Russian Chemical Reviews **66** (7) 579 – 596 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 548.562

Ion exchange on inorganic sorbents

A B Yaroslavtsev

Contents

I.	Introduction	579
II.	Thermodynamics of ion exchange	579
III.	Kinetics of ion exchange	582
IV.	The main types of inorganic ion-exchange substances	584
V.	Conclusion	593

Abstract. The principal features of the thermodynamics and kinetics of ion-exchange processes in inorganic ion exchangers are discussed. The literature data on the ion-exchange properties of oxide systems, globular hydrates, and salts of polyvalent cations are surveyed. The methods for carrying out ion-exchange processes and the characteristic features of their occurrence on typical inorganic ion-exchange materials are examined. The bibliography includes 306 references.

I. Introduction

Ion exchange on inorganic substances is characteristic of many natural and industrial processes. Even before the demonstration of the existence of ions as such, it was observed that treatment of soil specimens with solutions of ammonium salts entailed the reversible formation of calcium salts.[1,2] It was established that this is due to the presence of a series of clay minerals in soil. The first synthetic ion-exchange materials were later obtained — amorphous sodium aluminosilicates, which were used successfully to reduce the hardness of water.[3] Amorphous and crystalline substances of this type, called zeolites, were for a long time the main objects for the study of ion-exchange processes. A significant disadvantage of zeolites proved to be their low stability in experiments in highly acid and alkaline solutions. This stimulated chemists to seek new materials with analogous properties. Synthetic ion exchangers on a polymer matrix — ion-exchange resins[4] — rapidly displaced the inorganic analogues.

The revival of interest in inorganic sorbents began in the early 1960s. This was associated with the fact that ion exchangers with a fairly high thermal stability and resistance to ionising radiation were needed for many branches of industry; furthermore, an extremely high partition coefficient was observed in certain inorganic sorbents even for alkaline earth metal cations, which are comparatively difficult to separate. After the synthesis by Clearfield and Stynes[5] of the cryptocrystalline acid zirconium phosphate, which is now one of the most familiar inorganic ion exchangers, the stream of studies devoted to ion exchange on inorganic materials increased significantly. Crystalline zirconium phosphate is distinguished by a higher stability, compared with amorphous specimens, and a higher sorption capacity compared with zeolites. By employing it, it is possible to observe the structural changes in the substance in the course of the exchange. The latter stimulated a series of purely theoretical investigations.

However, one should note that there have been comparatively few review publications on the study of inorganic ion exchangers. Among these, one may point to Amphlett's monograph,[6] a book edited by Clearfield,[7] as well as the review by the latter,[8] devoted mainly to the description of the properties of various classes of ion-exchange substances. The remaining publications are more specific. The aim of the present review is a survey of the thermodynamic and kinetic ideas about ion exchange on inorganic matrices and also the use of these data for the analysis of the properties of various compounds, results that have not so far entered into review publications being emphasised.

A B Yaroslavtsev The Higher Chemical College, Russian Academy of Sciences, Miusskaya ploshad' 9, 125190 Moscow, Russian Federation. Fax (7-095) 200 42 04. Tel. (7-095) 978 82 57.
E-mail:yaroslav@rfbr.ru

Received 19 February 1997
Uspekhi Khimii **66** (7) 641 – 660 (1997); translated by A K Grzybowski

II. Thermodynamics of ion exchange

When substances containing groups of $\equiv E-O-H$ fragments accessible to the exchange of H^+ and OH^- come into contact with an aqueous solution, an equilibrium that is determined by the occurrence of the following reactions is established in the system:

$$\equiv E-O-H + H_2O \rightleftharpoons \equiv E-O^- + H_3O^+ , \quad (1)$$

$$\equiv E-O-H + H_2O \rightleftharpoons \equiv E-OH_2^+ + OH^- , \quad (2)$$

where E is a polyvalent element.

As a result, the entire volume of the substance or a proportion of it acquires a negative or positive charge and sorption from a solution of cations or anions becomes possible:

$$\equiv E-O-H + H_2O + \frac{1}{z}A^{z+} \rightleftharpoons \quad (3)$$

$$\rightleftharpoons \equiv E-O-A_{1/z} + H_3O^+ ,$$

$$\equiv E-O-H + \frac{1}{z}X^{z-} \rightleftharpoons \equiv E-X_{1/z} + OH^- . \quad (4)$$

The tendency of a substance to manifest cation- or anion-exchange properties is determined primarily by the acidity of the $\equiv E-O-H$ groups. Zirconium hydrogenphosphate $Zr(HPO_4)_2 \cdot \cdot H_2O$ is known to contain O_3POH groups the proton-accepting capacity of which is reduced as a result of their coordination to a cation with an appreciable polarising capacity. These groups tend to dissociate only *via* reaction (1) and the compound exhibits only cation-exchange properties.[8,9] The hydroxyapatites $[Ca_x(PO_4)_y(OH)_{2x-3y}]$ and the hydrogelcites having the compositions

$[M^{II}_3M^{III}(OH)_8]^+x^{z-}_{1/z}$, or $[M^{II}_2M^{III}(OH)_6]^+x^{x-}_{1/z}$,[10] as well as certain complex oxides[11] dissociate in accordance with reaction (2) and these substances therefore exhibit anion-exchange properties. Finally, both types of dissociation are characteristic of a series of compounds. This applies in the first place to the large class of hydrated oxides of Group III and IV elements such as aluminium, gallium, tin, and zirconium. The degree of conversion for reactions (1)–(4) and the ion-exchange capacities themselves of these compounds depend significantly on the method of synthesis of the latter and the acidity of the medium. Analysis of the dependence of the ion-exchange capacities of hydrated oxides on the pH of the medium, presented in Fig. 1, shows that the position of the equivalence point for the series of zirconium, tin, and silicon oxides diminishes from ~7 to ~6 and ~2 in strict correspondence with the decrease in the basicities of these compounds; the exchange of anions is altogether not characteristic of $HSbO_3 \cdot H_2O$. Since inorganic sorbents are distinguished by a high selectivity, the position of the equivalence point depends also on the nature of the sorbed ions.

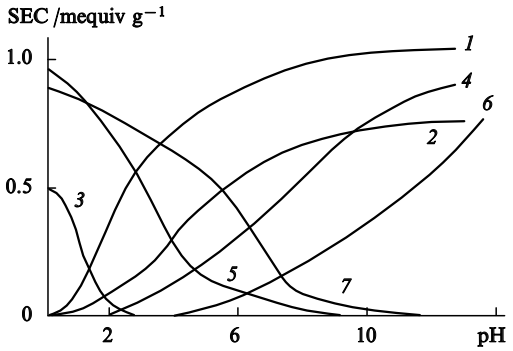


Figure 1. Dependence of the sorption exchange capacities (SEC) of the hydrated oxides of antimony (*1*), silicon (*2*, *3*), tin (*4*, *3*), and zirconium (*6*, *7*) on the pH of the medium in the sorption of sodium (*1*, *2*, *4*, *6*) and chloride (*3*, *5*, *7*) ions. The figure has been constructed on the basis of data from Kraus *et al.*[12] and Ahrland *et al.*[13]

It is noteworthy that, among the inorganic materials used as ion exchangers, cation exchangers are more common than anion exchangers. Anions have larger radii and this creates steric hindrance to their insertion into the bulk of the specimen. Furthermore, for the manifestation of anion-exchange activity by a substance, the latter must contain hydroxy-groups and must be able to substitute them by anions. However, the salts of polyvalent elements the OH groups of which more often possess distinctly acid properties show a greater tendency to sorb cations. In view of this, the thermodynamic features of ion exchange will henceforth be considered in relation to cations.

For reaction (3), which proceeds *via* a stage involving the formation of the solid solutions $x\text{R}-\text{O}-\text{A}_{1/z}\cdot y\text{R}-\text{O}-\text{H}$, the thermodynamic equilibrium constant may be represented by the expression

$$K_a = \frac{a(\text{H}_3\text{O}^+)^z_{\text{soln}}\, a(\text{A}^{z+})_{\text{s}}}{a(\text{H}_3\text{O}^+)^z_{\text{s}} a(\text{A}^{z+})_{\text{soln}}}, \qquad (5)$$

where a are the activities of the corresponding cations in solution (soln) and in the solid phase (s). By expressing the activity as the product of the concentration (c) and the activity coefficient (γ), we obtain

$$K_a = \frac{c(\text{H}_3\text{O}^+)^z_{\text{soln}}\, \gamma(\text{H}_3\text{O}^+)^z_{\text{soln}}\, c(\text{A}^{z+})_{\text{s}}\gamma(\text{A}^{z+})_{\text{s}}}{c(\text{H}_3\text{O}^+)^z_{\text{s}}\gamma(\text{H}_3\text{O}^+)^z_{\text{s}} c(\text{A}^{z+})_{\text{soln}}\, \gamma(\text{A}^{z+})_{\text{soln}}}, \qquad (6)$$

or, for the concentration equilibrium constant, we have

$$K_c = \frac{[\text{H}_3\text{O}^+]^z_{\text{soln}}[\text{A}^{z+}]_{\text{s}}}{[\text{H}_3\text{O}^+]^z_{\text{s}}[\text{A}^{z+}]_{\text{soln}}} = \frac{K_a\, \gamma(\text{H}_3\text{O}^+)^z_{\text{s}}\gamma(\text{A}^{z+})_{\text{soln}}}{\gamma(\text{H}_3\text{O}^+)^z_{\text{soln}}\, \gamma(\text{A}^{z+})_{\text{s}}}. \qquad (7)$$

A certain complication arises because the activity coefficients of the cations in the solid phase are difficult to estimate. On the other hand, in order to determine the thermodynamic functions of the exchange reactions it is necessary to know the thermodynamic equilibrium constant. Gaines and Thomas[14] proposed the following procedure for this purpose. The so-called 'mixed' equilibrium constant

$$K_{ac} = \frac{a(\text{H}_3\text{O}^+)^z_{\text{soln}}\, N(\text{A}^+)_{\text{s}}}{N(\text{H}_3\text{O}^+)^z_{\text{s}} a(\text{A}^+)_{\text{soln}}}, \qquad (8)$$

where N is the mole fraction of the corresponding cation in the solid phase, is calculated initially. The thermodynamic constant is found from the relation

$$\ln K_a = \int_0^1 \ln K_{ac}\, \text{d}N(\text{A}^+)_s \qquad (9)$$

It is noteworthy that the equilibrium exchange constant is usually not a constant quantity as a consequence of the change in the entropy of the system on contamination of the cationic sublattice of the initial substance or the product by microamounts of an impurity in the initial and concluding stages of the exchange reaction.[15–18]

Furthermore, in layered compounds the interplanar spacing and the size of the coordination polyhedra itself vary in the course of the exchange from values typical for the ion to be substituted to those characteristic of the incoming ion. The enthalpy and Gibbs free energy of exchange therefore decrease, while the equilibrium constant increases somewhat as the process proceeds (Fig. 2).

In many inorganic ion-exchange substances, the exchange proceeds in a two-phase region — the region corresponding to the existence of the substituted and unsubstituted forms. The process then takes place as a result of the displacement of the interface between these phases for a virtually unchanged composition of the latter. The formation of two phases during exchange on layered acid phosphates of tetravalent elements [α-$Ti(HPO_4)_2$ and α-$M^{I}TiH(PO_4)_2$ or α-$M^{I}TiH(PO_4)_2$ and α-$M^{I}_2Ti(PO_4)_2$] may

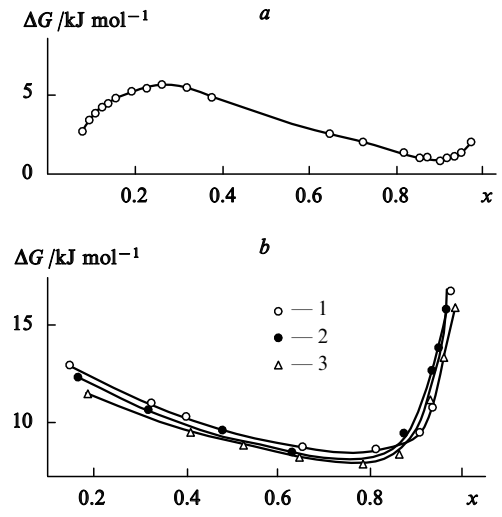


Figure 2. Dependence of the Gibbs free energy on the degree of substitution of the proton (x) in $K_xH_{1-x}Ta(PO4)_2$. The figure has been constructed on the basis of data from Guarido *et al.*,[15] Rullberg and Clearfield,[16] Yaroslavtsev *et al.*,[17] and Yaroslavtsev and Khrulev.[18]
(*a*) Overall curve; (*b*) for titration of the alkaline product of the interaction of $H_5O_2Ta(PO_4)_2$ with an excess of the corresponding alkali metal chloride: (*1*) NaOH; (*2*) LiOH; (*3*) KOH.

Table 1. Thermodynamic parameters of certain ion-exchange processes on inorganic sorbents.

Initial phase	Substituted phase	K_{298}	ΔG_{298} /kJ mol^{-1}	ΔH_{298} /kJ mol^{-1}	ΔS /J mol^{-1} K^{-1}	Ref.
Attapulgite (Li^+)	Attapulgite (Cs^+)	0.029	8.9	17	25	21
Attapulgite (Na^+)	Attapulgite (Cs^+)	0.041	8.0	16	24	21
Attapulgite (K^+)	Attapulgite (Cs^+)	0.13	5.1	12	24	21
Montmorillonite (K^+)	Montmorillonite (Cs^+)	0.076 (293 K)	6.3 (293 K)	–	–	22
Montmorillonite (Sr^{2+})	Montmorillonite (Cs^+)	1.9×10^{-3}	15.5	27	25	22
Montmorillonite (Y^{3+})	Montmorillonite (Cs^+)	3.8×10^{-4} (303 K)	19.7 (293 K)	28	27	23
Vermiculite (Li^+)	Vermiculite (Na^+)	7.7	−5.0	−21.3	−55	6
Shabasite (Na^+)	Shabasite (Ag^+)	11.4	−6.0	–	–	24
Clinoptilolite (Na^+)	Clinoptilolite (Th^{4+})	0.26	3.33	–	–	25
Mordenite (Na^+)	Mordenite (Th^{4+})	0.20	3.94	–	–	25
$(NH_4)_3PMo_{12}O_{40}$	$K_3PMo_{12}O_{40}$	4	−3.4	–	–	26
	$Rb_3PMo_{12}O_{40}$	192	−13.0	–	–	26
	$Cs_3PMo_{12}O_{40}$	5500	−21.3	–	–	26
$Zr(HPO_4)_2$ [a]	$Li^+-Zr(HPO_4)_2$	0.03	8.4	0	−28	27
	$Na^+-Zr(HPO_4)_2$	0.16	4.6	−11	−54	27
	$Na^+-Zr(HPO_4)_2$	0.02	9.7	−14	−77	28
	$K^+-Zr(HPO_4)_2$	0.4	2.3	−24	−88	27
	$Rb^+-Zr(HPO_4)_2$	48	−9.6	−40	−104	29
	$Rb^+-Zr(HPO_4)_2$	1.8	−1.4	−32	−103	30
	$Cs^+-Zr(HPO_4)_2$	2.7	−2.5	−36	−105	28
	$Cs^+-Zr(HPO_4)_2$	81	−10.9	−42	−105	29
	$Cs^+-Zr(HPO_4)_2$	4.8	−3.9	−37	−110	30
	$Ca^+-Zr(HPO_4)_2$	0.04	8.1	−3.6	−39	29
	$Sr^{2+}-Zr(HPO_4)_2$	0.06	7.1	4.4	−4	29
	$Ce^{3+}-Zr(HPO_4)_2$	0.10	5.6	2.7	−7	29
$Zr(O_3PC_6H_4SO_3H)_{0.43}(HPO_4)_{1.57}$	Na^+-ZPP	0.90	0.27	−8.3	−29	31
	Cs^+-ZPP	50	−9.7	−15.9	−21	31
	$Mg^{2+}-ZPP$	3.6	−3.2	0.9	14	31
	Na^+-ZPP	91	−11.2	−2.7	28	31
α-$Ti(HPO_4)_2$	α-$TiHLi(PO_4)_2$	5.2×10^{-4}	18.7	0.0	−63	32
	α-$TiHLi(PO_4)_2$	3.0×10^{-4}	19.6	–	–	18
α-$TiHLi(PO_4)_2$	α-$TiLi_2(PO_4)_2$	2.1×10^{-4}	21.0	−0.2	−71	32
	α-$TiLi_2(PO_4)_2$	5×10^{-6}	28.9	–	–	18
α-$Ti(HPO_4)_2$	α-$TiHNa(PO_4)_2$	1×10^{-3}	16.6	–	–	18
α-$TiHNa(PO_4)_2$	α-$TiNa_2(PO_4)_2$	3.7×10^{-6}	31.1	–	–	18
α-$Ti(HPO_4)_2$	α-$Ti(KPO_4)_2$	3×10^{-6}	31.2	15.5	−52	15
	α-$Ti(KPO_4)_2$	8.9×10^{-7}	34.5	–	–	18
γ-$Ti(HPO_4)_2$	γ-$TiH_{1.5}Li_{0.5}(PO_4)_2$	0.35	2.6	3.7	3.8	33
	γ-$TiH_{1.5}Li_{0.5}(PO_4)_2$	0.11	5.4	7.8	8	34
	γ-$TiH_{1.5}Na_{0.5}(PO_4)_2$	0.80	0.55	1.2	2.3	33
	γ-$TiH_{1.5}K_{0.5}(PO_4)_2$	1.8	−1.5	−1.1	1.6	33
	γ-$TiH_{1.5}Cs_{0.5}(PO_4)_2$	3.9	−3.4	−2.4	3.4	33
	γ-$TiH_{1.5}Cs_{0.5}(PO_4)_2$	17.6	−7.1	−5.1	7.0	35
γ-$TiH_{1.5}Li_{0.5}(PO_4)_2$	γ-$Ti(LiPO_4)_2$	0.3	3.0	−4.2	−24	33
	γ-$Ti(LiPO_4)_2$	0.08	6.3	−8.8	−51	34
γ-$TiH_{1.5}Na_{0.5}(PO_4)_2$	γ-$Ti(NaPO_4)_2$	0.5	1.6	−3.3	−17	33
γ-$TiH_{1.5}K_{0.5}(PO_4)_2$	γ-$Ti(KPO_4)_2$	0.9	0.17	−2.9	−10	33
γ-$Ti(HPO_4)_2$	γ-$TiHCu_{0.5}(PO_4)_2$	0.16	4.6	35.5	104	36
$Sn(HPO_4)_2$ [a]	$Na^+-Sn(HPO_4)_2$	0.3	3.1	−1	−29	37
	$K^+-Sn(HPO_4)_2$	9	−5.3	−15	−33	37
	$Rb^+-Sn(HPO_4)_2$	50	−9.5	−22	−42	37
	$Cs^+-Sn(HPO_4)_2$	125	−11.7	−17	−24	37
$Ce(HPO_4)_2$ [a]	$Li^+-Ce(HPO_4)_2$	2.8	−2.5	0.9	11	38
	$Na^+-Ce(HPO_4)_2$	1.0	0.0	0.8	3	38
	$K^+-Ce(HPO_4)_2$	2.7	−2.5	−0.2	3	38
$TaH(PO_4)_2$	$TaLi(PO_4)_2$	0.2	4	−35	−130	39
	$TaNa(PO_4)_2$	0.6	1	−36	−140	39
	$TaK(PO_4)_2$	0.3	3	8	12	39

Note. All the thermodynamic parameters were calculated for substitution of one mole of cations. [a] Amorphous.

serve as a typical example. The procedure for the determination of the thermodynamic parameters of the exchange described above is therefore inapplicable for compounds of this kind, but it has been used nevertheless in a large number of studies. Since the activities of the incoming cations A^{z+} and of the hydrogen in the solid phase remain constant, the equilibrium constant should be expressed by the relation [18]

$$K_a = \frac{a(H_3O^+)^z_{soln}}{a(A^{z+})_{soln}} = \frac{[H_3O^+]^z_{soln}\,\gamma(H_3O^+)^z_{soln}}{[A^{z+}]_{soln}\,\gamma(A^+)_{soln}} = \frac{K_c\,\gamma(H_3O^+)^z_{soln}}{\gamma(A^{z+})_{soln}}. \quad (10)$$

The error due to the calculation of the equilibrium constant using Eqns (6) and (7), which are erroneous for the given process, is to a large extent abolished on further mathematical treatment with the aid of Eqn (9). For this reason, the values of K_a and of the free energy of exchange obtained with the aid of this procedure may approach the true values.

There are several standard approaches to the description of the ion-exchange equilibrium. A number of workers have investigated the equilibrium after adding a definite amount of a salt to the ion exchanger in the hydrogen-form (hydroxo-form) and the reaction is frequently carried out with microamounts of a salt, which makes it possible to describe the equilibrium only in the initial stages of the exchange process. The most promising method involves the study of the curves for the titration of cation exchangers with alkali in the presence of a salt of the corresponding metal. The process then reduces to the neutralisation of the acid produced. This makes it possible to carry out experiments only in acid and weakly alkaline media and to reduce to a minimum the effect of hydrolysis even for readily hydrolysable compounds such as, for example, tantalum hydrogenphosphate.[17] In order that the exchange of ions occurs *via* the stage involving the formation of solid solutions, the concentration of hydrogen ions $[H^+]$ should vary in proportion to the mole fraction of the protons in the solid phase [in accordance with Eqn (8)]. For layered hydrogenphosphates of polyvalent elements, the equilibrium involving solid phases with different degrees of substitution should seemingly lead to a constant overall concentration of protons and metal cations.[6] However, when alkali is added, the concentration diminishes somewhat owing to the neutralisation reaction. For this reason, the titration curve is skewed for all the processes described in the literature.[19, 20]

Certain values of the thermodynamic parameters for exchange reactions on inorganic sorbents are presented in Table 1. It is noteworthy that the significant discrepancies between the parameters for the sorption of alkali metal cations on amorphous zirconium phosphate are due to the difference between the methods used to determine the required quantities and the methods for the preparation of the sorbents (in the course of their preparation, the ratio P/Zr varied from 1.2 to 1.9). Whereas for a high degree of reaction the equilibrium constant depends on the properties of the equilibrium phases, for a low degree of reaction it depends only on the nature of the active groups on the surface. Furthermore, for an equilibrium process there should be a possibility of attaining the final state from both the starting materials and from the final products. On the other hand, in the case of layered hydrogenphosphates of tetravalent elements, the reverse exchange frequently leads to the formation of compounds with a degree of hydration exceeding that for the initial substance and hence to a change in the equilibrium constant. Some investigators therefore do not believe at all that it is legitimate to employ the term 'equilibrium constant' for such quantities.

We shall now consider the factors that influence the thermodynamic parameters of ion exchange processes described by reaction (3). In the transfer of a cation A^{z+} with a radius R_A from a dilute solution to a singly charged ion-exchange group with a radius R_X, the electrostatic interaction energy

$$\Delta G = \frac{-z_A e^2}{R_A + R_X}, \quad (11)$$

is liberated and the hydration energy E_A is consumed. The change in energy on desorption of the cation B can be described similarly:

$$\Delta G = e^2\left(\frac{z_B}{R_B + R_X} - \frac{z_A}{R_A + R_X}\right) + E_A - E_B. \quad (12)$$

Using this relation, Eisenman[40] has calculated series of the variation of the affinity of alkali metal cations for the sorbent as a function of R_X.

The relations presented 'work well' in the case of biological systems and ion-exchange resins on a polymer matrix. On the other hand, for inorganic sorbents their use is limited. This is due primarily to the fact that the concentration of the groups with the affinity for cations in such sorbents is high and the coordination sphere of the A^{z+} ion with a fixed distance between the ionogenic groups is formed in the ion exchanger matrix. The energy of the interaction of the cation with the ion exchanger matrix is found to be initially specified fully or partially (if a displacement of the cation in the coordination polyhedron is possible). It follows from simple geometrical calculations that, when the cation A^{z+} is localised at the centre of an octahedron made up of oxygen atoms in the interlayer space in the layered phosphates $A_xY(PO_4)_2$ (Y = Ti, Zr, Hf, Sn, Pb, Sb, Ta), the distance A–O may vary from 4.8–5.2 Å in the absence of distortion to 2.8–3.0 Å for the unlikely limiting model of a planar hexagon when the octahedron is compressed along the threefold axis. Evidently, the cavity formed is large for any cation. The affinity of the matrix for the alkali metal cation therefore increases with increase in the heat of hydration, *i.e.* with increase in the radius of the given cation. This can explain the increase in the selectivity of the sorption in the Li^+–Cs^+ series. This type of effect is often abolished when part of the water is retained in the coordination spheres of the cations when the latter are incorporated in the ion exchanger matrix. The H_2O molecules also participate in the filling of the free volume.

The entropy of the sorption process may be determined as the difference between the entropies of the incoming and leaving groups in the sorbent and in the solution. The entropy is determined primarily by the change in the degree of hydration of the cations following their incorporation in the solid phase.[31] The transfer of one water molecule from the ion exchanger to the solution at room temperature is on average accompanied by an increase in the entropy of the system by 25 kJ mol^{-1}. The insignificant tendency of large cations to be hydrated is responsible for the additional increase in the partition coefficients when the cations are sorbed in the anhydrous or weakly hydrated form.

III. Kinetics of ion exchange

In the study of the kinetics of ion exchange on polymeric matrices, diffusion within the grain, the migration of ions in a thin film surrounding the ion exchanger grain (the so-called film kinetics), and diffusion in the liquid phase, which may make an appreciable contribution only for dilute solutions, are usually considered as the main processes.[41] In the study of ion exchange on inorganic sorbents, only the first two processes are considered, since the diffusion in solutions is significantly faster.

The quantitative description of diffusion processes of this kind is complicated by the following factors.

Firstly, it is extremely difficult to collect a fraction of crystals with a specified size. Secondly, the mutual diffusion coefficient (D_{AB}) of the exchanging ions varies during the process as the ratio of the mole fractions of the cations participating in the exchange (X_A and X_B) is varied:

$$\frac{1}{D_{AB}} = \frac{X_A}{D_A} + \frac{X_B}{D_B},$$

where D_A and D_B are the diffusion coefficients of the corresponding cations in the individual phases.[42] Thirdly, there is a possibility of a change in the diffusion conditions in the solid matrix as a consequence of its transformation in the course of the exchange (for example, for layered phosphates as a consequence of the change in the interplanar spacings and in the degree of hydration).[8] Fourthly, there is a possibility of a change in the size of the sorbent particles during the exchange process.[43–45] The vast majority of studies have therefore been devoted to a qualitative description of the ion exchange kinetics.

The rate-limiting stage of the diffusion of cations in the solid phase is their passage through the common face of two coordination polyhedra within the crystal. As a result of the consecutive fusion of occupied and unoccupied polyhedra, conductivity channels appear and may extend in the structure along one, two, or three directions and hence ensure one-, two-, or three-dimensional diffusion. The size of the cross-section of such a channel is determined by the number of anion atoms constituting it and their nature. The required size may be estimated on the hypothesis of the close packing of the anions and of the formation by the latter of regular planar polygons in the cross-section (Fig. 3). The results of the calculation of the cross-sections formed by oxygen ions (R = 1.40 Å) are presented in Table 2. The size of the cross-sections of the channels may increase somewhat when account is taken of the radius of the polyvalent cations binding the oxygen atoms.

Cation	Li^+	Na^+	K^+	Rb^+	Cs^+
Radius †	$\frac{0.59}{0.62}$	$\frac{0.99}{1.02}$	$\frac{1.37}{1.38}$	$\frac{-}{1.52}$	$\frac{-}{1.67}$

Furthermore, all the figures considered, starting with the tetragon, are nonrigid and the displacement of some of the ions from the plane of the channel cross-section leads to a decrease in their size.

Analysis of the data presented in Table 2 with allowance for the radii of the alkali metal cations makes it possible to conclude that the channels with a triangular cross-section are difficult to pass through by virtually all cations, while the channels with a tetragonal cross-section are difficult to pass through by all cations other than the lithium cation. The diffusion of the remaining cations requires at least pentagonal channels. However, it is known that lithium ions are capable of passing also through channels with a triangular cross-section made up of oxygen atoms.[48,49] This ability is due to the activation energy for the given process.

In individual instances (for example, in polyphosphates of polyvalent elements), channels with a comparatively large cross-section are formed between oxygen atoms belonging to neighbouring planes, which facilitates the diffusion of cations. In order to ensure the diffusion of cations in α-$M^{IV}(HPO_4)_2 \cdot H_2O$, it is necessary that they should pass through the face of a coordination polyhedron with a radius of 1.3 Å made up of oxygen atoms.[50] Small cations (Li^+, Na^+) permeate through it comparatively readily. For larger cations — with a radius > 1.3 Å (K, Rb^+, or Cs^+ for titanium phosphate and Rb^+ or Cs^+ for zirconium phosphate) — a considerable energy barrier must be overcome. In this case, for the implementation of the ion-exchange process it is necessary to maintain a high pH of the solution. The low activity of hydrogen ions is responsible for the possibility of the release of an additional number of protons from the ion-exchange material matrix. The latter acquires a negative charge and an electrostatic potential difference is created between the ion exchanger and the solution and is responsible for the diffusion of bulky cations into the cation exchanger. For this reason the exchange with lithium and sodium ions on α-$M^{IV}(HPO_4)_2 \cdot H_2O$ takes place in acid solutions, while the exchange with caesium occurs only in alkaline solutions.[33,50] In the case of γ-$M^{IV}(HPO_4)_2 \cdot 2H_2O$ with a significantly greater interplanar spacing, the energy barrier is virtually absent and the exchange of all the cations occurs readily in acid solutions.[33] Strictly speaking, the determination of the equilibrium thermodynamic parameters of H^+/K^+, H^+/Rb^+, and H^+/Cs^+ exchange processes for the α-phosphates of tetravalent elements is difficult and the characteristics presented in Table 1 refer to the 'pseudo-equilibrium' state.

† The number above the line is the radius of a cation with a coordination number of 4, while the number under the line is the radius of a cation with a coordination number of 6.[47]

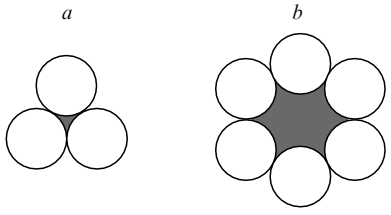


Figure 3. Schematic illustration of the formation of the triangular (*a*) and hexagonal (*b*) channels in the spherical close packing of oxygen atoms.

Table 2. Calculated radii of *n*-sided channels made up of oxygen atoms (Å).

Packing of oxygen atoms	n = 3	4	5	6	n = 8
Close packing	0.22	0.58	0.98	1.40	2.26
Channels with planar E_nO_n rings [a] in zeolites [46]	0.25	0.45	0.75	1.1	1.9
Close packing of oxygen atoms separated by sum of their van der Waas radii	0.28	0.73	1.22	1.75	2.8

[a] E = polyvalent cation.

Alberti *et al.*[50] and Troup and Clearfield[51] carried out the sorption of caesium ions on zirconium hydrogenphosphate in the presence of traces of sodium (Fig. 4). The cations of the latter substitute some of the protons on the surface of the crystals, as a result of which the interplanar spacing in the latter increase from 7.6 to 11.8 Å. The gap between the planes for $[M^{IV}(HPO_4)_2]_n$ then expands and caesium cations enter freely into the lattice already at a pH close to 4.

In order to estimate the kinetic parameters of the ion-exchange processes, Barrer's method is used.[52–54] The diffusion coefficients are calculated by means of the following equation:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \frac{-Dt\pi^2 n^2}{R^2}, \qquad (13)$$

where F is the degree of completion of the exchange process, n an integer, D the diffusion coefficient, t the time, and R the radius of the ion-exchanger particles. The series in the equation quoted above converges comparatively rapidly for large values of F.

The diffusion coefficients calculated from the results of the ion-exchange experiments are presented in Table 3.

The above method has been used also to investigate ion-exchange processes on layered hydrogenphosphates of tetravalent elements. The diffusion coefficients and the activation energies for diffusion presented in Table 3 for these compounds differ markedly. The differences are due to the fact that the size of intergrown crystals and not the crystals themselves was used in a number of studies. In this case, an average diffusion coefficient was determined, since the rate of diffusion can be significantly different in the intergranular space and in the grain itself. On this basis, Larsen and Cilley[38] concluded that the values obtained are too high and they were unable to convert kinetic curves into diffusion coefficients.

Another problem is that Eqn (13) was derived by Barrer for a homogeneous isotropic spherical grain with a continuous series of solid solutions of the type $A_yH_{1-y}X$. On the other hand, none of the above conditions holds for many materials, among which one

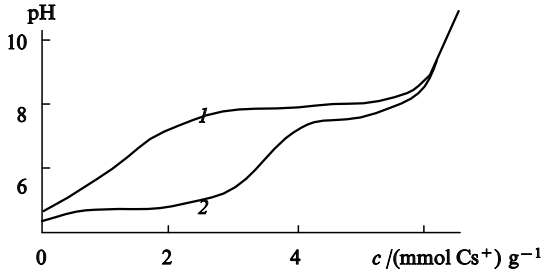


Figure 4. Curves for the titration of acid zirconium phosphate with caesium hydroxide in the presence of CsCl (*1*) and CsCl with added NaCl (*2*).

Table 3. Diffusion coefficients in certain inorganic ion-exchange materials calculated from experimental data.

Ions to be exchanged	T /°C	D /cm^2 s^{-1}	E /kJ mol^{-1}	Ref.
Basic cancrinite				
Na^+/Li^+	25[a]	5.5×10^{-16}	56	55
Analcite				
Na^+/Tl^+	25[a]	1.7×10^{-15}	62	56
Ultramarine				
Na^+/Ag^+	25[a]	1.6×10^{-16}	94	55
Ag^+/Na^+	25[a]	5.2×10^{-17}	92	55
Ag^+/Li^+	25[a]	5.6×10^{-15}	113	55
Ag^+/K^+	75	5.7×10^{-16}	–	55
Na^+/Ag^+	25[a]	7.2×10^{-16}	74	6
Na^+/Cu^{2+}	25[a]	1.4×10^{-16}	87	6
Na^+/Co^{2+}	25[a]	5.6×10^{-17}	93	6
Na^+/Ni^{2+}	25[a]	8.1×10^{-17}	103	6
Na^+/Mn^{2+}	25[a]	2.0×10^{-17}	99	6
Amberlite IR 1				
Na^+/Li^+	30	3.0×10^{-6}	–	55
Na^+/K^+	30	3.5×10^{-6}	–	55
α-$Zr(HPO_4)_2\cdot H_2O$				
H^+/Na^+	25	1.0×10^{-6}	–	6
H^+/Na^+	25	$(0.1-5)\times10^{-11}$	–	57
H^+/Cs^+	25	1.1×10^{-8}	–	6
α-$Sn(HPO_4)_2\cdot H_2O$				
H^+/Na^+	20	6×10^{-8}	31	37
H^+/K^+	20	5.3×10^{-8}	31	37
H^+/Cs^+	20	4.1×10^{-8}	46	37
α-$LiHTi(PO_4)_2\cdot H_2O$				
H^+/Li^+	20	8×10^{-12}	–	18
α-$NaHTi(PO_4)_2\cdot H_2O$				
H^+/Na^+	20	6×10^{-11}	–	18
α-$Li_2Ti(PO_4)_2\cdot H_2O$				
H^+/Li^+	20	2×10^{-13}	–	18
α-$Na_2Ti(PO_4)_2\cdot H_2O$				
H^+/Na^+	20	1×10^{-14}	–	18
α-$K_2Ti(PO_4)_2\cdot H_2O$				
H^+/K^+	20	1×10^{-13}	–	18
$H_5O_2Ta(PO_4)_2$				
H^+/Li^+	20	3.8×10^{-6}	26	58
$Li_{0.5}H_{0.5}Ta(PO_4)_2\cdot 2H_2O$				
H^+/Li^+	20	1.1×10^{-6}	21	58
$LiTa(PO_4)_2\cdot 2H_2O$				
H^+/Li^+	20	6.4×10^{-7}	20	58
$Cu_xH_{3-2x}(PW_{12})_{40}\cdot nH_2O$				
H^+/Cu^{2+}	25	6×10^{-8}	–	59

[a] The literature data have been recalculated for 25 °C.

may identify also the layered hydrogenphosphates of tetravalent elements. The exchange in these substances takes place as a result of the drift of the interface between the AX and HX phases with extremely narrow regions of homogeneity. The rate-limiting stage is then two-dimensional diffusion of A^+ and H^+ ions through the AX layer. In the latter case, one can therefore consider, as an alternative method for the study of ion exchange kinetics, the method of stationary concentrations where the pH of the solution is kept constant by adding an excess of alkali. The latter procedure is analogous to the method widely used in the description of topochemical solid-phase processes and is based on a simplified solution of the stationary diffusion equation

$$l^2 = Dt\,, \tag{14}$$

where l is the thickness of the substituted layer. The main disadvantages of this approach are the impossibility of taking into account the free energy of the exchange reaction, which determines the driving force of the diffusion process, and the probability of entering the region of nonstationary diffusion. Furthermore, the physical significance of the concept of 'the driving force of the diffusion process', believed as a rule to be the concentration gradient within the substance, is also lost. In compounds with a narrow region of homogeneity the concentration gradient is comparatively small.

The solution of the 'diffusion problem' for an ion exchange process occurring as a result of the migration of the interface between two phases, based on the consideration of the model of a species moving within the crystal in a field with a periodic potential and the chemical potential superimposed on it, has been examined by Yaroslavtsev and Khrulev.[18] The chemical potential difference ($\Delta\mu$) between the solution and the interface in the crystal was chosen as the driving force of the process. The resulting kinetic equations for one-, two-, and three-dimensional diffusion through a plane, a hollow cylinder, and a hollow sphere assume the following forms respectively:

$$\frac{dQ}{dt} = Dc_0\Delta\mu\frac{S/l}{RT}, \tag{15}$$

$$\frac{dQ}{dt} = \frac{2\pi Dc_0h\Delta\mu}{RT\ln(r_0/r)}, \tag{16}$$

$$\frac{dQ}{dt} = \frac{4\pi Dc_0\Delta\mu[rr_0/(r_0-r)]}{RT}, \tag{17}$$

where dQ/dt is the flux of diffusing ions, c_0 is the concentration of the migrating ions in the layer where diffusion takes place, S and l are respectively the area and thickness of the plate, h is the height of the cylinder, and r_0 and r are the outer and inner radii of the cylinder or sphere. The quantities l and r are variable and are determined by the thickness of the layer of the growing phase. In the course of the experiment, they can be determined from the amount of reagent added and its current concentration. The chemical potential difference between the interfaces can be found from the relation

$$\Delta\mu = RT\ln\frac{c_Mc'_H}{c_Hc'_M}\,, \tag{18}$$

where c and c' are respectively the equilibrium and current concentrations of the cations. The relations presented are valid also in the exchange for the large potassium, rubidium, and caesium cations. For these species, the passage of the interface between solid phases requires an additional chemical potential difference.[18]

IV. The main types of inorganic ion-exchange substances

Among inorganic ion-exchange compounds, it is possible to identify the following classes: complex oxides, globular hydrates, and salts of polyvalent elements.

1. Complex oxides

Complex oxides are most widely represented among inorganic ion-exchange compounds. They include all natural ion exchangers — clay minerals and zeolites. The advantages of complex oxides is their availability and thermal and (partially) chemical stability. However, in view of the tendency of oxides to be close-packed, most of them have channels with small cross-sectional areas which must be passed by cations in order to migrate in the lattice. Furthermore, the high energy of the crystal lattices of the oxides is responsible also for the high energy of formation of defects in the latter (ΔH_f). As a consequence of this, the cationic diffusion coefficient is low and at room temperature does not as a rule exceed 10^{-10} cm^2 s^{-1}.[60] The diffusion coefficient is defined by the relation

$$D = \frac{1}{6} fca^2 v_0 \exp\left(\frac{\Delta S_f}{2R}\right)\exp\left(-\frac{E + \Delta H_f/2}{RT}\right), \qquad (19)$$

where f is the correlation factor, which varies for the majority of substances from 0.33 to 0.78 as the coordination number of the cation increases, c is the concentration of the cations of the given type, a is the length of the elementary transfer step, v_0 is the pre-exponential factor for the transfer frequency in the range $10^{12}-10^{14}$ s^{-1}, ΔS_f and ΔH_f are the entropy and enthalpy of the defect formation process, and E is the activation energy for the mobility of defects.

Calculations by Eqn (13) have shown that between three days and one year is required to achieve 95% completion of the exchange process for 0.1–1 mm oxide particles.[60] Such duration is characteristic of geological processes, but it cannot satisfy experimenters. A simple solution to this problem has been found: since the activation energy for diffusion in oxides is 80–100 kJ mol^{-1}, an increase in temperature by 100 °C leads, in conformity with Eqn (19), to an increase in the diffusion coefficient and hence in the rate of the process by 3–4 orders of magnitude. Bearing this in mind, the ion exchange, which occurs slowly at room temperature, is carried out either under hydrothermal conditions or in a melt.[61,62] If this is insufficient and also if the thermal stability of the ion exchanger is low, experimenters attempt to reduce the enthalpy of formation of defects, for example by heterovalent doping. In particular, doping of $Li_2Y^{IV}O_3$ by a compound of a pentavalent element having the composition $LiZ^{V}O_3$ leads to formation of lithium vacancies in the structure:

$$x\mathrm{LiZ^{V}O_3} + (1-x)\mathrm{Li_2Y^{IV}O_3} = \mathrm{Li_{2-x}Z_xY_{1-x}O_3}\,. \qquad (20)$$

On the other hand, doping with the compound $Li_3Z^{III}O_3$ leads to the appearance of interstitial lithium ions:

$$x\mathrm{Li_3Z^{III}O_3} + (1-x)\mathrm{Li_2Y^{IV}O_3} = \mathrm{Li_{2+x}Z_xY_{1-x}O_3}\,. \qquad (21)$$

In materials of this kind, the energy of formation of defects is reduced to zero and the diffusion coefficient is defined by the relation

$$D = \frac{1}{12} fcxa^2 v_0 \exp\left(-\frac{E}{RT}\right). \qquad (22)$$

Even for $x = 0.01$, the diffusion coefficient increases significantly and may prove to be fully acceptable for ion exchange at a comparatively low temperature.

a. Zeolites and clay minerals

Typical representatives of complex oxides with ion-exchange properties are zeolites and clay minerals. The structural base of these compounds consists of alternating layers of SiO_4 and AlO_4 tetrahedra or AlO_6 octahedra. The general formula of such compounds can be expressed in the form $M_{x/z}[(AlO_2)_x.(SiO_2)_y]\cdot mH_2O$. All clay minerals have a layered structure and the blocks, approximately corresponding to the composition $Si_8Al_4O_{24}^{4-}$, are arranged at right angles to the crystallographic c axis (Fig. 5). The surface of the blocks is made up of oxygen atoms carrying a non-compensated negative charge. The electroneutrality of the compound is ensured overall by the incorporation in the interstitial space of alkali or alkaline earth metal cations or protons,[6] forming coordinate or valence bonds with the oxygen atoms of the $Si_8Al_4O_{24}^{4-}$ blocks. Some of these cations are capable of exchanging with the cations of the surrounding solution. The overall ion-exchange capacity of such materials ranges from hundredths to 1.5 mequiv g^{-1} and for compounds with compositions close to $H_4Si_8Al_4O_{24}\cdot nH_2O$ the ion-exchange capacities with respect to cations and anions are approximately the same.[6] A characteristic feature of such materials is their ability to swell in aqueous solutions or in water.

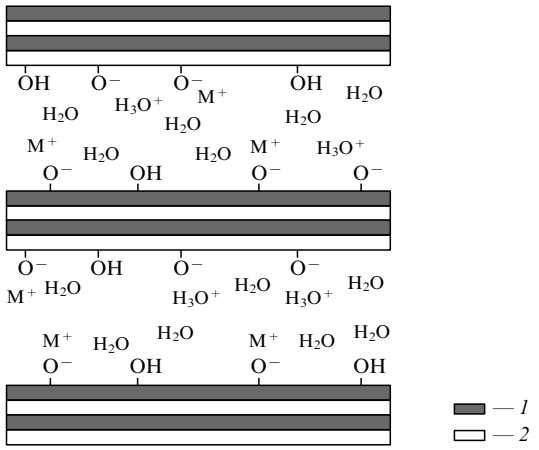


Figure 5. Schematic illustration of the structure of clay materials. (*1*) and (*2*) blocks of the layered structure; M^+ = alkali metal cation.

The silicon at tetrahedral sites can be partly substituted by aluminium cations, while aluminium at the octahedral sites can be substituted by a whole series of cations (divalent and trivalent iron, magnesium, and certain others with similar radii). Substitution by an ion with a smaller radius (Si^{4+}/Al^{3+}, Al^{3+}/Fe^{2+}, Al^{3+}/Mg^{2+}) increases the ion-exchange capacity with respect to cations. Therefore, for the majority of zeolites and clay minerals, the cation-exchange capacity exceeds the anion-exchange capacity. Clay minerals are distinguished by selectivity with respect to the sorption of large cations (Table 1). In the series of alkali metals, the selectivity increases from lithium to caesium.[21,22,63,64]

In zeolites, the joining of the AlO_4 and SiO_4 tetrahedra *via* vertices, edges, or faces leads to the formation of diverse structures — fibrous, layered, or structures with a three-dimensional framework. The chemical and ion-exchange properties of zeolites with fibrous and layered structures are close to those of clay minerals, while those of zeolites having a rigid framework in the structure may differ significantly. The crystal lattices of the latter can be regarded to a first approximation as a $(SiO_2)_n$ matrix with three-dimensional connections, some of the silicon ions in which have been substituted by aluminium ions. The excess negative charge is compensated by the insertion into the lattice of cations with a smaller charge or by the substitution of some of the oxygen atoms by anions of monobasic acids. All these 'defective' cations and ions and also a certain number of water molecules are located within channels having different cross-sections (Table 2). If the size of the ions is smaller than the size of the channels, they can migrate in the structure and can participate in ion exchange. In contrast to clay minerals, the volume of such substances hardly changes during exchange and their ion-exchange capacity is determined by the chemical composition and may be fairly high. Thus, for certain minerals of the type of feldspar, it approaches 10 mequiv g^{-1} (sodalite, ultramarine) or can actually exceed this

value (cancrinite).[65] Alkali metal cations are partly exchanged even on contact with water:

$$Na_{12}[Al_{12}Si_{12}O_{48}]\cdot aq + H_2O \rightleftharpoons \quad (23)$$
$$\rightleftharpoons Na_{12-x}H_x[Al_{12}Si_{12}O_{48}]\cdot aq + xNa^+ + xOH^- .$$

As a result of this, many zeolites in the initial form contain a certain number of protons.[66] In order to attain a more complete conversion into the hydrogen-form, zeolites are treated with solutions of ammonium salts at elevated temperatures, the ammonia formed being removed during annealing.[67,68]

Zeolites with a three-dimensional structure and a fixed size of the channels are used as 'ionic sieves'. Indeed, cations with a radius close to the radius of the cross-section of the channels are weakly sorbed, whilst still larger ones altogether fail to be sorbed. Thus ultramarine sorb effectively lithium, sodium, and silver ions and poorly rubidium and ammonium ions, while caesium does not participate in the exchange process.[65] Zeolites with a large size of the channels sorb weakly various alkylammonium cations,[6] but certain zeolites are capable of sorbing even bulky complex cations.[69]

The specific sorption properties of zeolites, their availability, low cost, and stability have led to their extensive practical application. For example, zeolites are used to extract heavy elements (including radioactive ones) such as caesium, thorium, and uranium from solutions.[25,63,70–73] Zeolites modified with the aid of ion exchange by copper, nickel, platinum, ruthenium, and certain other cations are promising as catalysts in reactions involved in organic synthesis and for the conversion of nitrogen oxides and carbon monoxide in exhaust and industrial gases.[74–82]

b. Complex oxides with a trivalent metal

Many complex oxides incorporating polyvalent elements have structures similar to those of the compounds examined above. The simplest representatives of complex oxides with a trivalent metal are alkali metal aluminates, chromates, and ferrites. The best known are the β-aluminates, also known as β-alumina having the composition $M_{1+x}Al_{11}O_{17+x/2}$ ($M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, H_3O^+, NH_4^+, Ag^+, Tl^+, *etc.*). These compounds are distinguished by a high ionic conductivity involving alkali metal cations or protons.[83–85]

The structure of β-aluminates is made up of $Al_{11}O_{16}$ spinel blocks containing four layers with close packing of oxygen, each fifth layer containing only a quarter of the oxygen atoms retaining these blocks next to one another in crystals (Fig. 6). Alkali metal cations are located in the same layer, five cavities of different types corresponding to each. The population of cavities of each type depends not only on the nature of the singly charged cations but also on the stoichiometry of the compound and even on temperature.[85,86–90] β-Gallates also have a similar structure.[91,92] The extremely low energy barriers to jumps between the cavities (the minimum values correspond to silver and sodium ions) give rise to the possibility of rapid ion transfer. It is remarkable that, contrary to the generally accepted view, the similar energies for the localisation of singly-charged cations at different crystallographic sites, for example $(NH_4)_{1+x}Al_{11}O_{17+x/2}$, lead to a decrease in the population of the principal Beaver–Ross sites and to an anomalously rapid increase in the concentration of ammonia in the interstices with increase in the nonstoichiometry index x.[93] This fact can be explained by the displacement of ammonia from the main sites by the cations located in close proximity in the interstices.[94] Within the framework of the theory developed by Bruce and Abrahams,[95] such displacement leads to the formation of alternating structural blocks with populated sites and interstices and to the cooperative transport of ions. accordingly, nonstoichiometric compounds with a large value of x‡ are characterised by a high cationic mobility.[96–100]

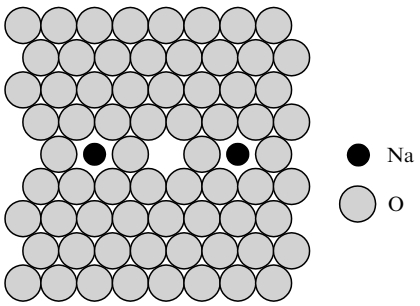


Figure 6. Schematic illustration of the structure of the oxygen sublattice of sodium β-aluminate with accommodation of the alkali metal cations in the conducting plane. The oxygen atoms in the conducting plane pass through the later.

The first communication about the occurrence of ion exchange in sodium β-aluminates for alkaline earth metals is that of Toporov and Stukalova.[101] Exchange of this kind occurs comparatively slowly at room temperature, but is significantly accelerated on raising it. It is therefore most suitable to carry out this process in nitrate melts at 300–350 °C.[102] Under such conditions, the diffusion coefficient of even caesium β-aluminate reaches 10^{-7} cm^2 s^{-1} and the tendency of the structure to sorb cations increases in the sequence $Ag^+ > Tl^+ > K^+ > Na^+ > Rb^+ > Li^+ > Cs^+$.[62,102] The ammonium-forms of the β-aluminate[62,85,99,103] and β-gallate,[98,104,105] as well as ammonium β-ferrite[106] can be obtained by exchange from the melt. In order to accelerate the removal of the alkali metal, the ammonium nitrate melt is electrolysed with a rubidium β-aluminate anode.[107] For the preparation of the oxonium forms of the β-aluminates, the exchange was carried out in inorganic acids at an elevated temperature[105,108–110] or the silver form of the β-aluminates was reduced with hydrogen.[62,111]

β-Aluminates are capable of sorbing multicharged cations, in particular the lanthanide cations.[112–116] The latter are also localised in the conducting plane[112,113,116] and are characterised by a comparatively high mobility.[116]

The α-$NaCrO_2$-type structures of lithium and sodium ferrites and chromites consist of close-packed oxygen atoms, among which the alkali metal and chromium ions occupy alternately octahedral cavities in the direction of the (111) crystallographic planes.[117] Interaction of these compounds with lithium and silver nitrate and copper(I) chloride melts leads to the formation of the compositions ABO_2 ($A = Li^+$, Ag^+, Cu^+; $B = Fe^{3+}$, Cr^{3+}).[60,118] When the corresponding process is carried out using a stoichiometric mixture of metallic palladium and palladium(II) chloride, the A sites may be occupied by palladium ions.[118] Analogous reactions have been described also for a series of aluminates of monovalent and divalent metals.[119,120] When sodium chromite is treated with a 300-fold excess of 25% nitric acid for 12 h, it is possible to achieve virtually complete substitution of the sodium ions by protons.[60] It is noteworthy that not all the compounds obtained retain the crystal structure of the initial substance.

c. Complex oxides with tetravalent, pentavalent, and hexavalent cations

The layered titanates $M_2Ti_nO_{2n+1}$ and $M_4Ti_nO_{2n+2}$, the structures of which are made up of $Ti_nO_{2n+1}^{2-}$ or $Ti_nO_{2n+2}^{4-}$ layers, are inorganic ion-exchange materials. On being combined *via* common edges or vertices, the TiO_6 octahedra form infinite cavities between which alkali or alkaline earth metal cations are located.[121–130] Since the latter possess a fairly high mobility, they can be substituted in solutions or melts by M^+ and M^{2+} cations or protons. A certain number of water molecules, can also

‡ Such compounds are frequently referred to as β″-aluminates (gallates, ferrites).

permeate into the interlayer space.[60, 126, 128, 130, 131] The exchange reactions in these compounds may prove to be hindered kinetically. Thus treatment of lithium titanate with a zinc chloride melt leads to only partial exchange.[60] This phenomenon can be explained by postulating that the cationic sites are nonequivalent: only some of them are capable of being substituted by zinc cations, as in lithium germanates described by Joubert and Durif.[132] A series of new titanates have also been synthesised in recent years, among which one may differentiate fibrous materials containing hydrogen or alkali metal cations within $Ti_8O_{18}^{4-}$ layers and octahedral $Ti_8O_{17}^{2-}$ tunnels. The cations within the layers tend to exchange rapidly, while those located within the tunnels are inert.[133]

One of the few representatives of hydrated oxides of polyvalent cations, capable of stoichiometric ion exchange, is polyantimonic acid $(H_3O)_2Sb_2O_6 \cdot H_2O$. Together with the method usually employed for the synthesis of hydroxides, namely deposition from solution, this acid can be obtained with the aid of the ion-exchange reaction occurring on treatment of potassium antimonate with nitric acid.[134] The compound formed has the pyrochlore structure with oxonium ions in the octahedral cavities.[134, 135] The protons of polyantimonic acid are capable of being quantitatively substituted by alkali metal cations. The selectivity series then assumes the following form: $Na^+ > K^+ > Rb^+ > Cs^+ > Li^+$, while the overall ion-exchange capacity reaches 5.1 mequiv g^{-1}.[136–139]

Alkali metal niobates and tantalates (pyrochlore structural type) are also capable of undergoing stoichiometric substitution of all the cations by hydrogen. The ion-exchange capacities of these compounds reach 2–3.3 mequiv g^{-1}. This is due to the appreciable polarisation of the oxygen ions, leading to the formation of weak bonds between the lattice and the exchanging cation and to the presence of comparatively large channels. The hydrogen-forms of these ion exchangers may be obtained as a result of the hydrolysis of the pentachlorides[8] or by the acid treatment of thallium,[134, 140] lithium,[141–145] or potassium[146] niobates at an elevated temperature. In contrast to antimonic acid, only half of the $(H_3O)HM_2O_6$ protons are hydrated in niobium and tantalum hydroxides. NMR data have also confirmed the presence of protons and oxonium ions in these substances.[134] Many investigators have concentrated particular attention on the study of the phases formed at intermediate stages of the exchange process.[142, 143, 145]

In order to obtain ion-exchange materials with a high capacity and high rates of exchange, it appears attractive to synthesise compounds with heterovalent substitution of the atoms in the ion-exchanger matrix. A considerable number of studies have been devoted to the preparation of mixed titanates, niobates, and tantalates with a layered or tunnel structure. The best known are the compounds MTi_nNbO_{2n+3}, and $M_3Ti_nNbO_{2n+4}$.[147–153] The monovalent cations in these substances ensure a charge balance in the structure, remaining weakly bound to the framework. The alternating TiO_6 and NbO_6 octahedra, joined together by common edges or vertices, form double layers between which singly charged cations, capable of being substituted, are located.[152] The reactivities of mixed titanates - niobates differ significantly. Thus the substitution of the alkali metal cation for a proton in $MTiNbO_5$ takes place comparatively easily, while the analogous process involving $CsTi_2NbO_7$ requires treatment with concentrated acid and the reaction product is the hydrate $HTi_2NbO_7 \cdot 2H_2O$. In the case of $K_3Ti_5NbO_{14}$, the maximum degree of substitution of potassium by hydrogen reaches only 80%.[148, 152]

Variable-composition compounds, incorporating singly, doubly, triply, and quintuply charged cations together with titanium, may be differentiated as a separate group. The formulae of such compounds can be written as $A^I_{2x}B^{II}_xTi_{2-x}O_4$, $A^I_xB^{III}_xTi_{2-x}O_4$, and $A^I_{1-x}Ti_{1-x}Nb_{1+x}O_5$.[148, 151, 154, 155] In the compounds of the first two types, the substitution of part of the titanium by atoms B with a lower valence leads to a deficiency of cations, which is compensated when the corresponding number of ions A^+ are inserted into the interstices. On the other hand, in compounds of the third type the compensation of the charge on substitution of titanium by niobium leads to the formation of vacancies in the cationic sublattice. Such a defective structure is distinguished by an increased cationic mobility, which helps to accelerate ion-exchange processes. On the other hand, the ion exchange of caesium for lithium, sodium, or potassium in $Cs_{0.7}Mg_{0.35}Ti_{1.65}O_4$ proceeds comparatively rapidly in melts at 300–400 °C. However, the completion of the exchange of caesium for sodium in an aqueous solution requires four days.[155]

Heterovalent substitution is possible in niobates and tantalates. The layered niobates and tantalates containing calcium or lanthanum were investigated vigorously in the 1980s–1990s.[156–162] Treatment of these compounds with concentrated acids at 60 °C leads to fairly rapid ion exchange.[157, 159] The proton conductivity of the hydrogen-form of a series of such materials reaches 10^{-3} S cm^{-1} at 400 °C.[162] Certain compounds containing niobium or tantalum together with tungsten or molybdenum also possess similar properties.[163–165] The complete substitution of potassium by hydrogen on treatment with concentrated hydrochloric acid even of the stoichiometric compound $KTaWO_6$ occurs at room temperature. The hydrate $HTaWO_6 \cdot H_2O$ formed exhibits an appreciable proton conductivity of 2×10^{-7} S cm^{-1} at 25 °C.[165]

d. Oxides with variable-valence cations

An effect analogous to heterovalent doping may be obtained on partial oxidation or reduction of the ions of the framework. A typical representative of sorbents with a variable valence of the lattice cations is manganese dioxide. It has long been noted that the freshly precipitated compound contains an appreciable amount of impurity ions which can be readily exchanged for cations present in the solution surrounding it.[166, 167] This is due to the fact that manganese dioxide contains divalent and trivalent manganese. Its composition may be represented by the formulae $Mn^{II}_nMn^{III}_yMn_{1-x-y}O_{2-2x-y}(OH)_{2x+y} \cdot mH_2O$ or $MnO_{2-x}(OH)_x \cdot nH_2O$ (the charge is compensated as a result of the insertion of protons, which form OH groups with oxygen). It was initially postulated that only hydroxy groups located on the surface of the particles of the test substance, may participate in the exchange process. However, it was later shown that the ion-exchange capacity of manganese dioxide may reach 4 mequiv g^{-1},[168, 169] which in no way agrees with this hypothesis. All the known modifications of manganese dioxide are made up of MnO_6 octahedra joined together in such a way that long channels are formed between them.[8] Singly and doubly charged cations are in fact located within these channels and readily migrate along them, ensuring the possibility of exchange processes.

Among other compounds with distinct ion-exchange properties, one may identify the tungsten and molybdenum blues and bronzes $A^I_xBO_3$, which possess both electronic and ionic conductivity. They can be readily obtained by the electro-chemical reduction of molybdenum or tungsten oxides and also by the interaction of the latter with the corresponding metal or hydrogen at an elevated temperature. Vanadium and niobium bronzes possess similar properties. In the simplest case, small cations are intercalated in the octahedral cavities of the tungsten or molybdenum oxide lattice. The formation of tunnel or layered structures is an alternative.[170] All these compounds have been thoroughly described in the literature, but they are not often used for ion-exchange processes. Therefore, without dealing in detail with their properties, we shall note only some of the latest studies where these compounds were examined.[171–173]

2. Globular hydrates

Globular hydrates are widely distributed compounds, typical representatives of which are loose deposits of hydrated oxides of polyvalent elements of the type $Al_2O_3 \cdot nH_2O$ and $ZrO_2 \cdot nH_2O$. Since such compounds are sparingly soluble, their formation reactions occur at a high degree of supersaturation of the solutions

where the rate of nucleation is very high and fully comparable to the rate of growth of the particles. The precipitated deposits represent a large number of very small and poorly formed (amorphous or weakly crystallised) particles. The geometry of small particles is in many respects determined by the requirement that the surface tension energy be minimised.[94] The formation of particles in the form of spheres (globules), the core of which usually has a composition close to that of the corresponding oxides is the most favourable. The extensive surface of the globules contains a multiplicity of uncompensated bonds, which may be stabilised as a result of the sorption of protons H^+ and OH^- groups from the solution,[136] as well as other ions and water molecules (Fig. 7*a*). The bonds between the sorbed particles and the core are comparatively weak, so that dissociation of the $\equiv E-O-H$ groups *via* an acid or base mechanism and the transfer of the resulting ions into the intergranular space are possible.[136]

The most significant difference between the globular hydrates and the substances described above is the variable and comparatively low ion-exchange capacity determined in the first place by their surface area. After prolonged storage or heating, particularly under hydrothermal conditions, olation, oxolation, and crystallisation processes involving the substances take place,[174] as a result of which the ion-exchange capacity may decrease by several orders of magnitude. Furthermore, we may recall that the ion-exchange capacity depends significantly on the pH of the solution in contact with the hydroxides[12, 13] and even the nature of the processess occurring on raising the pH changes from anion-exchange to cation-exchange reactions. Since the nature of the active centres on the surfaces of globular hydrates depends on the method of their preparation, the position of the equivalence point is not a fundamental characteristic of the substance but depends on its previous history. Nevertheless the relation between cation- and anion-exchange properties of hydrated oxides is determined primarily by the electronegativity of the polyvalent cation. Thus the distinctly acid hydrated antimony(V) oxide, mentioned above, may participate only in cation exchange.[136] On the other hand, the hydrated yttrium oxide, dissociating preferentially *via* a basic mechanism, is an anion exchanger.[20]

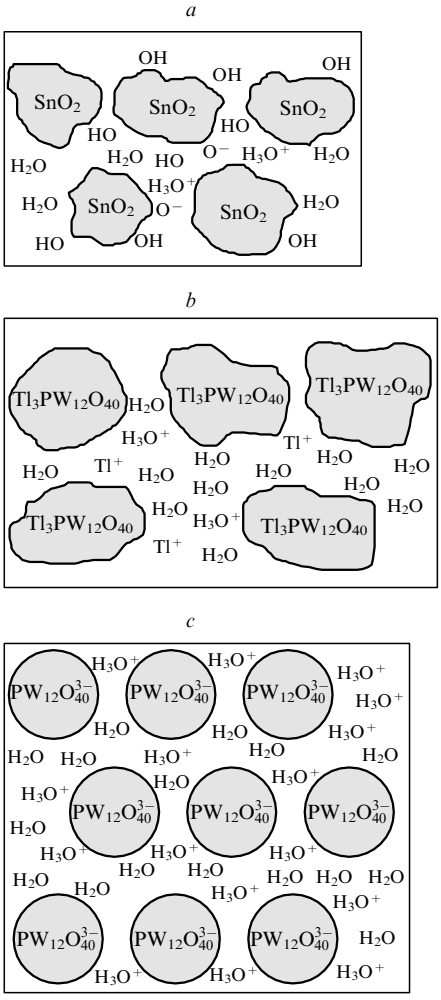


Figure 7. Schematic illustration of the structures of the globular hydrates $SnO_2 \cdot nH_2O$ (*a*), $Tl_{3-x}H_x(PW_{12}O_{40}) \cdot nH_2O$ (*b*), and $H_3PW_{12}O_{40} \cdot 29H_2O$ (*c*).

The presence of ion-exchange properties in globular hydrates may lead to their contamination and hence to an ambiguous treatment of the experimental results. For example, the hydroxides of trivalent elements are most often obtained by deposition with ammonia from solutions of salts of the corresponding metals. The deposition product is characterised by an appreciable content of the anions of the initial salts. This is due to the fact that the resulting solution is a buffer containing the $NH_4X + NH_4OH$ mixture.[20] The concentration of hydroxide ions in it in the presence of a 10% excess of the precipitant reaches only 2×10^{-6} and is several orders of magnitude lower than the concentration of the anions X^-. For this reason, the surface of the globules actively sorbs the anions. The content of nitrate ions in the yttrium hydroxide $Y(OH)_{3-x}(NO_3)_x \cdot 0.7H_2O$ ($0 < x < 0.5$), obtained by deposition from a nitrate solution, corresponds to the fraction of the cations localised on the surface of the particles.[20] For the complete conversion of the compounds thus obtained into the hydroxide, it is necessary to wash them with solutions of alkalis containing OH^- ions. Similar ion-exchange processes may occur also on much better formed deposits, for example on hydrated aluminium oxide.[173, 176]

Materials with distinct anion-exchange properties may be obtained by doping hydrated oxides having basic properties with an admixture containing a high-valence cation. It has been postulated[6, 177] that the excess positive charge is compensated as a result of the sorption of anions from the $Zn_{1-y}Al_y(OH)_2X_y$ solution. However, this interpretation appears doubtful, since the initial hydroxide already possesses similar properties and is characterised by a significant degree of disorder, which should abolish the effect of heterovalent doping.

Among globular hydrates, hydrated oxides of tetravalent elements (silicon, tin, titanium, and zirconium) are most often employed as ion-exchange materials. Their principal advantage is very low solubility in both acid and alkaline solutions. In the series of compounds quoted, the acid properties are somewhat weakened:[136] whereas silicon hydroxide can participate only in cation exchange, for the zirconium compound the zero-charge point is attained at a pH close to 7.[12, 13, 176, 178, 179] Dichromate and molybdate ions are sorbed in the anionic form, the latter being involved in octahedral coordination, which does not rule out the possibility of the condensation of polyanions on the surface of the hydroxides.[179] Hydrated vanadium(V) oxide also has properties close to those of the compounds listed above.[136, 180]

A series of specific, properties of hydrated oxides are determined by the characteristics of their structure. In the first place, such properties are determined by the nature of the highly mobile 'solution' in the interlayer space, which contains water molecules and ions formed on dissociation of the groups localised on the surface. In view of the extremely small size of the micropores (< 100 Å[181]) containing the intergranular solution and also as a consequence of the lack of order in the system of hydrogen bonds formed within it and on the surface of the globule, such a solution has a very high mobility. The latter vanishes only on cooling the specimen to temperatures close to the boiling point of nitrogen.[178, 181-183] The presence of proton defects (H_3O^+ or HO^-) in the solution is responsible for a fairly high proton conductivity of globular hydrates, the magnitude of which reaches 10^{-2} S cm^{-1} for the series of compounds (Table 4). The proton conductivity and the mobility of the proton-containing groups decrease sig-

Table 4. The proton conductivities of certain globular hydrates.

Oxide or heteropolyacid	Extent of solvation	$\sigma_{298\,K}$ /S cm^{-1}	Ref.
Ga_2O_3	$4H_2O$	10^{-4}	184
Cr_2O_3	$8.5H_2O$	10^{-5}	184
In_2O_3	$5-6\,H_2O$	$(1-3)\times10^{-3}$	184
ZrO_2	$1.7-5.6\,H_2O$	$10^{-4}-10^{-5}$	136
SnO_2	$2-3\,H_2O$	$(2-4)\times10^{-4}$	136
CeO_2	$2H_2O$	$10^{-5}-10^{-6}$	185
ThO_2	$3-5\,H_2O$	$5\times10^{-6}-4\times10^{-4}$	184
V_2O_5	$0.5-1.8\,H_2O$	$10^{-4}-10^{-2}$	185, 186
Sb_2O_5	$0.6-6.5\,H_2O$	$10^{-4}-3\times10^{-3}$	134, 184, 187, 188
Nb_2O_5	$0.3-0.8\,H_2O$	10^{-4}	134
Ta_2O_5	$0.5-1\,H_2O$	10^{-4}	134
$H_3PMo_{12}O_{40}$	$6-29\,H_2O$	$7\times10^{-5}-0.17$	189, 191
$H_3PW_{12}O_{40}$	$6-29\,H_2O$	$8\times10^{-4}-8\times10^{-2}$	191–193
	$6CH_3OH$	$4.5-10^{-4}$	193
	$6CH_3CN$	1.8×10^{-5}	193
	$6C_2H_5OH$	10^{-4}	193
	$6(CH_3)_2CO$	8×10^{-6}	193
	$6CH_3COC_2H_5$	5×10^{-6}	193
	$6(CH_3)_2SO$	2×10^{-7}	193

nificantly during the dehydration of the hydrated oxides.[136, 182, 184] The kinetics of the exchange processes depend on the relative permittivity of the solvent, since ion-exchange processes take place on the surface of the particles of the globular hydrates and in the intergranular solution. The rate of exchange and the capacity of the ion exchanger may therefore change, for example in the presence of alcohols.[194]

Alkali metal and thallium tungstophosphates, the ion-exchange properties of which have been examined by Yaroslavtsev *et al.*,[195, 196] are constructed similarly. The X-ray diffraction patterns of these compounds are identical with those of the anhydrous salts of the heteropolyacids constituting the cores of the globules, but differ by the broadening of the reflections corresponding to the formation of 80–200 Å particles. Water molecules are localised in the inter-granular space (Fig. 7*b*), their number varying from 7 to 12 per formula unit. In the interaction of solutions of heteropolyacids and alkali metal chlorides, a high concentration of hydrogen ions is maintained. For this reason, not only alkali metal cations but also protons are sorbed on the particles deposited from the solution. In the presence of an excess of the chloride, the trisubstituted salts $M_3PW_{12}O_{40}\cdot nH_2O$ are deposited, their formation being thermodynamically most favourable. In the presence of a deficiency of the chloride, their surface sorbs heteropolyanions and protons, which is equivalent to the deposition of acid salts in which the content of hydrogen ions may reach 1.05 per formula unit (for example, $Cs_{1.95}H_{1.05}PW_{12}O_{40}\cdot\cdot nH_2O$ characterised by a minimal solubility product and a minimal crystal size).[195]

It has been established by ^{205}Tl NMR that a significant proportion of the thallium ions in $Tl_3PW_{12}O_{40}\cdot11.5H_2O$ are in a mobile state.[196] Prolonged washing of the above compound with water leads to the disappearance of the line due to mobile thallium, which indicates its removal from the surface of the globules as a result of the reaction

$$Tl_3PW_{12}O_{40}\cdot nH_2O + (m + x - n)H_2O = \quad (24)$$
$$= Tl_{3-x}H_xPW_{12}O_{40}\cdot mH_2O + xTlOH\,.$$

The process described above leads to an increase in the ionic conductivity from 2.7×10^{-4} to 5×10^{-4} S cm^{-1} in view of the greater mobility of protons compared with Tl^+ ions.[196] The increase in ionic conductivity on passing from neutral to acid salts of heteropolyacids has been noted also for other cations.[195, 197]

From the standpoint of thermodynamics, the formation of particles smaller than 100 Å is difficult owing to the considerable expenditure of energy on the formation of the interface. There is therefore probably a limiting minimum size of the hydrate globules. However, the series of compounds examined is aptly supplemented by the hydrates of heteropolyacids with a high water content ($H_3PX_{12}O_{40}\cdot29H_2O$, where X = Mo, W), the anion of which, with a radius of ~12 Å, can be regarded as a microglobule (Fig. 7*c*).[198] The high mobility of the 'intergranular' $3H^+\cdot29H_2O$ solution disappears at very low temperatures.[59] The proton conductivity of these compounds is a maximum among all those measured at room temperature,[190] its magnitude decreasing significantly in the course of dehydration (Table 4). Similar properties are characteristic of numerous heteropolyacid solvates.[193] The conductivity of such solvates diminishes with increase in the volume of the solvent molecule (in conformity with the decrease in its rotational mobility, which is required for the transfer of a proton).

It is difficult to observe ion exchange for heteropolyacid hydrates because their crystal lattice is unstable and readily disintegrates on contact with the solvent. Nevertheless, an ion-exchange process was achieved when $H_3PW_{12}O_{40}\cdot29H_2O$ and $Cu_{3/2}PW_{12}O_{40}\cdot28H_2O$ single crystals came into contact.[59] The mutual diffusion of copper and hydrogen ions can be observed readily in this case from the change in the colour of the crystals. The coefficient of the mutual diffusion of H^+ and Cu^{2+} is $(3-7)\times10^{-8}$ cm^2 s^{-1}.

There are no fundamental differences between the structure of globular hydrates and that of the hydrated antimony and manganese oxides described above. However, the microstructures of the cores of the globules and the chemical individuality of the polyvalent cation in the latter determine the possibility of the occurrence of exchange processes throughout the bulk of the particles, which in fact serves as the basis for their assignment to the class of complex oxides. On the other hand, from the standpoint of the interpretation of the nature of the proton conductivity, all these compounds can be assigned to globular hydrates, because the conductivity within the grain is negligible compared with the surface component. The use of fractal geometry appears extremely productive in the treatment of the properties of compounds with a high surface area and porosity.[199]

3. Salts of polyvalent elements

a. The layered hydrogenphosphates and arsenates $H_yB(XO_4)_2$

Among the salts of polyvalent elements, the sparingly soluble phosphates and arsenates $H_yB(XO_4)_2$ are most widely used as inorganic ion-exchange materials. Zirconium hydrogenphosphate $Zr(HPO_4)_2\cdot nH_2O$ has been undoubtedly most thoroughly investigated. Investigators have shown particular interest in this compound after a communication had been published in 1943 concerning the possibility of separating with its aid uranium and plutonium from their fission products.[200] The communication of Clearfield and Stynes [5] about the synthesis of crystalline zirconium hydrogenphosphate stimulated the development of research into the nature of ion exchange on inorganic phosphates.

Zirconium hydrogenphosphate may be obtained after prolonged heating of a mixture of zirconium oxychloride with an excess of phosphoric acid or by evaporating the corresponding solution with added hydrofluoric acid. In this case, the slow disintegration of zirconium fluoride complexes results in the deposition of well formed $Zr(HPO_4)_2\cdot H_2O$ crystals. The latter consist of long $[Zr(HPO_4)_2]_n$ layers, in which zirconium ions are in an octahedral environment consisting of the oxygen atoms of the anions (Fig. 8). Only three oxygen atoms of the anion participate in the formation of the P–O–Zr linkages, while the fourth is oriented towards the interplanar space and is linked to hydrogen *via* a valence bond. The layers are retained next to one another *via* hydrogen bonds with water molecules ($O_3PO-H-OH_2$) 2.77 and 2.81 Å long.[50, 201] The acid nature of the HPO_4^{2-} groups and the nearly optimum lengths of the hydrogen bonds [202] create precon-

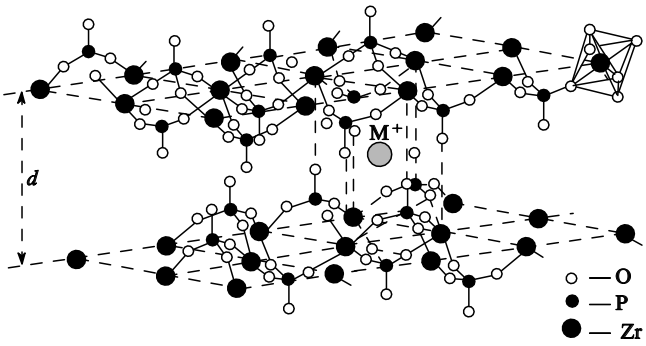


Figure 8. A fragment of the structure of acid zirconium phosphate with an indication of the preferred site where the cation is located in the distorted octahedron made up of oxygen atoms.

ditions for the appearance of proton conductivity in $Zr(HPO_4)_2 \cdot H_2O$ and, together with the possible cationic diffusion in the interlayer space, for the appearance of ion-exchange properties.

A considerable number of hydrogenphosphates of polyvalent elements are isostructural with the above compound, but, in view of the difficulty of obtaining large crystals, structural data are available only for a few of them.[203, 204] The main characteristics of these materials are the interlayer distance and the ion-exchange capacity (Table 5).

A new phase — α-$Zr(HPO_4)_2 \cdot 0.5H_2O$ with an interlayer distance of 7.42 Å — has been described and characterised

Table 5. Interlayer distances and calculated ion-exchange capacities of certain acid phosphates and arsenates of tetravalent elements.

Composition	Interlayer distance /Å	Ion-exchange capacity /mequiv g^{-1}	Ref.
α-$Ti(HPO_4)_2 \cdot H_2O$	7.60	7.75	203
α-$Ge(HPO_4)_2 \cdot H_2O$	7.71	7.08	205
α-$Zr(HPO_4)_2 \cdot H_2O$	7.56	6.64	50, 201, 206
α-$Sn(HPO_4)_2 \cdot H_2O$	7.87	6.09	207
α-$Hf(HPO_4)_2 \cdot H_2O$	7.58	5.15	204
α-$Pb(HPO_4)_2 \cdot H_2O$	7.95	4.79	205
α-$Ti(HAsO_4)_2 \cdot H_2O$	7.78	5.78	205
α-$Ge(HAsO_4)_2 \cdot H_2O$	7.86	5.40	205
α-$Zr(HAsO_4)_2 \cdot H_2O$	7.74	5.14	205
α-$Sn(HAsO_4)_2 \cdot H_2O$	7.89	4.80	205
α-$Hf(HAsO_4)_2 \cdot H_2O$	7.79	4.20	205
α-$Pb(HAsO_4)_2 \cdot H_2O$	7.97	3.96	205
γ-$Ti(HPO_4)_2 \cdot H_2O$	11.62	7.24	208, 209
γ-$Zr(HPO_4)_2 \cdot H_2O$	12.25	6.27	210
$H_5O_2Ta(PO_4)_2$	9.50	2.02	211, 212

structurally comparatively recently.[213] It differs from the monohydrate by the system of hydrogen bonds. The authors[213] note the stability of this phase — they did not observe its conversion into a mixture of the monohydrate and the anhydrous compound.

The interlayer distance in the γ-modifications of the acid phosphates γ-$M(HPO_4)_2 \cdot 2H_2O$ is significantly greater[208–210] than in the α-modification, which facilitates the occurrence of ion-exchange processes. The study of the structure of compounds of this type is complicated because only finely disperse specimens are obtained in the course of synthesis. For this reason, none of the information concerning their structure can be regarded as fully reliable. However, it has been established reliably with the aid of ^{31}P NMR that two nonequivalent PO_4 polyhedra, coordinated twice and four times to the multicharged cation, are present in the structure.[214] As a result of this, the $H_2PO_4^-$ anions are displaced into the interlayer space, which in fact leads to the layers moving apart (Table 5).

Tantalum hydrogenphosphate has a structure similar to that of the α-phosphates of tetravalent elements.[211, 212] However, the number of hydrogen ions in this compound is smaller by a factor of 2 and the negative charge of the basic layers is therefore smaller, the interaction between them is weaker, and the interlayer distance is greater.[212] Furthermore, the polarisation of the phosphate anion by the pentavalent cation decreases the proton-accepting capacity of the oxygen atoms and leads to the dissociation of the HPO_4^- groups giving rise to diaquahydrogen ions $H_5O_2^+$.[212]

In the course of ion exchange on α-phosphates, alkali metal cations permeate into the interlayer space and are disposed in the vicinity of the centre of the octahedron made up of the oxygen atoms of the anion (Fig. 8) not coordinated to the tetravalent cation. A type $AB(XO_4)_2$ lattice with the structure of an anhydrous alum is obtained. Numerous double antimony and tantalum phosphates with alkali metals are constructed in this way.[215–218] The coordination sphere of potassium in zirconium phosphate with a degree of substitution of 50% [$ZrKH(PO_4)_2$] is formed similarly.[219] The real radius of the octahedral cavities in such structures is equal to 4.7–5.3 Å and the radius of the cation in it should be 3.3–3.9 Å, which exceeds significantly the size of any alkali metal cation. The above octahedra therefore contract along the threefold axis and the interlayer distance diminishes. However, this contraction is insufficient and the excess space is filled with water molecules. The cation then shifts from the highly symmetrical position and the interlayer distance increases as a rule relative to that in the initial acid phosphate.[39]

The number of highly symmetrical sites at the centre of the octahedron is smaller by a factor of 2 than the number of monovalent cations in the structure of the products of the complete substitution of tetravalent elements in acid phosphates. As a result of this, the coordination sphere of the metal is formed in a specific manner — with partial involvement of the oxygen atoms of the anion and water molecules. Thus there are four nonequivalent cationic sites in $Na_2Zr(PO_4)_2 \cdot 3H_2O$ with coordination numbers of 7, 7, 6, and 4. Between one and four water molecules and between two and five oxygen atoms of the anion enter into the immediate environment of sodium. Among the oxygen atoms, there are also those involved in the formation of P–O–Zr linkages.[220] In $(NH_4)_2Zr(PO_4)_2 \cdot H_2O$, two nonequivalent types of ammonium ions are surrounded by respectively four and five oxygen atoms of the anion and are linked to a water molecule *via* a bridging hydrogen bond: $NH_4^+ - HOH - NH_4^+$.[221]

During ion exchange on acid phosphates, the structure of the $[M(PO_4)_2]_n$ layers is kept almost constant. Therefore, when the unit cell parameters a and b are similar, the interlayer distance changes significantly (usually increases), which is a sign of the occurrence of ion-exchange processes for the compounds $M(HXO_4)_2 \cdot H_2O$. The typical interlayer distances in certain products of ion exchange on acid phosphates with the ratio $M : XO_4 = 1 : 2$ are presented in Table 6 and their dependences on the degree of hydration and the radius of the cation in the monosubstituted sodium salts of zirconium α-phosphate and titanium γ-phosphate are shown in Fig. 9. The interlayer distance increases with increase in the radius of the sorbed cation and with the degree of hydration of the compound.

As a consequence of the structural nonequivalence of the hydrogen atoms in the hydrogenphosphates of tetravalent elements and the steric hindrance to the accommodation of a second cation, the exchange process on α-phosphates usually occurs in two stages. There is therefore a possibility of the formation of two substitution products — α-$AHM(HXO_4)_2 \cdot nH_2O$ and α-$A_2M.(HXO_4)_2 \cdot nH_2O$, where A is an alkali metal cation. The formation of only the product of the complete substitution of protons has been noted for large cations. It has been shown[18, 50] for potassium, rubidium, and caesium ions that this is caused by the kinetic inhibition of the exchange process. After the substitution of the

Table 6. Degrees of hydration (n) and interlyer distances (d) in the products of ion exchange on acid phosphates with the ratio $M : XO_4 = 1 : 2$.

Initial state	H^+		Li^+		Na^+		K^+		Ref.
	n	d, Å	n	d, Å	n	d, Å	n	d, Å	
100% substitution									
α-$Ti(HPO_4)_2 \cdot H_2O$	1	7.60	1	7.6	3	9.9	3	10.4	33
α-$Zr(HPO_4)_2 \cdot H_2O$	1	7.56	1	8.50	3	9.88	3	10.70	208, 220
γ-$Ti(HPO_4)_2 \cdot 2H_2O$	2	11.62	2	11.3	2	12.8	3	14.2	33
$H_5O_2Ta(Po_4)_2$	2	9.50	2	9.08	3	10.96	1	8.89	39
50% substitution									
α-$Ti(HPO_4)_2 \cdot H_2O$	1	7.60	1	7.6	4	10.4	–	–	33
α-$Zr(HPO_4)_2 \cdot H_2O$	1	7.56	3	10.1	5	11.87	–	–	222
γ-$Ti(HPO_4)_2 \cdot 2H_2O$	2	11.62	1.5	11.3	3	13.2	0	10.8	33

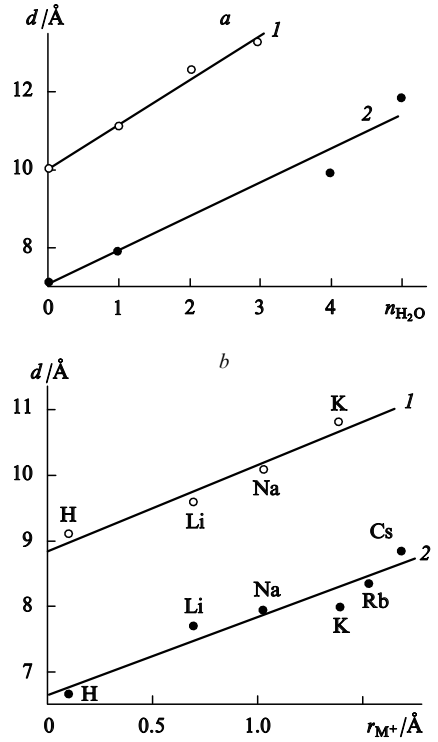


Figure 9. Dependence of the interlayer distance in the acid phosphates of tetravalent elements on the degree of hydration (*a*) and on the radius of the alkali metal cation in $AHB(PO_4)_2 \cdot nH_2O$ (*b*). (*a*) (based on the data of Llavona *et al.*[33] and Poojary and Clearfield[220]): (*1*) γ-NaHTiP; (*2*) α-NaHZrP; (*b*) (based on the data of Llavona *et al.*[33] and Scou *et al.*[222]): (*1*) γ-MHTiP; (*2*) MTaP.

first cation, the $[M(XO_4)_2]_n$ layers move apart and the insertion of a second cation between them becomes preferred to the migration of the singly substituted phase front into the bulk of the specimen. In particular, this conclusion has been confirmed by the possibility of obtaining α-$KHZr(PO_4)_2$ by other methods.[219] The removal of this limitation and the weakening of the interaction forces between the layers, for example for γ-$Zr(HPO_4)_2$, leads to the formation of two intermediate phases with degrees of substitution of 25% and 50%, in the course of the exchange.[33] In the case of tantalum hydrogenphosphate with an even weaker interaction between the layers, the solid solutions $M_xH_{1-x}Ta(PO_4)_2 \cdot nH_2O$ are formed.[39]

The proton/alkali metal cation ion-exchange processes in acid phosphates of polyvalent elements are due to the high mobility of the hydrogen ions and the incoming cations, which increases with increase in the degree of hydration and diminishes with increase in the radius and content of the alkali metal.[39, 224] The attempt to achieve the exchange of the protons of acid tin phosphate for Cu^{2+} cations showed that the ion exchange occurs only on the surface.[224] This is caused by the fact that the diffusion of doubly charged cations is kinetically hindered and that the double tin copper phosphate with a low mobility of the cations is formed on the surface. The nuclei of the new phase produced cover the conductivity channels and prevent further exchange.[224] However, it was possible to obtain the product $MgZr(PO_4)_2 \cdot 3H_2O$ by refluxing titanium hydrogenphosphate with magnesium acetate.[225] This method makes it possible to increase the diffusion coefficient by carrying out the process at an elevated temperature and by working in the region of comparatively low pH values, which are determined by the ratio of the concentrations of acetate ions and acetic acid in solution. An alternative method of synthesis of compounds with doubly and triply charged cations involves their preparation from the sodium-form of zirconium α-phosphate in accordance with the mechanism proposed by Scou *et al.*:[226]

$$\alpha\text{-}Zr(HPO_4)_2 \cdot nH_2O \xrightarrow{Na^+} \alpha\text{-}NaHZr(PO_4)_2 \cdot 5H_2O \xrightarrow{A^{z+}} \alpha\text{-}A_xH_{2-x}Zr(HPO_4)_2 \cdot nH_2O$$

Magnesium zirconium hydrogenphosphate α-$Mg_{0.5}HZr(PO_4)_2 \cdot 3H_2O$ and chromium zirconium hydrogenphosphate α-$Cr_{0.5}H_{0.5}Zr(HPO_4)_2 \cdot 5H_2O$ were thus synthesised at room temperature. The sorption of the ions $[Ru(NH_3)_6]^{2+}$ from the corresponding aqueous solution has been achieved similarly (with the intermediate formation of the ammonium analogue).[227]

The hydrated acid phosphates can be obtained from the potassium salts $K_xSb_xP_2O_{3x+5}$ by ion exchange with inorganic acids at an elevated temperature,[228] but this process is slow. The substitution of potassium in $KTa(PO_4)_2$ takes place more simply.[211] Chernorukov *et al.*[223] obtained double tantalum alkali metal phosphates by solid-phase synthesis from finely disperse tantalum hydrogenphosphate and the corresponding chlorides and hydroxides at 200–400 °C.

$$HTa(PO_4)_2 + ACl = ATa(PO_4)_2 + HCl\,.$$

The corresponding process cannot be carried out in solution owing to the hydrolysis of the tantalum hydrogenphosphate. However, the synthesis of the coarsely crystalline compound using the method proposed by Yaroslavtsev and Nikolaev[211] made it possible to achieve proton/alkali metal cation ion-exchange in aqueous solutions.[17, 39]

A multiplicity of other materials with ion-exchange and catalytic properties as well as proton conductivity have been obtained from hydrogenphosphates of polyvalent elements. Among them, mention should be made of a mixed zirconium hydrogenphosphate-arsenate[219] and numerous phosphonates and mixed phosphate-phosphites, which have been extensively investigated in recent years as promising ion exchangers with a high selectivity.[31, 230–235] The products of the intercalation of amines, alkohols, and other organic derivatives, containing functional groups and capable of forming bonds with a proton in the structure of acid zirconium phosphate, have also been studied intensely.[44, 236–245]

b. Structures of the NASICON type

Hydrogenphosphates of tetravalent elements with the ratio $M^{IV} : XO_4 = 2 : 3$ belong to the NASICON structural type. They have become widely known by virtue of the high cationic conductivity§ of a series of solid solutions $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$.[246, 247] A series of compounds $A^IB_2^{IV}(PO_4)_3$, where A^I is an alkali metal cation, while B^{IV} is the cation of a tetravalent metal, which is usually zirconium, have been synthesised. Solid-

§ Their name 'Na super-ion conductor' (NASICON) is due precisely to this property.

phase or hydrothermal synthesis as well as synthesis from the melt are normally employed.[248–255]

The joining together of BO_6 octahedra and PO_4 tetrahedra is characteristic of the NASICON type crystal structure, but, in contrast to the layered phosphates examined above, all the oxygen atoms of the anion participate in the formation of the P–O–B linkages. Channels extending along the crystallographic *c* axis are formed in the three-dimensional lattice. However, whereas 75% of the cavities remain unoccupied in $NaZr_2(PO_4)_3$,[247,249] they are all occupied in $Na_4Zr_2(SiO_4)_3$.[256,257] All the oxygen atoms in the structure described are simultaneously coordinated to quadruply and quintuply charged cations and they therefore possess comparatively weak electron-donating properties. Together with the partial occupation of the cavities, this ensures a high mobility of the cation and the possibility of the occurrence of ion-exchange reactions.

The cation exchange in the compounds $A^IB_2^{IV}(PO_4)_3$ is most often carried out by treating the initial phase with salt melts. The lithium, potassium, and silver derivatives can be obtained in this way from the sodium phase.[8,258–260] The attempts to obtain the hydrogen-form of zirconium phosphate by treating the sodium or ammonium compound with an acid under hydrothermal conditions were unsuccessful.[254] $(H_3O)B_2^{IV}(PO_4)_3$ was obtained by the interaction of $LiZr_2(PO_4)_3$ or $LiTi_2(PO_4)_3$ with an acid[7] and also as a result of the heat treatment of $NH_4Zr_2(PO_4)_3$ with subsequent maintenance of $HZr_2(PO_4)_3$ in water.[261] The substance obtained can serve in its turn as the initial basis for the synthesis of derivatives with other monovalent ions. Thus the preparation of $LiTi_xZr_{2-x}(PO_4)_3$ by ion exchange with lithium hydroxide under hydrothermal conditions has been described.[262]

In contrast to layered phosphates, the three-dimensional lattice of compounds with a NASICON type structure changes little when the cations are varied. However, there are structures of this type differing in symmetry. The assignment of a substance to a particular structural type is determined primarily by the number of singly charged cations per formula unit. The compounds $A_3^IB_2^{III}(PO_4)_3$, where B^{III} = Sc, B, or Fe,[263–266] exhibiting ion-exchange properties and cationic conductivity, have been obtained. As in the $NaZr_2(PO_4)_3$ structure, the number of singly charged cations (A^I) is found to be smaller than the number of sites available for their accommodation. Sodium and lithium ions arc then found to be statistically distributed between a pair of possible sites with nonequivalent populations, forming the so called statistical dipoles.[263,264,267]

c. Compounds based on the structure of $NbOPO_4$ and its derivatives

The oxide phosphates $BOXO_4$ (where B is, for example, V, Nb, or Mo and X = P or As) are characterised by one of the simplest types of isostructure, formed by the joining together of BO_6 octahedra and XO_4 tetrahedra. The crystal lattice of the oxyphosphates of pentavalent vanadium, niobium, and molybdenum is made up of planes of tetrahedra of phosphate anions and metal octahedra joined together by four vertices (Fig. 10 *a*).

The two remaining vertices of the octahedron are in the *trans*-position relative to one another and are combined with the analogous vertices of adjacent layers, ensuring bonding between them as a result of the formation of the –O–B–O–B–O– bridges.[268–270] The $BOXO_4$ structures are distinguished by a significant nonequivalence of the metal–oxygen bonds: one of the bonds formed is close to being a double bond, whilst the other is close to a very weak coordinate bond (Table 7).

By virtue of the features listed above, the intercalation of water molecules in compounds of this kind is possible.[278–281] This process proceeds particularly readily in vanadium oxyphosphate, the cation of which tends to form multiple bonds. Here it is assumed that, on dissociation of the –O–V–O– chain of bonds, $H_2O–V=O$ fragments are formed and the planes $(H_2VO_2PO_4)_n$ move apart in space, forming a layered structure (Fig. 10*b*).[271,272] The positions of protons and of the second water molecule in $VOPO_4 \cdot 2H_2O$ have not been determined. The formation of compounds with a higher degree of hydration is also possible. Analogous transformations under the influence of a hydrochloric acid solution occur in niobium oxide phosphate, where the metal–oxygen bonds differ less.[281] It has been established by NMR that the monohydrate and trihydrate contain two hydroxy groups, not bound to the phosphorus, per cation, (*i.e.* these substances are niobium hydroxophosphates $Nb(OH_2)PO_4$ and $Nb(OH)_2PO_4 \cdot 2H_2O$.[281]

The compounds formed may split off protons, which can migrate in the interlayer space. This follows, in particular, from the evident analogy between the structure of the hydrated oxyphosphates and uranyl phosphate — one of the best proton conductors at room temperature (1.8×10^{-3} S cm^{-1}).[274,282] The conductivity of niobium oxyphosphate trihydrate is lower almost by an order of magnitude (3×10^{-4} S cm^{-1}), probably as a consequence of the less-developed system of hydrogen bonds, while the activation energies for this process are virtually identical in the two compounds.[281] The conditions in the interlayer space are favourable for the migration of cations. Thus, conditions for ion-exchange processes are created in a series of compounds

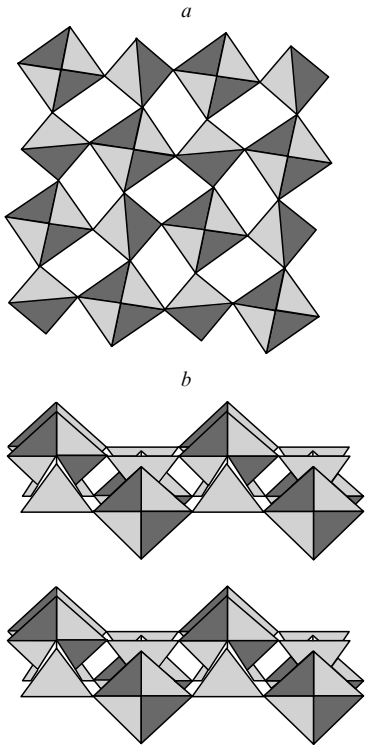


Figure 10. Fragments of the $VOPO_4$ (*a*) and $VOPO_4 \cdot 2H_2O$ (*b*) structures.

Table 7. The metal–oxygen bond lengths in certain compounds based on the $NbOPO_4$ structure.

Compound	The length of B–O bonds in octahedron /Å			Ref.
	B–O–(X)	B–O–(B)	B=O	
$NbOPO_4$	1.97	1.78	2.32	269
$MoOPO_4$	1.97	1.66	2.63	268
$VOPO_4$	1.87	1.58	2.87	270
$VOPO_4 \cdot 2H_2O$	1.92	1.43	2.49	271, 272
$NH_4(VO_2)(HPO_4)$	1.92	1.57	1.69	273
$HUO_2PO_4 \cdot 4H_2O$	2.31	1.75	1.78	274
$KMoO_2PO_4$	1.98, 2.19	1.69	1.69	275
$KTiOPO_4$	1.99	1.72	1.98	276, 277

$BOX_4 \cdot nH_2O$. $H_3OMoO_2PO_4$ and its potassium analogues have similar structures, although the metal – oxygen bonds are then in the *cis*-position in the molybdenum coordination polyhedron.[275, 283]

Hydrated vanadium and niobium oxyphosphates exhibit ion-exchange properties on interaction with solutions of alkalis, substituting one of the protons by a cation *via* the reaction [284–287]

$$H_2BO_2PO_4 \cdot nH_2O + MOH \rightleftharpoons \rightleftharpoons MHBO_2PO_4 \cdot nH_2O + H_2O,$$

where M = Li, Na, K, Rb, Cs, or NH_4.[284–287] The lengths of the metal — oxygen bonds are then significantly equalised even in the vanadium derivatives $NH_4(VO_2)(HPO_4)$ [273] and there is a simultaneous rearrangement of the structure with migration of the proton to the anion and the formation of a vanadium coordination polyhedron in the form of a square pyramid.[288] The compound $LiHBO_2PO_4$ with a high lithium conductivity has been obtained by the heat treatment (500 °C) of the products of the interaction of niobium oxyphosphate with lithium hydroxide.[287]

In uranyl phosphate, the oxygen atoms of the anion are coordinated to the metal and the remaining two participate in the formation of the uranyl ion. The 'anionic part of the framework' therefore manifests weak proton-accepting properties and the proton is transferred to the proton hydrate sub-lattice $H^+ \cdot 4H_2O$ localised in the interlayer space.[274] This is responsible for the high ionic conductivity and the distinct ion-exchange properties. Oxonium ions are readily substituted by an alkali or alkaline earth metal ion.[289] Uranyl phosphate readily sorbs cations even from dilute aqueous systems with formation of solid solutions. All the compounds formed have a fairly high ionic conductivity.[192, 291–293]

Another type of ion-exchange processes, occurring in hydrated vanadium oxyphosphate, is the reductive intercalation of hydrogen and singly or doubly charged cations with partial reduction of vanadium *via* the reaction [278, 293–298]

$$VOPO_4 \cdot nH_2O + xM^{y+} + xye^- \rightleftharpoons M_xVOPO_4 \cdot nH_2O\,.$$

An intermediate degree of oxidation of vanadium in the range $4 < z < 5$ was most frequently attained, but in the case of the reductive intercalation of lithium and hydrogen the limiting case with x = 1 occurred. The compounds $AVOPO_4 \cdot nH_2O$ can then be considered as the reduction products.[298] These substances may give rise to several crystal structures, differing in the type of binding of the octahedra and in the number of molecules of the water of hydration. A characteristic feature of these substances is the presence of the vanadyl ion with a shortened metal – oxygen distance ($\sim$1.5 Å). Three sites in the equatorial plane are occupied by the oxygen atoms of the anion and one site is occupied by the oxygen of water or the vanadyl ion ($R_{V-O} \approx 2.0$ Å). Weakly coordinated water molecules or the oxygen of a neighbouring vanadyl cation ($R_{V-O} \approx 2.3$ Å) are located in the *trans*-position relative to the oxygen of the V = O group.[298–301]

In compounds of the type $VOHPO_4 \cdot nH_2O$ the hydrogen phosphate anions are highly polarised and may dissociate with elimination of the proton. The substance formed on substitution of such a proton by an alkali metal cation retains the ability to exchange the latter for other cations (Na^+, K^+, Rb^+, NH_4^+, Ag^+, Tl^+).[303–306] The substitution products $AVOPO_4$ are constructed from distorted VO_6 octahedra, combined into chains *via* a pair of common vertices, and from PO_4 tetrahedra bound to them.[306] Such compounds belong to the $KTiOPO_4$ structural type characterised by the presence of channels along the crystallographic *c* axis,[276, 277] which are responsible for the ionic mobility and the ion-exchange properties.[265]

V. Conclusion

The data presented in the review show that inorganic sorbents are promising materials for the separation and extensive purification of various ions, including alkali metal cations, which are difficult to separate by other methods. Such ion exchangers are characterised by a high radiation stability and by the ability to sorb heavy metal cations. They are therefore actively employed in the atomic industry. The ability to extract selectively a series of cations from a large number of competing ions of the main substance is quite important. Inorganic sorbents are widely employed for the creation of different kinds of materials with an extensive specific surface, catalytic properties, and ionic conductivity. Furthermore, with the aid of ion exchange it is possible to obtain a series of substances, the synthesis of which by other methods is impossible owing to the thermodynamic instability of the initial compounds or the kinetic inhibition of their reactions.[81] All this provides grounds for the hypothesis that the use of inorganic sorbents will expand.

We believe that the employment of ion-exchange processes as model reactions for the comprehensive study of the thermodynamic and kinetic characteristics of certain phenomena occurring in solids (for example, the diffusion of ions, solid-phase reactions, *etc*.) is also promising. The possibility of selecting substances with different sizes of cavities, conductivity channels, and interplanar spacings makes it possible to trace in detail the influence of these parameters on the dynamics of the processes considered and to investigate the dependence of the affinity of the structure for particular ions on the geometry and nature of their potential environment, rigidly specified by the structure of the ion-exchange matrix. The simplicity and high accuracy whereby the changes in the concentrations of the reactants in solution may be monitored permit the modelling of many processes in solids.

This review has been written with the support of the Russian Fundamental Research Fund (project No. 97-03-33736).

References

1. H S Thompson *J. R. Agric. Soc., Engl.* **11** 68 (1850)
2. J F Way *J. R. Agric. Soc., Engl.* **11** 313 (1850)
3. R Gans *Jahrb. Preuss. Geol. Landesanstalf (Berlin)* **26** 179 (1905)
4. B A Adams, E L Holmes *J. Soc. Chem. Ind., London* **54** 1 (1935)
5. A Clearfield, J A Stynes *J. Inorg. Nucl. Chem.* **26** 117 (1964)
6. C B Amphlett *Inorganic Ion Exchangers* (Amsterdam: Elsevier, 1964)
7. A Clearfield (Ed.) *Inorganic Ion Exchange Materials* (Boca Ration, FL: CRC Press, 1982)
8. A Clearfield *Chem. Rev.* **88** 125 (1988)
9. G Alberti, U Costantino, S Allulli, A Massucci *J. Inorg. Nucl. Chem.* **37** 1779 (1975)
10. W T Reichle *Chemtech* 58 (1986)
11. I C Chisem, W Jones *J. Mater. Chem.* **4** 1737 (1994)
12. K A Kraus, H O Phillips, T A Carlson, J S Johnson, in *Proceedings of the IIth International Conference on Peaceful Uses of Atomic Energy* (Geneva: United Nations, 1958) p. 28
13. S Ahrland, I Grenthe, B Noren *Acta Chem. Scand.* **14** 1059 (1960)
14. G L Gaines, H C Thomas *J. Chem. Phys.* **21** 714 (1953)
15. C G Guarido, M Suarez, J R Garcia, J Rodriges *J. Chem. Soc., Dalton. Trans.* 1865 (1985)
16. L H Kullberg, A Clearfield *Solv. Ion Exch.* **8** 187 (1990)
17. A B Yaroslavtsev, A E Nikolaev, V A Tarnopolsky *Mendeleev Commun.* 56 (1996)
18. A B Yaroslavtsev, A A Khrulev *Zh. Neorg. Khim.* **42** 553 (1997) [a]
19. A Clearfield *Mater. Chem. Phys.* **351** 257 (1993)
20. A V Erin, Z N Prozorovskaya, A B Yaroslavtsev *Zh. Neorg. Khim.* **38** 200 (1993) [a]
21. C N Merriam, H C Thomas *J. Chem. Phys.* **24** 993 (1956)
22. G L Gaines, H C Thomas *J. Chem. Phys.* **23** 2322 (1955)
23. GR Frysiner, H C Thomas *J. Phys. Chem.* **64** 224 (1960)
24. R M Barrer, D C Sammon *J. Chem. Soc.* 2838 (1955)
25. C Constantopouiou, M Loizidou, Z Loizidou, N Spyrellis *J. Radioanal. Nucl. Chem. Artic.* **178** 143 (1994)
26. J R Smit, J J Jacobs, W J Robb *J. Inorg. Nucl. Chem.* **12** 95 (1959)
27. E M Larsen, D R Vissars *J. Phys. Chem.* **64** 1732 (1960)
28. L Kullberg, A Clearfield *J. Phys. Chem.* **85** 1578 (1981)
29. L Baetsle *J. Inorg. Nucl. Chem.* **25** 271 (1963)

30. C B Amphlett, P Eaton, L A McDonald, A J Miller *J. Inorg. Nucl. Chem.* **26** 297 (1964)
31. L H Kullberg, A Clearfield *Solv. Extr. Ion Exch.* **8** 195 (1990)
32. C G Guarido, M Suarez, J R Garcia, R Llavona, J Rodriguez *J. Chem. Thermodyn.* **17** 63 (1985)
33. R Llavona, M Suarez, J R Garcia, J Rodriguez *Inorg. Chem.* **28** 2863 (1989)
34. E Gonzalez, R Llavona, J R Garcia, J Rodrigez *J. Chem. Soc., Dalton. Trans.* 829 (1989)
35. E Gonzalez, R Llavona, J R Garcia, J Rodrigez *J. Chem. Soc., Dalton. Trans.* 1825 (1989)
36. C Alvarez, R Llavona, J R Garcia, M Suarez, J Rodrigez *J. Chem. Soc., Dalton. Trans.* 2045 (1987)
37. G I Smirnov, A S Chernyak, O N Kostromina *Zh. Prikl. Khim.* **62** 2202 (1989) [b]
38. E D Larsen, W A Cilley *J. Inorg. Nucl. Chem.* **30** 287 (1968)
39. A B Yaroslavtsev, V A Tarnopol'skii *Zh. Neorg. Khim.* **42** 548 (1997) [a]
40. G Eisenman *Biophys. J., Suppl.* **2** 259 (1962)
41. F Helfferich *Ionenaustauscher. Grundlagen Struktur. Herstellung. Theorie* Vol. 1 (Weinheim: Verlag Chemie, 1959)
42. W K Warburton, D Turnbull *Diffusion in Solids* (Amsterdam: North-Holland, 1975)
43. H van Olphen *An Introduction to Clay Colloid Chemistry* Ch. 1 (New York: Wiley, 1976)
44. G Alberti, M Casciola, U Constantino *J. Colloid Interface Sci.* **107** 256 (1985)
45. G Alberti, M Casciola, U Constantino, F di Gregorio *Solid State Ion.* **32/33** 44 (1989)
46. J V Smith *Chem. Rev.* **88** 149 (1988)
47. R D Shannon *Acta Crystallogr., Sect. A* **32** 751 (1976)
48. V B Kalinin, S Yu Stefanovich, in *Khimiya Tverdogo Tela, T. 8 (Ser. Itogi Nauki i Tekhniki)* [The Chemistry of the Solid State (Advances in Science and Engineering Series) Vol. 8] (Moscow: Izd. VINITI, 1992) p. 131
49. R I Smith, A R West *J. Mater. Chem.* **1** 91 (1991)
50. G Alberti, U Constantino, J P Gupta *J. Inorg. Nucl. Chem.* **36** 2109 (1974)
51. J M Troup, A Clearfield *Inorg. Chem.* **16** 3311 (1977)
52. R M Barrer *Diffusion in and through Solids* (Cambridge: Cambridge University Press, 1941) p. 29.
53. G E Boyd, A W Adamson, L S Myers *J. Am. Chem. Soc.* **69** 2836 (1947)
54. R M Barrer, J Falconer *Proc. R. Soc., London A* **236** 227 (1956)
55. R M Barrer *Proc. Chem. Soc.* 99 (1958)
56. R M Barrer, L Hings *J. Chem. Soc.* 1879 (1953)
57. G Alberti, G Bernasconi, M Casciola, U Constantino *Ann. Chim. (Rome)* **68** 1779 (1978)
58. A B Yaroslavtsev, I A Stenina *Zh. Neorg. Khim.* **42** (1997) (in the press) [a]
59. A B Yaroslavtsev, E M Yaroslavtseva, V F Chuvaev *Zh. Neorg. Khim.* **39** 951 (1994) [a]
60. W A England, J B Goodenough, P J Wiseman *J. Solid State Chem.* **49** 289 (1983)
61. L Sylvia, G H Nancolas *J. Inorg. Nucl. Chem.* **30** 273 (1968)
62. Y-F Y Yao, J T Kummer *J. Inorg. Nucl. Chem.* **29** 2453 (1967)
63. R Harjula, J Lehto, E H Tusa, A Paavola *Nucl. Technol.* **107** 272 (1994)
64. T C Watling, L V C Rees *Zeolites* **14** 687 (1994)
65. R M Barrer *Chem. Ind.* 1258 (1962)
66. R P Townsend, in *New Developments in Zeolite Science and Technology* (Tokyo: Kodansha, 1986) p. 273
67. M Lal, C M Johnson, A T Howe *Solid State Ion.* **5** 451 (1981)
68. K-D Kreuer, W Weppner, A Rabenau *Mater. Res. Bull.* **17** 501 (1982)
69. K J Balkus, A G Gabrielov, S L Bell, F Bedioui, L Roue, J Devynck *Inorg. Chem.* **33** 67 (1994)
70. P K Sinha, R V Amalraj, V Krishnasamy *Radiochim. Acta* **65** 125 (1994)
71. M T Olguin, M Soache, M Asomoza, D Acosta, P Bosch, P Bulbulian *Sep. Sci. Technol.* **29** 2161 (1994)
72. E Malliou, M Loizidou, N Spyrellis *Sci. Total Environ.* **149** 139 (1994)
73. K H Lieser *Radiochim. Acta* **70** 355 (1995)
74. J O Petunchi, W K Hall *Appl. Catal. B, Environ.* **3** 239 (1994)
75. Y J Li, J N Armor *Appl. Catal. B, Environ.* **4** 275 (1994)
76. Y F Chang, J G Mccarty, E D Wachsman, V L Wong *Appl. Catal. B, Environ.* **4** 283 (1994)
77. G Moretti *Catal. Lett.* **28** 143 (1994)
78. L X Dai, H Sakashita, T Tatsumi *Bull. Chem. Soc. Jpn.* **67** 1553 (1994)
79. H Sato, S Shimizu, N Abe, K Hirose *Chem. Lett.* 59 (1994)
80. V I Kanazirev, G L Price, K M Dooley *J. Catal.* **148** 164 (1994)
81. K Ebitani, M Morokuma, J H Kim, A Morikawa *J. Chem. Soc., Farad. Trans.* **90** 377 (1994)
82. W Grunert, N W Hayes, R W Joyner, E S Shapiro, M R H Siddiqui, G N Baeva *J. Phys. Chem.* **98** 10832 (1994)
83. J C Warn, M Gaffari, S Choi *J. Chem. Phys.* **63** 772 (1975)
84. G C Farrington, J L Briant *Mater. Res. Bull.* **13** 763 (1978)
85. J O Thomas, G C Farrington *Acta Crystallogr., Sect. B* **39** 227 (1983)
86. C R Peters, M Bettman, W Moore, M D Glick *Acta Crystallogr., Sect. B* **27** 1826 (1971)
87. J P Boilot, Ph Colomban, G Collin, R Comes *J. Phys. Chem. Solids* **41** 47 (1981)
88. J M Newsam, B C Tolfield *J. Phys. Chem., Solid State Phys.* **14** 1545 (1981)
89. J O Thomas, K J Frase, G C McIntyre, G C Farrington *Solid State Ion.* **9/10** 1029 (1983)
90. J O Thomas, G C McIntyre, J De Nuzzio *Solid State Ion.* **18/19** 642 (1986)
91. H Ikawa, T Tsurumi, M Ishimori, K Urabe, S Udagawa *J. Solid State Chem.* **60** 51 (1985)
92. T Tsurumi, H Ikawa, T Nishimura, K Urabe, S Udagawa *Solid State Ion.* **71** 154 (1987)
93. N Iyi, Y Yajima, S Kimura *J. Solid State Chem.* **92** 578 (1991).
94. A B Yaroslavtsev *Svoistva Tverdykh Tel Glazami Khimika* (The Chemist's View of the Properties of Solids) (Moscow: Moscow Aviation Institute, 1995)
95. P G Bruce, I Abrahams *J. Solid State Chem.* **95** 74 (1991).
96. N Baffier, J C Badot, Ph Colomban *Solid State Ion.* **13** 233 (1984)
97. S W Smoot, D H Whitmore, W P Halperin *Solid State Ion.* **18/19** 687 (1986)
98. T Tsurumi, H Ikawa, K Urabe, T Nishimura, T Oohashi, S Udagawa *Solid State Ion.* **25** 143 (1987)
99. J D DeNuzzio, G C Farrington *J. Solid State Chem.* **79** 65 (1989)
100. K Uchinokura, S Nariki, S Ito, N Yoneda *Solid State Ion.* **35** 207 (1989)
101. N A Toropov, M M Stuklova *Dokl. Akad. Nauk SSSR* **24** 459 (1939) [c]
102. L M Foster, M P Anderson, G V Chandrashekhar, G Burns, R B Bradford *J. Chem. Phys.* **75** 2412 (1981)
103. Ph Colomban, A Novak *Solid State Ion.* **5** 241 (1981)
104. H Ikawa, T Tsurumi, K Urabe, S Udagawa *Solid State Ion.* **20** 1 (1986)
105. T Tsurumi, H Ikawa, M Ishimori, K Urabe, S Udagawa *Solid State Ion.* **21** 31 (1986)
106. P Lenfant, D Plas, M Ruffo, Ph Colomban *Mater. Res. Bull.* **15** 1817 (1980)
107. K G Frase, G C Farrington, J O Thomas *Annu. Rev. Mater. Sci.* **14** 279 (1984)
108. M W Breiter, G C Farrington, W L Roth, J L Duffy *Mater. Res. Bull.* **12** 895 (1977)
109. Ph Colomban, G Lucazeau, R Mercier, A Novak *J. Chem. Phys.* **11** 5244 (1977)
110. Y Sheng, B Cobbledick, P S Nicholson *Solid State Ion.* **27** 233 (1988)
111. J M Newsam, A K Cheetman, C Tofield *J. Solid State Chem.* **60** 214 (1985)
112. F Rocca, A Kuzmin, J Purans, G Mariotto *Solid State Ion.* **70** 465 (1994)
113. F Rocca, A Kuzmin, J Purans, G Mariotto *Phys. Rev. B, Condens. Mater* **50** 6662 (1994)
114. G Mariotto, F Tietz, E Zanghellini, M Ferrari *J. Phys. IV, Collog.* **4** 474 (1994)
115. M Wolf, J O Thomas *J. Mater. Chem.* **4** 839 (1994)
116. T Dedecke, J Kohler, F Tietz, W Urland *Eur. J. Solid State Inorg. Chem.* **33** 185 (1996)
117. W Rudorff, H Becker *Z. Naturforsch. B, Chem. Sci.* **9** 614 (1954)
118. R D Shannon, B D Rogers, C T Prewitt *Inorg. Chem.* **10** 713 (1971)
119. E Thilo, W Geissner *Z. Anorg. Chem.* **345** 151 (1966)
120. W Geissner *Z. Anorg. Chem.* **352** 145 (1967)
121. S Andersson, A D Wadsley *Acta Crystallogr.* **14** 1245 (1961)
122. S Andersson, A D Wadsley *Acta Crystallogr.* **15** 194 (1962)
123. A D Wadsley, W G Mumme *Acta Crystallogr., Sect. B* **24** 392 (1968)
124. E K Beloev, N Sh Saifulin, N M Panasenko *Izv. Akad. Nauk SSSR, Neorg. Mater.* **4** 917 (1968) [d]
125. R Olazcuaga, J-M Reau, M Devalette, G Le Flem, P Hagenmuller *J. Solid State Chem.* **13** 275 (1975)

126. M Dion, Y Piffard, M Tournoux *J. Inorg. Nucl. Chem.* **40** 917 (1978)
127. M Watanabe, Y Bando, M Tsutsumi *J. Solid State Chem.* **28** 392 (1979)
128. R Marchand, L Brohan, R M'Bedi, M Tournoux *Mater. Res. Bull.* **15** 1129 (1980)
129. H Izawa, S Kikkawa, M Koizumi *J. Phys. Chem.* **86** 5023 (1982)
130. R Werthmann, R Z Hoppe *Anorg. Allg. Chem.* **519** 117 (1984)
131. J Lehto, A Clearfield *Radioanal. Chem.* **118** 1 (1987)
132. J C Joubert, A Durif *Bull. Soc. Fr. Miner. Cristallogr.* **87** 517 (1964)
133. T Sasaki, M Watanabe, Y Fujiki, Y Kitami *Chem. Mater.* **6** 1749 (1994).
134. U Chowdhry, J R Barkley, A D English, A W Sleight *Mater. Res. Bull.* **17** 917 (1982)
135. M A Subramanian, G Aravamudan, G V Subba Rao *Prog. Solid. State Chem.* **15** 55 (1983)
136. W A England, M G Cross, A Hamnett, P J Waiseman, J B Goodenough *Solid State Ion.* **1** 231 (1980)
137. L H Baetsle, D Huysn *J. Inorg. Nucl. Chem.* **30** 639 (1968)
138. J D Donaldson, M J Fuller *J. Inorg. Nucl. Chem.* **30** 1083 (1968)
139. M Abe *J. Inorg. Nucl. Chem.* **41** 85 (1979)
140. D Groult, C Michel, B Raveau *J. Inorg. Nucl. Chem.* **30** 61 (1968)
141. C E Rice, J L Jackel *J. Solid State Chem.* **41** 308 (1982)
142. C E Rice, J L Jackel *Mater. Res. Bull.* **19** 591 (1984)
143. C E Rice *J. Solid State Chem.* **64** 188 (1986)
144. V A Ganshin, I N Korkishko, T V Morozova, V A Fedorov *Zh. Tekh. Fiz.* **63** 166 (1993)
145. G R Pazpujalt, D D Tuschel, G Braunstein, T Blanton, S T Lee, L M Salter *J. Appl. Phys.* **76** 3981 (1994)
146. Y Piffard, M Dion, M Tournoux *C. R. Hebd. Seances Acad. Sci., Ser. C* **290** 437 (1980)
147. A D Wadsley *Acta Crystallogr.* **17** 623 (1964)
148. H Rebbah, G Desgardin, B Raveau *Mater. Res. Bull.* **14** 1125 (1979)
149. M Hervieu, B Raveau *J. Solid State Chem.* **32** 161 (1980)
150. M Hervieu, H Rebbah, G Desgardin, B Raveau *J. Solid State Chem.* **35** 200 (1980)
151. H Rebbah, G Desgardin, B Raveau *J. Solid State Chem.* **31** 321 (1980)
152. B Raveau *Rev. Chim. Miner.* **21** 391 (1984)
153. K Domen, Y Ebina, J Kondo *Res. Chem. Intermediates* **20** 895 (1994)
154. D Groult, C Mercey, B Raveau *J. Solid State Chem.* **32** 289 (1980)
155. W A England, J E Birkett, J B Goodenouch, P J Wiseman *J. Solid State Chem.* **49** 300 (1983)
156. M Dion, M Ganne, M Tournoux *Mater. Res. Bull.* **16** 1429 (1981)
157. A J Jacobsen, J W Johnson, J T Lewandoski *Inorg. Chem.* **24** 3727 (1985)
158. M Dion, M Ganne, M Tournoux *Rev. Chim. Miner.* **23** 61 (1986)
159. J Gopalakrishnan, B Vasudeva *Mater. Res. Bull.* **22** 413 (1987)
160. R A Ram, A Clearfield *J. Solid State Chem.* **112** 288 (1994)
161. T Matsuda, T Fujita, N Miyamae, M Takeuchi, I Kunou *J. Matter. Chem.* **4** 955 (1994)
162. V Thangadurai, A K Shukla, J Gopalakrishnan *Solid State Ion.* **73** 9 (1994)
163. B M Gatehouse *J. Solid State Chem.* **22** 404 (1977)
164. C Michel, A Guyomarc h, B Raveau *J. Solid State Chem.* **25** 251 (1978)
165. C M Mari, F Bonino, R Catti, R Pasinetti, S Pizzini *Solid State Ion.* **18/19** 1013 (1986)
166. B Ghosh *J. Chem. Soc.* 2605 (1926)
167. R S Johnson, W C Vosburgh *J. Electrochem. Soc.* **99** 317 (1952)
168. G V Leont'eva, V V Volkhin *Izv. Akad. Nauk SSSR, Neorgan. Mater.* **4** 728 (1968) [d]
169. G V Leont'eva, V V Volkhin *Izv. Akad. Nauk SSSR, Neorgan. Mater.* **5** 1224 (1969) [d]
170. A F Wells *Structural Inorganic Chemistry* (Oxford: Clarendon Press, 1986)
171. H Tagaya, K Ara, J Kadokawa, M Karasu, K Chiba *J. Mater. Chem.* **4** 551 (1994)
172. J Gopalakrishnan, N S P Bhuvanesh, A R Raju *Chem. Mater.* **6** 373 (1994)
173. A R Armstrong, P A Anderson *Inorg. Chem.* **33** 4366 (1994)
174. A Clearfield *Inorg.Chem.* **3** 146 (1964)
175. J Hietala, A Root, P Knuuttila *J. Catal.* **150** 46 (1994)
176. M A Lure, I Z Kurets, S M Krasnopolskaya, S A Reznikov, A F Babikov, F K Shmidt *Kinet. Catal.* **35** 405 (1994)
177. E J Duwell, J W Shepard *J. Phys. Chem.* **63** 2044 (1959)
178. A I Mun, Z N Prozorovskaya, A B Yaroslavtsev, V V Parshutkin, L G Gurvich *Zh. Neorg. Khim.* **29** 2780 (1984) [a]
179. V V Parshutkin, Z N Prozorovskaya, A B Yaroslavtsev *Zh. Neorg. Khim.* **32** 998 (1987) [a]
180. L Znaidi, N Baffier, D Lemordant *Solid State Ion.* **28/30** 1750 (1988)
181. R C T Slade, M G Cross, W A England *Solid State Ion.* **6** 225 (1982)
182. V V Parshutkin, A B Yaroslavtsev, Z N Prozorovskaya, A I Mun *Zh. Neorg. Khim.* **30** 56 (1985) [a]
183. Ph Colomban, C Doremieux-Morin, Y Piffard, M H Limage A Novak *J. Mol. Struct.* **213** 83 (1989)
184. D J Dzimitrowicz, J B Goodenough, P J Wiseman *Mater. Res. Bull.* **17** 971 (1982)
185. R C T Slade, J Barker, T K Halstead *Solid State Ion.* **24** 147 (1987).
186. Ph Barboux, N Baffier, R Morineau, J Livage *Solid State Ion.* **9/10** 1073 (1983)
187. J Connard, H Estrade-Szwarkopf, A J Dianoux, C Poinsignon *J. Phys. (Paris)* **45** 1361 (1984)
188. X Turillas, G Delabouglisse, J C Joubert, T Fournier, H Muller *Solid State Ion.* **17** 169 (1985)
189. L O Atovmyan, L I Erofeev, A I Korosteleva, L S Leonova, V P Tarasov, E A Ukshe, V G Shteinberg *Khim. Fiz.* **3** 1518 (1984) [e]
190. O Nakamura, T Kodama, I Ogino, Y Miyake *Chem. Lett.* 17 (1979)
191. O Nakamura, I Ogino, T Kodama *Solid State Ion.* **3/4** 347 (1981)
192. K-D Kreuer *J. Mol. Struct.* **177** 265 (1988)
193. V F Chuvaev, A B Yaroslavtsev, E M Yaroslavtseva, E Kh Oniani *Zh. Neorg. Khim.* **36** 2101 (1991) [a]
194. E M Mikhail, H F Ghoneimy, N Z Misak *Solid State Ion.* **82** 75 (1995)
195. A B Yaroslavtsev, E M Yaroslavtseva, V F Chuvaev *Zh. Neorg. Khim.* **39** 948 (1994) [a]
196. A B Yaroslavtsev, E M Yaroslavtseva, V F Chuvaev *Zh. Neorg. Khim.* **35** 2769 (1990) [a]
197. E A Ukshe, L S Leonova, A I Korosteleva *Solid State Ion.* **3/4** 219 (1989)
198. M-R Noe-Spirlet, G M Brown, W Z Busing, H A Levy *Acta Crystallogr., Sect. B* **33** 1038 (1977)
199. D W Scaeffer *Science* **243** 1023 (1989)
200. E R Russel, A W Adamson, J Schubert, G E Boyd *U.S.A.E. Commun., Report CN-508* (1943); quoted after 6
201. J Albertsson, A Oskarsson, R Tellgren, J O Tomas *J. Phys. Chem.* **81** 1574 (1977).
202. A B Yaroslavtsev, D L Gorbachev *Mendeleev Commun.* 46 (1995)
203. A Norlund Christensen, E Krogh Andersen, I G Krogh Andersen, G Alberti, M Nielsen, M S Lehmann *Acta Chem. Scand.* **44** 865 (1990)
204. I Nakai, K Imai, T Kawashima, K Ohsumi, F Izumi, I Tomita *Anal. Sci.* **6** 689 (1990)
205. M I Zhuk, N G Chernorukov, I A Korshunov, G F Sibrina *Zh. Neorg. Khim.* **29** 2253 (1984) [a]
206. G Schuck, R Melzer, R Sonntag, R E Lechner, A Bohn, K Langer, M Casciola *Solid State Ion.* **77** 55 (1995)
207. A B Yaroslavtsev, Z N Prozorovskaya, V F Chuvaev, V V Parshutkin, G G Shifanova *Zh. Neorg. Khim.* **34** 1188 (1989) [a]
208. G Alberti, U Costantino, M Luciani, M L Giovagnotti *J. Inorg. Nucl. Chem.* **41** 643 (1979)
209. V P Titov, S V Yakubovskaya, R Ya Mel'nikova, Yu G Zonov, N A Akulich *Zh. Neorg. Khim.* **33** 563 (1988) [a]
210. S Yamanaka, M Tanaka *J. Inorg. Nucl. Chem.* **41** 45 (1979)
211. A B Yaroslavtsev, A E Nikolaev *Mendeleev Commun.* 136 (1995)
212. A B Yaroslavtsev, A E Nikolaev, R Zonntag, V F Chuvaev *Zh. Neorg. Khim.* **42** 29 (1997) [a]
213. G Alberti, U Costantino, R Millini, G Perego, R Vivani *J. Solid State Chem.* **113** 289 (1994)
214. N J Clayden *J. Chem. Soc., Dalton Trans.* 1877 (1987)
215. S Oyetola, A Verbaere, Y Piffard, M Tournoux *Eur. J. Solid State Inorg. Chem.* **25** 259 (1988)
216. V P Nikolaev, G G Sadikov, A V Lavrov, M A Porai-Koshits *Izv. Akad. Nauk SSSR, Neorgan. Mater.* **19** 972 (1983) [d]
217. Y Piffard, S Oyetola, S Courant, A Lachgar *J. Solid State Chem.* **60** 209 (1985)
218. V P Nikolaev, G G Sadikov, A V Lavrov, M A Porai-Koshits *Izv. Akad. Nauk SSSR, Neorgan. Mater.* **22** 1369 (1986) [d]
219. P R Rudolf, A Clearfield *Inorg. Chem.* **24** 3714 (1985)
220. D M Poojary, A Clearfield *Inorg. Chem.* **33** 3685 (1994)
221. A Clearfield, J M Troup *J. Phys. Chem.* **18** 243 (1973)
222. E Scou, I G Krogh Andersen, E Krogh Andersen, M Casciola, F Guerrini *Solid State Ion.* **35** 59 (1989)

223. N G Chernorukov, T V Sharova, A I Kryukova, I A Korshunov *Zh. Neorg. Khim.* **30** 1177 (1985) [a]
224. A B Yaroslavtsev, Z N Prozorovskaya, V F Chuvaev *Zh. Neorg. Khim.* **35** 1379 (1990) [a]
225. V P Titov, L V Kul'bitskaya, Yu G Zonov *Zh. Neorg. Khim.* **33** 67 (1988) [a]
226. E Scou, R Palombari, F Guerrini, M Casciola *Solid State Ion.* **46** 129 (1991)
227. M J Hudson, A D Workman *J. Mater. Chem.* **4** 1337 (1994)
228. S Deniard-Courant, Y Piffard, P Barboux, J Livage *Solid State Ion.* **27** 189 (1988)
229. M L Berardelli, P Galli, A La Ginestra, M A Massucci, K G Varshnelly *J. Chem. Soc., Dalton Trans.* 1737 (1985)
230. A Clearfield, G D Smith *Inorg. Chem.* **8** 431 (1969)
231. G Alberti, U Costantino, S Allulli, N Tomassini *J. Inorg. Nucl. Chem.* **40** 1113 (1978)
232. G Alberti, U Costantino, M Casciola, R Vivani, A Peraio *Solid State Ion.* **46** 61 (1991)
233. G Alberti, M Casciola, R Palombari, A Peraio *Solid State Ion.* **58** 339 (1992)
234. G Alberti, M Casciola, U Costantino, A Peraio, E Montoneri *Solid State Ion.* **50** 315 (1992)
235. M E Thompson *Chem. Mater.* **6** 1168 (1994)
236. U Costantino *J. Chem. Soc., Dalton Trans.* 402 (1979)
237. J P Gupta, D V Nowell *J. Chem. Soc., Dalton Trans.* 1178 (1979)
238. R M Tindwa, D K Ellis, G Z Peng, A Clearfield *J. Chem. Soc., Faraday Trans. 1* **81** 545 (1985)
239. T Kijima, Y Matsui *Nature (London)* **322** 533 (1986)
240. M Casciola, U Costantino, L Di Croce, F Marmottini *J. Inc. Phenom.* **6** 291 (1988)
241. A Clearfield, B D Roberts *Inorg. Chem.* **27** 3237 (1988)
242. M Casciola, U Costantino, F Marmottini *Solid State Ion.* **35** 67 (1989)
243. M Casciola, S Chieli, U Costantino, A Peraio *Solid State Ion.* **46** 53 (1991)
244. M Casciola, U Costantino, A Caevi *Solid State Ion.* **61** 245 (1993)
245. U Costantino, F Marmottini, M Curini, O Rosati *Catal. Lett.* **22** 333 (1993)
246. H Y-P Hong *Mater. Res. Bull.* **11** 173 (1976)
247. C Delmas, J-C Viala, R Olazcuaga, G LeFlem, P Hagenmuller, F Cheraoui, R Brochu *Solid State Ion.* **3/4** 209 (1981)
248. B Malkovic, B Prodic, M Sljukic *Bull. Soc. Chim. Fr.* 1777 (1968)
249. L Hagman, P Kierkegaard *Acta Chem. Scand.* **22** 1822 (1968)
250. A Clearfield, S P Pack *J. Inorg. Nucl. Chem.* **37** 1283 (1975)
251. B E Taylor, A D English, T Berzins *Mater. Res. Bull.* **12** 171 (1977)
252. N G Chernorukov, I A Korshunov, T V Prokof'eva *Fiz. Kristallogr.* **23** 475 (1978)
253. R J Cava, E M Vogel, D W Johnson *J. Am. Ceram. Soc.* **65** C157 (1982)
254. A Clearfield, B D Roberts, M A Subramanian *Mater. Res. Bull.* **19** 219 (1984)
255. A Ono *J. Mater. Sci. Lett.* 936 (1985)
256. R L Sizova, V A Blinov, A A Voronkov, V V Il'yukhin, N V Belov *Fiz. Kristallogr.* **26** 165 (1981)
257. F Genet, M Barj *Solid State Ion.* **9/10** 891 (1983)
258. H Y-P Hong *Mater. Res. Bull.* **13** 117 (1978)
259. M Nagai, T Nishino, T Kanazava *Solid State Ion.* **18/19** 964 (1986)
260. A Ono *J. Mater. Sci.* **19** 2691 (1984)
261. M A Subramanian, B D Roberts, A Clearfield *Mater. Res. Bull.* **19** 1471 (1984)
262. M Casciola, U Costantino, I G Krogh Andersen, E Krogh Andersen *Solid State Ion.* **37** 281 (1990)
263. G Collin, R Comes, J P Boilot, Ph Colomban *J. Phys. Chem. Solids* **47** 843 (1986)
264. V V Tkachev, V I Ponomarev, L O Atovmyan *Zh. Strukt. Khim.* **25** 128 (1984) [f]
265. J Gopalakrishnan, S Uma, K K Rangan, N S P Bhuvanesh *Proc. Indian Acad. Sci., Chem. Sci.* **106** 609 (1994)
266. A Orliukas, R Vaitkus, A Kezionis, S Aukselis *Solid State Ion.* **40/41** 158 (1990)
267. V B Kalinin, A M Golubev *Kristallografiya* **37** 151 (1992) [g]
268. P Kierkegaard, M Westerlund *Acta Chem. Scand.* **18** 2217 (1964)
269. J Longo, P Kierkegaard *Acta Chem. Scand.* **20** 72 (1966)
270. B Jordan, C Calvo *Can. J. Chem.* **51** 2621 (1973)
271. H R Tietze *Austral. J. Chem.* **34** 2035 (1981)
272. M Tachez, F Theobald, J Bernard, A W Hewat *Rev. Chim. Miner.* **19** 291 (1982)
273. P Amoros, D Beltran-Porter, A Le Bail, G Ferey, G Villeneuve *Eur. J. Solid State Inorg. Chem.* **25** 599 (1988)
274. B Mrosin *Acta Crystallogr., Sect. B* **34** 3732 (1978)
275. R Peascoe, A Clearfield *J. Solid State Chem.* **95** 83 (1991)
276. I V Voloshina, R G Gerr, M Yu Antipin, V G Tsirel'son, N I Pavlova, Yu T Struchkov, R P Ozerov, I S Rez *Kristallografiya* **30** 668 (1985) [f]
277. N K Hansen, J Protas, G Marnier *Acta Crystallogr., Sect. B* **47** 660 (1991)
278. K Benke, G Lagafy *Inorg. Chem.* **22** 1503 (1983)
279. N Casan, P Amoros, R Ibanez, E Martinez, D Beltran *J. Inc. Phenom.* **6** 193 (1988)
280. D Beltran-Porter, A Beltran-Porter, P Amoros, R Ibanez, E Martinez, A Le Bail, G Ferey, G Villeneuve *Eur. J. Solid State Inorg. Chem.* **28** 131 (1991)
281. A B Yaroslavtsev, A E Nikolaev, V F Chuvaev *Zh. Neorg. Khim.* **41** 1255 (1996) [a]
282. L V Kobets, V A Filimonov *Izv. Akad. Nauk SSSR, Neorgan. Mater.* **24** 1327 (1988) [d]
283. M T Weller, R G Bell *Acta Crystallogr., Sect. C* **44** 1516 (1988)
284. F Preuss, H Schug *Z. Naturforsch., B, Chem. Sci.* **30** 334 (1975)
285. S Pulvin, E Bordes, M Ronis, P Courtine *J. Chem. Res. (S)* 29 (1981)
286. S Pulvin, E Bordes, M Ronis, P Courtine *J. Chem. Res. (S)* 362 (1981)
287. S Bruque, M M Lara, L Moreno, T Ramirezcardenas, J Chaboy, M Marziali, S Stizza *J. Solid State Chem.* **114** 317 (1995)
288. D Beltran-Porter, P Amoros, R Ibanez, E Martinez, A Beltran-Porter, A Le Bail, G Ferey, G Villeneuve *Solid State Ion.* **32/33** 57 (1989)
289. V Pekarek, M Benesova *J. Inorg. Nucl. Chem.* **26** 1793 (1969)
290. Ph Colomban, M Pham-Thi, A Novak *Solid State Commun.* **53** 747 (1985)
291. M Pham-Thi, Ph Colombasn *Solid State Ion.* **17** 295 (1985)
292. C M Vershoor, A B Ellis *Solid State Ion.* **22** 65 (1986)
293. G Ladwig *Z. Chem.* **8** 307 (1968)
294. E Bordes, P Courtine *J. Catal.* **57** 236 (1979)
295. J W Johnson, A J Jacobson *Angew. Chem., Int. Ed. Engl.* **22** 412 (1983)
296. A J Jacobson, J W Johnson, J F Brody, J C Scanlon, J T Lewandowski *Inorg. Chem.* **24** 1782 (1985)
297. M R Antonio, R L Barbour, P R Blum *Inorg. Chem.* **26** 1235 (1987)
298. P Amoros, R Ibanez, E Martinez, A Beltran-Porter, D Beltran-Porter, G Villeneuve *Mater. Res. Bull.* **24** 1347 (1989)
299. C C Torardi, J C Calabreste *Inorg. Chem.* **23** 1308 (1984)
300. M E Leonowicz, J W Johnson, J F Brodie, H F Shanson, J M Newsam *J. Solid State Chem.* **56** 370 (1985)
301. A Le Bail, G Ferey, P Amoros, D Beltran, G Villeneuve *J. Solid State Chem.* **79** 109 (1989)
302. A Le Bail, G Ferey, P Amoros, D Beltran *Eur J. Solid State Inorg. Chem.* **26** 419 (1989)
303. R Masse, J C Grenier *Bull. Soc. Fr. Mineral. Cristallogr.* **94** 437 (1971)
304. M M Eddy, T E Gier, N L Keder *Inorg. Chem.* **27** 1856 (1988)
305. M L Phillips, T E Gier, M M Eddy, N L Keder, G D Stuchy, J D Bierlein *Solid State Ion.* **32/33** 147 (1989)
306. M L F Phillips, W T A Harrison, T E Gier, G D Stuchy, G V Kulkarni, J K Burdett *Inorg. Chem.* **29** 2158 (1990)

[a] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[b] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*
[d] — *Inorg. Mater. (Engl. Transl.)*
[e] — *Russ. J. Chem. Phys. (Engl. Transl.)*
[f] — *J. Struct. Chem. (Engl. Transl.)*
[g] — *Crystallogr. Rep. (Engl. Transl.)*