Translated from *Uspekhi Khimii*, **44**, 2150-2170 (1975) U.D.C. 546.183-325

Hyprophosphorous Acid and Its Salts

N.V.Romanova and N.V.Demidenko

The review deals with the analysis of the literature on the synthesis, properties, and applications of hypophosphorous acid and its salts in pharmaceutical practice, for the surface treatment of metals, in analytical chemistry, etc.
The bibliography includes 168 references.

CONTENTS

I.	Introduction	1036
II.	Hypophosphorous acid: preparation and properties	1036
III.	The structure and properties of the hypophosphite ion	1036
IV.	Alkali metal and alkaline earth metal hypophosphites	1039
V.	The mechanism of the synthesis of hypophosphites in solution	1040
VI.	Hypophosphites and their classification	1041
VII.	Metal hypophosphite complexes	1043
VIII.	The reducing properties of the hypophosphite ion	1044
IX.	The applications of hypophosphites	1044

I. INTRODUCTION

Of the three main acids containing one phosphorous atom in the molecule—phosphoric, phosphorous, and hypophosphorous—the last has been least investigated and is most difficult to synthesise in a high yield; there have also been few studies on its salts (hypophosphites).

Hypophosphites have been attracting attention not only because of their extensive applications as reducing reagents, but also in connection with their possible use for the preparation of various polymeric materials.

Information about the synthesis of hypophosphorous acid and various alkali metal hypophosphites, their structures, and properties, and the conditions governing the formation of their complexes in aqueous and non-aqueous media is presented below.

II. HYPOPHOSPHOROUS ACID: PREPARATION AND PROPERTIES

Pure hypophosphorous acid $H(O_2PH_2)$ consists of white crystals melting at 26.5°C and decomposing above 50°C. Its heat of fusion is 2.4 kcal mole^{-1} [1-4] and the heat of solution of the crystalline acid in water is about −0.18 kcal mole^{-1}.

An interesting laboratory method for the preparation of $H(O_2PH_2)$ involves the oxidation of phosphine (PH_3) in an aqueous suspension of iodine[5]. Phosphine, obtained by the reaction of potassium phosphide with dilute hydrochloric acid, is passed into a flask containing a stirred suspension of iodine until the solution is decolorised. At a reduced pressure (40 mmHg) it is possible to remove hydrogen iodide and water, leaving behind pure $H(O_2PH_2)$. The latter is also formed on slow oxidation of white phosphorus in the presence of water, but its yield is insignificant. When white phosphorus is oxidised by passing moist air over its surface, only 10–12% of the initial amount of phosphorus is converted into $H(O_2PH_2)$.[6]

Hypophosphorous acid is obtained by the decomposition of alkaline earth metal phosphides with water. It is possible to synthesise the acid by treating an aqueous solution of calcium hypophosphite with an equivalent amount of H_2SO_4. A method for the purification of hypophosphorous acid by the recrystallisation of commercial 50% $H(O_2PH_2)$ has been described[7]. The pure acid can be obtained by converting technical sodium hypophosphite into hypophosphorous acid by ion exchange[8].

Hypophosphorous acid is a powerful monobasic acid. According to Kolthoff's data[9-13], its dissociation constant is 8.0×10^{-2}. The fact that hypophosphorous acid is monobasic shows that in this structure the phosphorus has a coordination number of four.

In studies of the kinetics of the oxidation of hypophosphorous acid by halogens by bromine and chlorine (Griffith and McKeown) and by iodine (Griffith et al.)[14-19] it was found that the rate-determining stage of the oxidation is the conversion of the inactive form of hypophosphorous acid $(H_3PO_2)_I$ into the active form $(H_3PO_2)_{II}$. It has been suggested that the $(H_3PO_2)_I$ form is a tautomer with two hydrogen atoms attached to phosphorus, while $(H_3PO_2)_{II}$ contains two hydroxy-groups attached to phosphorus. It is noteworthy that under identical conditions the reaction with chlorine is faster than that with bromine, while the reaction with iodine is slowest.

Fig. 1 presents titration curves for hypophosphorous acid and certain other lower acids of phosphorus. The dissociation constant of $H(O_2PH_2)$ has been compared with the K_{diss} for other acids and it has been shown that these values are consistent with calculated data[20,21].

Table 1 lists the dissociation constants of a number of phosphorus acids.

III. THE STRUCTURE AND PROPERTIES OF THE HYPOPHOSPHITE ION

The structure of the hypophosphite ion has been investigated by X-ray diffraction using ammonium hypophosphite[23,24]. This anion has the form of a distorted tetrahedron two corners of which are occupied by oxygen atoms and the other two by hydrogen atoms, with the phosphorus located in the centre of the tetrahedron. It has been shown that the P–O distance is 1.51 Å, the P–H distance about 1.5 Å, and the O–P–O and H–P–H angles are respectively 120° and 92°.

The structures of magnesium, nickel, and cobalt hypophosphite hexahydrates have been investigated similarly by X-ray diffraction[25,26]. It has been established that in the magnesium salt the $H_2PO_2^-$ anion has a nearly tetrahedral structure with a P–O distance of 1.52 Å and an O–P–O angle of 109°. The observed P–O distances correspond approximately to 0.6 of a π bond per σ bond, which is equivalent to 1.2π bonds per phosphorus atom.

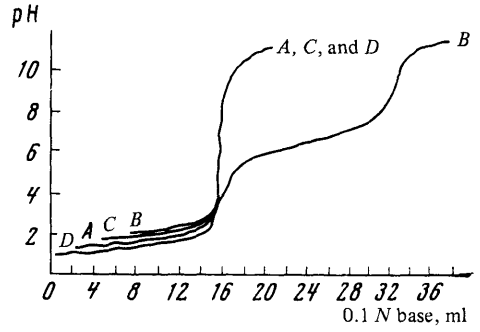


Figure 1. pH titration curves: *A*) for hypophosphorous acid; *B*) for phosphorous acid; *C*) for pyrophosphorous acid; *D*) for hydrochloric acid. The pH values were established relative to standard buffer solutions.

Table 1. Dissociation constants of various phosphorus acids at 20–25°C[22].

Acid	Formula	pK_1	pK_2	pK_3	pK_4
Hypophosphorous	$H^+ + H_2PO_2^-$	1.1	—	—	—
Phosphorous	$2H^+ + HPO_3^{2-}$	1.3	6.7	—	—
Monoethyl phosphite	$H^+ + (RO)HPO_2^-$	0.8	—	—	—
Methylphosphonic	$2H^+ + RPO_3^{2-}$	2.3	7.9	—	—
Propylphosphonic	$2H^+ + RPO_3^{2-}$	2.4	8.2	—	—
Phosphoric	$3H^+ + PO_4^{3-}$	2.1	7.1	12.3	—
Hypophosphoric	$4H^+ + {}^{-2}O_3PPO_3^{2-}$	(2.0)	(2.6)	7.2	10.0
Pyrophosphoric	$4H^+ + {}^{-2}O_3POPO_3^{2-}$	1.0	2.0	6.6	9.6

The ^{31}P NMR spectra[27–30] of hypophosphite solutions reveal 1 : 2 : 1 spin–spin splitting with a between-peak separation of 0.33 G (Fig. 2). Similarly the ^1H NMR spectrum has two peaks corresponding to 1 : 1 spin–spin splitting. This implies that two hydrogen atoms (nuclear spin 1/2) are bound covalently to the phosphorus atom (nuclear spin 1/2) so that, even if their mutual exchange or their exchange with water does occur, these processes are fairly slow (the half-exchange period is of the order of several minutes). According to published data, approximately 95% or more of the free acid or its salts exists in a form where four atoms are linked directly to phosphorus.

The hypophosphite ion has a $[^{31}P]$ spectrum with three peaks of relative intensities 1 : 2 : 1. The phosphite anion contains two peaks of equal intensities in its spectrum and trimethyl phosphite gives rise to nine peaks with the theoretical intensity ratios 1 : 9 : 36 : 84 : 126 : 84 : 36 : 9 : 1. The multiplet structure of the NMR spectra is due to the indirect spin–spin splitting by covalently bound hydrogen atoms.

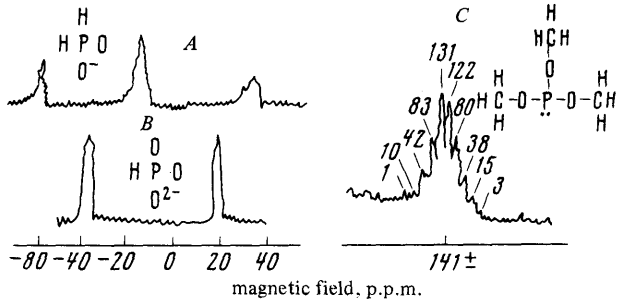


Figure 2. The NMR spectrum of phosphorus in hypophosphite and phosphite anions and in trimethyl phosphite: *A*) hypophosphorous acid; *B*) phosphorous acid; *C*) trimethyl phosphite.

In addition, the Raman spectra of hypophosphorous acid and some of its salts have been investigated[31–37] and it has been shown that the hypophosphite ion has C_{2v} symmetry, attributable to the tetrahedral species $H_2PO_2^-$.

Despite the fact that the acid and its alkali metal and alkaline earth metal salts contain tetracoordinate phosphorus, owing to the equilibrium between tautomeric forms it is possible to displace the equilibrium towards the form with tricoordinate phosphorus. This can be achieved under conditions where an electron acceptor (but not a hydrogen ion) can participate in utilising the free electron pair of the tricoordinate phosphorus atom. Possibly such conditions obtain in addition products or double salts of tin(II) hypophosphite with tin(II) bromide or iodide[38].

The kinetics of the isotope exchange between hypophosphites and water and between hypophosphites and other salts of phosphorus oxyacids have been thoroughly investigated. In earlier studies[39,40] it was stated that the two hydrogen atoms linked directly to the phosphorus atom of the hypophosphite anion are incapable of exchange with the hydrogen atoms of water. However, the latest investigations[41,42] established that this process does occur slowly but at a measurable rate. The rate of substitution of one hydrogen atom of the hypophosphite anion (linked directly to phosphorus) is given by the following equation in which the numerical constants refer to 30.0°C:

$$R = 3.33\,[H^+]\,[H_2PO_2^-] + 2.9\,[H_3PO_2]^2,$$

where R is expressed in litre mole^{-1}h^{-1}. This exchange is believed to be determined by the conversion, mentioned above, of the tautomeric form of the hypophosphite ion into one with tricoordinate phosphorus.

The exchange of oxygen between the hypophosphite ion and water in which it is dissolved has also been studied[43]. It was shown that the half-exchange periods for oxygen in the acid at 40° and 100°C are respectively 70 h and less than 0.2 h. The rate of exchange of oxygen for the sodium salt is so low that it cannot be detected even at 100°C. These data must be compared with the results obtained by the same workers in a study of the exchange of hydrogen

atoms[41,42]. The half-exchange period for hydrogen in $H(O_2PH_2)$ at 25°C is 16 min, while for $Na(O_2PH_2)$ at 100°C the period is 21 h. Possibly the lower rate of oxygen exchange for the sodium salt compared with the acid is a consequence of the presence of a hydrogen bond between the OH groups of the acid and water. This explanation is similar to the theory of electrical conduction proposed by Grotthus[44], according to which the hydrogen atoms joined directly to phosphorus form weaker hydrogen bonds with water than the hydrogen atoms of the OH group.

It has been shown[45-47] that the phosphorus atoms in the hypophosphite ion do not exchange with phosphites and phosphates in either acid or neutral solutions. It is interesting to note that the phosphorus exchange between hypophosphorous and phosphoric acid does not occur in the presence of iodine or iodides, although the oxidation of hypophosphorous acid to phosphorous acid by iodine might give rise to phosphorus exchange at a rate comparable to that of the oxidation-reduction reaction. In mixtures of arsenious and arsenic acids iodine promotes arsenic exchange at a rate which may be predicted from kinetic data for the oxidation-reduction reaction.

The absence of exchange between hypophorous and phosphorous acids in the presence of iodine has been explained on the hypothesis that the process consists of two stages: a slow transition of the inactive form of hypophosphorous acid into the active form and then a rapid irreversible oxidation of the active form by iodine. Thus in the first, reversible stage, the exchange cannot occur, while the second (oxidation-reduction) stage is not accompanied by the exchange owing to its irreversibility. The active form of hypophosphorous acid is probably a tautomeric structure based on tricoordinate phosphorus. This result and data for hydrogen exchange between hypophosphorous acid and water are consistent with the conclusions based on the oxidation of hypophosphites, which will be described below.

Hypophosphorous acid and hypophosphites are readily oxidised. On storage in the cold, the crystals of hypophosphorous acid are stable[7] but contaminated crystals readily decompose at room temperature. The decomposition products are mainly phosphine, phosphorus, phosphoric acid, and hydrogen. Similarly, on vigorous heating, hypophosphites decompose, giving rise to phosphine, red phosphorus, phosphites, phosphates, and possibly other compounds. This type of decomposition is evidently a consequence of self-oxidation-reduction.

The kinetics of the reaction between hypophosphite and hydroxide ions, in which phosphite ions and gaseous hydrogen are formed, have been investigated[48]. The rate equation for this reaction is

$$-\mathrm{d}[H_2PO_2^-]/\mathrm{d}t = K[H_2PO_2^-][OH^-]^2.$$

The rate constant K is approximately 3×10^{-4} min^{-1} at 100°C. It has been suggested that free hydrogen is more readily evolved from the hydroxide ion than from the hypophosphite ion[49].

Hypophosphites also decompose in neutral solutions at a moderate rate, evolving hydrogen in the presence of platinum black, palladium, and copper[48,50-55]. These metals are readily deposited in a colloidal state from solutions of their salts under the influence of sodium hypophosphite. The resulting colloidally dispersed metal then catalyses the decomposition of hypophosphite ions in which hydrogen is evolved.

The study of isotope exchange has shown that the hydrogen evolved from neutral hypophosphite solutions in the presence of metallic catalysts originates from water to the extent of 50%.[56] In this case the catalytic decomposition of the hypophosphite should be consistent with the following chemical equation:



A number of studies have been made of the oxidation of hypophosphites by various oxidising agents. The main product of these reactions is phosphite. The rate of oxidation of sodium hypophosphite in an alkaline medium is approximately three times higher than in a neutral medium: in the former case the completion of the reaction requires 60 min and in the latter 180–200 min.[57] The subsequent oxidation of phosphites to phosphates in an acid solution is much slower. The catalytic effect of freshly deposited nickel on the oxidation of sodium hypophosphite has been investigated[58]. It has been shown that the degree of oxidation of hypophosphite is influenced by temperature, oxidation, time, acidity of the solution, and the amount of catalyst.

As stated above, the kinetics of the oxidation of hypophosphorous acid by halogens have been studied and it has been found that the conversion of the inactive form of hypophosphorous acid $(H_3PO_2)_I$ into the active form $(H_3PO_2)_{II}$ determines the rate of oxidation. The interaction between the active form and halogens takes place after each collision. The constant for the equilibrium between the two forms of hypophosphorous acid has been calculated:

$$K = \frac{[(H_3PO_2)_{II}]}{[(H_3PO_2)_I]} = \frac{K_1}{K_2} \simeq 10^{-12}. \qquad (A)$$

The rate of interconversion of the two forms of hypophosphorous acid has been found to be directly proportional to the hydrogen ion concentration and to determine the rate of oxidation in an acid solution.

The kinetics of the oxidation of hypophosphorous acid by iodate ions have been studied[59-61] and a number of investigations have also been made of the slower reactions with bromates and chlorates[62,63]. The kinetics of the reaction between H_3PO_2 and iodate are close to those of the oxidation of hypophosphites by halogens. However, there are a number of complicating side reactions, for example the interaction of iodine with $H(O_2PH_2)$ and the reaction of phosphorous acid with iodine and iodate. Nevertheless in this case too the rate of oxidation is determined by the stage involving the conversion of $(H_3PO_2)_I$ into $(H_3PO_2)_{II}$. This proved to be the case also in a study of the kinetics of the oxidation of hypophosphite by copper(II)[64-67] and mercury(II)[68-70] salts at moderate concentrations of the oxidant in an acid medium.

The kinetics of the oxidation of hypophosphorous acid in an acid medium by chromate[71], silver[72], iron(III)[73], and arsenate[74] ions have been studied at moderate and high concentrations. It has been found that the type and concentration of oxidising agents have in essence no influence on the rate of the process, which increases appreciably with increasing acidity of the solution. This is reflected by the equation

$$\mathrm{d}[H_3PO_2]/\mathrm{d}t = K[H_3PO_2][H^+],$$

in which K is of the order of 0.24 litre mole^{-1}min^{-1} for all the reactions investigated.

The results of all the kinetic studies are consistent with the claim that the active form of the acid is present in extremely low amounts and that the rate of conversion of

the inactive form into the active form, being slow, determines the rate of the entire reaction under readily realisable experimental conditions.

These results are consistent with NMR data, which have shown that 95% or more of the hypophosphite ions are present in the tautomeric form based on tetracoordinate phosphorus. In conformity with Eqn. (*A*), the fraction of $HP(OH)_2$ in hypophosphorous acid is only 10^{-12} relative to $H_2P(O)(OH)$.

IV. ALKALI METAL AND ALKALINE EARTH METAL HYPOPHOSPHITES

Recently hypophosphites have been used extensively in many countries for chemical nickel plating of metals [75]. There is interest in the application of hypophosphites also in many other branches of industry [76]. In view of the increased requirement for hypophosphites there has been a growth in the amount manufactured. Thus during the period 1955–1960 the production of hypophosphites and hypophosphorous acid in the USA [77] increased from 100 000 lbs to 1 million lbs of the equivalent amount of phosphorus annually. In the USSR in 1967 the production of sodium hypophosphite increased by a factor of several tens compared with 1957.

One of the decisive factors on which the level of requirement of hypophosphites depends is their cost. The existing high cost of hypophosphite in USSR, which is responsible for the high cost of chemical nickel plating [78], is caused, on the one hand, by the low yield (about 36% relative to the phosphorus in the charge) of hypophosphite in the industrial preparation of Na_2HPO_2 via $Ca(H_2PO_2)_2$ and, on the other hand, by the relatively small scale of the industrial production. The low yield of hypophosphite in the reaction of phosphorus with hydroxide ions is due to the fact that the phosphorus in the charge is consumed not only in the formation of the hypophosphite but is also converted into phosphite and passes to the gas phase mainly in the form of phosphine.

The methods for the production of hypophosphites described [79-85] do not allow one to infer the particular factors which influence their yields. The maximum yield of hypophosphite of 70% claimed in a Swiss patent [86] is in no way justified. A low temperature of the synthesis of the solutions is specified in many patents, but its relation to the yield is never discussed. A method has been described [87] for the production of alkali metal hypophosphites in the presence of an aqueous suspension of insoluble alkaline earth metal phosphates, phosphites, sulphates, silicates, and oxalates and also aluminium, magnesium, and silicon oxides and various types of clays as catalysts. These suspensions increase the area of contact between the reactants, which in turn activates the reaction. The mixture is heated above the melting points of phosphorus. A highly pure product is obtained in 90% yield without an excess of the alkali metal or side products.

The method of synthesis of hypophosphites by the reaction of white phosphorus with alkali and alkaline earth metal hydroxides is classical (it was described as early as 1816) and is still used in the industrial production of hypophosphites. Different versions of the main reaction of phosphorus with hydroxides have been described [79,86,88-108]. The yield of the reaction products under laboratory and industrial conditions has been very low, but the increasing interest in hypophosphites has led to the method being patented. The conditions for the preparation of sodium hypophosphite reviewed by Uhlir et al. [82] have been developed on the basis of these patents.

The method used to manufacture sodium hypophosphite adopted in the USSR, consists of two stages. In the first state the reaction of yellow phosphorus with $Ca(OH)_2$ results in the formation of calcium hypophosphite via the reaction

$$8P + 3Ca(OH)_2 + 6H_2O = 3Ca(H_2PO_2)_2 + 2PH_3.$$

In the second stage the resulting calcium hypophosphite is decomposed with sodium carbonate and NaH_2PO_2 is obtained:

$$Ca(H_2PO_2)_2 + Na_2CO_3 = 2NaH_2PO_2 + CaCO_3.$$

The technological parameters of this method are very poor, the degree of utilisation of the initial phosphorus being at best 16–18%. The consumption of lime is four times the stoichiometric amount. The rate of synthesis of calcium hypophosphite is low, the concentration of the resulting solutions is 7–8 g litre^{-1}, and the consumption of steam in the evaporation of such solutions is high. The effluent gases from the synthesis (PH_3) are not used. In the method adopted the most important stage, responsible for the low efficiency of the entire industrial cycle, is the synthesis of calcium hypophosphite.

Soviet scientists developed recently a number of improvements to this method leading to a higher yield and a faster process. The existing view that the reaction between yellow phosphorus and calcium hydroxide in an aqueous medium is "sluggish" proved to be incorrect; an increase in the specific surface of phosphorus accelerates the synthesis by a factor of several powers of ten. Above 90–93 °C, the rate of reaction increases very rapidly and near 100 °C the process is completed in 2–3 min in the presence of a high specific surface.

Under these conditions, it is possible to obtain solutions containing 12–13% of calcium hypophosphite. The attainment of high rates and high hypophosphite concentrations during the synthesis makes it possible to reduce by a factor of 15 the consumption of steam in the evaporation of the solutions and to reduce sharply the volume of the reactors. The possibility of a considerable decrease of the consumption of calcium hydroxide has been established. Instead of a 400% excess, one can use an excess of approximately 25% relative to stoichiometry. The employment of closed reactors-emulsifiers makes it possible to utilise the PH_3 obtained in the synthesis by its combustion to P_2O_5 with subsequent synthesis of phosphoric acid, which increases the degree of utilisation of phosphorus to 75–80%.

The following conditions for the synthesis in reactors-emulsifiers must be regarded as optimal: the temperature of synthesis 90–93 °C and molar proportions of phosphorus and lime (P : CaO) of 1 : 0.45, which corresponds to an approximately 25% excess of lime. The amount of water introduced into the synthesis is calculated to give 12–13% solutions.

Morgunova and Averbukh [109] made a detailed study of the synthesis of sodium hypophosphite from (1) yellow phosphorus and sodium hydroxide, (2) yellow phosphorus, calcium hydroxide, and sodium carbonate, (3) yellow phosphorus, sodium hydroxide, and calcium hydroxide, (4) yellow phosphorus, barium hydroxide, and sodium carbonate, and (5) yellow phosphorus, sodium hydroxide, and barium hydroxide. During their investigations, they established that an increase of the yield of sodium hypophosphite to 55–59% of the phosphorus in the charge can be ensured by preparing the sodium hypophosphite solution in a single stage by the reaction of phosphorus with hydroxide

ions in the presence of both Na^+ ions alone and in the joint presence of Na^+ and Ca^{2+}. When Ca^{2+} ions are replaced by Ba^{2+}, the yield falls. The overall amount of hydroxide ions introduced into the process, which can ensure the complete utilisation of the phosphorus in the charge, should be not less than 1.0–0.9 mole per gram-atom of phosphorus. A decrease of the content of phosphite formed during the synthesis is achieved by precipitating it in the form of insoluble alkaline earth metal phosphites. The amount of alkaline earth metal required to precipitate the phosphite may be 0.25–0.30 mole per gram-atom of phosphorus, which is determined by the amount of phosphite formed in the synthesis.

In the synthesis of sodium hypophosphites in the presence of hydroxide ions introduced as the alkaline earth metal hydroxide, Na^+ ions can be introduced both as the hydroxide and as the carbonate. When sodium ions are added as the carbonate, the required amount of hydroxide ions must be introduced in the form of the alkaline earth metal hydroxide. The amounts of reactants in the charge should ensure the molar ratios $P : Na^+ : Ca^{2+}(\text{or } Ba^{2+}) : OH^- = 1 : 0.50–0.60 : 0.25–0.30 : 0.90–1.0$.

V. THE MECHANISM OF THE SYNTHESIS OF HYPOPHOSPHITES IN SOLUTION

There exist various views on the relation between the composition of the gas phase and that of the products formed in the synthesis of hypophosphites in solution[80]. Some investigators believe that the amount of hydrogen evolved is proportional to the amount of phosphite formed in the oxidation of hypophosphite:

$$P_4 + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3; \quad (1)$$

$$H_2PO_2^- + OH^- \rightarrow HPO_3^{2-} + H_2 \uparrow, \quad (2)$$

while others state that hydrogen is formed in an amount proportional to the amount of hypophosphite.

Reactions which agree best with practical results according to the authors have been put forward[81]:

$$P_4 + 4OH^- + 4H_2O \rightarrow 4H_2PO_2^- + 2H_2; \quad (3)$$

$$P_4 + 4OH^- + 2H_2O \rightarrow 2HPO_3^{2-} + 2PH_3. \quad (4)$$

Different amounts of phosphite and phosphine are formed by reactions (3) and (4). There exist also other views on the pathways followed in the formation of phosphites and hydrogen[80], but the presence of both components in the gaseous mixture is never denied. According to one investigation[82] the synthesis of sodium hypophosphite involves other reactions, apart from those quoted above, in which molecular hydrogen and diphosphine are formed:

$$3P_4 + 8OH^- + 8H_2O \rightarrow 8H_2PO_2^- + P_2H_4; \quad (5)$$

$$H_2PO_2^- + 2OH^- \rightarrow PO_4^{3-} + 2H_2; \quad (6)$$

$$15P_2H_4 \rightarrow P_{12}H_6 + 18PH_3. \quad (7)$$

In his most complete and latest monograph on phosphorus, Van Wazer[110] quotes the same reactions as Tsuboi[31].

Soviet investigators[111] made a fairly detailed study of the mechanism of the synthesis of hypophosphite in solution. They showed that, when phosphorus interacts with hydroxide ions, hypophosphite and phosphite are formed simultaneously. Presumably both hydrogen and phosphine can be evolved under these conditions.

Morgunova and Averbukh quote in their paper[111] the free energies of some of the reactions calculated from Latimer's data[112] (Table 2). All the reactions listed in the Table, except the last, are thermodynamically probable. In order to determine which reactions actually occur, the authors studied the composition of the gas phase in the synthesis of hypophosphite solutions.

Table 2. The free energies of certain reactions (Latimer's data[112]).

No. of reaction	Reaction	Free energy, kJ
1	$P_4 + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3$	−336.0
2	$H_2PO_2^- + OH^- \rightarrow HPO_3^{2-} + H_2$	−142.8
3	$P_4 + 4OH^- + 4H_2O \rightarrow 4H_2PO_2^- + 2H_2$	−472.2
4	$P_4 + 4OH^- + 2H_2O \rightarrow 2HPO_3^{2-} + 2PH_3$	−485.2
8	$P_4 + 4OH^- + 8H_2O \rightarrow 4HPO_3^{2-} + 8H_2$	−722.8
9	$P_4 + 6H_2O \rightarrow 3H_3PO_2 + PH_3$	−126.4
10	$H_2PO_2^- + 2OH^- \rightarrow PO_4^{3-} + 2H_2$	−199.5
11	$HPO_3^{2-} + 3OH^- \rightarrow PO_4^{3-} + 2H_2O$	−217.1
12	$3H_3PO_2 \rightarrow PH_3 + 3H_3PO_3$	−125.5
13	$H_3PO_2 + H_2O \rightarrow H_3PO_3 + H_2$	−96.6
14	$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4$	+3.8

Their investigations showed that the composition of the gas phase depends on which hypophosphite is synthesised. In the synthesis of calcium hypophosphite the gas phase contains more phosphine than hydrogen. Three times as much PH_3 as H_2 is always present in the gas phase. A clear-cut dependence of the change in the composition of the gas phase on time has not been observed.

In the synthesis of sodium hypophosphite the content of hydrogen is approximately three times greater than that of PH_3. The $H_2 : PH_3$ ratio then decreases, reaching in some cases approximately 0.6 at the end of the synthesis. The average $H_2 : PH_3$ and hypophosphite : phosphite ratios in the synthesis of calcium hypophosphite are 0.3 and about 1.4, while in the synthesis of sodium hypophosphite from yellow phosphorus and NaOH the ratios are 1.8 and 3.5 respectively.

Table 3. The contributions of reactions (1), (4), (3), and (8) to the synthesis (%).

Sodium hypophosphite				Calcium hypophosphite			
(1)	(4)	(3)	(8)	(1)	(4)	(3)	(8)
—	35.7	64.3	—	impossible			
88.3	—	—	16.7	impossible			
impossible				26.7	53.4	19.9	—
80.6	—	1.6	17.8	impossible			
—	31.6	63.5	0.4	impossible			

Possible combinations of reactions which ensure the formation of both hydrogen and phosphine in the above proportions and which are the most probable on thermodynamic grounds [reactions (1), (4), (3), and (8) in Table 2] have been elucidated. The possible combinations of reactions in the synthesis of hypophosphites are indicated in Table 3, which shows that the combination of reactions

(4) and (3) is feasible only in the synthesis of sodium hypophosphite solutions and is impossible in the synthesis of calcium hypophosphite. This has also been pointed out in other investigations[82,112]. The synthesis of hypophosphites may involve the simultaneous occurrence of reactions (1), (4), (3), and (8) with formation of hypophosphite. Apart from phosphine, the gas phase contains diphosphine, which causes the self-ignition of the evolved gases in air. Furthermore, a certain amount of elemental phosphorus passes to the gas phase.

VI. HYPOPHOSPHITES AND THEIR CLASSIFICATION

The available literature data are mainly concerned with studies on alkali metal phosphites. The following alkali metal hypophosphites are known[80]: $Li(O_2PH_2).H_2O$, $K(O_2PH_2)$, $Na(O_2PH_2).H_2O$, and the ammonium salts $(NH_4)(O_2PH_2)$ and $(NH_3OH)(O_2PH_2)$. They are all readily soluble in water. However, there are no reliable data for their solubilities[114] except for the solubilities of the sodium salt in two glycols. At 25°C $Na(O_2PH_2)$ dissolves in an amount of 33.01 g in 100 g of ethylene glycol and 9.70 g in 100 g of propylene glycol. The heats of solution of the sodium, ammonium, calcium, and barium salts have been determined by Bright and Carson[113].

The following Group II metal hypophosphites are known[80]: $Mg(O_2PH_2).6H_2O$, $Ca(O_2PH_2)_2$, $Sr(O_2PH_2)_2$, $Ba(O_2PH_2)_2$, and $Ba(O_2PH_2)_2.H_2O$. These salts are also extremely soluble in water, the solubilities of $Ca(O_2PH_2)_2$ and $Ba(O_2PH_2)_2$ at room temperature being respectively 17 and 29 g per 100 g of water.

As a rule, other metal hypophosphites are obtained by the reaction of the metal oxide or hydroxide with hypophosphorous acid. In many cases, when the metal can be readily reduced, an oxidation-reduction takes place instead of the formation of the salt. Such processes occur, for example, when copper and silver oxides are used. However, salts such as copper hypophosphite can sometimes be obtained by cooling or by rapid salting-out with alcohol[114].

The physical properties and solubilities of some hypophosphites which we have found in the literature are compiled in Table 4.

Myants and Matrosov[115] studied the infrared spectra of metal hypophosphites and carried out calculations on various vibrational models. The salts were obtained by the double decomposition of the metal with barium and potassium hypophosphites. Drying in a Fisher pistol over P_2O_5 at 77°C (the salts decomposed at a higher temperature) resulted in only a partial loss of the water of crystallisation. The starting materials and the compositions of the salts obtained are listed in Table 5.

Table 5. The hypophosphites which have been synthesised and investigated.

Starting materials	Composition of resulting salt	Composition of salt after drying
$(NH_4)_2SO_4$ and $Ba(H_2PO_2)_2$	$NH_4H_2PO_2$	$NH_4H_2PO_2$
Li_2SO_4 and $Ba(H_2PO_2)_2$	$LiH_2PO_2 \cdot H_2O$	LiH_2PO_2
Na_2SO_4 and $Ba(H_2PO_2)_2$	$NaH_2PO_2 \cdot \frac{1}{3} H_2O$	NaH_2PO_2
$MgSO_4 \cdot 7H_2O$ and $Ba(H_2PO_2)_2$	$Mg(H_2PO_2)_2 \cdot 6H_2O$	$Mg(H_2PO_2)_2 \cdot H_2O$
$ZnSO_4 \cdot 7H_2O$ and $Ba(H_2PO_2)_2$	$Zn(H_2PO_2)_2 \cdot \frac{1}{2} H_2O$	$Zn(H_2PO_2)_2 \cdot \frac{1}{2} H_2O$
$CdSO_4 \cdot \frac{8}{3} H_2O$ and $Ba(H_2PO_2)_2$	$Cd(H_2PO_2)_2 \cdot 2H_2O$	$Cd(H_2PO_2)_2 \cdot H_2O$
Tl_2SO_4 and $Ba(H_2PO_2)_2$	TlH_2PO_2	TlH_2PO_2
$Th(NO_3)_4$ and KH_2PO_2	$Th(H_2PO_2)_4 \cdot 3H_2O$	$Th(H_2PO_2)_4 \cdot 3H_2O$
$Pb(NO_3)_2$ and KH_2PO_2	$Pb(H_2PO_2)_2 \cdot H_2O$	$Pb(H_2PO_2)_2 \cdot H_2O$
$MnSO_4 \cdot 7H_2O$ and $Ba(H_2PO_2)_2$	$Mn(H_2PO_2)_2 \cdot 3H_2O$	$Mn(H_2PO_2)_2 \cdot 2H_2O$
$Fe_2(SO_4)_3 \cdot 9H_2O$ and $Ba(H_2PO_2)_2$	$Fe(H_2PO_2)_3 \cdot H_2O$	$Fe(H_2PO_2)_3$
$NiSO_4$ and $Ba(H_2PO_2)_2$	$Ni(H_2PO_2)_2 \cdot 6H_2O$	$Ni(H_2PO_2)_2$
$CoCO_3$ and H_3PO_2	$Co(H_2PO_2)_2 \cdot 2H_2O$	$Co(H_2PO_2)_2 \cdot H_2O$

Despite the wide variety of metals, the salts investigated have mainly similar spectra. The infrared spectra of the salts in the solid state (KBr discs) have been investigated in the range 400–3000 cm^{-1} on IKS-14 apparatus; the spectra of aqueous solutions have also been obtained for salts which are readily soluble in water. The presence of two bands due to the vibrations of the P–O bond (antisymmetric at 1115–1200 cm^{-1} and symmetric at 1020–1060 cm^{-1}) is characteristic of all the salts; this shows that the structure of the anion with equalised PO

Table 4. Physical properties of certain hypophosphites.

Formula	Mol.wt.	Colour, crystalline form, refractive index	Density	B.p., °C	M.p., °C	Solubility, g/100 g of solvent		
						in cold water	in hot water	in other solvents
$NH_4H_2PO_2$	83.03	colourless, orthorhombic	2.515	240*	200	sol.	v.sol.	soluble in alcohol NH_3, insoluble in acetone
$Ba(H_2PO_2)_2 \cdot H_2O$	285.33	white lustrous, polyhedral	2.87(10°)	—	**	28.6	33.3	moderately sol. in alcohol
$Fe(H_2PO_2)_3$	250.81	pale grey, porous	—	—	**	0.043(25°)	0.083(100°)	sol. in citrate salt soln.
KH_2PO_2	104.09	white, deliquescent, hexagonal	—	—	**	v.sol.	v.sol.	sol. in chloroform (11.1 at 25°C) and very slightly sol. in abs. alcohol
$Ca(H_2PO_2)_2$	170.05	pale grey, polyhedral	—	—	**	15.4(25°)	12.5(100°)	insol. in alcohol
$Mg(H_2PO_2)_2 \cdot 6H_2O$	262.39	white cryst.	—	—	—	20	—	insol. in alcohol and ether
$Mn(H_2PO_2)_2 \cdot H_2O$	202.93	pink cryst.	—	150	—	12.5	16.7	insol. in alcohol
$NaH_2PO_2 \cdot H_2O$	155.99	colourless, polyhedral	—	200	—	100(25°)	667(100°)	v. sol. in alcohol and slightly sol. in NH_3
$Ni(H_2PO_2)_2 \cdot 6H_2O$	296.80	green, cubic	1.82(20°)	—	100*	sol.	—	—
H_3PO_2	63.98	cryst.	—	—	—	reacts	reacts	—
$Zn(H_2PO_2)_2 \cdot H_2O$	213.36	colourless, hygr., cryst.	—	—	—	sol.	—	reacts with alkali

* Decomposition temperature.
** Compound decomposes.

bonds persists in all cases. The bands in the region of 1150–1160, 1080, and 810 cm^{-1}, which are associated with the variation of the angles α and γ in the phosphorus tetrahedron, remain at the same wavenumbers in the spectra of all the salts. For salts which exist in the form of hydrates, the intense bands in the range 2300–2500 cm^{-1} correspond to the vibration frequency of the water of crystallisation involved in strong hydrogen bonding.

The spectra of the alkali metal salts are similar and can be satisfactorily interpreted in terms of the ionic model. Furthermore, they resemble the spectrum of the tetraalkylammonium salt, which is ionic. This makes it possible to attribute an ionic structure to them.

The spectra of a number of the metal salts show changes relative to those of the alkali metal salts (the spectra of the anion), which depend on the nature of the metal: (1) new bands appear in the range 400–600 cm^{-1}; (2) the P–O bond vibration frequencies exhibit an appreciable bathochromic shift. These changes suggest the formation of the M–O coordinate bond and the similarity of the spectra of all the salts (including the alkali metal salts) shows that the equalisation of the PO bonds persists in all cases.

In the spectra of $Mg(H_2PO_2)_2$, $Ca(H_2PO_2)_2$, and TlH_2PO_2 the shift of the P–O vibration frequencies is slight, which demonstrates that the interaction of the metal with the oxygen atoms of the anion is weak. These salts have a nearly ionic structure. A chain model, in which the metal is linked to one of the oxygen atoms of each anion forming the coordination sphere of the metal, has been proposed for other salts with an appreciable amount of covalent character.

Thallium hypophosphite has been obtained and investigated in detail[8]. The authors concluded that the following method is most suitable for the preparation of large amounts of the pure salt: a TlOH solution is prepared by shaking thin plates of metallic thallium with an 80% excess of water, the mixture being simultaneously bubbled with oxygen. The solution is then filtered and saturated with carbon dioxide; after partial evaporation and cooling, Tl_2CO_3 precipitates and may be recrystallised from water. The thallium carbonate crystals are treated with hypophosphorous acid, and the resulting solution is filtered and concentrated *in vacuo*. A large amount of n-propyl or isopropyl alcohol (3 litres of the alcohol per 100 ml of the saturated salt solution) is added to the residual solution and the resulting mixture is cooled at 5°C for one week. The white acicular crystals formed are washed with fresh isopropyl alcohol and the product is then dried in a vacuum desiccator. The melting point of TlH_2PO_2 has been determined as 114°C. The salt is usually seen to undergo a slight decomposition near its melting point. On heating, thallium hypophosphite gradually blackens. Heating for 6–7 h at 95°C is needed before blackening begins. It has been suggested[8] that under these conditions TlH_2PO_2 is slowly oxidised by atmospheric oxygen to thallium phosphite TlH_2PO_3. Thallium hypophosphite is sensitive to light: the same black colour appears in sunlight as on heating.

The existence of the complex Tl^{3+}–$H_2PO_2^-$ is doubtful[116]; the only evidence for it is the properties of the $H_2PO_2^-$ ligand, which forms complexes with other metals. The following mechanism has been proposed for the formation of the complex of $H_2PO_2^-$ with Tl^{3+} before the oxidation stage:

$$Tl^{3+} + H_2PO_2^- \rightleftarrows (TlH_2PO_2)^{3+}$$
$$(TlH_2PO_2)^{3+} + H_2O \rightarrow Tl^+ + H_3PO_3 + 2H^+.$$

The decomposition of the complex is not a simple process; it involves the addition of an oxygen atom to form H_3PO_3, which takes place by the substitution of one hydrogen atom linked directly to phosphorus by an OH group of water.

The properties of anhydrous $Co(H_2PO_2)_2$, $Zn(H_2PO_2)_2$, $Fe(H_2PO_2)_2$, $Cu(H_2PO_2)_2$, and $Ni(H_2PO_2)_2$ have been described[117]. The first two compounds were obtained by crystallisation from aqueous solutions. The salts $Fe(H_2PO_2)_2$ and $Cu(H_2PO_2)_2$ have been prepared by precipitation from acetone solution. Iron hypophosphite is a pale-blue powder insoluble in water. Copper hypophosphite is unstable at room temperature and decomposes with formation of metallic copper a few minutes after precipitation.

Nickel hypophosphite, consisting of an amorphous yellow powder, has been prepared by dehydrating the hexahydrate or by precipitation from acetone solution and dehydration in the presence of P_2O_5.[117] The behaviour of cobalt, zinc, iron, copper, and nickel hypophosphites in relation to anhydrous pyridine has been studied. Cobalt and zinc hypophosphites form the readily crystallising compounds $Co(H_2PO_2)_2Py_2$ and $Zn(H_2PO_2)_2Py_2$. They lose pyridine at 20°C, being reconverted into the corresponding hypophosphites.

It has been found that the interaction of M^{2+} (M = Cu, Co, or Ni) and $H_2PO_2^-$ in aqueous solution at 19° ± 2°C, an ionic strength of 3 ($NaClO_4$), and pH 3.7–3.9 results in the formation of relatively unstable hypophosphite complexes[118] The composition of cobalt and nickel hypophosphites with the ratio $M^{2+}:H_2PO_4^- = 1:1$ has been established by the method of continuous variations. The equilibrium constant for the reaction $M^{2+}H_2PO_2^- \rightleftharpoons MH_2PO_2^+$ (for M = Co) has been calculated as 0.82 ± 0.09.[119]

The synthesis of aluminium hypophosphite by two methods has been described[120]. One of them reduces to heating aluminium hydroxide or an aluminium salt solution with 50% H_3PO_2 at 80–90°C for 1 h with subsequent slow precipitation of $Al(H_2PO_2)_3$. The second method involves heating an aluminium salt with sodium hypophosphite, the precipitation being even slower than in the first method. $Al(H_2PO_2)_3$ is insoluble in water and H_3PO_2. It is soluble in warm sodium hydroxide solution, dilute H_2SO_4, and dilute and concentrated HCl. On heating, aluminium hypophosphite decomposes, without fusion, at approximately 220°C with evolution of phosphine and the formation of a reddish-brown deposit. The conditions under which hypophosphorous acid might reduce aluminium compounds to the metal have not been found.

Scandium, yttrium, and lanthanum hypophosphites $R(H_2PO_2)_3$ have been obtained by the interaction of the hydroxides of the first two elements and of $La_2(CO_3)_3$ with hypophosphorous acid[121]. The resulting hypophosphites are crystalline substances insoluble in water and organic solvents. They crystallise in a system with low symmetry. Scandium hypophosphite decomposes *in vacuo* at 350°C, yttrium hypophosphite at 450°C, and lanthanum hypophosphite at 300–350°C. The infrared spectra of scandium, yttrium, and lanthanum hypophosphites have sharp maxima. The spectra recorded in the range 400–3000 cm^{-1} are mainly those of the anions. The influence of the cations on the spectrum is manifested mainly in the range 400–500 cm^{-1}.

The anhydrous lanthanide hypophosphites having the composition $R(H_2PO_3)_3$ and the double hypophosphites $CeR(H_2PO_2)_6$, where R = Er, Tm, Yb, or Lu, have been synthesised[122,123]. The former are crystalline substances with the colour characteristic of the lanthanide ion, which, however, is less intense than that of the nitrates, chlorides,

and other salts. The results of heating to 105–108 °C showed that they do not contain water of crystallisation. Heavy lanthanide hypophosphites are less soluble in water than light lanthanide hypophosphites. They tend to form supersaturated solutions, this tendency being most marked for the light lanthanides.

Lanthanum hypophosphite $La(H_2PO_2)_3.H_2O$ and europium hypophosphite $Eu(H_2PO_2)_3.H_2O$ have been investigated by X-ray diffraction[124] and it has been shown that the chemical properties of these compounds in solutions are somewhat different.

Praseodymium hypophosphite $Pr(H_2PO_2)_3$ crystallises in the form of green prisms when a 1% of H_3PO_2 solution is neutralised with praseodymium oxide and then evaporated on a water bath. The salt is fairly sparingly soluble in water.

The double hypophosphites $CeR(H_2PO_2)_6$, where R = Er, Tm, Yb, or Lu, have been analysed chemically and their thermal decomposition has been studied[123]. It has been established that the decomposition takes place instantaneously in the temperature range 300–370 °C. The decomposition products are oxidised in the range 440–600 °C.

VII. METAL HYPOPHOSPHITE COMPLEXES

The existence in solution of cationic complexes $MH_2PO_2^{2+}$ formed by lanthanide and hypophosphite ions has been confirmed spectrophotometrically for praseodymium, neodymium, and erbium. The equilibrium constants and the formation constants of the complexes have been calculated[125]. The interaction of lanthanide ions with hypophosphorous acid was studied using an SF-10 recording spectrophotometer. The absorption spectra of solutions of praseodymium(III), neodymium(III), and erbium(III) complexes were recorded in the ranges 420–505, 490–615, and 500–560 nm respectively 10 min after mixing the solutions (this time interval was sufficient for equilibration). The absorption spectra do not change in the course of the next 2–3 h, but for an $H_3PO_2 : M^{2+}$ ratio exceeding 8 or at pH 3.0 a precipitate is formed.

The optical densities of solutions of the hypophosphite complexes at the absorption band maxima of the Pr^{3+} and Nd^{3+} ions are lower and in the case of Er^{3+} higher than the optical densities D_{chl} of solutions of their chlorides. The Pr^{3+} and Nd^{3+} absorption band maxima undergo bathochromic or hypsochromic shifts. The split erbium band has maxima at 522.5 and 519 nm. A study of the influence of the pH on ΔD at the absorption band maxima showed that the formation of lanthanide complexes of $H_2PO_4^-$ begins at a pH greater than 1, reaching a maximum at pH 2.5 for praseodymium and neodymium and at 1.6 for erbium. When the pH of solutions of the praseodymium and neodymium complexes is greater than 6.5 and that of the erbium complex greater than 3, precipitates are gradually deposited from the solutions at a rate which is higher the higher the pH and the greater the $H_2PO_2^- : M^{3+}$ ratio.

The compositions of the complexes have been investigated[125] spectrophotometrically by the isomolar series method and by the restricted logarithmic method. Experiments were performed at pH 2.9–3.4 where the difference between the optical densities of solutions of the complexes reaches a maximum. The formation of highly dissociated complexes with the probable component ratio $H_3PO_2^- : M^{3+} = 1 : 1$ has been established.

The reaction between lanthanide ions and hypophosphorous acid can be represented by the equation

$$M^{3+} + H_3PO_2 \rightleftarrows MH_2PO_2^{2+} + H^+.$$

The values of $\lg K_{eq}$ and $\lg K_{form}$ obtained are listed in Table 6, which shows that those for the praseodymium, neodymium, and erbium complexes differ insignificantly from one another.

Table 6. The logarithms of the equilibrium constants and the formation constants of lanthanide complexes of H_3PO_2.

Complex	K_{eq}	K_{form}
$PrH_2PO_2^{2+}$	0.23±0 03	1.33±0.03
$NdH_2PO_2^{2+}$	0.00±0.04	1.10±0.04
$ErH_2PO_2^{2+}$	0.37±0.03	1.47±0.03

The kinetics of the formation of iron[126] and chromium[127] monohypophosphite complexes have been studied. The existence of the complexes $CrH_2PO_2^{2+}$ and $Fe(H_2PO_2)_2^{2+}$ has been confirmed and their stability constants have been determined. The preparation of tin(IV) hypophosphite has been described[128]. A saturated solution of SnO in H_3PO_2 was saturated with oxygen until colourless $Sn(H_2PO_2)_4$ crystals formed, this being the first example of a solid compound containing tin(IV) and an anion with a high reduction potential. The possibility of the formation of zirconium and hafnium hypophosphite complexes has been studied. It has been shown by ion exchange[129] that the anionic complexes $[Zr(H_2PO_2)_6]^{2-}$ and $[Hf(H_2PO_2)_6]^{2-}$ are formed when hydrated zirconium(IV) and hafnium(IV) oxides are dissolved in an aqueous H_3PO_2 solution (maximum concentration 0.3 N).

The formation of insoluble compounds of the type $M[Zr(H_2PO_2)_6]$ and $M[Hf(H_2PO_2)_6]$ when bivalent metal salts are added (M = Mg, Ca, Mn, Co, Ni, Fe, Zn, or Cd) is of interest. It has been shown[129] that these insoluble bivalent metal hypophosphitozirconates and hypophosphitohafnates do not contain water and decompose at 210–300 °C. Apart from the calcium salt, they are all isomorphous. According to infrared spectroscopic data, both terminal and bridging H_2PO_2 groups have been detected in $M[Zr(H_2PO_2)_6]$ and $M[Hf(H_2PO_2)_6]$. Consequently the hypophosphitozirconates and hypophosphitohafnates are polycondensed complexes. It has been found[130] that H_3PO_2 forms with molybdenum(VI) a complex having a high optical density at 400 nm whatever the acid concentration, while the complex with PO_4^{3-} is not formed at a solution acidity of about 1.6 N. A spectrophotometric method for the determination of hypophosphite in the presence of phosphates has been developed on this basis.

Like phosphites, hypophosphites form addition products[131] with hydrogen halides (HCl, HBr, and HI). Whereas phosphates can combine with three molecules of the hydrogen halide, hypophosphites and phosphites can combine with two molecules. A typical compound of this type is $Cd(H_2PO_2)_2.2HCl$. In these compounds the hydrogen halide is linked to the hypophosphite molecule, similarly to water in hydrates, i.e. is coordinated to the metal ion.

Interesting germanium(II) complexes have been described[132]: $Ge(H_2PO_2)_2.GeCl_2$ and $3Ge(H_2PO_2)_2.GeBr_2$. The former salt (m.p. 124 °C) was synthesised by heating

activated germanium oxide, obtained by dissolving the normal oxide in alkali and reprecipitating it with 6 *N* HCl and 50% H_3PO_2 in the course of 30 min. After allowing the mixture to stand for 12 h, the crystals were separated, washed with dilute H_3PO_2 and absolute alcohol, and dried *in vacuo* at room temperature. The latter salt (m.p. 129°C) was obtained using GeO, 35% HBr, and 50% H_3PO_2. Crystals separated on slow cooling. The compounds obtained are extremely stable in air, but are hydrolysed in water, forming germanium hydroxide.

When germanium dioxide is heated with H_3PO_2, it is reduced, dissolving with formation of a yellow-green solution. This behaviour is the opposite to that of SnO_2, which, although soluble in H_3PO_2, is not reduced to the bivalent state in the absence of HCl.[132] Everest[133] states that the double salts $Sn(H_2PO_2)_4.SnCl_4$ and $Sn(H_2PO_2)_2.SnCl_2$ exist.

VIII. REDUCING PROPERTIES OF THE HYPOPHOSPHITE ION

Many studies have been made on the reducing properties of hypophosphite ions. Pyrolysis of NaH_2PO_2 in the presence of LiH (molar ratio 1 : 22) or LiOH (molar ratio 1 : 5) has been investigated in the range 210–250°C.[132] The possibility of the following reactions has been suggested:

$$NaH_2PO_2 + LiH \rightarrow NaHPO_2 + Li + H_2 , \quad (15)$$

$$NaH_2PO_2 + 2LiH \rightarrow NaPO_2 + 2Li + 2H_2 , \quad (16)$$

$$6NaH_2PO_2 + 3LiH \rightarrow 2Na_3PO_4 + P_4H_4O + 3LiOH + H_2 , \quad (17)$$

$$NaH_2PO_2 + 4LiH \rightarrow PLi_3 + NaOH + LiOH + 3H_2 , \quad (18)$$

$$NaH_2PO_2 + LiOH \rightarrow NaLiHPO_3 + H_2 , \quad (19)$$

$$NaPO_2 + LiOH \rightarrow NaLiHPO_3 , \quad (20)$$

$$NaH_2PO_2 + 3LiOH \rightarrow NaLiH_2PO_4 + 2H_2 , \quad (21)$$

$$2NaH_2PO_4 \rightarrow PH_3 + Na_2HPO_4. \quad (22)$$

The compound P_4H_4O, obtained in reaction (17), is a mixture of red polymeric products. It is insoluble in water, acids, and organic solvents. It has been shown[134] that P_4H_4O is satisfactorily described by the formula $(P_4H_4O)_n$. The possible structure of $(P_4H_4O)_n$ has been considered on the basis of the infrared spectra and possible structural formulae, containing the P–P bond, have been put forward. It has been suggested that P–O–P or –P=O and HO–P– linkages may be formed. P_4H_4O is not formed in the interaction of NaH_2PO_2 with LiOH.

The reduction of $K_3[Co(CN)_6]$ by hypophosphorous acid in 1 *N* HCl solution in an atmosphere of nitrogen, resulting in the formation of $Co(CN)_2.2H_2O$, has been studied[135]. The hypothesis that the reduction reaction proceeds via the intermediate complexes $[Co(CN)_5.OP(O)H_2]^{4-}$ or $[(CN)_5CoOPH_2OCo(CN)_5]_n$ has been confirmed by infrared spectra, which contain absorption bands characteristic of the P–O and P–H groups.

The high reducing capacity of the hypophosphite ion constitutes the basis of many methods for its determination. Thus a procedure has been developed[135] for potentiometric titration with vanadate of hypophosphite and phosphite in their mixtures, based on the oxidation of $H_2PO_2^-$ to PO_4^{3-} (via HPO_3^{2-}) by vanadate in the presence of a silver salt; in the absence of silver, phosphite is not oxidised to PO_4^{3-}.

A volumetric method for the determination of hypophosphite with iodine has been described[137]. It consists in the oxidation of hypophosphite to phosphite:

$$H_3PO_2 + I_2 + H_2O \rightarrow H_3PO_3 + 2HI.$$

Under certain conditions, the resulting phosphite may be oxidised by iodide to phosphate:

$$H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2HI.$$

In a strongly acid medium the first reaction mainly occurs.

A procedure has been developed[138] for the determination of hypophosphite ions in acid chemical nickel-plating solutions based on weighing the nickel–phosphorus coating obtained as a result of the reaction of Ni^{2+} by hypophosphite. Phosphite (up to 50 g litre^{-1}) and reducing agents do not interfere with the determination.

It has been established[139] that in a borate buffer IO_4^- oxidises $H_2PO_2^-$, HPO_3^{2-}, SeO_3^{2-}, and TeO_3^{2-} on heating and in all cases IO_3^- is formed. The excess IO_4^- may be titrated iodometrically in a buffer medium and the content of any of the above substances can thus be found. A procedure has been proposed for the photometric determination[140,141] of $H_2PO_2^-$, based on the decrease of the optical density of the solution at 530 nm due to the reduction of Fe^{3+} to Fe^{2+} by the hypophosphite ion.

Sodium hypophosphite may be determined[142], after the preliminary removal of iron from solution, by oxidising NaH_2PO_2 with an iron(III) salt solution, this being followed by the titration of the Fe^{2+} formed with a cerium(IV) sulphate solution. The kinetics and mechanism of the oxidation of phosphite by cerium(IV) in sulphuric acid solution have been studied[143]. Conditions have been described for the oxidation of hypophosphite ions by various oxidants: nitric acid[144], permanganate[145,146], cerium(IV) salts[147,148], dichromate solution in the presence of silver ions[149], bromide-bromate[150], an iron(III) salt[151], and persulphate (catalysed by bivalent copper in perchloric acid solution)[152].

Organic derivatives of hypophosphorous acid—phosphinous and disubstituted phosphinic acids—are of interest. One or two hydrogen atoms attached to phosphorus in hypophosphorous acid can be substituted by alkyl or aryl groups. When one hydrogen atom is substituted, the resulting compounds are called alkylphosphinous or phosphinous acids RHPOOH. Little is known about the monoesters of these acids, but a number of diesters have been obtained. The acids formed as a result of the substitution of two hydrogen atoms attached to phosphorous in hypophosphorous acid are called dialkylphosphinic (diarylphosphinic) acids or "secondary" phosphinic acids.

The free acids $R_2P(O)(OH)$ and the corresponding esters $R_2P(O)(OR)$ are known.

IX. THE APPLICATIONS OF HYPOPHOSPHITES

From the economic point of view, the applications of hypophosphites for the surface treatment of metals are the most important[153]. This advanced method was proposed in the USA after the Second World War[154] and was subsequently extended, investigated theoretically, and continually improved[155].

Investigations showed[156–159] that metallic plates can be coated chemically by nickel, cobalt, or their alloys with the aid of hypophosphite ions, the resulting thin coating (less than 0.025 mm) being extremely hard, non-porous, and strongly attached to the metal. The thickness of the layer of deposited metal may be regulated. A great advantage of the method is the possibility of treating also non-metallic materials—ceramics, glass, and plastics. In semiconductor engineering it is possible to deposit metallic contacts directly onto ceramics or other materials in the manufacture of transistors[159].

Hypophosphites are also used for the electroplating of various articles[160,161].

The reducing properties of hypophosphites permitted their use in the manufacture of explosives[160]. For example, a mixture of equal amounts of barium hypophosphite and potassium chlorate, the latter subjected to preliminary drying at 100°C, rapidly ignites in open air with a weak explosion. In a closed vessel the mixture detonates. It is readily ignited by an electric spark and is very sensitive to impact and friction.

In view of the use of hypophosphites in pharmaceutical practice at the end of the 19th century, their toxicity has been investigated in very great detail[163-167]. No evidence indicating their toxicity to mammals has been obtained; in the mammallian organism they remain unchanged and are rapidly eliminated.

Hypophosphites have been recently finding increasingly frequent applications in analytical chemistry. Thus a method employing hypophosphite has been developed[168] for the titrimetric determination of iron in the presence of copper ions as the catalyst.

REFERENCES

1. J. Thomsen, Ber., 7, 994, 996 (1874).
2. J. Thomsen, J. prakt. Chem., 11, 113 (1875).
3. J. Thomsen, Thermochem. Untersuch., 1, 178, 195, 297 (1883).
4. J. Thomsen, Thermochem. Untersuch., 2, 212, 225 (1884).
5. R. Paris and P. Tardy, Compt. rend., 223, 242 (1946).
6. T. Milobedzki and M. Maculec, Roczniki Chem., 23, 13 (1949).
7. W. A. Jenkins and R. T. Jones, J. Amer. Chem. Soc., 74, 1353 (1952).
8. W. A. Jenkins and D. M. Jost, J. Amer. Chem. Soc., 73, 2945 (1951).
9. I. M. Kolthoff, Rec. Trav. Chim., 46, 350 (1927).
10. W. V. Bhagwat and N. R. Dhar, J. Indian Chem. Soc., 6, 781 (1929).
11. C. Morton, Pharm. J., 125, 102 (1930).
12. C. Morton, Chemist and Druggist, 113, 138 (1930).
13. A. D. Mitchell, J. Chem. Soc., 117, 957 (1920).
14. R. O. Griffith, A. McKeown, and R. P. Taylor, Trans. Faraday Soc., 36, 752 (1940).
15. R. O. Griffith and A. McKeown, Trans. Faraday Soc., 30, 530 (1934).
16. A. D. Mitchell, J. Chem. Soc., 117, 1322 (1920).
17. B. D. Steele, J. Chem. Soc., 91, 1641 (1908).
18. B. D. Steele, J. Chem. Soc., 92, 1659 (1908).
19. P. Nylen, Z. anorg. Chem., 230, 385 (1937).
20. J. E. Ricei, J. Amer. Chem. Soc., 70, 109 (1948).
21. G. Schwarzenbach, Helv. Chim. Acta, 19, 1043 (1936).
22. T. D. Farr, "Phosphorus, Properties of the Element and Some of Its Compounds", Tenn. Valley Authority, Wilson Dam., Ala., 1950 (TVA Chem. Eng. Rept. No. 8).
23. W. A. Zachriasen and R. C. L. Mooney, J. Chem. Phys., 2, 34 (1934).
24. M. L. Huggins, Phys. Rev., 21, 719 (1923).
25. Rodriguez Pedrazuela A., S. Carcia-Blanco, and L. Rivoir, Anales real. soc. espaň. Fís. Quím., 49A, 255 (1953).
26. A Farrari and C. Colla, Gazzetta, 67, 294 (1937).
27. H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys., 21, 279 (1953).
28. H. S. Gutowsky and D. W. McCall, J. Chem. Phys., 22, 162 (1954).
29. J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, J. Amer. Chem. Soc., 78, 5715 (1956).
30. W. E. Quinn and R. M. Brown, J. Chem. Phys., 21, 1605 (1953).
31. M. Tsuboi, J. Amer. Chem. Soc., 79, 1351 (1957).
32. T. J. Hanwick and P. O. Hoffmann, J. Amer. Chem. Soc., 19, 708 (1951).
33. J. P. Mathieu and J. Jacques, Compt. rend., 215, 346 (1942).
34. A. Simon and F. Feher, Z. anorg. Chem., 230, 289 (1937).
35. J. C. Ghosh and S. K. Das, J. Phys. Chem., 36, 586 (1932).
36. D. E. C. Corbridge and E. J. Lowe, J. Chem. Soc., 493 (1954).
37. L. W. Daasch and D. C. Smith, Anal. Chem., 23, 853 (1951).
38. D. A. Everest, J. Chem. Soc., 4698 (1954).
39. H. Erlenmeyer, W. Schoenauer, and G. Schwarzenbach, Helv. Chim. Acta, 20, 726 (1937).
40. H. Erlenmeyer and H. Gärtner, Nature, 134, 327 (1934).
41. A. I. Brodskii and L. V. Sulima, Dokl. Akad. Nauk SSSR, 85, 1277 (1952).
42. W. A. Jenkins and D. M. Jast, J. Chem. Phys., 20, 538 (1952).
43. A. I. Brodskii and L. V. Sulima, Dokl. Akad. Nauk SSSR, 92, 589 (1953).
44. S. Glasstone, "Textbook of Physical Chemistry", 2nd Edition, D. Van Nostrand Co. Inc., New York, 1946, pp. 887, 898.
45. A. I. Brodskii, D. N. Strazhesko, and L. A. Chervyatsova, Dokl. Akad. Nauk SSSR, 75, 823 (1950).
46. V. D. Ionin, A. F. Lukovnikov, M. D. Neiman, and An. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 67, 463 (1943).
47. C. Perrier and E. Sergé, Ricerca sci., 9, 638 (1938).
48. A. Sieverts and R. Loessner, Z. anorg. Chem., 76, 10 (1912).
49. D. M. Jost and H. Russel, "Systematic Inorganic Chemistry", Prentice Hall, Inc., New York, 1946, Vol. 6, p. 191.
50. A. Sieverts and E. Peters, Z. phys. Chem., 91, 199 (1916).
51. A. Sieverts, Z. anorg. Chem., 64, 29 (1910).
52. P. Bretean, Bull. Soc. chim. France, 9, 515 (1911).
53. J. Bougault, Compt. rend., 148, 415 (1909).
54. H. Wieland and W. Franke, Bayr. Acad. Wissenschaften zu München, Ann., 464, 101 (1928).
55. P. Hersh, J. Chem. Educ., 20, 376 (1943).
56. W. Franke, J. Mönch, Annalen, 550, 1 (1941).
57. E. M. Morgunova and N. D. Maslova, Zhur. Prikl. Khim., 45, 2071 (1972).
58. E. M. Morgunova and A. S. Shubin, Zhur. Prikl. Khim., 46, 957 (1973).
59. P. Hayward and D. M. Yost, J. Amer. Chem. Soc., 71, 915 (1949).
60. V. Hovorka, Coll. Czech. Chem. Comm., 2, 559 (1930); 2, 609 (1930).
61. P. Neogi and B. Sen, J. Indian Chem. Soc., 8, 725 (1931).
62. B. Nath Sen., Coll. Czech. Chem. Comm., 10, 321 (1938).
63. B. Nath Sen., Gazzetta, 78, 423 (1948).
64. A. D. Mitchell, J. Chem. Soc., 121, 1624 (1922).

65. G. S. Vozdvizhenskii and A. F. Gerasimov, Trudy Kazan. Khim-Tekhnol. Inst. im. Butlerova, No. 1, 108 (1934).
66. P. Neogi and S. Mukerji, J. Indian Chem. Soc., **6**, 529 (1929).
67. J. E. Myers and J. B. Firth, Z. anorg. Chem., **80**, 93 (1913).
68. A. D. Mitchell, J. Chem. Soc., **125**, 1013 (1924).
69. A. D. Mitchell, J. Chem. Soc., **119**, 1266 (1921).
70. C. O. Gerfen, Univer. Microfilms Pub. No. 2678, Ann. Arbor. Mich., 113 (1951).
71. A. D. Mitchell, J. Chem. Soc., **125**, 564 (1924).
72. A. D. Mitchell, J. Chem. Soc., **123**, 629 (1923).
73. A. F. Bogoyavlenskii, Uch. Zap. Kazan. Univ. im. Ul'yanova-Lenina, **100**, 69 (1940).
74. G. F. Vozdvizhenskii and A. F. Gerasimov, Zhur. Russ. Fiz.-Khim. Obshch., **62**, 409 (1930).
75. A. Brenner and G. Riddel, J. Res. Nat. Bur. Stand., **37**, 31 (1946); **39**, 385 (1947).
76. R. R. Pahud, Chimie et Industrie, **87**, 759 (1962).
77. J. R. Van Wazer, "Phosphorus and Its Compounds", Monsanto Chemical Company, St. Louis, Missouri, 1961, Vol. 11.
78. K. M. Gorbunova and A. V. Nikiforova, "Fiziko-Khimicheskie Osnovy Protsessa Khimicheskogo Nikelirovaniya" (Physicochemical Principles of Chemical Nickel Plating), Izd. Akad. Nauk SSSR, Moscow, 1960.
79. J. R. Van Wazer, "Encyclopedia of Chemical Technology", Interscience Publ., New York, 1953, Vol. 10, pp. 488–494.
80. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans Green and Co., London, 1928, Vol. 8, p. 879.
81. B. Topley and B. Raistrick, "Thorpe's Dictionary of Applied Chemistry", Longmans Green and Co., London, 1947, Vol. 9, pp. 502–508.
82. Z. Uhlir, S. Schoole, and J. Beneš, Chem. Prum., 8, 291 (1958).
83. J. Novotny and V. Penel, Chem. Prum., 8, 301 (1958).
84. I. V. Sterzhnev, E. M. Morgunova, and E. L. Gabova, Zhur. Prikl. Khim., **34**, 953 (1963).
85. I. V. Sterzhnev, E. M. Morgunova, and E. L. Gabova, Zhur. Prikl. Khim., **34**, 1873 (1963).
86. German P. 442 210 (1927); Zhur. Prikl. Khim., 40, 274 (1962).
87. Japanese P. 43621 (applied for on 10. 7. 67; Published on 24. 12. 1971); Ref. Zhur. Khim., 19L44P (1972).
88. Swiss P. 322 980 (1957); Zhur. Prikl. Khim., 40, 274 (1962).
89. Swiss P. 322 981 (1957); Zhur. Prikl. Khim., 40, 274 (1962).
90. Swiss P. 360 378 (1962); Zhur. Prikl. Khim., 40, 274 (1962).
91. French P. 1 155 025 (1956); Zhur. Prikl. Khim., 40, 274 (1962).
92. French P. 1 181 938 (1957); Zhur. Prikl. Khim., 40, 274 (1962).
93. French P. 155 025 (1958); Zhur. Prikl. Khim., 40, 274 (1962).
94. French P. 1 152 431 (1958); Zhur. Prikl. Khim., 40, 274 (1962).
95. French P. 1 164 005 (1958); Zhur. Prikl. Khim., 40, 274 (1962).
96. French P. 1 202 859 (1958); Zhur. Prikl. Khim., 40, 274 (1962).
97. French P. 1 240 383 (1959); Zhur. Prikl. Khim., 40, 274 (1962).
98. French P. 1 256 459 (1961); Zhur. Prikl. Khim., 40, 274 (1962).
99. Italian P. 456 918 (1950); Zhur. Prikl. Khim., 40, 274 (1962).
100. Italian P. 556 786 (1957); Zhur. Prikl. Khim., 40, 274 (1962).
101. BRD P. 1 029 809 (1959); Zhur. Prikl. Khim., 40, 274 (1962).
102. BRD P. 1 078 552 (1960); Zhur. Prikl. Khim., 40, 274 (1962).
103. BRD P. 1 119 237 (1961); Zhur. Prikl. Khim., 40, 274 (1962).
104. BRD P. 1 112 054 (1961); Zhur. Prikl. Khim., 40, 274 (1962).
105. BRD P. 1 145 588 (1963); Zhur. Prikl. Khim., 40, 274 (1962).
106. US. P. 2 938 770 (1960); Zhur. Prikl. Khim., 40, 274 (1962).
107. US. P. 2 977 192 (1961); Zhur. Prikl. Khim., 40, 274 (1962).
108. Dutch P. 102 461 (1962); Zhur. Prikl. Khim., 40, 274 (1962).
109. E. M. Morgunova and T. D. Averbukh, Zhur. Prikl. Khim., 40, 274 (1962).
110. J. R. Van Wazer, "Phosphorus and Its Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1962, Vol. 1.
111. E. M. Morgunova and T. D. Averbukh, Zhur. Prikl. Khim., 40, 1660 (1967).
112. W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions" (Translated into Russian), Inostr. Lit., Moscow, 1954.
113. N. F. Bright and T. Carson, Canad. J. Techn., 31, 221 (1953).
114. R. Engel, Compt. rend., **129**, 518 (1899).
115. O. S. Mayants and E. I. Matrosov, Izv. Akad. Nauk SSSR, Neorg. Materialy, 1, 546 (1965).
116. K. S. Gupta and J. K. Gupta, J. Chem. Soc. (A), 256 (1970).
117. B. Gerard and D. Mireille, Compt. rend., **272**, 1866 (1971).
118. L. V. Mitrofanova, V. N. Medvedkov, and B. V. Erofeev, Uch. Zap. Moskov. Gos. Ped. Inst. im. Lenina, 464, 120 (1971).
119. R. I. Novoselov and V. I. Belevantsev, Zhur. Neorg. Khim., 17, 1001 (1972) [Russ. J. Inorg. Chem., No. 4 (1972)].
120. D. A. Everest, J. Chem. Soc., 2945 (1952).
121. J. Pokorný, Chem. Zvesti, 19, 628 (1965).
122. V. V. Serebrennikov, "Khimiya Redkozemel'nykh Elementov" (The Chemistry of the Lanthanide Elements), Izd. Tomsk. Univ., Tomsk, 1969, Vol. 1, p. 378.
123. T. G. Shvalova, G. A. Seryakova, and A. T. Malinina, Sbornik Nauch. Trudov Kuzbas. Politekh. Inst., 52, 34 (1973).
124. M. A. Porai-Koshits, L. A. Aslanov, and V. M. Ionov, Izv. Akad. Nauk SSSR, Ser. Khim., 1450 (1972).
125. N. S. Poluektov, R. S. Lauer, and S. F. Ognichenko, Zhur. Neorg. Khim., 8, 2133 (1970) [Russ. J. Inorg. Chem., No. 8 (1970)].
126. J. H. Espenson and D. F. Dustin, Inorg. Chem., 8, 1760 (1969).
127. J. H. Espenson and D. E. Binau, Inorg. Chem., 5, 1365 (1966).

128. W. B. Simpson, Chem. Comm., 1100 (1967).
129. J. Deabriges, Bull. Soc. chim. France, 2, 485 (1970).
130. A. Anton, Analyt. Chem., 37, 1422 (1965).
131. F. Ephraim and A. Schärer, Ber., 61B, 2161 (1928).
132. D. A. Everest, J. Chem. Soc., 1670 (1952).
133. D. A. Everest, J. Chem. Soc., 2903 (1951).
134. R. Rudnicki and J. Kolitowska, Roczniki Chem., 42, 21 (1968).
135. P. S. Poskorim, Inorg. Nuclear Chem. Letters, 5, 933 (1969).
136. N. A. Suvorovskaya and Yu. S. Kuznetsova, "Nauchnye Soobshcheniya Instituta Gornogo Dela im A. A. Skochinskogo" (Scientific Reports of the Skochinskii Mining Institute), 1969, p. 47.
137. J. R. McClosky, Plating, 51, 689 (1964).
138. A. A. D'yakov and R. G. Rozenblyum, Zavod. Lab., 30, 1216 (1964).
139. R. L. Kaushik and R. Prosad, J. Indian Chem. Soc., 46, 923 (1969); Ref. Zhur. Khim., 24G114 (1969).
140. V. I. Volokhova, R. S. Vakhidov, and A. I. Luk'yanitsa, Zavod. Lab., 39, 932 (1973).
141. J. P. Randin and H. E. Hintermann, J. suisse horlog, Ed. suisse, 1972, No. 11–12, 325.
142. V. K. Sidel'nikov, S. P. Zhulebina, and A. N. Yagubets, Izv. Akad. Nauk Mold. SSR, Ser. Fiz.-Tekh. i Mat. Nauk, No. 3, 84 (1969).
143. S. K. Mishra and J. K. Gupta, J. Inorg. Nuclear Chem., 29, 1643 (1967).
144. G. Charlot, "Les Méthodes de la Chimie Analytique. Analyse Quantitative Minérale" (Translated into Russian), Izd. Khimiya, Moscow–Leningrad, 1965, p. 866.
145. J. R. Pound, J. Chem. Soc., 307 (1942).
146. D. Kőszegi and E. Salgó, Z. anal. Chem., 150, 262 (1956).
147. M. N. Sastri and C. Kalidas, Rec. Trav. chim., 74, 1045 (1955).
148. K. B. Rao and G. G. Rao, Z. anal. Chem., 147, 279 (1955).
149. G. G. Rao and K. B. Rao, Z. anal. Chem., 154, 333 (1956).
150. "Reaktivy i Preparaty dlya Laboratornykh Rabot, Neorganicheskie. Tekhnicheskie Usloviya" (Reagents and Preparations for Laboratory Work in Inorganic Chemistry. Technical Conditions), Standardizdat, Moscow, 1957, p. 97.
151. M. N. Sastri and C. K. Kalidas, Rec. Trav. chim., 75, 1122 (1956).
152. R. Swaroop and G. K. Gupta, J. Chem. Soc., Dalton Trans., 7, 851 (1972).
153. P. Švehla, Chem. Průmysl, 15, 668 (1965).
154. K. Holeček, "Bezporoudove niclování. Stud. zprava", 82008/7, 1960.
155. A. A. Sutyagina, K. M. Gorbunova, and M. O. Glazunov, Dokl. Akad. Nauk SSSR, 147, 1133 (1962).
156. A. Brenner, D. E. Couch, and E. K. Williams, J. Res. Nat. Bur. Stand., 44, 109 (1950).
157. G. E. Zamar, Iron Age, 171, No. 24, 115 (1953).
158. W. Blum, Can. Metals, 15, No. 5, 52 (1952).
159. S. Šebek and B. Machánová, Chem. Průmysl, 15, 307 (1965).
160. A. Brenner, D. E. Couch, and E. K. Williams, US.P. 264 322 (1953); J. R. Van Wazer, "Phosphorus and Its Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1962, Vol. 1.
161. T. H. Bonn and D. C. Wendell, US.P. 2 644 787 (1953); J. R. Van Wazer, "Phosphorus and Its Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1962, Vol. 1.
162. A. Berg and L. Cari-Mantraud, Monit. Sci., 14, 271 (1893).
163. M. Paguelin and L. Joly, Compt. rend., 86, 1505 (1878).
164. M. Paguelin and L. Joly, J. pharm. chim., 28, 314 (1878).
165. P. Schulz, Arch. exp. Pathol., 18, 174 (1884).
166. G. Polk, Pharm. J., 5, 425 (1874).
167. T. Panzer, Untersuch. Nahr. und Genussm., 5, 11 (1902).
168. P. Norkus and R. Markeviciene, Trudy Akad. Nauk Lit. SSR, B, 51, No. 4, 85 (1967).

Gorky Kiev State
Pedagogic Institute