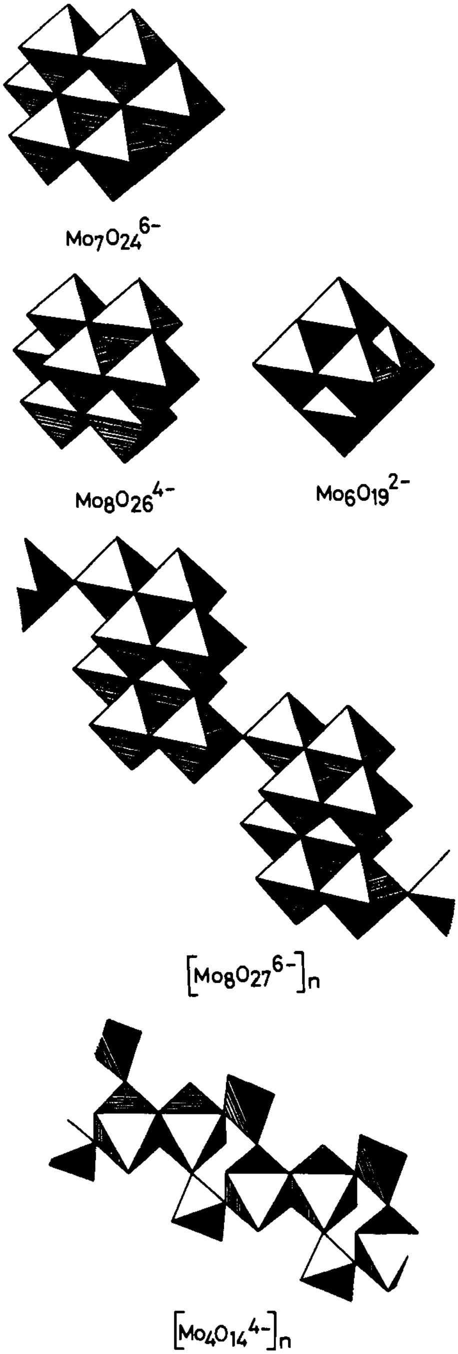
A. SOLID ISOPOLYMOLYBDATES

The classic method of preparing isopolymolybdates and isopolytungstates is crystallization of alkali (including ammonium), and sometimes also alkaline earth, salts from acidified aqueous metalate solutions. A variant of the preparation with regard to acidification consists in the use of "molybdic acid" or "tungstic acid" ($MO_3 \cdot H_2O$, $MO_3 \cdot 2H_2O$) (*7*) and, with regard to deposition, in the precipitation of the ions from acidified aqueous alkali salt solutions as sparingly soluble salts (K, Ba, tri- and tetraalkylammonium salts, etc.) (*7, 31, 74, 151*). Commercially available "ammonium molybdate," $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, is obtained by crystallization after dissolution of molybdenum trioxide in aqueous ammonia solution. During the past decade some other methods have also become known: controlled hydrolysis of the tetraesters of the metallic acids in organic solvents and in the presence of organic bases or salts (cf. Section III, B, 1, b) (*8, 109–112, 152*); reaction of the metal oxides or oxide hydrates with organic bases, either as liquids or dissolved in organic solvents (occasionally also in water) (*153, 103, 124*); and reaction of polymetalate salts with organic cations to give those with inorganic cations (*74, 124*).

Salts having inorganic cations are hardly soluble in organic solvents, whereas those with organic cations dissolve well. The latter can, therefore, be recrystallized from organic solvents with comparative ease (*74, 111*). A further advantage is that equilibrium reactions between polymetalate ions (reactions involving H_2O) are suppressed in the absence of water.

1. *Crystallization or Precipitation from Aqueous Solution* (*27*)

Whereas normal molybdates ($A_2MoO_4 \cdot yH_2O$) crystallizing from "neutral" [$P(!) = 0$] aqueous molybdate solutions contain the tetrahedral ion MoO_4^{2-} (*1, 154*), all salts of known structure hitherto obtained from acidified molybdate solutions comprise polyanions made up of MoO_6 octahedra. Ammonium (1:2)-molybdate obtained from solutions having $P \approx 0$ consists of MoO_6 octahedra and MoO_4 tetrahedra.



$Mo_7O_{24}^{6-}$

$Mo_8O_{26}^{4-}$

$Mo_6O_{19}^{2-}$

$[Mo_8O_{27}^{6-}]_n$

$[Mo_4O_{14}^{4-}]_n$

FIG. 6. Polymolybdate ions of known structure. (The structure of the "decamolybdate" ion has been omitted. It is too complicated to be depicted in the same manner.)

(3:7)-Molybdates (*65, 66*), the so-called paramolybdates, crystallize from solutions having $Z \approx 1.1$. They are heptamolybdates containing the discrete ion $Mo_7O_{24}^{6-}$ ($Z^+ = 8/7 = 1.14$), whose structure has been determined and repeatedly confirmed (*90–95*) (Fig. 6). The known salts include $Na_6Mo_7O_{24} \cdot 22H_2O$, $Na_6Mo_7O_{24} \cdot 14H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $K_6Mo_7O_{24} \cdot 4H_2O$ (*155, 9, 1, 27*).

At $Z \approx 1.3$, the so-called "trimolybdates," (1:3)-molybdates of formula $A_2O \cdot 3MoO_3 \cdot yH_2O$, are deposited as a very voluminous, fibrous mass of crystals (*155, 1, 9, 156*). Only the Z^+ value (1.33, from analysis) and fingerprints [X-ray powder diagram (*156*), IR (*156*) and Raman spectra (*27*)] are known. The fingerprints show that the same polymetalate species is present in all cases. The known salts include $Na_2O \cdot 3MoO_3 \cdot yH_2O$, $(NH_4)_2O \cdot 3MoO_3 \cdot yH_2O$, $K_2O \cdot 3MoO_3 \cdot yH_2O$. Some uncertainty attaches to the value of y owing to the voluminous texture of the products. For the sodium salt having $y = 3$, a chain-type structure was postulated (*156*).

Solutions of $Z \approx 1.5$ afford the crystalline metamolybdates or "tetramolybdates," (1:4)-molybdates of formula $A_2O \cdot 4MoO_3 \cdot yH_2O$ ($Z^+ = 1.50$). The known salts are $Na_2O \cdot 4MoO_3 \cdot 6H_2O$ (yellowish), $(NH_4)_2O \cdot 4MoO_3 \cdot 2H_2O$ or $\cdot 2.5H_2O$, and $(NH_4)_2O \cdot 4MoO_3$ (without H_2O) (*155, 1, 9, 27*). A potassium salt cannot be prepared; under the appropriate conditions the "trimolybdate" if always formed instead (*14, 27*). According to their Raman and IR spectra the three salts contain different polymetalate ions (*27*). The structure of salt $(NH_4)_2O \cdot 4MoO_3 \cdot 2.5H_2O$ or $\cdot 2H_2O$ is known: It contains discrete octamolybdate ions having the formula $Mo_8O_{26}^{4-}$ (*15, 16*) (Fig. 6). However, mechanistic studies also allow the presence of (structurally different) $Mo_8O_{26}^{4-}$ (cf. Section III, A, 2, c) in the other two salts (*23*).

At $Z \approx 1.8$, crystallization occurs of (1:9)-molybdates (*26, 27*) containing a discrete highly aggregated molybdate ion of probable formula $Mo_{36}O_{112}^{8-}$ ($Z^+ = 64/36 = 1.78$) (*26*). The known sodium, ammonium, potassium, and barium salts crystallize with $\approx 80H_2O$ and display identical Raman spectra (*27*). The structure of the ion has yet to be determined. A structural proposal (*26*) compatible with all available data received no support from mechanistic studies because no explanation can be given for the fast formation of this structure. A new proposal, which appears to satisfy this aspect too (*23*), is put forward in Fig. 7.

Solutions having $P = 2.0$ ($Z \approx 1.8$) to $P = 4$ (the acidification of such solutions can no longer be satisfactorily described by a Z value; cf. Fig. 1) precipitate the so-called decamolybdates, (1:10)-molybdates of formula $A_2O \cdot 10MoO_3 \cdot yH_2O$ ($Z^+ = 1.80$) as small hexagonal

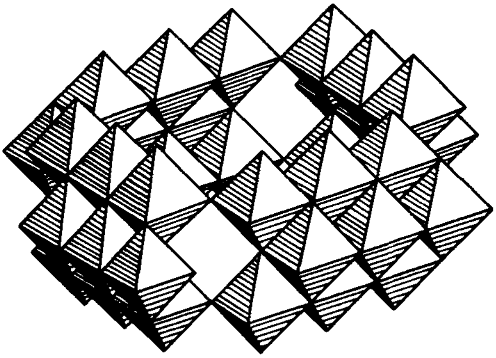


FIG. 7. New proposed structure for the $Mo_{36}O_{112}^{8-}$ ion.

prisms (*157*, *43*, *27*, *106*). The known sodium, ammonium, and potassium salts are shown by their Raman and IR spectra (*27*, *106*) to represent defined substances based on the same polymolybdate ion. No discrete polyanion is present; the basic structural units are double chains of MoO_6 octahedra linked together in three dimensions via shared octahedral corners (*106*). Structural studies indicate $[AHMo_5O_{16}(H_2O)\cdot H_2O]_n$ to be the most appropriate formulation.

The polymolybdates described so far crystallize readily from the acidified alkali (including ammonium) molybdate solutions; although the "trimolybdates," metamolybdates, and "decamolybdates" require a little time to do so (several days). Several further polymolybdates can be obtained on observation of certain conditions (from aqueous solution).

After several hours of heating of an ammonium molybdate solution of $-0.5 \leqslant P \leqslant 0.5$ at $>60°C$ (sealed vessel or replenishment of evaporating ammonia), a crystalline (1:2)-molybdate of formula $(NH_4)_2O\cdot 2MoO_3$ (*158*, *1*, *27*, *159*, *125*) appears. This salt does not contain discrete polyanions but a chain-type polytetramolybdate ion $[Mo_4O_{14}^{4-}]_n$ ($Z^+ = 4n/4n = 1.00$) (*105*, *24*) (Fig. 6). The corresponding sodium and potassium salts are unknown.

If an ammonium heptamolybdate solution is allowed to stand for a very long period (*160*, *161*) or acidified to $Z \approx 1.20$ and treated with ammonium chloride (*162*), it deposits crystals of a (3:8)-molybdate having the formula $3(NH_4)_2O\cdot 8MoO_3\cdot 4H_2O$. This is likewise devoid of discrete polyanions, containing a chain-type polyoctamolybdate ion $[Mo_8O_{27}^{6-}]_n$ ($Z^+ = 10n/8n = 1.25$) (Fig. 6) (*104*, *22*). The corresponding sodium and potassium salts are again unknown.

From solutions of $Z \approx 1.7$, addition of tetrabutylammonium salts precipitates a yellow (1:6)-molybdate; complete agreement of its IR spectrum with that of (1:6)-tungstate indicates the presence of the $Mo_6O_{19}^{2-}$ ion ($Z^+ = 10/6 = 1.67$) (*112*) (Fig. 6). The salt crystallizes without water.

Apart from the alkali salts of the normal monomolybdate, the heptamolybdate, and the 36-molybdate ion, all these substances are sparingly soluble in water (*27*).

According to older literature (*163*), many more polymolybdates should be obtainable from aqueous solution. However, since several decades ago only inadequate methods of identification were available —products were characterized practically only by elemental analysis and appearance—the same products were probably often described as being different, owing to analytical errors (cf. Section III, A, 4, c), and mixtures of different products or mixed crystals as homogeneous substances*.

2. *Preparation by Hydrolysis of Esters*

Since a pure molybdic ester soluble in organic solvents is not yet available, the ester–ammonia adduct $3MoO_2(OC_2H_5)_2 \cdot 2NH_3$ has been used. In this way, salts $(NH_4)_6Mo_7O_{24}$ (without H_2O) ($Z^+ = 1.14$), $(NH_4)_2O \cdot 4MoO_3$ (without H_2O) ($Z^+ = 1.50$), and $2(NH_4)_2O \cdot 6MoO_3 \cdot H_2O$ ($Z^+ = 1.33$) could be prepared (*152*).

3. *Preparation by Reaction of Molybdenum Trioxide with Organic Bases*

Reaction of molybdenum trioxide with hexakis(dimethylamino)-cyclotriphosphazene in aqueous suspension affords the 10,6-molybdate $[HN_3P_3(N(CH_3)_2)_6]_2Mo_6O_{19}$ whose anion has the structure shown in Fig. 6 (*103*). (Remarkably, the proton of the base is located on a ring nitrogen atom.)

B. ISOPOLYMOLYBDATE IONS IN (AQUEOUS) SOLUTION

Studies on aqueous alkali metalate solutions have been performed in some instances without adopting any special measures regarding the ionic medium and in others at greater or lesser ionic strengths. Measurements in which the law of mass action is applied (e.g., methods of Sections III, A, 3, c and A, 5, b) require constant ionic strength for the whole set

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* The polymolybdate types listed above are those that we (*27*) too have obtained from aqueous solution on systematic variation of the conditions of preparation (acidification, crystallization time, temperature, initial concentration of molybdate) and by using cations Na^+, NH_4^+, and K^+.

of experimental data (*49*). High ionic strengths favor aggregation reactions, equilibrium constants become larger (*5*, *164*, *165*), and the measured effects more pronounced (potential jumps, breaks in titrations, etc.) (*31*, *52*, *63*). Rate constants also increase (*166*); however, in disaggregations not only positive (*166*) but also negative effects (*167*, *168*) have been observed. These effects apparently arise by complex formation between the polyions and the alkali metal ions (*2*, *5*, *6*, *169*, *166*, *144*). Nevertheless, since obviously all aggregation reactions are affected in a similar manner, the same species always appear regardless of the ionic strength (cf. Section IV, B, 3, b). Differences reported in the literature are no doubt largely due to the authors' interpretation of their measurements. The sole experimentally confirmed case of the ionic medium having an influence on a reaction seems to be that of the "acidic paratungstate ion" (*170*).

Equilibration of the reactions occuring in molybdate solutions is complete within several minutes at the latest (*5*, *9*, *27*, *143*, *171*). In this respect, the molybdate system differs considerably from the tungstate system. Subsequent reactions are related to the gradual precipitation of sparingly soluble solids (*27*, *172*) (cf. Sections III, A, 2, d and IV, B, 3).

1. Protonated Monomolybdate Species

On acidification of a monomolybdate solution, the MoO_4^{2-} ion is protonated to give HMO_4^- and subsequently H_2MoO_4. Even though the occurrence of these reactions must be regarded as self-evident, their experimental proof is very difficult since the aggregation reactions following simple mono- and diprotonation are very fast (requiring use of flow methods) and quantitative (requiring action concerning concentrations) (*143*).

Studies using a flow technique and plotting potentiometric titration curves as function of the concentration at a time of 10^{-2} sec after acidification showed that no changes in the curves occur only for (initial) concentrations of MoO_4^{2-} of 2×10^{-4} *M* and below, that is, separation of the pure protonation reactions (of the monomolybdate ion) from the aggregation reactions could be accomplished (*143*). (The concentration limit would lie higher for shorter times.) Equilibrium constants for the mono- and diprotonation reaction could be estimated from the shape of the curve (see Table I). Ultrasonic relaxation methods (*150*) afforded a rate constant of 5×10^9 M^{-1} sec^{-1} for monoprotonation of the MoO_4^{2-} ion. This value is about one power of ten lower than that of diffusion-controlled reactions and is explained in terms of structural changes of the monomolybdate ion on protonation (see below).

TABLE I

OVERALL FORMATION CONSTANTS β, OVERALL STANDARD REACTION ENTHALPIES ΔH_r^0, AND OVERALL STANDARD REACTION ENTROPIES ΔS_r^0 FOR FORMATION OF MOLYBDATE SPECIES (p,q)

Parameter	Species (1,1)	(2,1)	(8,7)	(9,7)	(10,7)	(11,7)	(12,8)	(34,19)	(64,36)	(5,2)	Medium	Temp. (°C)	Ref.
Log β	$\approx$3.88	7.75	—	—	—	—	—	—	—	—	0.1 M (KCl)	20	*143*
Log β	4.00	8.21	—	—	—	—	—	—	—	—	$\mu = 0.0023$	20	*175*
Log β	4.68	8.68	—	—	—	—	—	—	—	—	$\mu = 10.5$ (?)	—	*176*
Log β	3.89	7.50	57.74	62.14	65.68	68.21	—	196.30	(373.69[a])	$\approx$19	3 M Na(ClO$_4$)	25	*87*
Log β	3.55	7.20	52.81	57.39	61.02	63.40	—	—	—	—	1 M Na(Cl)	25	*5*
Log β[b]	3.53	7.26	52.80	57.42	60.84	—	71.56	—	—	—			
ΔH_r^0 (kcal)	14 ± 7	—	−56.0	−53.4	−52.6	−53.2	—	—	—	—	3 M Na(ClO$_4$)	25	*134*
ΔS_r^0 (cal deg^{-1})	65 ± 23	—	76	105	124	134	—	—	—	—			

[a] This value was calculated assuming that a 64,36 ion (*87*) and not a 34,19 (*26*) is formed.

[b] Alternative set of species with a 12,8 ion instead of the 11,7 ion.

Detection of the two protonated species with static methods, that is, at equilibrium since in the $H^+/MoO_4{}^{2-}$ system after a few minutes changes no longer occur, has all the more chance of success the greater the contribution made by the pertinent species to the sum of all molybdate species (with the exception of the $MoO_4{}^{2-}$ ion). As a consequence of the law of mass action, this is the case for minimum possible initial concentrations of $MoO_4{}^{2-}$ and minimum possible Z values for the $HMoO_4{}^-$ ion and maximum possible Z values for H_2MO_4 (about 1–2). The lower limit for the $MoO_4{}^{2-}$ initial concentration and the Z value are set by the sensitivity of the method of investigation. Using this approach [evaluation of potentiometric (Z, $\log c_{H^+}$, $C_{MoO_4{}^{2-}}$) equilibrium curves], both $HMoO_4{}^-$ and H_2MoO_4 could be detected (*87*, *5*) and their formation-constants and thermodynamic parameters $\Delta H_r{}^0$ and $\Delta S_r{}^0$ (*134*) (Table I) determined.

The two consecutive dissociation constants of molybdic acid $K_1 = \beta_{2,1}/\beta_{1,1}$ and $K_2 = \beta_{1,1}$ are practically equal while they differ by a factor of about 10^{-5} for other polybasic acids (*173*, *174*). This is generally rationalized in terms of a structural change accompanying protonation, specifically a transition from tetrahedral to octahedral coordination of M according to (*143*, *175*, *176*, *150*)

$$MO_4{}^{2-} \xrightarrow{+H^+,\ +2H_2O} [MO(OH)_5]^- \xrightarrow{+H^+} M(OH)_6 \qquad (8)$$

Our own studies (*177*) of this problem have shown that the occurrence of $[MO(OH)_5]^-$ and $M(OH)_6$ is even less likely than that of $[MO_3(OH)]^-$ and $MO_2(OH)_2$ but that the problem can be solved quite well by assuming the species $[MO_3(OH)(H_2O)_2]^-$ and $MO_2(OH)_2(H_2O)_2$.

2. *Primary Aggregation Products*

We use the term *primary aggregation products* to mean (a) transient species with $q > 1$ requiring investigation techniques suitable for fast reactions, and (b) species detectable also in equilibrium by static methods having $1 < q < q_H$ and $Z^+ \leqslant Z^+{}_H$ and, additionally, those with $q = q_H$ and $Z^+ < Z^+{}_H$, where H is the initial major product occurring on successive acidification of the solution—in this case the $Mo_7O_{24}^{6-}$ ion. Since such species must be fundamentally capable of existence for mechanistic reasons, there has been no lack of attempts to detect them. The detection of di-, tri-, tetra-, and hexamolybdate ions is reported in the literature (*178*, *164*, *169*, *58*, *61*, *179*, *59*, *145*, *146*, *148*; additional data in Refs. *1*, *5*, *52*), these species being described, however, in some cases as major products and not as primary products.

On the basis of model calculations (*108*) with the computer program mentioned in Section III, A, 7, it will now be shown that primary aggregation products cannot be recognized by static methods, especially those given in Sections III, A, 3, a and A, 4, a, if their Z^+ value differs by less than 0.2–0.3 units from that of the main product, as is the case for the 6,6 ion (*58*, *179*, *59*). Those methods permitting recognition of several species coexisting in equilibrium and their characterization with respect to p and q represent exceptions; the only methods of this kind to be used so far are those based on mathematical analysis of (Z, log c_{H^+}, $C_{MO_4{}^{2-}}$) equilibrium curves given in Section III, A, 5, b. For example, assuming that $Mo_7O_{24}^{6-}$ is the initial major product of acidification, as is generally accepted nowadays, we introduce this ion and its overall formation constant, and a second species p,q whose Z^+ value lies between 0.9 and 1.2 (e.g., species 6,6) into the computer program and vary the formation constant for this second ion. We then find that for none of the species p,q does there exist an equilibrium constant that would lead to c_i values giving straight-line sections subject to unequivocal characterization in an $X(Z) = \Sigma_j \chi_j c_j$ plot for $C_{MoO_4{}^{2-}}$ = const. in the range $0 < Z \leqslant 1.2$.

No primary aggregation products were found on mathematical analysis of (Z, log c_{H^+}, $C_{MoO_4{}^{2-}}$) equilibrium curves. Whenever a species with $q < 7$ has been postulated (*178*, *164*, *169*) in such studies, it has actually been a main product occurring at higher Z values. Very detailed studies of the range $0 < Z \leqslant 1.1$ by means of intensity difference diagrams of Raman spectra failed also to indicate primary aggregation products (*27*, *180*). Thus even the very recently reported detection of a 1,2- (*58*, *61*, *59*) or a 6,6-molybdate ion (*58*, *179*, *59*) in a break titration cannot be correct. Such species are clearly at a thermodynamic disadvantage compared to the heptamolybdate ion, as is also apparent from mechanistic studies (*23*).

Relaxation studies by the temperature jump method (*145*, *146*) on 7×10^{-3}–2.5×10^{-2} M molybdate solutions at acidifications P = 0.01–0.11 [pH = 5.3–5.6; medium, 0.3 M Na(NO$_3$)] indicated the existence of a very rapidly formed tetramolybdate ion (Z^+ = 6?/4) as primary aggregation product. At higher ionic strength [3 M Na(ClO$_4$)] but otherwise similar conditions, however, a hexamolybdate ion (p = 6–7, q = 6) was found (*148*).

3. *The Main Reaction Products*

The term *main product* will be used to describe all polymetalate species that can be detected by static techniques, with the exception of those defined as primary aggregation products. Under certain conditions (initial concentration of MO_4^{2-}, acidification, time, temperature), they practically all occur at some time in significant concentrations, although this does not follow from the above definition. Apart from the main products, the solutions will certainly contain numerous other species in such low concentrations that they are undetectable. The existence of such species is also indicated by mechanistic reasoning and investigations (*13*, *19–21*, *27*, *23*). In particular, the discrete polyions evading detection in aqueous solution but crystallizing out of solution as salts (e.g., the ammonium octamolybdate having the structure determined by Lindqvist and tetrabutylammonium 10,6-molybdate) must already be present in solution (cf. also Section III, A, 2, d). The same applies to polymetalates whose crystal lattice is not composed of discrete polyions if the macropolyion itself, however, is clearly formed from discrete polyions [e.g., ammonium polyoctamolybdate (*22*) and ammonium polytetramolybdate (*24*)]. Extensive formation of these salts can be explained in terms of their sparing solubility (which is, however, only rarely demonstrable directly) and removal of their constitutent species from an equilibrium that is unfavorable for them (*22*, *24*, *27*).

a. Range $0 < Z \leqslant 1.14$. Very precise investigation of the range $0 < Z \leqslant 1.1$ by means of intensity difference diagrams of Raman spectra (see preceding Section) reveal that a spectroscopically uniform reaction occurs, within the limits of experimental accuracy (*27*, *180*).

Formation of 7,6- ($Z^+ = 1.167$) or 8,7-molybdate ions ($Z^+ = 1.143$) as initial aggregation product in solution was deduced from breaks in pH, conductivity, and other titration curves (references cited in Refs. *1*, *5*, *9*, *52*). It is very difficult to distinguish between these two ions because their Z^+ values differ only slightly, thus necessitating an accuracy superior to $\approx 0.5\%$ in the Z value of the titration break. Moreover, these studies provide no information about the degree of aggregation: 14,12- or 16,14-Molybdate ions or even higher aggregates could just as easily be present. However, molar mass determinations by ultracentrifugation of solutions with $Z \approx 1.15$ have indicated the degree of aggregation to be 7 or 8, although 6 could not be entirely ruled out (*5*, *52*).

Mathematical analysis of potentiometric (Z, $\log c_{H^+}$, $C_{MoO_4^{2-}}$) equilibrium curves led Sasaki and Sillén (*87*, *9*) to postulate a hydrolysis scheme involving the 8,7-molybdate ion as initial main product. However, Aveston *et al.* (*5*) were able to show that a scheme involving the 9,8-molybdate ion as first main product leads only to an insignificantly greater standard deviation in Z.

Preference for the 8,7-ion over the 7,6- and the 9,8-ion apparently arises because the paramolybdates, whose structure has been known since 1950 (*90*), contain $Mo_7O_{24}^{6-}$ ions ($Z^+ = 8/7$) and crystallize from solutions with $Z = 1.14$.

The good agreement found on comparison of the Raman spectrum of a solution acidified to $Z = 1.14$ with those of crystalline heptamolybdates (*5, 27*) was first utilized by Aveston *et al.* to demonstrate that the $Mo_7O_{24}^{6-}$ ion (see Fig. 6) is, indeed, the first main product to appear in solution. We can thus formulate the overall formation equation for the heptamolybdate ion as

$$8H^+ + 7MoO_4^{2-} \longrightarrow Mo_7O_{24}^{6-} + 4H_2O \qquad (9)$$

This is the only equation we shall give for the molybdate system. Experimental results only permit formulation of overall formation equations or equations in which the species of the initial and final states appear. Such equations are merely of interest so far as techniques of conducting or evaluating the reaction are concerned. In extreme cases the polymetalate species of the initial state can be the direct precursor of that of the final state; however, it may also undergo extensive prior degradation. Statement of a reaction equation for the first main product appearing in solution can be justified inasmuch as the overall formation equation and the equation relating the initial and final state of the system are then identical, i.e., the degradation reactions are redundant.

Apart from the overall formation constant (*87, 9, 5*) for the heptamolybdate ion, ΔH_r^0 and ΔS_r^0 (*134*) for the overall formation reaction could be determined by mathematical analysis of enthalpy titration curves (see Table I).

b. Range $1.14 \leqslant Z \leqslant 1.6$. Investigation of the range $1.14 \leqslant Z \leqslant 1.6$ with the aid of intensity difference diagrams of Raman spectra showed that on successive acidification there is no uniform reaction but instead at least three extensively superimposed consecutive reactions take place (*27*).

Before this direct evidence for the occurrence of several reactions became available, Sasaki and Sillén (*87, 9*) had already drawn up a hydrolysis scheme with several species for this region based on the mathematical analysis of potentiometric (Z, $\log c_{H^+}$, $C_{MoO_4^{2-}}$) equilibrium curves. They assumed formation of 8,7-, 9,7-, 10,7-, and 11,7-molybdate ions. However, Schwing *et al.* (*178, 164*) postulated 8,7-, 8,6-, and 9,6-molybdate ions again on the basis of mathematical analysis of potentiometric equilibrium curves, and Aveston *et al.*

using the same method found that, although the hydrolysis scheme of Sillén and Sasaki with only heptamolybdate ions gives the best fit with their own experimental data, schemes with a 12,8 instead of the 11,7 ion or only with octamolybdate ions (9,8, 10,8, 11,8, and 12,8 ions) also fitted nearly as well (*5*). Sillén subsequently found that Schwing's data were most readily compatible with his hydrolysis scheme too (*181*). Thus, it is seen that, in spite of the precise and, apart from the effects of varying ionic media [Sasaki and Sillén, 3 *M* $Na(ClO_4)$; Schwing, 3 *M* Na(Cl); Aveston 1 *M* Na(Cl)], mutually consistent experimental data of the three research groups no unequivocal conclusion can be drawn about the species occurring in the range under discussion. In addition to protonated heptamolybdate ions and unprotonated and protonated octamolybdate ions, individual hexa- and 9-molybdate ions (in conjunction with the other ions) are certainly also compatible with the experimental data.

The hydrolysis scheme for 1 *M* $Mg(ClO_4)_2$ as ionic medium with 6,6-, 9,8-, and 8,6-molybdate ions (*169*), which the authors believe to arise because of more pronounced complex formation of Mg^{2+} with the polyion than occurs with Na^+, is probably also identical with that having sodium salts as ionic medium, as shown by the standard deviations of other sets of species. Meanwhile, we have been able to prove this for the initial main product by means of Raman spectroscopy: The 8,7-molybdate ion is, indeed, formed also in this case (*180*).

Hydrolysis schemes proposed on the basis of breaks in titration curves and including more than three species (*46*, *58*, *59*, *62*) certainly lack a secure experimental foundation. As a consequence of the superposition of several reactions, deduced from both intensity difference diagrams and model calculations ($\Delta Z^+ < 0.2$; see Section III, A, 7), there are no sufficiently defined straight-line sections for determination of intersections (breaks). Schemes containing only two species (*52*, *61*) must, of course, also be incorrect.

An indication that protonated heptamolybdate ions occur might be seen in the minimal changes of the UV spectrum of the solution reported by Pungor and Halasz (*53*) for the range $1.14 \leqslant Z \leqslant 1.43$. Support for a 12,8-molybdate ion was deduced from a certain degree of resemblance between the Raman spectrum of a molybdate solution having $Z = 1.50$ with the spectrum of crystalline $(NH_4)_4Mo_8O_{26} \cdot 4H_2O$ ($Z^+ = 1.50$), as reported by Aveston and co-workers (*5*). In fact, the presence of 12,8-molybdate ions in solution at $Z = 1.50$ had already been deduced from the very existence of this ammonium 12,8-molybdate (*1*, *51*). Although Aveston himself expresses considerable caution concerning the existence of a 12,8 ion having the structure found by

Lindqvist on the basis of the above-mentioned spectral comparison, it is accepted as well-founded (*182*, *183*, *53*, *147*, *58*, *61*) by most research groups since publication of these experiments.

Our own studies of the solid-state and solution Raman spectra of several polymolybdates and polytungstates revealed much better agreement between the spectra when the same species is clearly present in the solid state and in solution than in the case in question (*27*). Thus the presence of a 12,8 ion, with the structure found by Lindqvist, in solution (at room temperature) seems to be at least "unproven." Recently, using a stopped-flow spectrophotometer, Mellström and Ingri (*142*) found two signals on disaggregation of the polyions present in molybdate solutions at $0 < Z < 1.5$ with excess OH^- ions, one of which was assignable to degradation of the $Mo_7O_{24}^{6-}$ ion and, if occurring, its protonated forms (which are not distinguishable by this method). The signal appearing at higher Z values indicates the presence of a further unidentified (and probably difficult to identify) species. This could be an octamolybdate ion; however, the possible presence of the molybdatosilicate ion formed from silicate contaminants could not be excluded. Acidified molybdate solutions being studied by the temperature-jump method (*147*) exhibited two relaxation signals, assigned to formation of $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$. Since these investigations rest on the foundation of previous work, namely equilibrium studies [by Aveston and co-workers (*5*)], the finding that a further species appears alongside $Mo_7O_{24}^{6-}$ (and possibly its protonated forms) warrants special attention, more so than does the claim of its identification as a $Mo_8O_{26}^{4-}$ ion.

For mechanistic reasons (*23*) we also consider the occurrence of 12,8 ions to be highly probable. However, the ion having the structure found by Lindqvist cannot play a very important role (at room temperature). We would definitely rule out the presence of 6,6-, 8,6-, 9,6-, 9,8-, and 11,8-molybdate ions in significant concentration.

A rate constant of $7 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ was deduced for protonation of the 8,7-molybdate ion from ultrasonic relaxation measurements (*150*). This value corresponds to that of diffusion-controlled reactions.

c. Range $1.6 \leqslant Z < 2$. By using intensity difference diagrams of Raman spectra, we found that yet another uniform polymolybdate ion surprisingly appears in the range $Z > 1.6$ at $Z \approx 1.8$ (*26*). This range had formerly been little investigated, no doubt because of difficulties besetting precise determination of Z. The equilibrium concentration of H^+ is already rather high so that errors in its potentiometric determination are consequently large; a further serious difficulty lies in the fact that the equilibrium concentration of H^+ steadily approaches the order of magnitude of the initial concentration, with the result that the reacted H^+ concentration, as the small difference between two large numbers, cannot be determined very accurately. However, we have already pointed out that intensity difference diagrams are completely insensitive to errors in Z values if they are employed merely to identify a uniform species.

The degree of aggregation of the species could be specified as 34–40, a surprisingly high value, by molar mass determination in an ultracentrifuge (sedimentation equilibrium technique) (*26*).

Additional information about the species was gained by studying the salts crystallizing out of the solutions, since complete agreement of the Raman spectra indicates the presence of the same polymolybdate species in solution and in the salts (*26*). Thus, combining the results of molar mass determination by ultracentrifugation with X-ray studies (see Section III, A, 5, a) yielded the degree of aggregation of $q = 36$, and the stoichiometric coefficient for the H^+ ion could be determined as $p = 64$ (even number) from the Z^+ value (1.77 ± 0.03) resulting from analysis of the solid (*26*). Structural models developed on the basis of mechanistic consideration led to the formula $Mo_{36}O_{112}^{8-}$ (*26*, *23*) (cf. Section IV, A, 1 and Fig. 7).

Earlier attempts to determine the molar mass [salt cyroscopy (*8*), ultracentrifugation (*5*), dialysis techniques (*184*)] had merely shown that the degree of aggregation and the polydispersity increase steeply beyond $Z = 1.5$. Mathematical analysis of potentiometric (Z, log c_{H^+}, $C_{MoO_4{}^{2-}}$) equilibrium curves led to a best fit between calculated and experimental data assuming participation of a 34,19-molybdate ion (*87*). Our own calculations (*26*) in which the 34,19 ion was replaced by the 64,36 ion gave only a slightly greater standard deviation in Z for the set of species with the 64,36 ion.

At still higher acidification, cationic species appear in the solution (*9*, *11*, *53*, *185–187*).

4. Disaggregation with OH^-

All polymolybdate ions are rapidly transformed by OH^- ions into polyions corresponding to the Z value of the solution. Accordingly, an excess of OH^- ions effects complete disaggregation to $MoO_4{}^{2-}$. Disaggregation of the $Mo_7O_{24}^{6-}$ ion is a first-order reaction with regard to both $Mo_7O_{24}^{6-}$ and OH^- ions (*167*, *168*, *188*, *142*). The reaction has also been studied with various organic bases (*168*, *188*, *189*) (cf. also Section IV, B, 3, b).

5. *Isopolymolybdate Ions Occurring in Solution and in the Solid State*

Some polymolybdate ions occur only in solution, and others only in solids. However, several ions exist both in solution and in the solid state. The polyions of the last-mentioned group are the most important

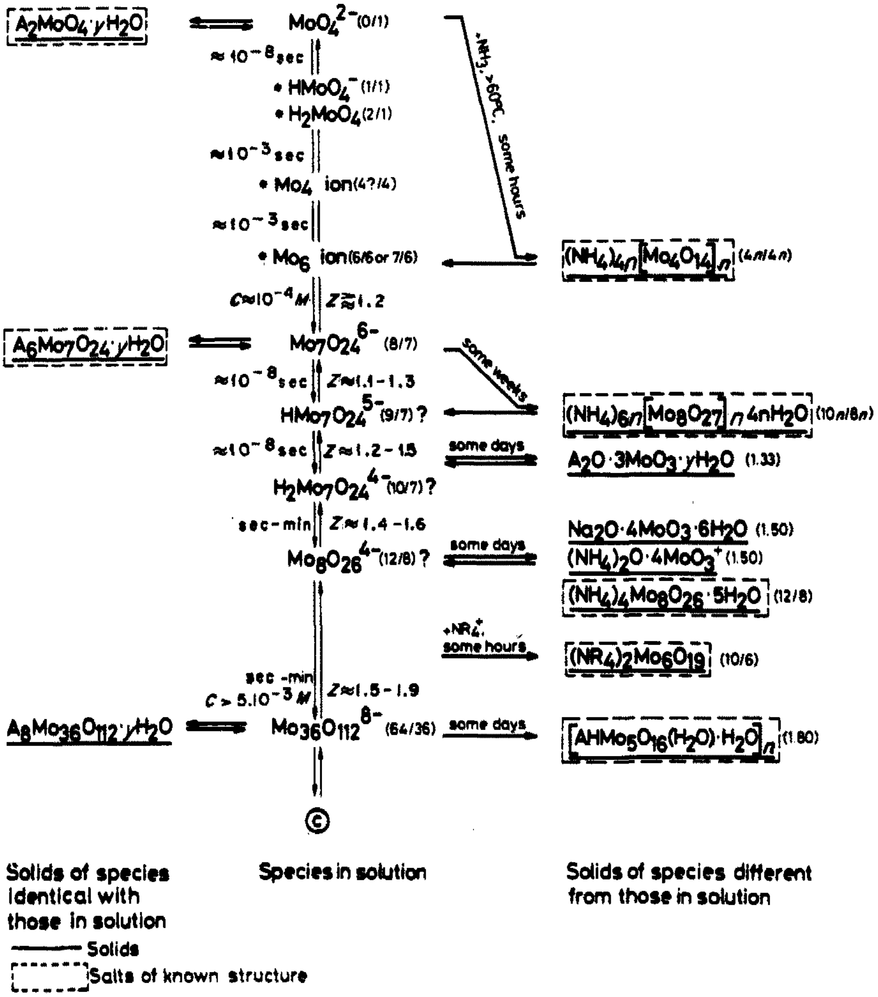

FIG. 8. Reaction scheme for the processes occurring in acidified aqueous molybdate solutions. In field c, probably only cationic species occur. In parentheses: p/q resp. Z^+. *Short-lived species that occur at equilibrium in small amounts only. †For this species reverse reaction does not take place.

for deriving reaction mechanisms: On the one hand these ions, as main products, are the thermodynamically preferred species since they are subject to the law of mass action in solution, and on the other hand, more experimental data are available for them, their structural data being of particular interest. Apart from the tetrahedral (*190*) MoO_4^{2-} ion, only the $Mo_7O_{24}^{6-}$ ion (see Fig. 6) and the $Mo_{36}O_{112}^{8-}$ ion occur both in (aqueous) solution and in the solid state.

The experimental results of Section IV are summarized as a reaction scheme in Fig. 8.

V. Isopolytungstates

A. SOLID ISOPOLYTUNGSTATES

1. *Crystallization or Precipitation from Aqueous Solution* (*27*)

The normal tungstates $A_2WO_4 \cdot yH_2O$ crystallizing from "neutral" ($P = 0$) aqueous tungstate solutions contain the tetrahedral WO_4^{2-} ion (*154*, *2*),* whereas polyanions made up of WO_6 octahedra occur in the salts obtained from acidified tungstate solutions, insofar as their structures have been determined. In this respect there is no difference between molybdates and tungstates. Differences do occur, however, in the course of the aggregation reactions, with the result that there is hardly a single polyionic species in either of the systems that has its counterpart in the other.

Solutions having $Z \approx 1.17$ deposit crystalline (5:12)-tungstates (*31*, *67*, *68*), the so-called paratungstates B,† crystallization requiring several days. Paratungstates B are dodecatungstates containing the discrete

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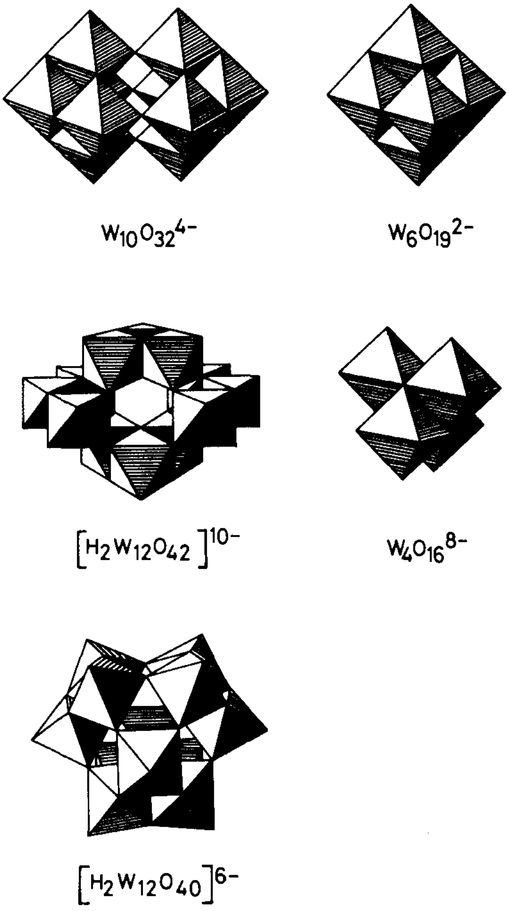
* Salt $7Li_2WO_4 \cdot 4H_2O$ is an exception. It contains at the center of the primitive cubic unit cell a $W_4O_{16}^{8-}$ group made up of WO_6 octahedra (Fig. 9) and WO_4^{2-} tetrahedra at the mid-points of the edges (*191*, *8*, *192*).

† Up to the mid-1940s only paratungstates are mentioned in the literature. In 1943, Souchay recognized that paratungstate solutions ($Z = 1.17$) are not homogeneous but contain two species in equilibrium. They were distinguished as paratungstate A and B ions. Solutions freshly acidified to $Z = 1.17$ were reported to contain only the para A ion, and the freshly prepared solutions of crystalline paratungstate ($Z^+ = 1.17$) only the para B ion. Subsequently, a further species was postulated for solutions having $Z = 1.17$ and designated as para B ion, Souchay's original para B ion being renamed as para Z ion. In the present article the designation introduced by Souchay is retained and other ions on the paratungstate level are designated A or B with subscripts, depending on whether the ion is regarded as a hexameric or a dodecameric particle. This is also expedient in view of the fact that we can hardly reserve the entire alphabet for the paratungstate level. Meanwhile, other species that are not precursors of the para Z ion have been designated Y and X.



$W_{10}O_{32}^{4-}$ $W_6O_{19}^{2-}$

$[H_2W_{12}O_{42}]^{10-}$ $W_4O_{16}^{8-}$

$[H_2W_{12}O_{40}]^{6-}$

FIG. 9. Polytungstate ions of known structure.

ion $[H_2W_{12}O_{42}]^{10-}$ ($Z^+ = 14/12 = 1.17$), whose structure has been determined by X-ray methods (Fig. 9) (*96*, *193*, *97–100*). The two H atoms are located in the interior of the W—O framework (*98*, *99*, *119*)* (cf. Section III, B, 1, c). The known salts include $Li_{10}[H_2W_{12}O_{42}]\cdot$

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* Although they are, in principle, acidic according to our theory of formation mechanisms and structures of polymetalate ions, the two H atoms are practically unable to exert an acid function owing to their location in the interior of the W—O skeleton. As a result of the structures of the W—O skeletons the shielding of the H atoms is less effective in the paratungstate B ion than in the metatungstate ion, which is also apparent from rapid alkalization experiments (*144*) (cf. Sections V, B, 3, a and b).

$32H_2O$, $Na_{10}[H_2W_{12}O_{42}] \cdot 27H_2O$, $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 10H_2O$, $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$, $K_{10}[H_2W_{12}O_{42}] \cdot 11H_2O$ (*2*, *7*, *194*, *195*).

From solutions having $Z \approx 1.5$, the X-ray amorphous pseudo-(ψ-) metatungstates can be precipitated (*31*, *7*, *151*, *196*). They are (1:4)-tungstates for which a probable degree of aggregation of about 24 has been deduced from the identity of the Raman spectra of solids and of solutions (*27*) and from molar mass determinations conducted with solutions (cf. V, B, 3, b). Salts $3K_2O \cdot 12WO_3 \cdot 15H_2O$ and $3BaO \cdot 12WO_3 \cdot 24H_2O$ ($Z^+ = 1.5$) are known (*31*, *7*). Recent investigations have shown the potassium salt to deviate somewhat from the ratio $a:b = 1:4 = 3:12$ [$2.58(K,Na)_2O \cdot 12WO_3 \cdot 17H_2O$ ($Z^+ = 1.57$) (*151*), $3K_2O \cdot 11.2WO_3 \cdot 12.9H_2O$ ($Z^+ = 1.46$) (*196*)].

After standing for several months or prolonged heating of a solution with $Z \approx 1.5$, again (1:4)-tungstates crystallize; this time the so-called true metatungstates are formed. They are dodecatungstates, shown by their isomorphism (*120*) with the 12-tungstatophosphate ion (*121*) of known structure to contain the discrete $[H_2W_{12}O_{40}]^{6-}$ ion ($Z^+ = 18/12 = 1.50$) (Fig. 9). Further proof of structure comes from the close resemblance among UV spectra of metatungstate, dodecatungstatophosphate, and dodecatungstatosilicate ions in solution (*7*). By X-ray structural analysis on aqueous solutions of the last-mentioned species, it could be shown that the structure of the $[SiW_{12}O_{40}]^{4-}$ anion is retained on dissolution in water (*36*). The two H atoms are situated in the interior of the W—O skeleton (*118*, *119*) (cf. Section III, B, 1, c; see also footnote on p. 281). The known salts include $Na_6[H_2W_{12}O_{40}] \cdot 21H_2O$ and $K_6[H_2W_{12}O_{40}] \cdot 11H_2O$ (*7*). (5:24)-Tungstates can be precipitated from the metatungstate solution by addition of trialkylammonium acetates (alkyl, e.g., pentyl and isopentyl) (*74*). They are acidic metatungstates having the formula $(HNR_3)_5[H_3W_{12}O_{40}]$ (without water of crystallization) ($Z^+ = 19/12 = 1.58$). Their appearance is probably due to the pronounced bulk of the trialkylammonium ion (*74*). One of the H atoms of the anion must be "peripherically" bonded.

If a tungstate solution is rapidly acidified to $Z \gtrsim 1.6$, then the yellowish (1:5)-tungstates, the so-called polytungstates Y can be precipitated (*74*, *151*). These salts contain the discrete decatungstate ion $W_{10}O_{32}^{4-}$ ($Z^+ = 16/10 = 1.60$) whose structure was first deduced from theoretical considerations (*197*) and has meanwhile been experimentally verified (*101*) (see Fig. 9). Among these salts, we know $K_4W_{10}O_{32} \cdot 4H_2O$, $(HNR_3)_4W_{10}O_{32}$, and $(NR_4)_4W_{10}O_{32}$ (without water of crystallization) (R = propyl, butyl, pentyl, isopentyl) (*151*, *74*).

Addition of acetone to tungstate solutions freshly acidified to $Z \approx 1.17$, which contain the paratungstate A ion ($Z^+ = 7/6 = 1.17$)

(cf. Section V, B, 3, a) whose salts do not, however, crystallize, precipitates a salt, regarded as paratungstate A, that is contaminated with the salt of the mineral acid used for acidification (*198*).

Concerning the preparation of a salt of another polytungstate species having $Z^+ = 1.50$, see footnote on p. 292 (Section V, B, 3, b).

2. *Preparation by Hydrolysis of Esters*

Controlled hydrolysis of tungstic tetraesters in organic solvents usually in the presence of organic bases or salts (*8*, *109*, *111*, *112*) opens a route to polytungstates, which in some cases can only be prepared impure, if at all, from aqueous solution. Which polyion actually is formed depends mainly on the solvent and the strength of the base. The salts generally crystallize without water (cf. Section III, B, 1, b).

It was possible to prepare the following salts: guanidinium monotungstate (*109*), ammonium, piperidinium, and pyridinium paratungstate A $\{A_5[HW_6O_{20}(OH)_2]$ or $A_5[HW_6O_{21}]$ (*109*)$\}$; ammonium paratungstate A_1 (*8*; cf. footnote †, p. 280); quinolinium and quinaldinium ψ-metatungstate (*109*); trialkylammonium polytungstates Y (alkyl = ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, isopentyl) (*112*); and tetraalkylammonium hexatungstates $(NR_4)_2W_6O_{19}$ (R = ethyl, *n*-propyl, *n*-butyl) (*111*). In the last-named salts, (1:6)-tungstates, the discrete $W_6O_{19}^{2-}$ ion (*102*) ($Z^+ = 10/6 = 1.67$) is present; its structure is depicted in Fig. 9. This ion cannot be detected in aqueous solution.

Salts of the polytungstate ions formed by aging (paratungstate B ion, metatungstate ion) have not yet been obtained by this method (*109*).

3. *Preparation by Reaction of* $WO_3 \cdot H_2O$ *with Organic Bases*

Piperidinium paratungstate A has been obtained by reaction of $WO_3 \cdot H_2O$ with piperidine as a medium-strength organic base (*153*).

4. *Preparation of Polytungstates Having an Inorganic Cation from Those Having an Organic Cation*

According to this method, the tributylammonium salt of the hydrogen metatungstate ion, $(HNR_3)_5[H_3W_{12}O_{40}]$ (cf. Section V, A, 1), dissolved in acetone was reacted with a solution of potassium iodide in acetone to form anhydrous potassium metatungstate $K_6[H_2W_{12}O_{40}]$, and, *inter alia*, the hydrogen metatungstate ion identified as such (*74*).

B. ISOPOLYTUNGSTATE IONS IN (AQUEOUS) SOLUTION

In the tungstate system too, investigations have been performed in some cases without adopting any special measures regarding the ionic medium and in others at greater or lesser ion strengths. The remarks made in the case of the molybdate system, where references pertinent to the tungstate system are also cited, also apply in the present section.

In contrast to the molybdate solutions, very fast reactions (*143*, *144*, *12*) and those reaching completion within a few minutes at the latest (*31*, *2*, *7*, *166*, *27*) are accompanied by very slow reactions (*31*, *2*, *7*, *166*, *27*) in tungstate solutions.

1. *Protonated Monotungstate Species*

On acidification of a monotungstate solution, the WO_4^{2-} ion is protonated to HWO_4^- and thence to H_2WO_4. Occurrence of these reactions is even more difficult to prove than in the analogous molybdate case, since the subsequent aggregation reactions start at even lower metalate concentrations and, thus, also proceed even faster (*143*, *144*).

Studies employing a flow method (*143*, *144*), as indicated for the molybdate system, showed no changes in the shape of curve for a time 5×10^{-3} sec after acidification only when the initial concentration of WO_4^{2-} was $\approx 7 \times 10^{-5}$ M or less (separation of the pure protonation reactions of the monotungstate ion from the aggregation reactions). Here, too, the equilibrium constants of the mono- and diprotonation reaction could be estimated from the shape of the curve (see Table II).

With static methods [evaluation of potentiometric (Z, log c_{H^+}, $C_{WO_4^{2-}}$) equilibrium curves], H_2WO_4 could not be detected at all, and detection of the HWO_4^- ion and determination of its formation constant (see Table II) could be accomplished only by the method developed especially for measurements at low Z values (*88*).

Concerning the two dissociation constants of tungstic acid and the conclusions drawn from their magnitude regarding the structure $\{[WO_3(OH)]^-$, $[WO(OH)_5]^-$, or $[WO_3(OH)(H_2O)_2]^-$ and $WO_2(OH)_2$, $W(OH)_6$, or $WO_2(OH)_2(H_2O)_2\}$, the same situation applies as in the molybdate system.

2. *Primary Aggregation Products*

In the tungstate system too, there has been no lack of attempts to detect primary aggregation products. In particular, the occurrence of di- and tritungstate ions (*54*, *199*, *200*) has been repeatedly claimed. Since paratungstate B and metatungstate ions can be pictured as being made up of tritungstate units, it was considered necessary to stipulate tritungstate ions for structural reasons (*200*). The feasibility of detecting such species is subject to the same restrictions as have been mentioned

TABLE II

OVERALL FORMATION CONSTANTS β, OVERALL STANDARD REACTION ENTHALPIES $\Delta H_r{}^0$, AND OVERALL STANDARD REACTION ENTROPIES $\Delta S_r{}^0$ FOR FORMATION OF TUNGSTATE SPECIES (p,q)

Parameter	Species							Medium	Temp. (°C)	Ref.
	(1,1)	(2,1)	(1,2)	(6,6)	(7,6)	(14,12)	(18,12)			
Log β	≈4.05	8.1	—	—	—	—	—	0.1 M (KCl)	20	*143*
Log β	≈3.5	8.1	—	—	—	—	—	0.1 M ($NaClO_4$)	20	*144*
Log β	≈3.8	—	≈5.8	≈51.7	≈59.7	—	—	3 M $Na(NO_3)$	22	*88*
Log β	—	11.3(?)	—	52.46	60.76	123.24	—	3 M $Na(ClO_4)$	25	*201*
Log β	—	—	—	—	53.98	111.03	132.51	3 M Li(Cl)	50	*6*
Log β	—	—	—	—	59.98	—	—	3 M Na(Cl)	25	*165*
$\Delta H_r{}^0$ (kcal)	—	—	—	−57.1	−62.5	−126.9	—	3 M $Na(ClO_4)$	25	*135*
$\Delta S_r{}^0$ (cal deg^{-1})	—	—	—	49	68	138	—			

in our discussion of the molybdate system. Accordingly, all attempted detections except those considered in the following lack a firm experimental foundation.

Mathematical analysis of (Z, log c_{H^+}, $C_{WO_4^{2-}}$) equilibrium curves revealed a 6,6- (*201*, *88*) and a 1,2-tungstate ion (*88*). The former appears only at very low Z values and, according to our concepts of the formation mechanisms and structures of polymetalate ions, should be formulated as $[W_6O_{20}(OH)_2]^{6-}$ (*19*). It has no acid/base relationship with the paratungstate A ion (see Section V, B, 3, a). The 1,2-tungstate ion, which we formulate as $[W_2O_7(OH)]^{3-}$ (*13*), could only be detected by the method developed especially for measurements at low Z values. It occurs at relatively high tungstate concentrations but only with very low Z values. (As an exception to the rule that polymetalate ions are built up of MO_6 octahedra, this ion must also contain an MO_4 tetrahedron according to our ideas about the formation mechanism of polymetalate ions.)

Relaxation measurements by the temperature-jump method (*149*) on 0.5×10^{-2} to 2.2×10^{-2} M tungstate solutions at Z values up to 0.2 ($-\log c_{H^+} \approx 7$) indicated the existence of a very rapidly formed tetratungstate ion. Our mechanistic concepts (cf. Section VI, A) require that this species be formulated as $[W_4O_{12}(OH)_4]^{4-}$ ($Z^+ = 4/4 = 1.00$) (*13*).

Schwarzenbach and co-workers (*143*, *144*) had likewise detected a tetratungstate ion ($Z^+ = 5/4 = 1.25$) using the flow technique by recording potentiometric titration curves at 5×10^{-3} sec after acidification. We formulate this ion as $[HW_4O_{12}(OH)_4]^{3-}$. It occurs in a different pH range (pH ≈ 3) from that found by the temperature-jump method (pH ≈ 7), thus explaining protonation beyond $Z^+ = 1$.

Apart from the overall formation constants for the 1,2- (*88*) and 6,6-tungstate ion (*201*, *88*), mathematical analysis of enthalpy titration curves also afforded ΔH_r^0 and ΔS_r^0 of the overall formation reaction for the 6,6 ion (*135*) (see Table II).

Remarkably enough, more primary aggregation products have been detected in the tungstate system than in the molybdate system, although it might be thought an easier task in the latter case owing to the less pronounced tendency to undergo aggregation (*19*).

3. *The Main Reaction Products*

a. Range $0 < Z \leqslant 1.17$. Precise investigations of the range $0 < Z \leqslant 1.17$ using intensity difference diagrams of Raman spectra showed that a spectroscopically uniform reaction occurs, within the limits of experimental accuracy, if the time of acidification of the solution is adopted as reference point (*27*).

Breaks in pH, conductivity, and other titration curves, in conjunction with molar mass determinations by the diffusion technique and by salt cryoscopy led to postulation of 7,6-tungstate ions ($Z^+ = 1.167$) (method as described in Section III, A, 5, a; references cited in Refs. *2*, *6*, *7*). 8,7-Tungstate ions ($Z^+ = 1.143$) have only been postulated occasionally, although precisely the same problem is met as in the molybdate system: The Z^+ values of the two species lie so close together that the Z value of the break has to be known to within less than $\approx 0.5\%$. Molar mass determinations by ultracentrifugation, which were performed because of the inaccuracy of the diffusion technique and salt cryoscopy, confirmed a degree of aggregation of 6 to 8 (*6*, *7*, *75*). [This polytungstate ion is one of the few species for which the degree of aggregation previously determined by the diffusion method (*60*, *77*, *202*) or by salt cryoscopy (*31*) was confirmed as being of the correct order.]

Mathematical analysis of potentiometric (Z, log c_{H^+}, $C_{WO_4^{2-}}$) equilibrium curves led to the postulation of hydrolysis schemes in which a 7,6-hexatungstate ion again features as the initial main product (*50*, *201*, *6*).

The polytungstate ion under discussion is usually formulated as 7,6 ion "$HW_6O_{21}^{5-}$." This formula contains the lowest possible number of H atoms. Controlled hydrolysis of tetraethyltungstate in ethanol led, in the presence of ammonia, piperidine, and pyridine as bases, to crystalline polytungstates, which displayed the same properties as the above tungstate ion on dissolution in water and may, therefore, be regarded as salts of this ion (*109*). According to the results of analysis, these salts can be formulated as 7,6-tungstates containing the ions $[HW_6O_{21}]^{5-}$ or $[HW_6O_{20}(OH)_2]^{5-}$ ("$HW_6O_{21}^{5-} \cdot H_2O$") (with r as 3 or 2) (*109*). Bearing in mind the analytical difficulties to be surmounted with the readily crystallizing heptamolybdates (*65*, *66*) and paratungstates B (*67*, *68*, *31*) in order to establish whether they are (5:12)- or (3:7)- (i.e., 7,6- or 8,7-)metalates, there is no choice but to accept an alternative interpretation as 8,7-tungstates for these poorly crystallizing and not very stable substances. The (Z, log c_{H^+}, $C_{WO_4^{2-}}$) equilibrium curves certainly allow also a set of species including an 8,7 ion (cf. the difficulties attending a decision between the hepta- and octamolybdate species).

Thus we see that the presence of 7,6-tungstate ions in solutions acidified to $Z \approx 1.17$ is by no means experimentally established, although their occurrence is accepted as certain by nearly all authors. A theoretical approach to the mechanisms of formation and structures of polymetalates (see Sections VI, B, 1–4) has led us to propose a structure (see Fig. 16) having the formula $[HW_6O_{20}(OH)_2]^{5-}$ ($r = 2$) (*19*). Accordingly we can write the formula equation for the ion as

$$7H^+ + 6WO_4^{2-} \longrightarrow [HW_6O_{20}(OH)_2]^{5-} + 2H_2O \qquad (10)$$

(cf. the comments regarding the formation equation for the heptamolybdate ion).

In solution, the 7,6- (or possibly 8,7-)tungstate ion is subject to slow conversion into another ion having the same Z^+ value until equilibrium is reached (*31*, *7*, *44*, *27*). Since tungstates having $Z^+ = 1.17$ are designated as paratungstates, the 7,6 ion occurring in tungstate solutions freshly acidified to $Z = 1.17$ has been called paratungstate A, and the other, paratungstate B (*31*). At high concentrations ($C_{WO_4^{2-}} \geqslant 0.1\ M$) equilibrium lies on the para B side, and, at low concentrations ($C_{WO_4^{2-}} \leqslant 0.1\ M$), on the side of the para A ion (*6*, *27*). As a consequence of the law of mass action, this concentration dependence provides some indication that the para B ion has a considerably higher degree of aggregation than the para A ion. Mathematical analysis of potentiometric (Z, log c_{H^+}, $C_{WO_4^{2-}}$) equilibrium curves identified the para B ion as a 14,12 ion ($Z^+ = 1.167$) (*6*). However, this finding requires confirmation by another method of study, for a 13,11 or a 15,13 ion ($Z^+ = 1.182$ and 1.154) no doubt fits the experimental data just as well as a 14,12 ion (cf. the difficulties attending a decision between the hepta- and octamolybdate species).

Freshly prepared solutions of the paratungstates crystallizing from tungstate solutions at $Z = 1.17$ exhibit the same behavior as the paratungstate B ion (*31*, *7*, *27*). In these solutions equilibrium between paratungstate A and B ions is approached from the para B ion (*31*, *7*, *27*). Molar mass determinations on freshly prepared solutions in an ultracentrifuge again showed the presence of a 12-tungstate ion (*7*, *6*, *75*). However, the experimental error of these measurements could extend this result to an 11- or 13-tungstate ion too. There appear to be several reasons favoring a 12-tungstate ion: (a) As has long (*96*) been known, the paratungstates crystallizing from solution contain discrete 12-tungstate ions; (b) interconversion of hexa-para A and dodeca-para B ions could be explained by a dimerization step in the conversion mechanism; (c) an ion having a degreee of aggregation that is already so high should (since it is probably made up of several small structural units of the same kind) have a symmetrical structure, i.e., an even degree of aggregation {cf., however, the highly symmetrical ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (*203*)!}. Comparison of the Raman spectra recorded for crystalline paratungstates with those of their (freshly prepared) solutions provided experimental evidence for the 12-tungstate ion (*6, 27*). Thus, the paratungstate B ion is assigned the formula $[H_2W_{12}O_{42}]^{10-}$ (see Fig. 9), and the crystalline paratungstates are paratungstates B.

The equilibrium between the paratungstate A and B ions can be formulated as

$$2[HW_6O_{20}(OH)_2]^{5-} \rightleftharpoons [H_2W_{12}O_{42}]^{10-} + 2H_2O \qquad (11)$$

Nevertheless, it should be clearly pointed out that no experimental proof has been obtained for a dimerization step in the interconversion of paratungstate A and B ions.

Fast acidification experiments in a flow apparatus (*144*) showed that the para A ion is hardly protonated down to a pH value of 3, affording a pK_a value of $\leqslant$ 2 for $[H_2W_6O_{20}(OH)_2]^{4-}$ [ionic medium 1 *M* Na(Cl)]. By contrast, protonation of the para B ion starts at considerably higher pH values [with 1 *M* Na(Cl) as ionic medium at pH $\approx$ 6] and the pK_a values are 5.0 for the $[H_3W_{12}O_{42}]^{9-}$ ion and 4.3 for the $[H_4W_{12}O_{42}]^{8-}$ ion. Fast alkalization experiments (*144*) afforded a pK_a value of $\approx$ 11 [1 *M* Na(Cl)] for the $[H_2W_{12}O_{42}]^{10-}$ ion. The authors give no pK_a for the $[HW_6O_{20}(OH)_2]^{5-}$ ion but a value $>$11 [1 *M* Na(Cl)] can be derived from the titration curve reported, which is readily compatible with our structural proposal for the para A ion (*19*). On the other hand, a pK_a value of 8.30 [3 *M* Na(ClO$_4$)] and 8.0 [3 *M* Na(NO$_3$)] would result from the overall formation constants for the 7,6 (para A) and 6,6 ion if the two ions are regarded as a conjugate acid/base pair. We, therefore, consider the experimentally detected 6,6 ion not to be the deprotonated para A ion, as does Arnek (*135*), but an ion of different structure for which we have put forward proposals (*19*).

Among the thermodynamic data, in addition to the overall formation constants for the para A (*50, 6, 201*) and para B ion (*6, 201*), ΔH_r^0 and ΔS_r^0 of the overall formation reactions have been established by mathematical analysis of enthalpy titration curves (*135*) (see Table II).

According to Boyer and Souchay (*170, 166*), at low tungstate concentrations and low ion strengths, an "acidic paratungstate" ion ($Z^+ \approx$ 1.33) appears in place of the paratungstate A ion ($Z^+ \approx$ 1.17). This ion is stabilized by $N(CH_3)_4{}^+$ ions and destabilized by Na^+ owing to ion pair formation between Na^+ and para A ions. At higher tungstate concentrations ($>$0.1 *M*) and on use of the sodium salt, the acidic paratungstate ion no longer appears because the Na^+ ion of the salt itself will suffice for ion pair formation with the para A ion.

b. Range $1.17 \leqslant Z \leqslant 1.6$. In the tungstate system too, aggregation reactions are not complete at $Z \approx$ 1.17. Up to $Z \approx$ 1.6, further reactions occur which, in contrast to the molybdate system, exhibit a pronounced time dependence.

The "acidic paratungstate" ion ($Z^+ \approx 1.33$), which appears in place of the para A ion under certain conditions, has already been discussed in the preceding section.

Conductivity, pH, and other titration curves show a break at $Z \approx 1.50$ (references cited in Refs. *2*, *6*, and *7*). A precise investigation has shown that not just one, but three or even four species having a Z^+ value close to 1.50 appear consecutively (*44*, *25*, *166*).

The first to appear directly (ca. 1 min) after acidification is designated as the metatungstate A ion (*44*). It is distinguished unequivocally from the subsequently appearing species, but characterized only by its approximate Z^+ value. The species is assumed to be the doubly protonated paratungstate A ion (*44*); however, the opinion has recently been voiced that it is identical with the polytungstate Y ion described below (*124*).

The metatungstate A ion is transformed within several hours into the ψ-metatungstate ion (*44*). This transformation manifests itself in a change in the shape of pH and conductivity titration curves, the shift of the long-wave UV absorption edge toward shorter wavelengths, and the appearance of a polarographic half-wave potential (*44*). The degree of aggregation is still a matter of dispute. Salt cryoscopy indicated sixfold tungstate aggregation (*31*). Investigations with an ultracentrifuge (Archibald technique) surprisingly yielded 24-aggregation (*7*).This result ($q = 24 \pm 3$) was confirmed by the same research group using the sedimentation equilibrium technique (*204*). A degree of aggregation of 24 has for a short period also been postulated by another group (*205*), but later this group claimed the ψ-metatungstate ion to have $q = 12$ (sedimentation equilibrium and velocity methods) (*75*). The ψ-metatungstate ion can be precipitated as the potassium and the barium salt (*31*, *7*). Comparison of Raman spectra shows that the same polytungstate species are present in the solid state and in solution (*27*). According to ^{1}H NMR studies the ion still possesses OH groups (*7*, *119*). The Z^+ value can be given approximately as 1.50 (cf. Section V, A, 1).

The ψ-metatungstate ion is irreversibly transformed in the course of weeks or months—faster on heating—into the true metatungstate ion, which appears to be the thermodynamically most stable species at $Z = 1.50$ (*31*, *44*, *7*). This transformation can be readily followed by UV (*7*, *25*) and Raman spectroscopy (*27*), as well as by the disappearance of the polarographic half-wave potential of the ψ-meta ion (*31*).

The metatungstate ion was identified by molar mass determinations in the ultracentrifuge as a dodecatungstate ion (*7*, *73*, *75*), and, thus, an 18,12-tungstate ion. Mathematical analysis of potentiometric (Z, log c_{H^+}, $C_{WO_4^{2-}}$) equilibrium curves of aged tungstate solutions (*6*) likewise indicated an 18,12 ion. As in other cases, the experimental accuracy of the molar mass determinations and of the potentiometric measurements is certainly not so great as to rule out an 11- or 13-tungstate ion. However, the presence of a dodecatungstate ion is verified by the good agreement between Raman spectra recorded for the solution and the solid state (*34*, *27*), and by the agreement existing among the UV spectra of solutions of metatungstate, dodecatungstatophosphate, and dodecatungstatosilicate ions (*7*). As already mentioned, it was demonstrated for the last-named species that the structure of the anion $[SiW_{12}O_{40}]^{4-}$ is retained on dissolution in water (*36*, *206*). Accordingly, the metatungstate ion should also be formulated as $[H_2W_{12}O_{40}]^{6-}$ ($Z^+ = 18/12 = 1.50$) in solution (see Fig. 9) [the two H atoms are located in the interior of the W—O skeleton (*118*, *119*)]. Fast acidification and alkalization experiments show the metatungstate ion to be aprotic in the pH range of 3 to 10 (*144*). Salts of the protonated ions can, however, be obtained from metatungstate solutions by precipitation with trialkylammonium acetate solution (*74*) (cf. Sections V, A, 1 and V, A, 4).

Interestingly enough, the metatungstate ion is not only formed in (aged) solutions having $Z \approx 1.5$ (or in the range $Z \approx 1.17$–1.50). At low tungstate concentrations, it also appears in considerable concentrations in (aged) solutions at $Z \approx 1.17$ (and lower) alongside the paratungstate A and B ions co-existing in equilibrium (*6*, *7*, *207*). This is simply a consequence of the pronounced thermodynamic stability of the metatungstate ion and the law of mass action: In dilute metalate solutions, the pH value for the same Z value lies considerably lower than in concentrated solutions, so that the high H^+ concentration required for formation of the 18,12 ion is present. Under these conditions, the ψ-metatungstate ion does not occur at all. Since the metatungstate ion possesses a higher Z^+ value than would correspond to the Z value of the solution, a further species having $Z^+ \ll 1.17$ must also be present in such solutions. This is the unprotonated monotungstate ion WO_4^{2-} ($Z^+ = 0$).

It has recently been found that yet another species, called polytungstate X, intervenes between the ψ-metatungstate and the metatungstate ion (*25*). Molar mass determinations in an ultracentrifuge show that it is probably also a dodecatungstate ion (*75*) like metatungstate, and the Z^+ value is most likely also 1.50. The UV spectrum of the solution and the polarographic half-wave potential are available as fingerprints (*25*).*

If a paratungstate A (or a monotungstate) solution is *rapidly* acidified to $Z \ngtr 1.6$, a further species is formed, the so-called polytungstate Y ion (*7*), which is characterized by typical UV (*7, 151, 74*) and Raman spectra (*27*). With regard to the acidification, the optimum conditions for the occurrence of this species lie at $Z \approx 1.6$ (*166, 27*). Anhydrous trialkylammonium, tetraalkylammonium (alkyl = propyl, butyl, pentyl, isopentyl), and tetraphenylphosphonium salts of composition $A_2O \cdot 5WO_3$ (*74, 124*) as well as the potassium salt (*151*) $K_2O \cdot 5WO_3 \cdot 4H_2O$ (*74*) can be precipitated from solution. Raman spectra show the same polytungstate species to be present in the salts as in their aqueous solutions (*27*). For mechanistic reasons (*197*), a species having $c = 0$ and a base/acid ratio of 1:5 can only be a decatungstate ion, $W_{10}O_{32}^{4-}$ ($Z^+ = 16/10 = 1.60$) whose structure is shown in Fig. 9. Molar mass determination in water and in acetone as solvent (*74*) and X-ray structure determination (*101*) confirm the presence of decatungstate ions. Thus, contrary to former assumptions (*7, 151, 75, 166*), dodecameric ions are not present. In (freshly) acidified aqueous solutions, the polytungstate Y ion is always accompanied by the ψ-metatungstate ion and is not stable for any length of time (at room temperature); it is transformed into the ψ-metatungstate ion within a few hours (*7, 151, 74, 27*). In fact, however, the two ions are in a temperature-dependent equilibrium that lies on the side of the ψ-meta ion at room temperature and on the side of the poly Y ion at higher temperatures (at 80°C the equilibrium in a $C = 1.2 \times 10^{-1}$ M solution lies to the extent of 60% on the side of the poly Y ion) (*205*).

Possibly, the polytungstate Y ion is identical with the metatungstate A ion. Evidence in support of this conclusion is provided not only by approximately equal rates of conversion into the ψ-meta ion and the unidirection shift of the long-wave UV absorption edge, but also by the break in the conductivity titration curve that lies at $Z = 1.56$ (*44*) instead of exactly at $Z = 1.50$.

Transformation of polytungstate ions Y into ψ-meta, ψ-meta into X,

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* The authors were able to employ a trick to prepare pure polytungstate X (*138*): They reduced a ψ-metatungstate solution under defined conditions at a mercury cathode, allowed the reduced ψ-metatungstate ion to transform into the reduced polytungstate X ion, oxidized it to the polytungstate X ion, and precipitated it as the cesium salt after prior removal of small amounts of the decomposition products of the ψ-meta and poly X ion by precipitation as the potassium salts.

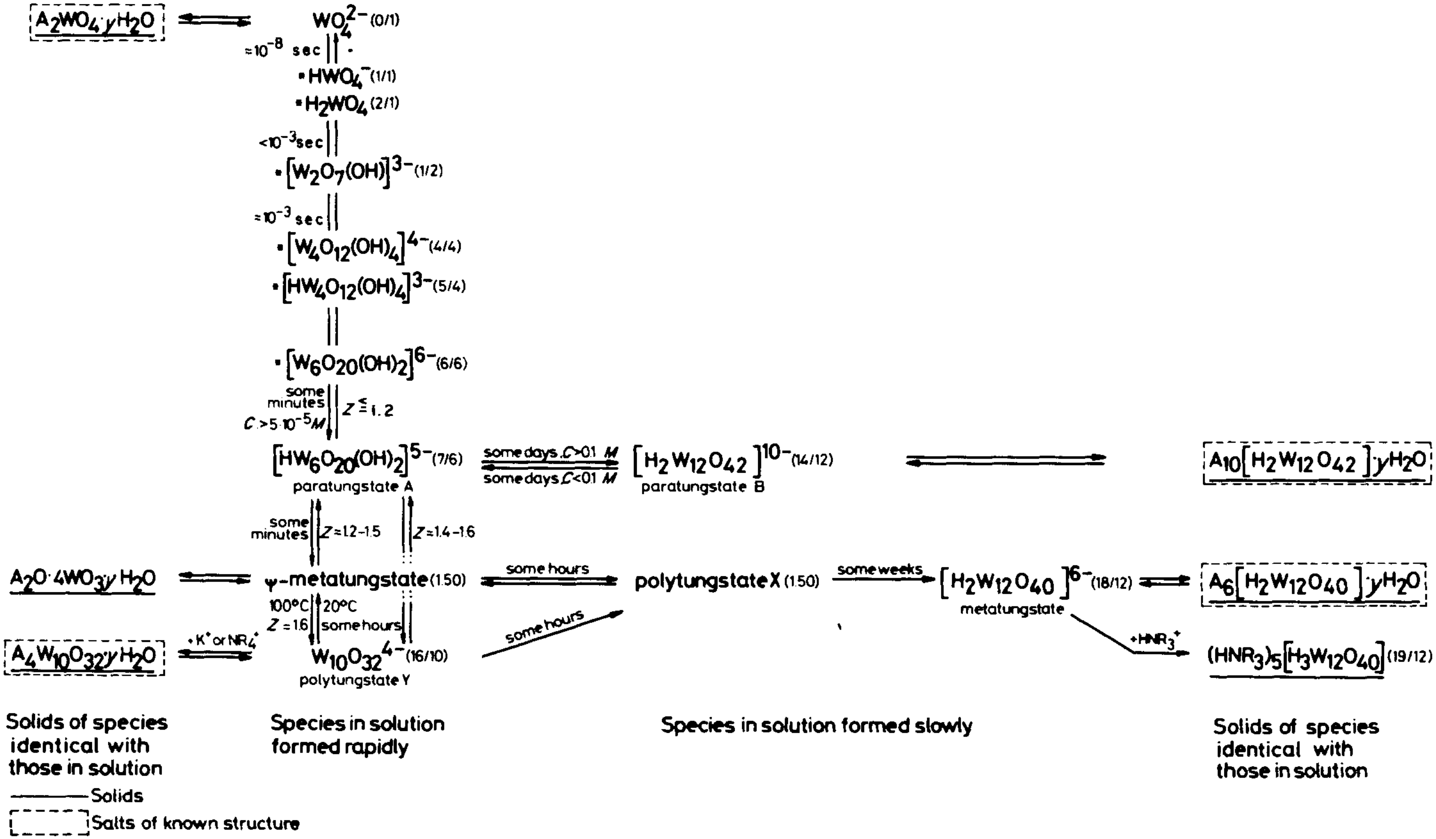

FIG. 10. Reaction scheme for the processes occurring in acidified aqueous tungstate solutions. In parentheses: p/q resp. Z^+. *Short-lived and other thermodynamically unfavorable species that occur at equilibrium in small amounts only.

Y into X, X into meta, meta into para A, X into para A, X into ψ-meta, ψ-meta into para A, and Y into para A has also been studied at defined pH values in buffered solution (*25*, *151*, *166*). It was found that all reactions are first-order in the polytungstate ion. Transformation of poly Y ion into the ψ-meta ion and into the para A ion is also first-order with respect to the OH^- ion. The reacton rate is independent of OH^- concentration for conversion of polytungstate X into meta, X into ψ-meta, and X into para A. (In the last case there is no OH^- dependence because the ψ-meta ion occurs as intermediate and its formation is the rate-determining step.)

4. Disaggregation with OH^-

In unbuffered solution all polytungstate ions are converted by OH^- ions into those polyions corresponding to the *Z* values of the solution and the time. There appears to be a rule that slowly formed anions also disaggregate slowly. With an excess of OH^-, ions, complete disaggregation to WO_4^{2-} takes place. Disaggregation of the metatungstate ion is first-order in metatungstate and in OH^- ion (*208*).

5. Isopolytungstate Ions Occurring in Solution and in the Solid State

The importance of possessing maximum information about precisely those species that occur both in solution and in the solid state has already been mentioned in the context of the isopolymolybdates. Apart from the tetrahedral (*190*) WO_4^{2-} ion, such species comprise the $[H_2W_{12}O_{42}]^{10-}$, the ψ-metatungstate, the $[H_2W_{12}O_{40}]^{6-}$, and the $W_{10}O_{32}^{4-}$ ions. Within certain limits this also applies to the paratungstate A (*27*) and polytungstate X ion (*138*).

The experimental results of Section V are summarized in the reaction scheme in Fig. 10.

VI. Formation Mechanisms of Polymetalates

We shall now broach the questions of why usually well-defined species occur under certain conditions instead of complex polymer mixtures, why particular structures are formed, why completely different species appear in the molybdate and tungstate systems, why some species are formed very rapidly and others very slowly, etc.

The structure of heteropolyanions was first considered by Miolati (*209*) who applied Werner's coordination theory to this class of compound. This theory was then extended by Rosenheim and co-workers (*210*) and applied to isopolyanions too. Once the first structural elucidation of a (hetero)polyanion, with the discovery of octahedral coordination of the M atoms with six O atoms, had become available (*121*), the theory was seen to be untenable. However, even prior to that discovery, Pauling (*211*) had become convinced that heteropolymetalates contain MO_6 octahedra with shared edges, even though his proposal was found to be incorrect for (1:12)-heteropolymetalates. The further development of polymetalate chemistry was decisively influenced by the first structural studies on isopolymetalates by Lindqvist (*90*, *15*, *96*), from whom the first ideas about the systematics of isopolymolybdate structures also originate (*1*). Similar views concerning heteropolymolybdate structures were later expressed by Kepert (*212*), who also attempted to derive the existence of the various (iso- and hetero)polymetalate structures solely on the basis of the size and charge of the metal atoms (*212*).

A first attempt to elucidate the mechanism of aggregation, i.e., the geometrical course of the individual successive aggregation steps is due to Freedmann (*200*). Starting from the [unsound (*2*, *213*)] experimental finding that a tritungstate ion should be the initial aggregation product on hydrolysis of a WO_4^{2-} solution (which seemed to be confirmed by the presence of W_3 units in the polytungstate structures then known), the author presents a series of geometrical steps purported to lead from the protonated tetrahedral monotungstate ion, via an increase in coordination from tetrahedral to octahedral, to a tritungstate as the preliminary product according to the building principle adopted. The result of these geometrical considerations could not be correct because, apart from other objections (*23*), the author had incorrectly counted the O atoms in the structures (*13*). Another attempt to derive the existence and isotope exchange behavior of a trimetalate group from particular geometric aspects (*214*) is also geometrically incorrect (*23*). By contrast, the geometrical building principle proposed by Kepert (*2*), which entails an increase in tungsten coordination from tetrahedral to octahedral with simple addition of a bidentate ligand, appears highly reasonable, even though in this case too (again owing to an error in counting of the O atoms) no adequate result was obtained (*13*).

Yet another attempt to put forward certain structural and mechanistic (partial) conclusions about isopolymetalates is due to Chojnacki (*215*, *216*). He proposed a "core + links" hypothesis resembling that of Sillén (*49*). The principal deviations from the latter are that the "core" may also be made up of several M atoms; that the core possesses the local Z^+ value of 2 (or possibly 3) and its M atoms, therefore, display octahedral coordination toward oxygen; that the number of "links" having the local Z^+ value of 1 (or possibly 0) and tetrahedral coordination with oxygen is limited to the number of peripheral O atoms in the core; and that information about the pH range of existence of a species is derived from the ratio of the M atoms in the core to those in the links. Since a polyion composed entirely of octahedra accordingly has to have a Z^+ value of at least 2 and no polyions exist for $Z^+ = 1$, all structures known so far contradict this hypothesis.*

We shall now present our own mechanistic views (*13*, *19–23*) on the formation of isopolymetalates, which embrace not only purely geometrical aspects but also consideration of acid/base properties of polymetalate ions and of their thermodynamic and kinetic stability.

A. THE ADDITION MECHANISM (*13*, *23*)

According to the studies we have performed so far, the addition mechanism is the simplest of all conceivable aggregation mechanisms. As such it serves especially for the formation of primary aggregation products.

1. Construction of Octahedra by the Addition Principle; Fundamental Geometrical Alternatives (*13*)

A prerequisite for the occurrence of aggregation is doubtless the very fast ($\approx 10^{-8}$ sec) protonation of the MO_4^{2-} ions to HMO_4^- and possibly H_2MO_4. In both species, M—O bonding is extended owing to protonation (*2*), and there is a possibility of attaining octahedral coordination for the M atom by addition of two monodentate or one bidentate ligand (Fig. 11a). A possible monodentate ligand is H_2O, which would yield species $[MO_3(OH)(H_2O)_2]^-$ and $MO_2(OH)_2(H_2O)_2$ proposed earlier (cf. Section IV, B, 1). However, reaction with biden-

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* Assumption of a core + links principle, also with a polynuclear core, is not irrelevant. If our following theory of the formation mechanisms and structures of isopolymetalate ions is correspondingly applied to heteropolymetalate ions (*23a*), the heteroatom polyhedron [e.g., $Te(OH)_6$] acts as aggregation nucleus ("core") and the HMO_4^- or H_2MO_4 function as "links" according to the addition or condensation principle (i.e., with raising of the coordination number of M). Hence an MO_6 octahedron [e.g., $MO_2(OH)_2(H_2O)_2$] can, at least in principle, also be taken as an aggregation nucleus (*23*). The final result on operation of the addition and condensation mechanism is the same as for the tetranuclear tetrametalate ion (formed only by the addition mechanism) as core, because the final product actually formed is decided by the acid/base properties (acidic and nonacidic H atoms) and the thermodynamic and kinetic stability of the competing species, granted that the same geometrical principles govern the constructional steps.

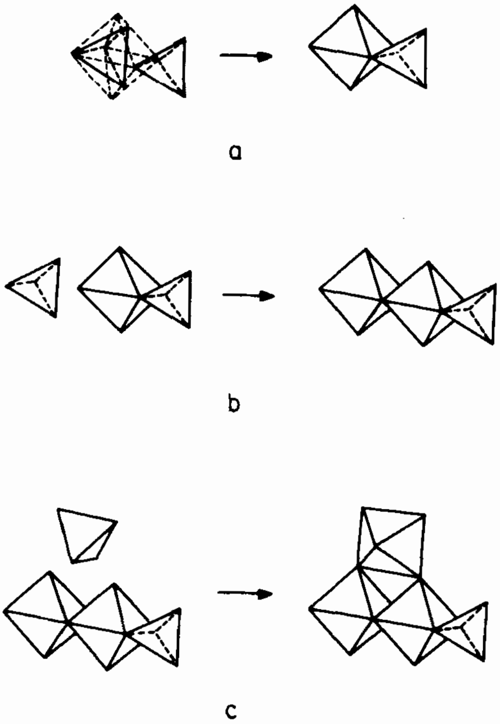

FIG. 11. Construction of an octahedron by the addition principle. (a) Addition of an MO_4 tetrahedron (HMO_4^-, H_2MO_4) to a tetrahedral edge (MO_4^{2-}, HMO_4^-, H_2MO_4), (b) to an octahedral edge (polymetalate ion already formed having MO_6 octahedra), (c) to the corners of two adjacent octahedra (larger polymetalate ion already formed).

tate ligands is no doubt more favorable. We assume the MO_4^{2-} ion, a further HMO_4^- ion or H_2MO_4 molecule (Fig. 11a), and already formed polymers containing MO_6 octahedra (Figs. 11b and c) to be capable of acting as such. Numerous polymeric species can be built up in compliance with this principle. We can classify them according to structure as follows.

A. Open (chainlike) polymetalates. Apart from MO_6 octahedra these also contain a MO_4 tetrahedron.

1. Unbranched (straight or angled) chains
    a. Tetrahedral group in terminal position
    b. Tetrahedral group within the chain

2. Branched chains
    a. Octahedron as branching point
    b. Tetrahedron as branching point
    c. Branching from the corners of two octahedra.

B. Closed (cyclic) polymetalates. These are made up exclusively of octahedra, and thus contain no tetrahedron. They arise on occurrence of intramolecular addition, i.e., when two O atoms of a polymeric ion act as dentic groups toward the tetrahedral group of the same ion (Fig. 12).

1. Unbranched (planar or puckered) rings
    a. Four-membered "rings"
    b. Six- and higher-membered rings
2. Rings bearing side chains (including branched ones)
    a. Side-chain linkage via an octahedral edge
    b. Side-chain linkage via the corners of two octahedra

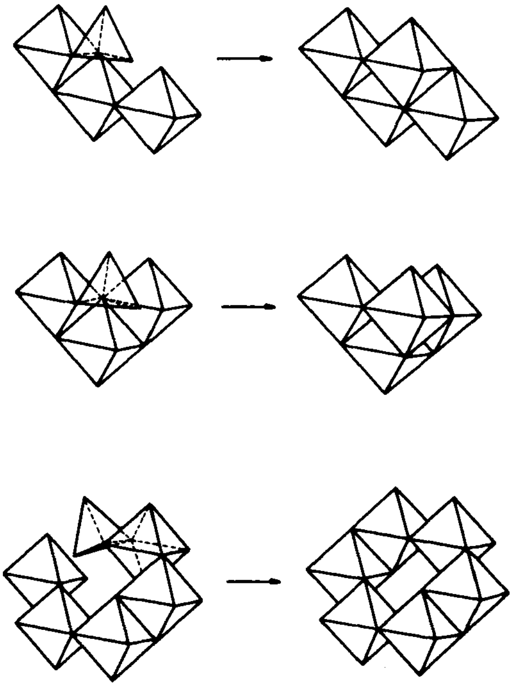

FIG. 12. Intramolecular addition with ring closure illustrated for formation of the two four-membered "rings" and a six-membered ring.

Among these numerous polymetalate structures, the cyclic structural units (without side chains) are distinguished from the others, *inter alia,* by requiring simultaneous disruption of two octahedra on removal of an MO_4 group, whereas only one octahedron is destroyed in all other cases. Moreover, of the cyclic structures, the four-membered "rings" are favored for purely statistical reasons by a factor of 10^3–10^4 over the next-highest representatives, the six-membered rings. This is simply explained: The probability that, of all the numerous possible addition sites, precisely the two ends of a long, angled, and relatively rigid chain should unite is extremely low.

If the (initial) concentration of MO_4^{2-} is very small, the aggregation reactions are disfavored by the law of mass action and H_2O plays an increasing role as ligand (cf. Sections IV, B, 1 and V, B, 1). The same applies also to the small amounts of protonated monometalate ions necessarily present in equilibrium (*23*).

2. *Acid/Base Functions of Polymetalate Ions; Number and Positions of H Atoms (19)*

The H atoms of the HMO_4^- ions forming the polymetalate ion are essential for the maintenance of octahedral coordination (Fig. 13) and, therefore, cannot be acidic as a general principle. It is worthwhile to consider which positions these H atoms will occupy and whether more H atoms than dictated by the ratio $1H^+/MO_4^{2-}$ (for an ion made up exclusively of octahedra) will be required for any particular reason.

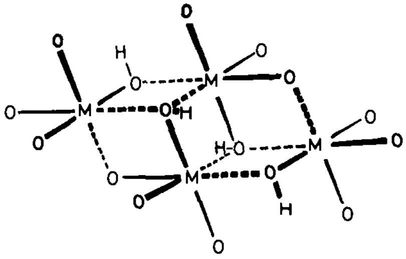

FIG. 13. "Meshing" of four HMO_4^- ions to form the $[M_4O_{12}(OH)_4]^{4-}$ ion.

Each octahedron is built up from an HMO_4^- ion and two further O atoms (belonging to 1 or 2 other HMO_4^- ions) (cf. Fig. 13) and thus bears a negative charge, i.e., it corresponds to a basic function in the aggregate. Now there are two kinds of O atoms in each octahedron: nonterminal O atoms (O atoms in M—O—M bridges and in OH groups) and terminal O atoms. In the pH range in which aggregation occurs, only terminal O atoms participate in charge acceptance. Inspection of all possible structures reveals that the following octahedra occur:

$$M(O_6)^- \quad M(O_5)O^- \quad M(O_4)O_2^- \quad M(O_3)O_3^-$$

The O atoms shown in parentheses are those belonging to M—O—M bridges and OH groups. It is seen from this formulation that the more stable base functions, i.e., those that have many O atoms outside the parentheses, occur when the (nonacidic) H atoms occupy positions on the O bridges. [Another reason why such positions are more favorable for H atoms than the others will become apparant later (Section VI, A, 3, b)]. Thus, the positions of the nonacidic H atoms are largely determined.

We can estimate the p*K*a values of the acid functions corresponding to these base functions by comparison with those of the mononuclear oxo acids. Table III shows that, in the pH range where significant aggregation takes place, the base functions $M(O_6)^-$ and $M(O_5)O^-$ can only occur in the protonated form. Hence the number and positions of further H atoms are established, which are, however, acidic.* Provided that protonation of the $M(O_4)O_2^-$ and $M(O_3)O_3^-$ functions does not take place, the base and acid functions are largely independent of each other (*23*).

3. *Energetics* (*19*, *20*, *23*)

a. Reaction and Structural Components of Favorable and Unfavorable Energy. We must now examine what factors favor aggregation and what factors disfavor the process.

Coordination of the bidentate ligands to HMO_4^- or H_2MO_4, i.e., construction of an octahedron, is doubtless the most important energy-producing process; a large portion of this energy will certainly come from the chelate effect. Since the oxygen has only four bonding orbitals it will avoid a coordination number of 5 wherever possible.

Both the repulsive forces acting among the negative charges and those among the M atoms as the central atoms of the octahedra are to be regarded as unfavorable. These interactions have a pronounced detrimental effect on the construction of highly aggregated polymetalates of compact structure. In particular, these compact structures also restrict the ability of the M atoms to minimize mutual repulsion by

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* The $M(O_6)H$ function can, however, be regarded as practically nonacidic (*19*). Polymetalate ions are no longer formed at the high pH values required for its deprotonation.

TABLE III

RELATION BETWEEN FORMULA OR STRUCTURE AND pK_a VALUE OF OXO ACIDS AND ACID FUNCTIONS OF POLYMETALATE IONS

		Examples		
Acid/base	pK_a	Chlorine acids [X = Cl]	Polymetalate octahedra [X = M(O$_n$)]	
$XO_3(OH)/XO_4^-$	Very small	$ClO_3(OH)/ClO_4^-$	Nonexistent	
$XO_2(OH)/XO_3^-$	$-3 \cdots 0$	$ClO_2(OH)/ClO_3^-$	$M(O_3)O_2(OH)/M(O_3)O_3^-$	$(3O_t)$
$XO(OH)/XO_2^-$	$1 \cdots 4$	$ClO(OH)/ClO_2^-$	$M(O_4)O(OH)/M(O_4)O_2^-$	$(2O_t)$
$X(OH)/XO^-$	$7 \cdots 10$	$Cl(OH)/ClO^-$	$M(O_5)(OH)/M(O_5)O^-$	$(1O_t)$
Nonexistent for mononuclear oxo acids	>11	—	$M(O_6)H/M(O_6)^-$	$(0O_t)$

moving away from the octahedral (or tetrahedral) centers. The repulsive forces among the negative charges are reduced by the additional protonation of the $M(O_6)^-$ and $M(O_5)O^-$ functions, when these base functions are present in a structure. The base functions should be considered relative to one another. The more stable, i.e., energetically favorable, functions are those with many terminal O atoms.

b. Free Energy of Reaction for the Various Aggregates. We have seen that there are energetically favorable and unfavorable reaction and structural components among the polymetalate ions. They appear in varying proportions for the different structures. If a structure and the reaction pathway by which it is formed is resolved to a sufficient extent, then the free energy of reaction $\Delta G^0_{r,i}$ for species i can be thought of as made up of increments for the individual reaction and structural components:

$$\Delta G^0_{r,i} = \sum_e h_{e,i}\, g_e \tag{12}$$

Term $h_{e,i}$ is the frequency of the component e for species i, and g_e is the increment of $\Delta G^0_{r,i}$ for the single occurrence of component e. (For components whose frequency cannot be counted out on the structure or reaction equation, e.g., the energy of electrostatic repulsion among negative charges, an appropriate standardization must be performed.)

However, we now have to render comparable the $\Delta G^0_{r,i}$ values for the various species. This is done by standardizing all $\Delta G^0_{r,i}$ values in such a manner that they correspond to experimental or imagined conditions. In the acidification range up to $Z \approx 1$, for instance, this means that the frequencies of the reaction and structural components have to be normalized for the initial amount of H^+ ions (h) as the reactant in which the system is deficient:

$$\Delta G^{0,h}_{r,i} = \sum_e h^h_{e,i}\, g_e \tag{13}$$

Components to be treated in this way include: construction of an octahedron (O); presence of an octahedron formed by coordination of one or two H_2O molecules (T_1, T_2); occurrence of coordination number 5 for oxygen (K); electrostatic repulsive energy among the negative charges (E); electrostatic repulsive energy among the M atoms (Z'); differing abilities of the M atoms to undergo displacement from the octahedral centers for octahedra with three adjacent, two adjacent, one, or no free corners (A_3, A_2, A_1); occurrence of an $M(O_3)O_3^-$ and $M(O_4)O_2^-$ base function (in the structure regarded as final product) (N_3, N_2); and protonation of an $M(O_5)O^-$ function appearing during the course of aggregation (H).

In order to obtain from Eq. (13) information about the thermodynamic stability of the numerous species possible according to the addition mechanism, we adapt it to the use of *relative* g_e values, e.g.,

$$\Gamma_i^h \equiv \Delta G_{r,i}^{0,h}/g_{\mathrm{O}} = \sum_e h_{e,i}^h \, (g_e/g_{\mathrm{O}}) \equiv \sum_e h_{e,i}^h \, \gamma_e \tag{14}$$

Now we can apply the equation to the aggregation products, estimating limiting values with an adequate safety factor for each γ_e. We find that in the case of *a scarcity of* H^+ *ions* ($Z \leqslant 1$) the maximum Γ^h (i.e., minimum $\Delta G_r^{0,h}$) occurs for the cyclic aggregates ($Z^+ = q/q = 1$), except for the compact four-membered "ring" ($Z^+ = 5/4 = 1.25$), within wide limits for the γ_e values .The estimated limiting values for γ_e were ($\gamma_{\mathrm{O}} \equiv 1$):

$$\begin{array}{rlcrl}
\gamma_{T_1} & = -0.75 \cdots -0.5 & \qquad & \gamma_{A_3} & \approx 1.5\gamma_{A_2} \\
\gamma_{T_2} & = -0.5 \cdots 0 & & \gamma_{A_1} & \approx 0.5\gamma_{A_2} \\
\gamma_K & \approx -0.5 & & \gamma_{N_3} & = 0 \cdots 0.5 \\
\gamma_E & = -0.15 \cdots 0 & & \gamma_{N_2} & = 0 \cdots \gamma_{N_3} \\
\gamma_{Z'} & = 0 \cdots 0.7\gamma_E & & \gamma_H & = -0.2 \cdots 0.2 \\
\gamma_{A_2} & = -0.4\gamma_{Z'} \cdots 0 & & &
\end{array}$$

The reason the planar 4,4-tetrametalate ion (and the other cyclic but statistically disfavored polymetalate ions) are so favorable thermodynamically is to be seen in the minimal Z^+ value of only 1 for this species; for nearly all other species constructued entirely from octahedra, $Z^+ > 1$. However, if Z^+ is unity the maximum possible number of octahedra (high energy gain) can be formed for a given amount of H^+ ions. If $Z^+ > 1$, then H^+ ions are required for simple protonation of the base functions $M(O_6)^-$ and $M(O_5)O^-$; although this is also energetically advantageous because it reduces the electrostatic repulsion among the negative charges, the energy gain cannot compare with that resulting on construction of an octahedron.

The necessity of protonating the base functions $M(O_6)^-$ and $M(O_5)O^-$ is a further reason for the nonacidic H atoms occupying O-bridge positions (cf. Section VI, A, 2) since this reduces the number of $M(O_5)O^-$ functions.

The reaction pathway leading to the planar 4,4-metalate ion is shown in Fig. 14. The principle governing the course of aggregation from the thermodynamic aspect when there is a scarcity of H^+ ions is to achieve, for a given number of protons, a maximum number of octahedra, preferably having two and three terminal O atoms, on the one hand, and a minimum accumulation of negative charge and of M atoms, on the other.

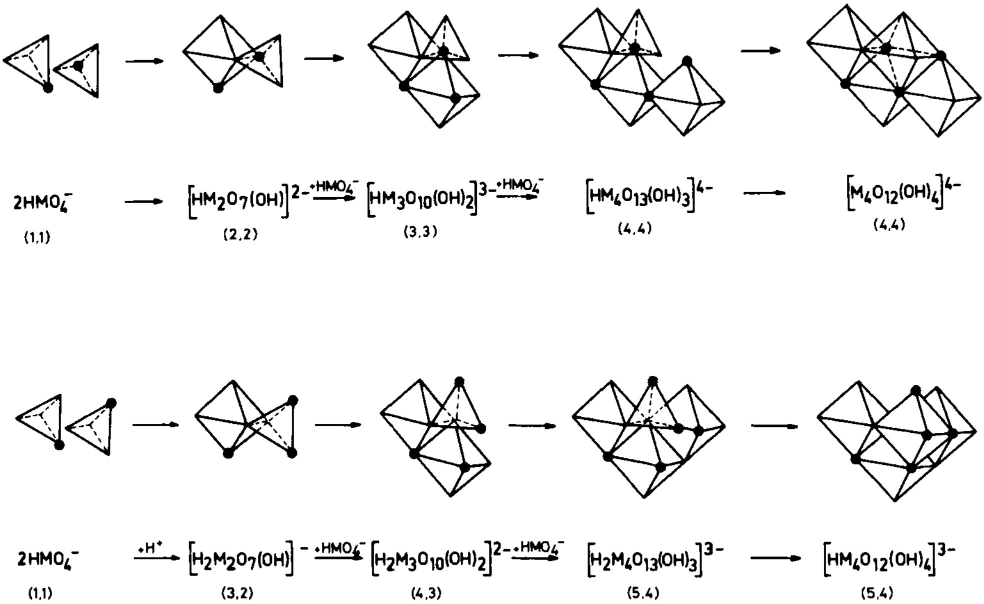


FIG. 14. Reaction pathway to the (planar) 4,4- and the (compact) 5,4-metalate ion according to the addition mechanism. (●) Positions of H atoms.

If there is an *adequate supply of H^+ ions*, the higher Z^+ value of the compact 5,4-metalate ion no longer opposes its formation. For geometrical reasons (cf. Section VI, A, 4), even the compact tetrametalate ion is now favored. The reaction pathway leading to the compact 5,4-metalate ion is also depicted in Fig. 14.

4. *Kinetics* (*13*, *23*)

Geometrically, construction of octahedra according to the addition principle is a very simple process. This explains the high rate of formation of polymetalate ions formed by addition: The rate constants of the primary bimolecular aggregation steps lie in the region of 10^6 M^{-1} sec^{-1} and higher.

The assumption that aggregation is favored when the (protonated) monomeric metalate species already possess octahedral coordination is sometimes found, accompanied by references to the construction of polymetalate ions from MO_6 octahedra, in the literature (*147*, *176*) (cf. Section IV, B, 1). However, the above geometrical considerations demonstrate that this is by no means necessary. On the contrary, aggregation even becomes more difficult for the postulated monomers

$[MO(OH)_5]^-$ and $M(OH)_6$ since simple addition is no longer possible. If our proposed monomer structures $[MO_3(OH)(H_2O)_2]^-$ and $MO_2(OH)_2(H_2O)_2$ were to apply, on the other hand, they could readily be incorporated into the aggregation scheme of the addition mechanism (*13*).

Comparison of the reaction steps leading from the (same) trimetalate structure to the planer and the compact tetrametalate structures reveals that from a geometrical standpoint the step leading to the compact structure is the more favorable of the two [see Fig. 4 in Tytko and Glemser (*13*)]. With an adequate supply of H^+ ions, when the more favorable Z^+ value is not the crucial factor, formation of the compact 5,4-tetrametalate ion is thus favored.

As previously mentioned, removal of an MO_4 group from a cyclic structural unit leads to simultaneous destruction of at least two octahedra, but of only one in all other cases. This means that elimination of an HMO_4^- ion from a ring is more difficult, i.e., the cyclic structural units are kinetically more stable than all other structural groups. When viewed with regard to the number of sites where elimination of an HMO_4^- ion can occur with disruption of the minimum number of octahedra, the compact tetrametalate structure is again favored (*13*).

5. *Comparison with Experimental Results*

Comparison of these results obtained on the basis of purely theoretical concepts with the experimental results for tungstate solutions indicates excellent agreement. The addition mechanism predicts not only the fast formation of primary aggregation products (and their structures) but also their p,q values, i.e., 4,4 for scarcity of, and 5,4 for a sufficient supply of H^+ ions. For the molybdate system (see Section IV, B, 2), agreement with the (6,4) species for a scarcity of H^+ ions exists for q but not for p. Presumably the experimental value of $p = 6$ is incorrect, since no other species having a Z^+ value far in excess of unity is formed in either the molybdate or the tungstate system when there is a scarcity of H^+ ions.

B. THE CONDENSATION MECHANISM (*19*, *20*, *23*)

1. *Octahedron Formation by the Condensation Principle*

Further aggregation to give higher polymetalates requires a new constructional principle. Stepwise buildup of new octahedra is possible only via condensation of H_2O. However, here too, addition

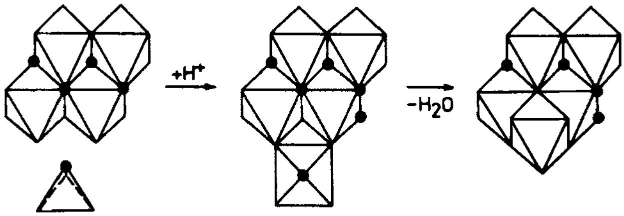


FIG. 15. Construction of an octahedron according to the condensation principle. (●) Positions of H atoms.

is the preliminary step and only then does the actual condensation occur (Fig. 15), which requires an OH group in a suitable position of the growing polymetalate ion. We can regard the growing polymetalate ion as a tridentate ligand: Two coordination sites on HMO_4^- are occupied by addition, thereby expanding the coordination sphere of the M atom; occupation of the third coordination site requires prior expulsion of the "monodentate ligand" OH from the $(HO)MO_3^-$ ion. This contructional principle can also lead to a multitude of polymetalate ions.

2. *Acid/Base Functions of Condensed Polymetalate Ions; Significance of* OH *Groups*

The function of the nonacidic H atoms in octahedra formed by the addition route, i.e., extension of the M—O bond as a prerequisite for octahedral coordination of the M atoms, is now exerted either partly or entirely by M atoms, according to the number of condensed H_2O molecules. This is why condensation products possess fewer nonacidic H atoms.

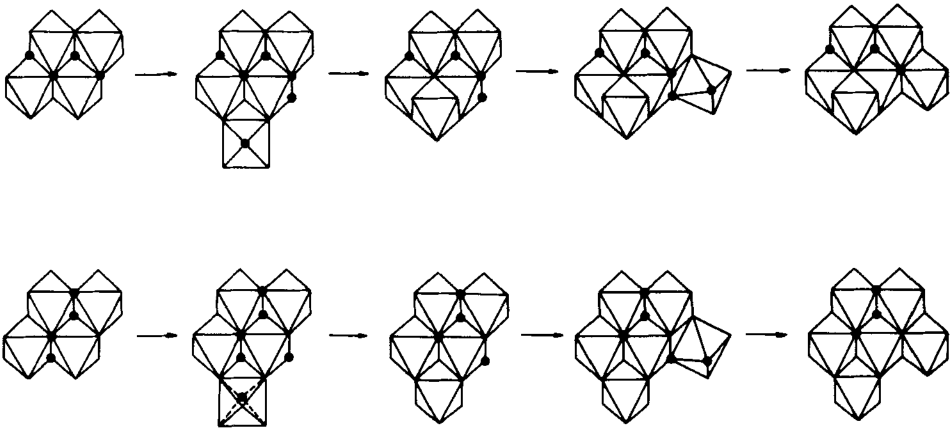
The number and positions of the acidic H atoms depend (in the pH range $\ngtr 3$) on the $M(O_6)^-$ and $M(O_5)O^-$ base functions. Whereas the occurrence of $M(O_6)^-$ and $M(O_5)O^-$ functions in the addition mechanism is unfavorable for a given species if there is a scarcity of H^+ owing to the consumption of H^+ beyond $Z^+ = 1$ (cf. Section VI, A, 3, b), such a generalization is invalid for the condensation mechanism. Once the four nonacidic H atoms present in the tetrametalate ion have been consumed, the H atoms of the $M(O_6)H$ and $M(O_5)OH$ functions satisfy the requirements for continued condensation.

3. *Energetics*

Adoption of the same approach as applied to the addition mechanism requires inclusion of an additional reaction component, namely condensation of an H_2O molecule (W), which should make a considerable contribution to the stability of the polymetalate ions. The limiting values adopted were

$$\gamma_W = 0 \cdots 2$$

a. Condensation Reactions without Participation of H_2MO_4 *and with a Scarcity of* H^+ *Ions* ($Z \leqslant 1.1$) (*Formation of the Paratungstate* A *Ion*). We first examined which species are possible for reasons of geometry and acid/base properties, assuming that only HMO_4^-, and not H_2MO_4, participates in condensation. We then applied Eq. (14) to these species. The calculation [Figs. 7 and 8 in Tytko and Glemser (*19*)] shows that, in the range of limiting values for γ_e given for the addition mechanism and the foregoing limits for γ_W, there exist regions in which $\Gamma_i^h = \Gamma_{\max}^h$ only for the species (4,4) (i.e., no condensation at all), (7,6), and (14,10). Formation of species other than (7,6) or (14,10) is not to be expected according to the condensation mechanism for a scarcity of H^+ ions ($Z \leqslant 1.1$), provided that only HMO_4^-, and not H_2MO_4, participates in condensation. However, the paratungstate A ion is a 7,6 ion. Apparently, the correct γ_e values lie in the range determined for a 7,6 ion. Above all, the size of γ_W and γ_E is important. For the tungstate system, γ_W is ≈ 0.7 and $\gamma_E \leqslant 0.04$.



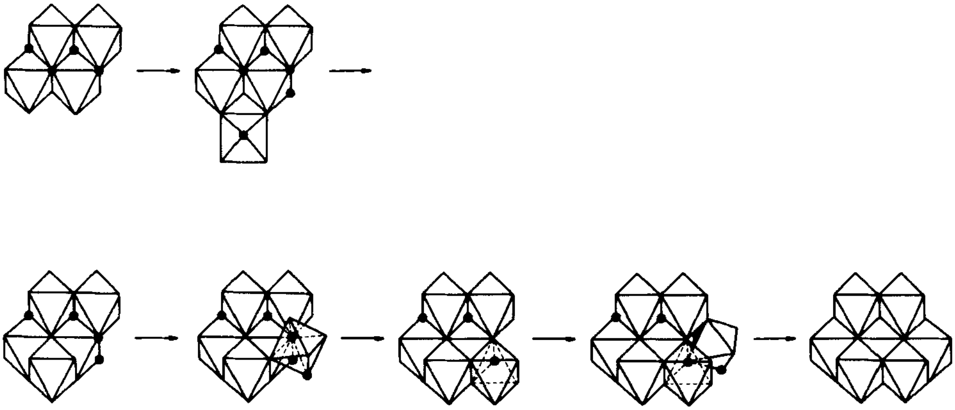
$$\underset{(4,4)}{[M_4O_{12}(OH)_4]^{4-}} \xrightarrow{+HMO_4^-} \underset{(6,5)}{[HM_5O_{15}(OH)_5]^{4-}} \xrightarrow[-H_2O]{} \underset{(6,5)}{[HM_5O_{16}(OH)_3]^{4-}} \xrightarrow{+HMO_4^-} \underset{(7,6)}{[HM_6O_{19}(OH)_4]^{5-}} \xrightarrow[-H_2O]{} \underset{(7,6)}{[HM_6O_{20}(OH)_2]^{5-}}$$

FIG. 16. Two of the reaction pathways leading to 7,6-metalate ions. (●) Positions of H atoms.

The principle governing the thermodynamics of the course of aggregation for a scarcity of H^+ ions is, with a given number of protons, the formation of a maximum number of octahedra (preferably with three and two terminal O atoms) and the condensation of a maximum number of H_2O molecules, on the one hand, and accumulation of a minimum of negative charge and of M atoms, on the other.

Two of the reaction pathways leading to 7,6 ions are shown in Fig. 16, which reveals that the formula $[HW_6O_{20}(OH)_2]^{5-}$ applies to the para A ion.

b. Condensation Reactions with Participation of H_2MO_4 *and Scarcity of* H^+ *Ions* ($Z \leqslant 1.1$) (*Formation of the Heptamolybdate Ion*) (*20, 23*). If not only HMO_4^- but also H_2MO_4 participate in the condensation mechanism, it is possible that two H_2O molecules can be lost in one condensation step. Consideration of all the structures possible owing to participation of one (or more) such condensation steps and their comparison with those resulting on exclusive participation of HMO_4^- leads, for a scarcity of H^+ ions, to an 8,7-metalate ion having the formula $M_7O_{24}^{6-}$ as the species of most favorable energy. Its precursor is a 7,6 ion. The reaction pathway leading to the 8,7-metalate ion is depicted in Fig. 17.



$$[HM_5O_{16}(OH)_3]^{4-} \xrightarrow{+HMO_4^-} [HM_6O_{19}(OH)_4]^{5-} \xrightarrow[-H_2O]{} [HM_6O_{20}(OH)_2]^{5-} \xrightarrow{+H_2MO_4} [HM_7O_{22}(OH)_4]^{5-} \xrightarrow[-2H_2O \atop -H^+]{} M_7O_{24}^{6-}$$

(6,5) (7,6) (7,6) (9,7) (8,7)

FIG. 17. Reaction pathway leading to the 8,7-metalate ion. (●) Positions of H atoms.

4. *Kinetics*

The enhanced geometrical complexity of the condensation steps explains the lower rate of formation of the condensation products.

5. *Comparison with Experimental Results*

Comparison of the results obtained from the condensation mechanism on the basis of purely theoretical concepts with experimental findings indicates agreement for both the tungstate and the molybdate system: In the pH range in which the paratungstate A ion is formed (pH $\geqslant$ 6), less than 1% of the protonated monomer is present as H_2WO_4; in the pH range in which the heptamolybdate ion is formed (pH $\geqslant$ 4.5), up to 25% of the protonated monomer is present as H_2MoO_4. Hence a rapidly formed 7,6 ion is to be expected for the tungstate system, and a likewise rapidly formed 8,7 ion for the molybdate system. The most impressive result is the correct prediction of the structure of the heptamolybdate ion. Formation of the analogous planar heptametalate structure is impossible owing to the absence of H atoms in positions suitable for the condensation step leading to loss of two H_2O molecules (*23*).

C. OTHER FORMATION MECHANISMS

A systematic search for further geometrical principles for building up (iso)polymetalate ions has revealed the following possibilities (*21*): union (essentially dimerization) of larger aggregates by addition (*21, 23*); union of larger aggregates by condensation of water (*22, 23*); rearrangements without condensation of water (*23*); and rearrangements with condensation of water (*21, 23*). For instance, the paratungstate B ion is formed by simple dimerization (without condensation of water) of two enantiomeric 7,6-tungstate ions, with the more compact of the structures derived as above, and subsequent rearrangement of a WO_6 octahedron in each half-structure with condensation of one H_2O molecule each (*21*) .The polyoctamolybdate ion arises by polycondensation of octamolybdate ions of formula $[H_2Mo_8O_{28}]^{6-}$, formed by the condensation mechanism, which are themselves energetically very unfavorable (*22*).

REFERENCES

1. Lindqvist, I., *Nova Acta Regiae Soc. Sci. Upsal.* **15**, No. 1 (1950).
2. Kepert, D. L., *Progr. Inorg. Chem.* **4**, 199 (1962).

3. Kepert, D. L., "The Early Transition Metals." Academic Press, New York, 1972.
4. Kepert, D. L., *in* "Comprehensive Inorganic Chemistry" (A. F. Trotman-Dickenson *et al.*, eds.), Vol. 4, p. 607. Pergamon, Oxford, 1973.
5. Aveston, J., Anacker, E. W., and Johnson, J. S., *Inorg. Chem.* **3**, 735 (1964).
6. J. Aveston, *Inorg. Chem.* **3**, 981 (1964).
7. Glemser, O., Holznagel, W., Höltje, W., and Schwarzmann, E., *Z. Naturforsch. B* **20**, 725 (1965).
8. Jahr, K. F., and Fuchs, J., *Angew. Chem.* **78**, 725 (1966); *Angew. Chem., Int. Ed. Engl.* **5**, 689 (1966).
9. Sasaki, Y., and Sillén, L. G., *Ark. Kemi* **29**, 253 (1968).
10. Souchay, P., "Polyanions et Polycations." Gauthier-Villars, Paris, 1963.
11. Souchay, P., "Ions minéraux condensés," Masson, Paris, 1969.
12. Glemser, O., and Tytko, K. H., *Z. Naturforsch. B* **24**, 648 (1969).
13. Tytko, K. H., and Glemser, O., *Chimia* **23**, 494 (1969).
14. Wempe, G., *Z. Anorg. Chem.* **78**, 298 (1912).
15. Lindqvist, I., *Ark. Kemi* **2**, 349 (1950).
16. Atovmyan, L. O., and Krasochka, O. N., *Z. Strukt. Chim.* **13**, 342 (1972).
17. Gatehouse, B. M., and Leverett, P., *Chem. Commun.* p. 740 (1970).
18. Gatehouse, B. M., and Leverett, P., *J. Chem. Soc. A* p. 2107 (1971).
19. Tytko, K. H., and Glemser, O., *Z. Naturforsch. B* **26**, 659 (1971).
20. Tytko, K. H., *Angew. Chem.* **83**, 935 (1971); *Angew. Chem., Int. Ed. Engl.* **10**, 860 (1971).
21. Tytko, K. H., *Abstr. Meeting Int. Soc. Study Solute-Solute-Solvent Interactions, 1st, 1972.*
22. Tytko, K. H., *Z. Naturforsch. B* **28**, 272 (1973).
23. Tytko, K. H., unpublished investigations on the mechanisms of formation and structures of isopolymetalate ions; presented at the Universities of Gothenborg and Umeå, KTH Stockholm, and at the Gordon Research Conference on Inorganic Chemistry, New Hampton, New Hampshire, 1974.
23a. Tytko, K. H., unpublished investigations on the mechanisms of formation and structures of heteropolymetalate ions; presented at the University of Umeå (Sweden) and at the 16th International Conference on Coordination Chemistry, Dublin 1974.
24. Tytko, K. H., *Z. Naturforsch. B* **31** (1976) (in press).
25. Souchay, P., Chauveau, F., and Le Meur, B., *C. R. Acad. Sci., Ser. C* **270**, 1401 (1970).
26. Tytko, K. H., Schönfeld, B., Buss, B., and Glemser, O., *Angew. Chem.* **85**, 305 (1973); *Angew. Chem., Int. Ed. Engl.* **12**, 330 (1973).
27. Tytko, K. H., Schönfeld, B., Cordis, V., and Glemser, O., presented at the *Int. Conf. Coord. Chem., 15th, 1973*, partly published in *Z. Naturforsch. B* **30**, 471, 834 (1975).
28. Duncan, J. F., and Kepert, D. L., *J. Chem. Soc.* (*London*) p. 5317 (1961); 205 (1962).
29. Chojnacka, J., *J. Inorg. Nucl. Chem.* **33**, 1345 (1971).
30. Wolff, C. M., and Schwing, J. P., *C. R. Acad. Sci., Ser. C* **268**, 571 (1969).
31. Souchay, P., *Ann. Chim.* [11] **18**, 61, 73, 169 (1943).
32. Le Meur, B., and Chauveau, F., *Bull. Soc. Chim. Fr.* p. 3834 (1970).
33. Charreton, B., Chauveau, F., Bertho, G., and Courtin, P., *Chim. Anal.* **47** 17 (1965).

34. Cordier, M., Murgier, M., and Theodoresco, M., *C. R. Acad. Sci.*, **211**, 28 (1940); M. Theodoresco, *ibid.* **210**, 297 (1940).

35. Johansson, G., Pettersson, L., and Ingri, N., *Acta Chem. Scand., Ser. A* **28**, 1119 (1974).

36. Levy, H. A., Agron, P. A., and Danford, M. D., *J. Chem. Phys.* **30**, 1486 (1959).

37. Pettersson, L., Lyhamn, L., Strandberg, R., Hedman, B., and Ingri, N., *Proc. Int. Conf. Coord. Chem., 15th, 1973,* p. 524.

38. Tytko, K. H., unpublished results.

39. Tytko, K. H., Thesis, Aachen, 1967.

40. Tytko, K. H., unpublished.

41. Mauser, H., *Z. Naturforsch. B* **23**, 1021, 1025 (1968).

42. Dumanski, A. V., Buntin, A. P., Dijatschkovski, S. Y., and Kniga, A. G., *Kolloid-Z.* **38**, 208 (1926).

43. Jander, G., Jahr, K. F., and Heukeshoven, W., *Z. Anorg. Allg. Chem.* **194**, 383 (1930).

44. Jander, G., and Krüerke, U., *Z. Anorg. Allg. Chem.* **265**, 244 (1951).

45. Cannon, P., *J. Inorg. Nucl. Chem.* **13**, 269 (1960).

46. Beltrán, J., and Puerta, F., *An. R. Soc. Esp. Fis. Quim., Ser. B* **59**, 271 (1963).

47. Saxena, R. S., and Saxena, G. P., *Z. Phys. Chem.* [N.F.] **29**, 181 (1961).

48. Blume, R., Lachmann, H., Mauser, H., and Schneider, F., *Z. Naturforsch. B* **29**, 500 (1974).

49. Sillén, L. G., *Acta Chem. Scand.* **8**, 299, 318 (1954).

50. Sasaki, Y., *Acta Chem. Scand.* **15**, 175 (1961).

51. Lindqvist, I., *Acta Chem. Scand.* **5**, 568 (1951).

52. Glemser, O., Holznagel, W., and Ali, S. I., *Z. Naturforsch. B* **20**, 192 (1965).

53. Pungor, E., and Halász, A., *J. Inorg. Nucl. Chem.* **32**, 1187 (1970).

54. Bettinger, D. J., and Tyree, S. Y., *J. Amer. Chem. Soc.* **79**, 3355 (1957).

55. Liska, M., and Plsko, E., *Chem. Zvesti* **11**, 390 (1957).

56. Ripan, R., and Szekely, Z., *Acad. Rep. Pop. Rom., Fil. Cluj, Stud. Cercet. Chim.* **8**, 187 (1957).

57. Liska, M., *Chem. Zvesti* **10**, 549 (1956).

58. Wiese, G., and Böse, D., *Z. Naturforsch. B* **27**, 897 (1972).

59. Wiese, G., and Böse, D., *Z. Naturforsch. B* **29**, 630 (1974).

60. Jander, G., and Heukeshoven, W., *Z. Anorg. Allg. Chem.* **187**, 60 (1930).

61. Jespersen, N. D., *J. Inorg. Nucl. Chem.* **35**, 3873 (1973).

62. Lagrange, P., and Schwing, J. P., *Bull. Soc. Chim. Fr.* p. 718 (1967).

63. Britton, H. T. S., *J. Chem. Soc.* (*London*) p. 147 (1927).

64. Szarvas, P., and Kukri, E. C., *Z. Anorg. Allg. Chem.* **305**, 55 (1960).

65. Lindqvist, I., *Acta Chem. Scand.* **2**, 88 (1948).

66. Sturdivant, H. J., *J. Amer. Chem. Soc.* **59**, 630 (1937).

67. Vallance, R. H., *J. Chem. Soc.* (*London*) p. 1421 (1931).

68. Saddington, K., and Cahn, R. W., *J. Chem. Soc.* (*London*) p. 3526 (1950).

69. Sillén, L. G., *in* "Coordination Chemistry" (A. E. Martell, ed.), Vol. 1, p. 491. Van Nostrand-Reinhold, New York, 1971.

70. Harvey, J. F., Redfern, J. P., and Salmon, J. E., *J. Chem. Soc.* (*London*) p. 2861 (1963).

71. Cooper, M. K., and Salmon, J. E., *J. Chem. Soc.* (*London*) p. 2009 (1962).

72. Heitner-Wirguin, C., and Cohen, R., *J. Inorg. Nucl. Chem.* **26**, 161 (1964).

73. Stock, H. P., and Plewinsky, B., *Kolloid-Z. Z. Polym.* **249**, 1148 (1971).

74. Birkholz, E., Fuchs, J., Schiller, W., and Stock, H. P., *Z. Naturforsch. B* **26**, 365 (1971).

75. Boyer, M., and Souchay, P., *Rev. Chim. Miner.* **8**, 591 (1971).

76. Glemser, O., and Höltje, W., *Z. Naturforsch. B* **20**, 492 (1965).

77. Jahr, K. F., and Witzmann, H., *Z. Anorg. Allg. Chem.* **208**, 145 (1932).

78. Jander, G., and Jahr, K. F., *Kolloid-Beih.* **41**, 1 (1934).

79. Jander, G., and Ertel, D., *J. Inorg. Nuclear Chem.* **14**, 75 (1960).

80. Brintzinger, H., and Ratanarat, C., *Z. Anorg. Allg. Chem.* **224**, 97 (1935); **222**, 317 (1935).

81. Baker, L. C. W., and Pope, M. T., *J. Amer. Chem. Soc.* **82**, 4176 (1960).

82. von Kiss, A., and Acs, V., *Z. Anorg. Allg. Chem.* **247**, 190 (1941).

83. Tobias, R. S., *J. Inorg. Nucl. Chem.* **19**, 348 (1961).

84. Sillén, L. G., *Acta Chem. Scand.* **16**, 159 (1962); **18**, 1085 (1964).

85. Ingri, N., and Sillén, L. G., *Acta Chem. Scand.* **16**, 173 (1962).

86. Ingri, N., Sillén, L. G., *Ark. Kemi* **23**, 97 (1964).

87. Sasaki, Y., and Sillén, L. G., *Acta Chem. Scand.* **18**, 1014 (1964).

88. Tytko, K. H., and Glemser, O., *Z. Naturforsch. B* **25**, 429 (1970).

89. Tytko, K. H., unpublished results.

90. Lindqvist, *Ark. Kemi* **2**, 325 (1950).

91. Shimao, E., *Nature* (*London*) **214**, 170 (1967); *Bull. Chem. Soc. Jap.* **40**, 1609 (1967).

92. Evans, H. T., *J. Amer. Chem. Soc.* **90**, 3275 (1968).

93. Gatehouse, B. M., and Leverett, P., *Chem. Commun.* p. 901 (1968).

94. Sjöbom, K., and Hedman, B., *Acta Chem. Scand.* **27**, 3673 (1973).

95. Evans, H. T., Gatehouse, B. M., and Leverett, P., *J. Chem. Soc., Dalton Trans.* p. 505 (1975).

96. Lindqvist, I., *Acta Crystallogr.* **5**, 667 (1952).

97. Weiss, G., *Z. Anorg. Allg. Chem.* **368**, 279 (1969).

98. Allmann, R., *Acta Crystallogr., Sect. B* **27**, 1393 (1971).

99. d'Amour, H., and Allmann, R., *Z. Kristallogr.* **136**, 23 (1972); **138**, 5 (1973).

100. Tsay, Y. H., and Silverton, J. V., *Z. Kristallogr.* **137**, 256 (1973).

101. Fuchs, J., Hartl, H., and Schiller, W., *Angew. Chem.* **85**, 417 (1973); *Angew. Chem., Int. Ed. Engl.* **12**, 420 (1973).

102. Henning, G., and Hüllen, A., *Z. Kristallogr.* **130**, 162 (1969).

103. Allcock, H. R., Bissell, E. C., and Shawl, E. T., *Inorg. Chem.* **12**, 2963 (1973).

104. Böschen, I., Buss, B., and Krebs, B., *Acta Crystallogr., Sect. B* **30**, 48 (1974); Böschen, I., Buss, B., Krebs, B., and Glemser, O., *Angew. Chem.* **85**, 409 (1973); *Angew. Chem. Int. Ed. Engl.* **12**, 409 (1973).

105. Knöpnadel, I., Hartl, H., Hunnius, W. D., and Fuchs, J., *Angew. Chem.* **86**, 894 (1974); *Angew. Chem., Int. Ed. Engl.* **13**, 823 (1974).

106. Krebs, B., and Böschen, I., *Acta Crystallogr., Sect. B* **30**, 1795 (1974).

107. The computer program used was written by one of the authors. The program HALTAFALL [N. Ingri, W. Kakołowicz, L. G. Sillén, and B. Warnqvist, *Talanta* **14**, 1261 (1967)] can be used in the same way.

108. Tytko, K. H., unpublished results.

109. Jahr. K. F., Fuchs, J., Witte, P., and Flindt, E. P., *Chem. Ber.* **98**, 3588 (1965).

110. Jahr, K. F., and Fuchs, J., *Chem. Ber.* **96**, 2457 (1963).

111. Jahr, K. F., Fuchs, J., and Oberhauser, R., *Chem. Ber.* **101**, 477 (1968).

112. Fuchs, J., and Jahr, K. F., *Z. Naturforsch. B* **23**, 1380 (1968).

113. Schott, G., and Harzdorf, C., *Z. Anorg. Allg. Chem.* **288**, 15 (1956).

114. Kolli, I. D., Pirogova, G. N., and Spitsyn, V. I., *Z. Neorg. Chim.* **1**, 470 (1956).

115. Kiss, A. B., Gadó, P., and Hegedüs, A. J., *Acta Chim. Acad. Sci. Hung.* **72**, 371 (1972).

116. Babushkin, A. A., *Izv. Akad. Nauk. SSSR., Ser. Fiz.* **22**, 1131 (1958).

117. Babushkin, A. A., Yuknevich, G. N., Berezkina, Y. F., and Spitsyn, V. I., *Z. Neorg. Chim.* 4, 823 (1959); *Russ. J. Inorg. Chem.* 4, 373 (1959).

118. Pope, M. T., and Varga, G. M., *Chem. Commun.* p. 653 (1966).

119. Spitsyn, V. I., Lunk, H. J., Čuvaev, V. F. and Kolli, I. D., *Z. Anorg. Allg. Chem.* **370**, 191 (1969).

120. Signer, R., and Gross, H., *Helv. Chim. Acta* **17**, 1076 (1934).

121. Keggin, J. F., *Proc. Roy. Soc. (London) Ser. A* **144**, 75 (1934).

122. Mattes, R., Bierbüsse, H., and Fuchs, J., *Z. Anorg. Allg. Chem.* **385**, 230 (1971).

123. Kiss, B. A., Holly, S., and Hild, E., *Magy. Kem. Foly.* **77**, 418 (1971).

124. Fuchs, J., *Z. Naturforsch. B* **28**, 389 (1973).

125. Hunnius, W. D., *Z. Naturforsch. B* **29**, 599 (1974).

126. Kiss, B. A., *Acta Chim. Acad. Sci. Hung.* **75**, 351 (1973).

127. Spitsyn, V. I., *Acta Chim. Acad. Sci. Hung.* **12**, 119 (1957).

128. Spitsyn, V. I., and Torchenkova, E. A., *Dokl. Akad. Nauk SSSR* **95**, 289 (1954).

129. Ripan, R., and Marcu, G., *Acad. Rep. Pop. Rom., Fil. Cluj, Stud. Cercet. Chim.* **10**, 201 (1959).

130. Spitsyn, V. I., Aistova, R. I., and Vasil'ev, V. N., *Dokl. Akad. Nauk SSSR* **104**, 741 (1955).

131. Yukhnevich, G. V., *Z. Neorg. Chim.* 4, 1459 (1959); *Russ. J. Inorg. Chem.* **4**, 656 (1959).

132. Kabanov, V. Ya., and Spitsyn, V. I., *Dokl. Akad. Nauk. SSSR* **148**, 109 (1963).

133. Spitsyn, V. I., and Berezkina, Y. F., *Dokl. Akad. Nauk. SSSR* **108**, 1088 (1956).

134. Arnek, R., and Szilard, I., *Acta Chem. Scand.* **22**, 1334 (1968).

135. Arnek, R., *Acta Chem. Scand.* **23**, 1986 (1969).

136. Pope, M. T., *Inorg. Chem.* **11**, 1973 (1972).

137. Launay, J. P., Souchay, P., and Boyer, M., *Collect. Czech. Chem. Commun.* **36**, 740 (1971).

138. Boyer, M., *J. Electroanal. Chem. Interfacial Electrochem.* **31**, 441 (1971).

139. Boyer, M., *C. R. Acad. Sci. Ser. C* **274**, 778 (1972).

140. Boyer, M., and Souchay, P., *J. Electroanal. Chem. Interfacial Electrochem.* **38**, 169 (1972).

141. Tourné, C., *Bull. Soc. Chim. Fr.* pp. 3196, 3199, 3214 (1967).

142. Mellström, R., and Ingri, N., *Acta Chem. Scand. Ser. A* **28**, 703 (1974).

143. Schwarzenbach, G., and Meier, J., *J. Inorg. Nucl. Chem.* **8**, 302 (1958).

144. Schwarzenbach, G., Geier, G., and Littler, J., *Helv. Chim. Acta* **45**, 2601 (1962).

145. Glemser, O., and Höltje, W., *Angew. Chem.* **78**, 756 (1966).

146. Asay, J., and Eyring, E. M., unpublished results.

147. Honig, D. S., and Kustin, K., *Inorg. Chem.* **11**, 65 (1972).

148. Wagner, G., Thesis, Göttingen, 1970.

149. Glemser, O., and Tytko, K. H., *Z. Naturforsch. B* **24**, 648 (1969).

150. Honig, D. S., Kustin, K., *J. Phys. Chem.* **76**, 1575 (1972).
151. Chauveau, F., Boyer, M., and Le Meur, B., *C. R. Acad. Sci., Ser. C* **268**, 479 (1969).
152. Fuchs, J., Jahr, K. F., and Nebelung, A., *Chem. Ber.* **100**, 2415 (1967).
153. Neu, F., and Schwing-Weill, M. J., *Bull. Soc. Chim. Fr.* p. 4821 (1968).
154. Cotton, F. A., and Wilkinson, G., "Anorganische Chemie," p. 875. Verlag Chemie, Weinheim (Bergstrasse), 1967.
155. Byé, J., *Ann. Chim.* [11] **20**, 463 (1945).
156. Chojnacki, J., and Hodorowicz, S., *Rocz. Chem.* **47**, 2213 (1973); **48**, 1399 (1974).
157. Rosenheim, A., and Felix, J., *Z. Anorg. Chem.* **79**, 292 (1913).
158. Svanberg, L., and Struve, H., *J. Prakt. Chem.* **44**, 282 (1848).
159. Hallada, C. J., *J. Less-Common Metals* **36**, 103 (1974).
160. Glemser, O., Wagner, G., Krebs, B., and Tytko, K. H., *Angew. Chem.* **82**, 639 (1970); *Angew. Chem., Int. Ed. Engl.* **9**, 639 (1970).
161. Foote, H. W., and Bradley, W. M., *J. Amer. Chem. Soc.* **58**, 930 (1936).
162. Hunnius, W. D., Thesis, Freie Universität, Berlin, 1970.
163. "Gmelins Handbuch der Anorganischen Chemie," 8th ed., Molybdän, System No. 53. Verlag Chemie, Berlin, 1935.
164. Haeringer, M., and Schwing, J. P., *Bull. Soc. Chim. Fr.* p. 708 (1967).
165. Goldstein, G., Wolff, C. M., and Schwing, J. P., *Bull. Soc. Chim. Fr.* p. 1201 (1971).
166. Souchay, P., Boyer, M., and Chauveau, F., *Kgl. Tek. Hoegsk. Handl. No.* **259** (1972) (Contributions to Coordination Chemistry in Solution, Stockholm, 1972, p. 159).
167. Lagrange, P., and Schwing, J. P., *Bull. Soc. Chim. Fr.* p. 1340 (1970).
168. Collin, J. P., and Lagrange, P., *Bull. Soc. Chim. Fr.* p. 777 (1974).
169. Baldwin, W. G., and Wiese, G., *Ark. Kemi* **31**, 419 (1968).
170. LeMeur, B., and Souchay, P., *Rev. Chim. Miner.* **9**, 501 (1972).
171. Angus, H. J. F., Briggs, J., and Weigel, H., *J. Inorg. Nucl. Chem.* **33**, 697 (1971).
172. Chojnacka, J., and Madejska, M., *Rocz. Chem.* **46**, 553 (1972).
173. Pauling, L., "General Chemistry." Edward Bros., Ann Arbor, Michigan, 1944.
174. Ricci, J. E., *J. Amer. Chem. Soc.* **70**, 109 (1948).
175. Rohwer, E. F. C. H., and Cruywagen, J. J., *J. South Afr. Chem. Inst.* **16**, 26 (1963); **17**, 145 (1964); **22**, 198 (1969).
176. Jain, D. V. S., *Indian J. Chem.* **8**, 945 (1970).
177. Tytko, K. H., unpublished results.
178. Schwing, J. P., Ph.D. Thesis, Strassbourg, 1961.
179. Wiese, G., *Z. Naturforsch. B* **27**, 616 (1972).
180. Tytko, K. H., and Petridis, G., unpublished results.
181. Sillén, L. G., *Pure Appl. Chem.* **17**, 55 (1968).
182. See Cotton and Wilkinson (154), p. 878.
183. Griffith, W. P., and Lesniak, P. J. B., *J. Chem. Soc., A* p. 1066 (1969).
184. Babko, A. K., and Gridchina, G. I., *Russ. J. Inorg. Chem.* **13**, 61 (1968).
185. Byé, J., Fischer, R., Krumenacker, L., Lagrange, J., and Vierling, F., *Kgl. Tek. Hoegsk. Handl. No.* **255** (1972) (Contributions to Coordination Chemistry in Solution, Stockholm, 1972, p. 99).
186. MacInnis, M. B., Kim, T. K., and Laferty, J. M., *J. Less-Common Metals* **36**, 111 (1974).

187. Ojo, J. F., Taylor, R. S., and Sykes, A. G., *J. Chem. Soc., Dalton Trans.* p. 500. (1975),

188. Collin, J. P., Lagrange, P., and Schwing, J. P., *J. Less-Common Metals* **36**, 117 (1974).

189. Collin, J. P. and Lagrange, P., *Bull. Soc. Chim. Fr.* p. 773 (1974).

190. Busey, R. H., and Keller, O. I., *J. Chem. Phys.* **41**, 215 (1964).

191. Hüllen, A., *Naturwissenschaften* **51**, 508 (1964); *Angew. Chem.* **76**, 588 (1964).

192. Borisov, S. V., Klevtsova, R. F., and Belov, N. V., *Kristallografija* **13**, 1980 (1968); *Sov. Phys. Crystallogr.* **13**, 852 (1969).

193. Lipscomb, W. N., *Inorg. Chem.* **4**, 132 (1965).

194. Ressel, H., Thesis, Technische Universität, Berlin, 1961.

195. Hähnert, M., *Z. Anorg. Allg. Chem.* **318**, 222 (1962).

196. Čuvaev, V. F., Lunk, H. J., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **180**, 133 (1968).

197. Tytko, K. H., unpublished results [cited in Tytko and Glemser (19)].

198. Wolff, C. M., and Schwing, J. P., *C. R. Acad. Sci., Ser. C* **272**, 1974 (1971).

199. Pan, K., and Hseu, T. M., *Bull. Chem. Soc. Jap.* **26**, 126 (1953); Pan, K., Lin, S. F., and Sheng, S. T., *ibid.* **26**, 131 (1953).

200. Freedman, M. L., *J. Amer. Chem. Soc.* **80**, 2072 (1958).

201. Arnek, R., and Sasaki, Y., *Acta Chem. Scand., Ser. A* **28**, 20 (1974).

202. Schulz, H., and Jander, G., *Z. Anorg. Allg. Chem.* **162**, 141 (1927); Jander, G., Mojert, D., and Aden, T., *Z. Anorg. Allg. Chem.* **180**, 129 (1929).

203. Johansson, G., *Acta Chem. Scand.* **14**, 771 (1960).

204. Cordis, V., unpublished results.

205. Boyer, M., and Souchay, P., *C. R. Acad. Sci., Ser. C* **268**, 2073 (1969).

206. Babad-Zakhryapin, A. A., and Gorbunov, N. S., *Izv. Akad. Nauk SSSR, Ser. Chim.* p. 1870 (1962).

207. Wolff, C. M., and Schwing, J. P., *C. R. Acad. Sci., Ser. C* **268**, 1339 (1969).

208. Glemser, O., Holznagel, W., and Höltje, W., *Z. Anorg. Allg. Chem.* **342**, 75 (1966).

209. Miolati, A., *J. Prakt. Chem.* **77**, 239, 417 (1908).

210. Rosenheim, A., *et al.*, *Z. Anorg. Chem.* **69**, 247 (1910); **70**, 73, 418 (1911); **75**, 141 (1912); **77**, 239 (1912); **89**, 224 (1914); **93**, 273 (1915); **96**, 139 (1916); **100**, 304 (1917); **101**, 215 (1917); **220**, 73 (1934).

211. Pauling, L., *J. Amer. Chem. Soc.* **51**, 2868 (1929).

212. Kepert, D. L., *Inorg. Chem.* **8**, 1556 (1969).

213. Tytko, K. H., unpublished results.

214. Babad-Zakhryapin, A. A., and Berezkina, Y. F., *Z. Strukt. Chim.* **4**, 346 (1963).

215. Chojnacki, J., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **11**, 365 (1963).

216. Chojnacki, J., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **11**, 369 (1963).