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Novokuibyshev Branch,
Scientific Research Institute
for Synthetic Alcohols and
Organic Products

U. D. C. 543.544

THE USE OF ION-EXCHANGE CHROMATOGRAPHY FOR STUDYING THE STATE OF IONS OF HIGH-VALENCY ELEMENTS IN SOLUTION

B. I. Nabivanets

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I. INTRODUCTION

Advances in the chemistry and technology of the rarer elements have set research workers a number of problems involving investigations into the state of ions from high-valency elements in solution. Generally, such ions cannot exist in the free state in aqueous solutions, owing to their relatively high ionic potential, and undergo hydrolysis or form complexes with various ligands; the formation of hydrolysed polymeric species is also characteristic of these ions.

The state of ions of high-valency elements greatly affects their reactivity with various reagents and the composition of the reaction products. This is of particular importance in analytical chemistry and in the hydrometallurgical processing of ores where one requires to separate metals, to isolate them from solution, and to obtain compounds or reaction products having a specific composition.

The nature of the reactions between complex ions [for example, TiO_2^{2+}, $Zr(OH)_x^{(4-x)+}$, NbO_2^+, MoO_4^{2-}, WO_4^{2-}, etc.] or polymeric species and various ligands, and thus the compositions and properties of the complexes formed, depends to a great extent on the state of the highly-charged ions in solution under given conditions; in addition, there may also be changes in the degree of hydrolysis or polymerisation of high-valency ions during the complex formation process [1].

To elucidate the formation mechanism and the true composition of complexes formed from highly-charged ions we must study the state of the latter under complex-forming conditions, as well as the changes which take place with highly-charged ions in the complex-forming process itself. Only by taking such data into account is it possible to determine that most important characteristic of complexes, their stability constants.

The principal characteristics of the states of high--valency ions in solutions are the sign and magnitude of the charge, the degree of hydrolysis, the polymerisation factor, and the composition and stability of complexes containing different ligands.

These characteristics can be determined by ion-exchange chromatography using ion exchangers having different chemical and physical properties.

II. QUALITATIVE DETERMINATION OF THE FORM IN WHICH THE ELEMENT BEING STUDIED EXISTS IN SOLUTION

The absorption of the element under investigation by strongly acid cation exchangers is direct evidence of the existence of cationic species in a solution, but if the investigation is carried out in highly acid solutions then the presence of large amounts of foreign ions (for example, H^+) can lead to a shift in the equilibrium towards the displacement of ions of the element from the cation exchanger. For example, while it has been established in a number of investigations that Ti^{IV}, [2-6] Zr^{IV}, [2] and Mo^{VI} [7] are hardly absorbed at all by cation exchangers in 1 *N* HCl, 3 *N* HCl, and 3 *N* HNO_3 respectively, electromigration experiments [8-10] have shown convincingly that Ti,[8] Zr,[9] and Mo [10] exist predominantly as cationic species in these media; the predominance of the cationic species $ZrCl^{3+}$, $ZrCl_2^{2+}$, and $ZrCl^+$ in 3 *N* HCl also depends on the stability constants of the zirconium chloro--complexes [11].

Account should be taken of the possibility of disturbing the equilibrium between the various ionic species during the absorption of the element by cation exchangers. For example, at pH 3–5 there is a marked absorption of sexivalent molybdenum ions by cation exchangers [10] although electromigration experiments [7], the determination of the isoelectric point of molybdic acid by a solubility method [7,12] as well as a calculation from the dissociation constants of molybdic acid [13] show that at this acidity practically all the Mo is present as hydrogen molybdate and molybdate ions or as isopolymolybdates [14-16].

Similar complications arise in the absorption by anion exchangers of the element being studied. For example, at pH > 12 Mo^{VI}, Mo^V, Ta^V, and Ge^{IV} are not absorbed by anion exchangers due to competition from OH^- ions although under these conditions these elements occur in solution as monomeric or polymeric anions of molybdic [10,14-16], niobic [17,18], tantalic [17,19,20], and germanic [21] acids. The competing effect of foreign ions can lead to false conclusions, particularly when studying low-stability complexes formed at high ligand concentrations, for under these conditions the ligand itself can be an ion displacer. For example, it has been established in a number of studies that an increase in sulphate ion concentration above a certain level leads to a reduction in the absorption of Ti^{IV}, [22] Zr^{IV}, [23] and Nb^V [23] by anion exchangers, although electromigration experiments [8,24] show that under these conditions these elements are present in solution as anionic sulphato--complexes.

Similar equilibrium disturbances are found in anion exchange. For example, Mo^{VI} is appreciably absorbed by anion exchangers in 0.2–1.0 *N* nitric acid [7] although molybdenyl cations predominate under these conditions [10].

Furthermore, anion exchangers containing $-NH_2$, =NH, or ≡N groups can absorb metal salt molecules to form complexes with the amino-groups of the resins. Such processes are characteristic of compounds of elements capable of coordinating with nitrogen atoms in various reagents. For example, it has been established that there is marked absorption of Cu, Co, Ni, Cd, and Zn by different types of anion exchangers from weakly acidic solutions, in which cationic species of these elements predominate [25]. The absorption under these conditions is due to the formation of complexes having the composition $[R_2M(H_2O)_2]X$, where R is an anion exchanger containing $-NH_2$, =NH, or ≡N, M a doubly-charged metal cation, and X^- represents Cl^- or NO_3^-.

The method of effluent curves is also used for making a qualitative determination of the form in which an element exists in solution [26]. Here one analyses successive individual portions of the test solution flowing from a column containing a cation or anion exchanger. If only ionic species are present in solution, then on passing a known volume of the solution through an ion-exchange column the ions under investigation are found to emerge in the filtrate, their concentration in individual portions of the filtrate increasing gradually and reaching a value equal to that in the initial solution. Such a curve has been obtained, for example, in the absorption of oxalato-complexes of Nb by EDE-10 anion-exchange resin† (curve *1*, Fig. 1) [26]; Nb is not absorbed under these conditions by KU-2 cation-exchange resin‡ (curve *2*, Fig. 1). If neutral molecules are present in solution the substance under investigation is not absorbed by ion exchangers, the effluent curve *2* in Fig. 1 being characteristic of this case. If colloidally dispersed particles predominate in the solution, however, then the adsorption is physical in nature, that is, it is independent of the charge sign of the active groups in the ion exchanger; in this case the effluent curves have the form of curves *3* and *4* in Fig. 1. Similar curves are obtained for colloidally dispersed particles of niobium hydroxide on an anion exchanger (curve *3*) and a cation exchanger (curve *4*) [26].

If there are several forms of the element in solution then it is impossible to detect the presence of the several different species from the first effluent curve, in which

† EDE-10 is a polyfunctional weakly or strongly basic anion--exchange resin prepared by the condensation of polyethylenepolyamines with epichlorohydrin, and contains secondary, tertiary, and quaternary nitrogen groups (Ed. of Translation).

‡ KU-2 is a monofunctional, strongly acid cation-exchange with $-SO_3H$ active groups, prepared by treating a swollen styrene--divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

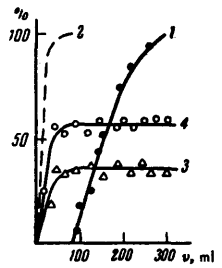


Fig.1. Relationship between the Nb^V concentration in the filtrate and the volume of solution passed through the column (for microconcentrations of niobium)[26]:
1) effluent curve for EDE-10 anion-exchange resin;
2) on KU-2 cation-exchange resin in oxalate solution;
3) effluent curve for EDE-10 anion-exchange resin;
4) on KU-2 cation exchanger in $NaNO_3$ solution.

case "secondary" effluent curves are obtained. For this purpose the filtrate solutions remaining after recording the primary curve are passed through a cation or anion exchanger not containing the ions under investigation. For example, the primary and secondary effluent curves obtained on passing a solution of niobium in 1 *N* HNO_3 through an ion exchanger[26] are shown in Fig. 2; the nature of the curves indicates that under these conditions electrically neutral complexes of Nb which are hardly absorbed at all by the cation or anion exchanger (curves *c'*, *a'*, *c''*, *a''*, Fig. 2) and colloidal Nb species whose absorption is physical in nature (curves *c*, *a*, Fig. 2) are present in equilibrium in the solution.

Colloidal species of an element can only be detected by the effluent-curve method in microconcentrations, where the number of colloidal particles physically adsorbed on

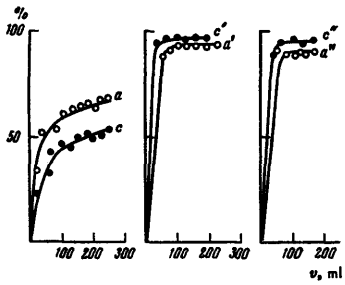


Fig.2. Effluent curves for micro-amounts of niobium in 1 *N* HNO_3:[26] *c*), *a*) are the first effluent curves on a cation exchanger (*c*) and an anion exchanger (*a*); *c'*), *a'*) are the secondary effluent curves after the cation exchanger on a cation exchanger (*c'*) and an anion exchanger (*a'*); *c''*), *a''*) are the secondary curves after the anion exchanger on a cation exchanger (*c''*) and an anion exchanger (*a''*).

the surface of the ion-exchanger granules represents an appreciable fraction of the total amount of the element concerned. For these reasons (equilibrium displacement, competition from foreign ions, etc.) the results of investigations by the effluent curve method can indicate only the presence of certain ionic species of the element under investigation in a given system; it is impossible, however, to show that these species predominate in the solution under the given conditions by this method.

III. DETERMINATION OF THE MAGNITUDE OF THE IONIC CHARGE

Determining the magnitude of the ionic charge of complex ions formed by hydroxo-cations — TiO^{2+}, $Zr(OH)_x^{(4-x)+}$, NbO_2^+, etc. — can frequently serve as one of the principal methods of establishing the composition and formation mechanism of complex ions in solution.

Over the last 7–8 years the ion-exchange method has been used for determining the charge on the sulphato-complexes of uranyl[28], Ge,[29] Nb, and Ti;[30] the oxalato-complexes of Ge,[31] Zr, and Hf;[32] the chloro-complexes of Ru;[33] and the hydroxo-complexes of Ti,[34] germanate[21], isopolyvanadates[35], vanadyl[36], molybdenyl[7], Zr,[37] Pa,[38] and certain polynuclear complexes of Ru.[39]

The methods for determining the magnitude of the ionic charge can be divided into two groups, the first being based on the equivalence and reversibility of ion-exchange reactions and the second being based on the swelling of ion exchangers during the absorption of ions.

1. Methods Based on the Equivalence and Reversibility of Ion-Exchange Reactions

The absorption of the ions of an element under investigation M^z by an ion exchanger loaded with ions $M_1^{z_1}$ having a known charge z_1 can be expressed by the equilibrium:

$$z_1 M^z + z\overline{R_{z_1}M_1} \rightleftarrows z_1\overline{R_z M} + z M_1^{z_1}. \qquad (1)$$§

This equilibrium can pertain to both cation and anion exchange. Three methods are available for determining the required charge magnitude z.

The first method is based on determining the exchange capacity of the ion exchanger for the element being studied M^z. For this we must know the total exchange capacity of the ion exchanger for an ion $M_1^{z_1}$ having a known charge z_1 and then completely displace the equilibrium (1) to the right by saturating the ion exchanger with the ions being studied M^z. The charge z is found from the relationship

$$z = \frac{Q}{G}, \qquad (2)$$

where Q is the capacity of a given weight of ion exchanger expressed in g-equiv. of absorbed $M_1^{z_1}$ ions, and G the amount of the element M^z in g-moles absorbed by the same weight of ion exchanger.

This method of determining the charge magnitude can involve substantial errors for a number of reasons, the chief ones being as follows. When determining the exchange capacity of an ion exchanger, H^+, Na^+, or Ca^{2+} ions (for cation exchangers) and Cl^- ions (for anion

§ Both here and subsequently the bar lines indicate the ion-exchanger phase.

exchangers) are usually used as $M_1^{z_1}$. These ions have relatively small radii and therefore readily penetrate into the pores of the ion exchanger to occupy practically all the active sites. In the absorption of high-valency ions or complex ions and polymeric species, however, which have larger ionic radii, these do not always succeed in occupying all the active sites of the ion exchanger. Furthermore, owing to the absorption of M^z ions the concentration of $M_1^{z_1}$ in solution is increased, which prevents the displacement of equilibrium (1) to the right. All of this can lead to excessively high results in the determination of z. Finally, a shift in equilibrium (1) towards ion-exchanger saturation by M^z ions is only possible with a substantial increase in the concentration (or absolute quantity) of the latter; this makes it difficult to determine the charge magnitude at low concentrations of the element.

Thus, a determination of the charge by using the total exchange capacity of an ion exchanger is not always reliable. For example, when using this method to find the charge on the cations of quadrivalent zirconium in perchloric acid solutions it was found[40] that the charge on the zirconium ions is increased on lowering the concentration of $HClO_4$, which contradicts the results obtained[41] by using the stability constants of zirconium hydroxo-complexes[42].

The second method is based on the relationship between the number of $M_1^{z_1}$ ions displaced and the charge magnitude z of the absorbed M^z ions. Experimentally this method is carried out by determining concentration changes for the ions under investigation (ΔM^z) and the displaced ions ($\Delta M_1^{z_1}$) on bringing the solution into contact with an ion exchanger $\overline{R_{z_1}M_1}$. The specific charge is calculated from the relationship

$$z = \frac{\Delta M_1^{z_1}}{\Delta M^z}. \qquad (3)$$

where $\Delta M_1^{z_1}$ is expressed in g-equiv. and ΔM^z in g-moles.

A necessary condition for obtaining reliable results is sufficient sensitivity in determining ΔM^z and $\Delta M_1^{z_1}$. Most analytical methods enable element concentrations of 10^{-4}–10^{-5} M and above to be determined in solution. Frequently, however, the charge magnitude has to be determined in the presence of foreign electrolytes whose concentration considerably exceeds the concentration of the element under investigation. In such cases the ion exchanger must first be saturated with ions of the foreign electrolyte. Consequently, while the element (M^z) is being absorbed it dislodges from the ion exchanger the foreign electrolyte ions ($M_1^{z_1}$), whose concentration even before absorption was appreciable. Thus, $\Delta M_1^{z_1}$ must be determined at a substantial concentration of $M_1^{z_1}$, which is only possible if the concentration of M^z ions being absorbed is fairly high. A reliable determination of $\Delta M_1^{z_1}$, is possible by changing the concentration of $M_1^{z_1}$ by at least 10%; therefore in determining the charge magnitude from relationship (3) the concentration of the element being studied should be not less than 10% of the concentration of foreign electrolyte (calculated per g-equiv.).

Table 1 shows the results of charge determinations for Ti^{IV} cations at various pH.[34] The values of z show that at pH < 1.17 doubly-charged titanyl cations TiO^{2+} predominate in solution and on raising the pH hydrolysis occurs to form singly-charged cations¶

$$TiO^{2+} + H_2O \rightleftarrows TiO(OH)^+ + H^+. \qquad (4)$$

¶ The absence of titanium poly-ions in solution under these conditions has been proved by a study of the ion-exchange kinetics and by dialysis[43].

TABLE 1. Magnitude of the charge on Ti^{IV} cations*.

Initial solution			Equilibrium solution			z
pH_1	$[H^+]_1$	$[Ti]$	pH_2	$[H^+]_2$	$[Ti]$	
0.50	$3.16\cdot10^{-1}$	$4.95\cdot10^{-2}$	0.40	$3.98\cdot10^{-1}$	$1.25\cdot10^{-2}$	2.21
1.17	$6.76\cdot10^{-2}$	$9.46\cdot10^{-2}$	1.05	$8.91\cdot10^{-2}$	0	2.24
1.40	$3.98\cdot10^{-2}$	$1.20\cdot10^{-2}$	1.33	$4.68\cdot10^{-2}$	$5.27\cdot10^{-2}$	0.99
5.75	$1.78\cdot10^{-6}$	—	3.50	$3.16\cdot10^{-4}$	—	—

* All concentrations are molar.

A similar principle is used for determining the charge of anions by using anion exchangers. For example, a study of the absorption of germanate ions by IRA-400 anion-exchange resin in the OH^- and Cl^- forms showed[21] that at pH ≃ 9 the absorption of 2.5 moles Ge leads to the displacement of one g-equiv. of OH^- or Cl^- ions. Thus, under these conditions Ge is present in solution as pentagermanate ions $Ge_5O_{11}^{2-}$ (according to these results).

The third method is based on displacing the equilibrium of reaction (1) [27,28] and consists of studying the effect of varying concentrations of $M_1^{z_1}$ on the absorption of the ions being studied, under the conditions $[\overline{R_{z_1}M_1}] \simeq$ const. In this case the equilibrium constant of (1) is

$$K = \frac{[\overline{R_zM}]^{z_1}\,[M_1^{z_1}]^z}{[M^z]^{z_1}} = (K_d)^{z_1}\,[M_1^{z_1}]^z. \qquad (5)$$

Here K_d is the coefficient for the distribution of element M^z between the ion exchanger and the solution, determined from the relationship

$$K_d = \frac{a}{100-a} \times \frac{v}{m}, \qquad (6)$$

where a is the amount of absorbed element in the equilibrium state (%), v is the volume of solution (ml), and m is the weight of ion exchanger (g).

Eqn. (5) supposes that the ratio of the activity coefficients of M^z ions in solution and in the ion-exchanger phase remains constant over a certain range of concentration. Putting Eqn. (5) in logarithmic form we obtain

$$\log K_d = -\frac{z}{z_1}\log[M_1^{z_1}] + \frac{1}{z_1}\log K. \qquad (7)$$

The ratio z/z_1 and thus the charge magnitude z, can be found from the slope of the curve of $\log K_d$ against $(-\log[M_1^{z_1}])$.

It was indicated above that the condition $[R_{z_1}M_1] \simeq$ const. must be observed while carrying out this method. This means that the amount of ion exchanger taken for each experiment should be fairly high, so that the absorption of M^z is hardly reflected at all in the amount of ion exchanger in the $[\overline{R_{z_1}M_1}]$ form. A determination of the charge magnitude using Eqn. (7) gives reliable results if the amount of $[\overline{R_{z_1}M_1}]$ is changed by not more than 1–2% during the absorption of M^z.

This condition can be written in the following form

$$mQ \geqslant v[M^z]z \times 50, \text{ or}$$

$$[M^z] \leqslant \frac{Q}{50z\ v/m}. \qquad (8)$$

Here $[M^z]$ is the molar concentration of M^z in the solution under investigation prior to contacting it with the ion exchanger, Q is the total exchange capacity of the ion exchanger (mg-equiv. g^{-1}), z the expected value of the

charge†, m the mass of ion exchanger (g), and v the volume of solution (ml).

To avoid a substantial change in the volume of the solution, arising from the swelling of the ion exchanger, the experiments are usually carried out by observing the relationship

$$\frac{v}{m} \geqslant 50. \qquad (9)$$

Taking condition (9) into account, the concentration of M^z can be readily calculated from Eqn. (8), which ensures that the determination of z by using Eqn. (7) is reliable.

By way of example, the results of charge determinations on Ti^{IV} cations in perchloric acid solutions[34] are shown in Fig. 3. In this case $M_1^{z_1} = H^+$ ($z_1 = 1$), so that the slope of the curve in Fig. 3 relative to the abscissa axis gives the value of z directly. According to Fig. 3, doubly-charged cations predominate in solution at pH < 1, these clearly being titanyl ions TiO^{2+}. At higher pH values hydrolysis occurs to form singly-charged $TiO(OH)^+$ cations, which agrees with the data in Table 1.

It is convenient to use the equivalence of ion exchange to determine the charge magnitude for relatively high concentrations of the ions under investigation (of the order of 10^{-2} M and above); at lower concentrations (of the order of 10^{-3} M and below) we generally employ the equilibrium displacement method.

2. Methods Based on the Swelling of Ion Exchangers

In an investigation of ion exchange on swelling ion exchangers it was found[37] that the exchange selectivity of ions having different valency depends very greatly on the swelling power of the ion exchanger. Therefore the amounts of ions absorbed can be expressed in the exchange isotherm equation as equivalent concentrations by including the specific volume of the swollen resin (V) in the equation:

$$\frac{g_1^{1/z_1} V^{1/z_1} \bar{f}_1^{1/z_1}}{g_2^{1/z_2} V^{1/z_2} \bar{f}_2^{1/z_2}} = K \frac{C_1^{1/z_1} f_1^{1/z_1}}{C_2^{1/z_2} f_2^{1/z_2}}. \qquad (10)$$

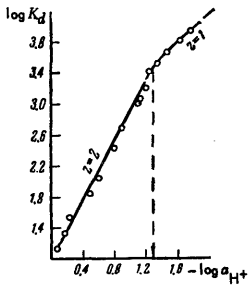


Fig. 3. Effect of the activities of hydrogen ions on the absorption of titanium by KU-2 cation-exchange resin[34]. Initial titanium concentration 2×10^{-4} M.

† Usually $z \leqslant 4$ in aqueous solutions.

Here g_1, g_2 and $\bar{f}_1$, $\bar{f}_2$ are the equivalent amounts of ions absorbed by the ion exchanger and their activity coefficients in the ion-exchanger phase respectively; C_1, C_2 and f_1, f_2 are the concentrations and activity coefficients of the exchanging ions in solution respectively; z_1 and z_2 are the ionic charges.

If one of the exchanging ions is a microcomponent (g_1), then the specific capacity of the ion exchanger for the macrocomponent (g_2) is equal to the total specific capacity of the resin and the concentration of macrocomponent in solution (C_2) will be the constant total concentration of the solution. In this case the activity coefficients of the ions in solution remain constant.

The distribution of microcomponent under investigation between the solution and resin is given by the coefficient:

$$K_{d_1} = \frac{g_1}{C_1} = K' \frac{g^{z_1/z_2} \bar{f}_2^{z_1/z_2}}{C^{z_1/z_2} \bar{f}_1 V^{z_1 - z_2/z_2}}. \qquad (11)$$

Eqn. (11) shows how the distribution coefficient of the element under investigation depends on the specific capacity of the resin (g), the total concentration of the solution (C), the specific volume of the resin (V), and the activity coefficients of the ions in the ion-exchanger phase. It follows from this equation that for $z_1 = z_2$ the distribution coefficient of the element is independent of the swelling power of the resin.

The selectivity in the absorption of the element under investigation on to two resin samples having different swelling powers can be expressed by the relative exchange selectivity coefficient β_1:

$$\beta_1 = \frac{K_{d_1}^{\mathrm{I}}}{K_{d_1}^{\mathrm{II}}} = \left(\frac{g^{\mathrm{I}}}{g^{\mathrm{II}}}\right)^{z_1/z_2} \left(\frac{V^{\mathrm{II}}}{V^{\mathrm{I}}}\right)^{z_1 - z_2/z_2} \left(\frac{\bar{f}_2^{\mathrm{I}}}{\bar{f}_2^{\mathrm{II}}}\right)^{z_1/z_2} \left(\frac{\bar{f}_1^{\mathrm{II}}}{\bar{f}_1^{\mathrm{I}}}\right). \qquad (12)$$

In this equation the indices I and II relate to resin samples having different swelling powers. It has been found experimentally that the activity coefficients of ions in the resin phase are independent of its swelling power, so that the ratio of the activity coefficients in Eqn. (12) is unity. For investigations in which resins having different swelling powers and the same total specific capacity ($g^{\mathrm{I}} = g^{\mathrm{II}}$) are used, Eqn. (12) assumes the form

$$\frac{K_{d_1}^{\mathrm{I}}}{K_{d_1}^{\mathrm{II}}} = \left(\frac{V^{\mathrm{II}}}{V^{\mathrm{I}}}\right)^{z_1 - z_2/z_2}. \qquad (13)$$

Using univalent ions as the macrocomponent ($z_2 = 1$) the equation for determining the charge has the form:

$$z = \frac{\log \dfrac{K_d^{\mathrm{I}}}{K_d^{\mathrm{II}}}}{\log \dfrac{V^{\mathrm{II}}}{V^{\mathrm{I}}}} + 1. \qquad (14)$$

To determine z we must have two resin samples of different swelling powers and the same specific capacity. In essence the experiment consists of determining the distribution coefficients K_d^{I} and K_d^{II} for the element under investigation on the two resin samples under strictly identical conditions; the specific volumes V^{I} and V^{II} of the swollen resins are determined pyknometrically under the same conditions. The concentration of the element should be at least 100 times less than the concentration of macrocomponent ions, in order to obtain reliable results.

As an example, the results of charge magnitude determinations for Zr^{IV} ions in nitric acid solutions[37] are presented in Table 2. They show that quadruply-charged Zr^{4+}

TABLE 2. Determination of the magnitude of the charge on Zr^{IV} ions as a function of nitric acid concentration[37].

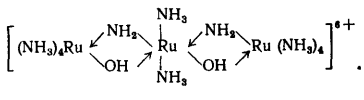
$[HNO_3]$, N	pH	K_d^I on a resin containing 12% divinylbenzene	K_d^{II} on a resin containing 2% divinylbenzene	V^I ml g^{-1}	V^{II} ml g^{-1}	z
5.0	—	6.4	4.5	0.578	0.775	+2.21
3.0	—	10.8	6.8	0.623	0.820	+2.70
2.5	—	40.0	19	0.630	0.835	+3.66
2.0	—	72.5	30	0.637	0.855	+3.99
1.5	—	140	82	0.645	0.905	+2.66
1.0	—	383	292	0.655	0.940	+1.83
0.5	—	397	373	0.670	0.997	+1.19
0.3	—	517	490	0.710	1.08	+1.13
0.1	1.0	535	535	0.720	1.09	+1.00
—	1.2	602	602	0.720	1.13	+1.00
—	1.5	760	685	0.720	1.16	+1.21
—	1.8	805	710	0.720	1.19	+1.12

ions are formed only over a narrow range of acid concentrations (2–2.5 N); the charge is reduced at higher NHO_3 concentrations owing to the formation of nitrato-complexes of Zr, and at lower acid concentrations due to the hydrolysis of Zr cations.

3. Some Special Aspects of Determining the Charge Magnitude of High-Valency Ions.

High-valency ions generally exhibit a strong tendency towards complex-forming reactions. Therefore, in certain cases, as was indicated earlier, they may be absorbed by ion exchangers by a molecular mechanism, which makes it impossible to determine their charge. To avoid such complications when determining the magnitude of the ionic charge it is necessary to use strongly acid cation exchangers containing active $-SO_3H$ groups (KU-2 or Dowex 50) and strongly basic anion exchangers containing active $\equiv\overset{+}{N}-OH$ groups (AV-17‡ or Dowex 1). These ion exchangers absorb high-valency ions virtually only by an ion-exchange mechanism.

In determining the charge magnitude of poly-ions the treatment of the results obtained by any of the methods described above depends on the method by which the amount of element absorbed by the ion exchanger is determined. If the total amount of absorbed element is determined in g-atoms then the result obtained is the value of the specific charge, that is, the charge attached to one atom of the element concerned in the poly-ion. The determination of the charge magnitude of polygermanate ions[21] mentioned above may be quoted as an example. However, if we determine the amount of absorbed poly-ions of the element under investigation by some method then we obtain the value of the effective (overall) charge of the poly-ion§. This quantity was obtained, for example, in a determination of the charge on the polynuclear complex Ru ion[39].



‡ AV-17 is a strongly basic anion-exchange resin containing quaternary nitrogen groups. It is based on styrene and trimethylamine (Ed. of Translation).

§ In the absence of poly-ions the specific charge is also the effective charge of the complex ion.

In this case the change in the concentration of the polynuclear complex in solution during absorption by a cation exchanger was determined spectrophotometrically from the characteristic maximum in the absorption spectrum of the polynuclear complex.

When low-stability complexes are formed in solution the degree of bonding of a highly-valent element in the complex depends on the excess concentration of ligand (in the case of hydroxo-complexes, on the pH). At the same time the ligand concentration in solution can differ considerably from that in the ion-exchanger phase[45]. For example, it has been found experimentally[46] that for the cation exchanger Dowex 50, with 1–2 N HCl in the aqueous phase, the concentration of HCl in the ion-exchanger phase was 0.09 and 0.2 N respectively. This gives reason to suppose that the state of highly-valent elements in the ion-exchanger phase may differ from that in the solution.

Nevertheless, under certain experimental conditions it is possible to obtain results which will yield the charge magnitude of the ions in solution. Let us suppose that in the absorption of a polymeric action $M_p(OH)_x^{(pq-x)+}$ by a cation exchanger the poly-ion dissociates and there is a change in the degree of hydrolysis, which leads to the formation of a cation $M(OH)_{\frac{x}{p}+y}^{\left(q-\frac{x}{p}-y\right)+}$ in the ion-exchanger phase (q is the valency of the central metal). This process can be represented by the equilibrium

$$M_p(OH)_x^{(pq-x)+} + p\left(q-\frac{x}{p}-y\right)\overline{RH} + py\,H_2O \rightleftarrows \rightleftarrows p\,\overline{R_{q-\frac{x}{p}-y}M(OH)_{\frac{x}{p}+y}} + z\,H^+. \quad (15)$$

A similar equation can be written for any change in the polymerisation factor p or for the similar case of only monomeric ions (p = 1) being present in solution.

The absorption of the complex $M_pA_x^{(pq-x)-}$ by an anion exchanger to form a complex $MA_{\frac{x}{p}+y}^{\left(q-\frac{x}{p}-y\right)-}$ in the ion-exchanger phase can be expressed by the equilibrium

$$M_pA_x^{(pq-x)-} + p\left(q-\frac{x}{p}-y\right)\overline{RA} \rightleftarrows p\,\overline{R_{q-\frac{x}{p}-y}MA_{\frac{x}{p}+y}} + z\,A^-. \quad (16)$$

A similar equation can be written for any change in the polymerisation factor p and the ratio M : A. It is readily seen that in Eqns. (15) and (16) $z = pq - x$, that is, the number of cations or anions displaced by ion exchange is equivalent to the charge in solution of the ions under investigation.

Eqns. (15) and (16) show that to determine the magnitude of the charge on ions present in solution it is necessary to use ion exchangers loaded with ions which are present in the complex ion being studied, or are connected by a chemical equation with ions present in it. In Eqn. (16) these are the A^- ions, in Eqn. (15) they are the H^+ ions connected with OH^- ions by the chemical equation $H^+ + OH^- \rightleftharpoons H_2O$.

This condition is not guaranteed when determining the charge on complex ions having high stability, whose composition cannot be changed with differences in ligand concentration in solution and in the ion-exchanger phase.

When determining the charge magnitude of ions one frequently has to deal with solutions containing ions having

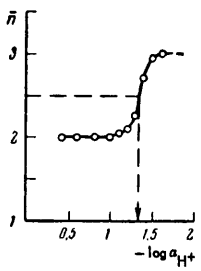


Fig.4. Relationship between $\bar{n}$ and the acidity of the medium in the formation of the hydroxotitanyl complex (calculated from the curve in Fig.3)[34].

different charge magnitudes in equilibrium. On contacting such a solution with an ion exchanger, ions having the higher charge will be absorbed first, and this can lead to a considerable disturbance in the equilibrium between the various ionic species. However, this disturbance in equilibrium is equivalent to the change in the composition of the ions in the ion-exchanger phase, so that by observing the conditions given above we obtain the mean charge magnitude of the ions in solution prior to absorption at given concentration conditions.

The results of charge magnitude determinations for ions can, in certain cases, be used to calculate the instability constants of the complexes. It follows from Eqn. (7) that

$$z = z_1 \frac{\Delta \log K_d}{\Delta \log [M_1^{z_1}]}. \qquad (17)$$

In complex formation involving a metal cation M^{q+} (q being the valency of the metal) the relationship between the Bjerrum formation constant $\bar{n}$ and the charge of the complex ion is expressed by the equation

$$\bar{n} = q - z = q - z_1 \frac{\Delta \log K_d}{\Delta \log [M_1^{z_1}]}. \qquad (18)$$

If a ligand or another ion, whose concentration is proportional to the ligand concentration, is taken as $M_1^{z_1}$ then it is possible to determine the composition of the complexes formed and their instability constants from the relationship

$$\bar{n} = f([M_1^{z_1}]).$$

This method has been used[34] to determine the instability constants of the hydroxotitanyl complex $TiO(OH)^+$. The variation of K_dTi with pH on KU-2 cation-exchange resin in the hydrogen form was studied, that is, the OH^- ion, whose concentration is connected with the H^+ concentration by the ionic product of water was taken as $M_1^{z_1}$. The relationship $\bar{n} = f(\text{pH})$ is shown in Fig. 4; the instability constant of the hydroxotitanyl complex, which is numerically equal to the OH^- concentration at $\bar{n} = 2.5$, was found graphically from this curve:

$$K_{\text{instab}} = \frac{[TiO^{2+}][OH^-]}{[TiO(OH)^+]} = 1.5 \times 10^{-3} \text{ at } 18°.$$

A similar result has been obtained by the solubility method[34].

IV. DETERMINATION OF THE POLYMERISATION FACTOR

Two methods can be used for determining the polymerisation factor by using ion exchangers. The first is based on the fact that ion-exchange processes on synthetic ion exchangers obey the law of mass action[47,48], thus making it possible to use the equilibrium displacement method, which enables the coefficients in the chemical equations to be determined. The second method[48] is based on the rate of diffusion of ions within the cation exchanger being a function of their sizes[49] a study of the ion-exchange kinetics thus enabling one to determine the conditions under which the polymeric species exist in solution and, in certain cases, to judge approximately the polymerisation factor of the ions under investigation.

1. The Equilibrium Displacement Method

It has been shown in studies of the polymerisation processes of Zr, Nb, Ta ions[17,50,51] that the polymeric species dissociate during the formation of stable complexes. Synthetic ion exchangers may be considered as macromolecular insoluble reagents[52]; with a fairly stable bond between the element under investigation and the ion exchanger (a high K_d value) it may be assumed that the polymeric species will dissociate in the ion-exchanger phase. In this case the ion-exchange reaction can be expressed by the equation

$$pz\overline{RM_1} + M_p^z \rightleftarrows p\overline{R_zM} + pzM_1, \qquad (19)$$

where M_1 is a singly-charged ion and p is the polymerisation factor.

It follows from Eqn. (19) that for $[\overline{RM_1}] \simeq$ const and $[M_1] \simeq$ const the distribution coefficient for the element under investigation (K_d) between the solution and the ion exchanger depends on the concentration of M_p^z. This enables the polymerisation factor p to be determined from the change in total concentration of the element.

Under these conditions the distribution coefficient assumes the form

$$K_d = \frac{G^p}{[M_p^z]} \times \frac{v}{m}. \qquad (20)$$

Here G is the amount of the element, in g-atoms, absorbed by the ion exchanger under the given conditions, $[M_p^z]$ the equilibrium concentration of poly-ions in solution, v the volume of the solution under investigation (ml), and m the mass of ion exchanger (g).

Eqn. (20) shows that K_d depends on the polymerisation factor p; a definite value of the distribution coefficient corresponds to each polymeric species, this remaining constant in a series of experiments in which the concentration of the element under investigation varies, if p is not altered.

The equilibrium concentration of polymeric species in solution can be expressed in terms of the total analytical concentration C:

$$[M_p^z] = \frac{1}{p} \times C. \qquad (21)$$

Combining Eqns. (20) and (21) we obtain:

$$K_d = \frac{G^p}{\frac{1}{p} \times C} \times \frac{v}{m}. \qquad (22)$$

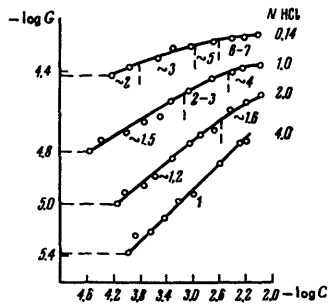


Fig. 5. Relationship between the amount of Zr absorbed by KU-1 cation-exchange resin and its equilibrium concentration[48]. The figures under the curves denote the polymerisation factor p.

G and C are found experimentally and the ratio v/m is constant in a given series of experiments. Expressing Eqn. (22) in logarithmic form we obtain:

$$p \log G = \log C + \log \frac{1}{p} + \log K'_d. \qquad (23)$$

For a definite constant polymerisation factor (p = const, K'_d = const), Eqn. (23) assumes the form

$$p \log G = \log C + \text{const}. \qquad (24)$$

On plotting $\log G$ against $\log C$ the polymerisation factor p can be determined from the slope of the curve relative to the ordinate axis. If p alters with a change in the concentration (C) of M^z, then the slope of the curve reflecting the relationship $\log G = f(\log C)$ will alter accordingly.

The results of experiments for Zr^{IV} in perchloric acid solutions[48] are shown in Fig. 5. H^+ ions were used as the M_1 ions having constant concentration. The experiments were carried out under static conditions using a sulphonated KU-1 cation-exchange resin¶ in the hydrogen form†. The slope of the curves in Fig. 5 relative to the ordinate axis shows that in 4 N $HClO_4$ at zirconium concentrations of 1×10^{-4}–1×10^{-2} M there are only monomeric species in solution; the polymerisation factor is increased by lowering the acid concentration or increasing the zirconium concentration. Similar results have been obtained by a dialysis method[50].

2. Ion-Exchange Kinetics.

Ion-exchange kinetics curves have a varying steepness depending on the rate at which equilibrium is established. A convenient way of comparing the kinetic curves is to determine graphically the time over which half the element being studied is absorbed, compared with the equilibrium state[48]. It has been proposed to call this time the half-equilibrium time and to represent it by $\tau_{\frac{1}{2}}$. Various types of kinetic curves are shown in Fig. 6. Curve *1* corresponds to the absorption by a cation exchanger of Co^{2+} ions, which do not form polymeric species, and curves *2* and *3* to the absorption of zirconium cations for various polymerisation factors. If the transition to the horizontal section on the ion-exchange-kinetics curve occurs over a long interval of time (curve *3*, Fig. 6) then it is necessary to determine the percentage absorption in the equilibrium state (A), to read off half this value (B) from the ordinate axis and to find the corresponding value of $\tau_{\frac{1}{2}}$ (curve *3*).

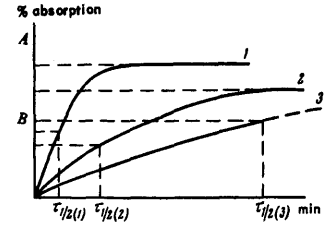


Fig. 6. Graphical determination of the half-equilibrium time $\tau_{\frac{1}{2}}$.[48]

TABLE 3. Variation in the polymerisation factor* and the rate of ion exchange of zirconium in perchloric acid solutions[48]. The calculated data obtained from the approximate formula $\tau'_{\frac{1}{2}} p \simeq \tau_{\frac{1}{2}} p'$ are in parentheses.

$[HClO_4]$, M	Zirconium concentration, M					
	1×10^{-2}		1×10^{-3}		1×10^{-4}	
	$\tau_{\frac{1}{2}}$ (min)	p	$\tau_{\frac{1}{2}}$ (min)	p	$\tau_{\frac{1}{2}}$ (min)	p
0.14	95	8	40	4	22	2
0.50	70	(6)	—	—	19	(1.8)
1.0	36	4	28	2	14	1.5
2.0	—	1.6	14	1.2	11	1.1

* The values of p are taken from Fig. 5.

As an illustration, the results of studies on the rate of ion exchange of zirconium cations in perchlorate solutions of KU-1 cation exchanger[48] are shown in Table 3. The data show that the polymerisation factor p and the half-equilibrium time $\tau_{\frac{1}{2}}$ are directly proportional. A similar method has been used in a study of the state of Ti^{IV} in hydrochloric acid solutions[43].

A calculation using the energy characteristics for ion interactions indicates that polyhydroxo-cations are ring-like structures[54]. Therefore it is to be expected that the plot of $\tau_{\frac{1}{2}}$ against p will be a straight line for the formation of polyhydroxo-cations in solution (for example, see Table 3). It is possible that this enables the kinetic method to be used not only for determining the conditions under which poly-ions exist in solution, but also for estimating approximately the mean polymerisation factor of polyhydroxo-cations.

¶ KU-1 is a difunctional, strongly acid cation-exchange resin with $-SO_3H$ and $-OH$ active groups, prepared by the condensation of p-phenolsulphonic acid with formaldehyde in acid (Ed. of Translation).

† Zirconium forms fairly stable sulphato-complexes[53], during which the polymeric species dissociate[24]. Therefore it may be assumed that polymeric cations of zirconium dissociate during absorption by a cation exchanger containing active sulphonate groups.

V. DETERMINATION OF THE COMPOSITION AND STABILITY OF COMPLEXES IN SOLUTION

Ion exchange has been widely used for determining the composition and stability constants of the complexes of many elements, including high-valency elements. For example, it has been used to study the chloro-[11], nitrato-[11,55], sulphato-[56], and oxalato-complexes[57] of Zr^{IV} and Hf^{IV}, the complexes of these elements with certain hydroxy-acids[58,59], the chloro-complexes of Ru^{IV},[60] the oxalato-complexes of Pu^{IV},[57] and the nitrato-complexes of Th^{IV}.[61]

The theory and practice of studying complex formation under static conditions using cation exchangers[59,62-66] and anion exchangers[66-69], as well as the study of complex formation under dynamic conditions[70-72], are described in sufficient detail in the literature. In this review we shall restrict ourselves merely to setting out the principles of carrying out an experiment and the basic formulae for the methods of Schubert[62-64], Fronaeus[65], and Paramonova[66], which have been most widely used.

Schubert's method[62,63] is used for studying systems in which only one complex, which is not absorbed by a cation exchanger, is formed. An indication of the formation of a single complex over a certain range of ligand concentration is a linear relationship for $1/K_d = f([A^{y-}])$, where K_d is the distribution coefficient of the element under investigation between the cation exchanger and the solution, and $[A^{y-}]$ is the equilibrium ligand concentration. It can be shown[64] that when working with microconcentrations of the element under investigation in the presence of a macroconcentration of singly-charged ions, the stability constant of a complex formed by the reaction $M + nA \rightleftharpoons MA_n$ can be calculated from the formula

$$\beta_n = \frac{[MA_n]}{[M][A]^n} = \frac{K_{d_0}/K_d - 1}{[A]^n}. \quad (25)$$

Here K_{d_0} and K_d are, respectively, the distribution coefficients of the element in the absence of the ligand A and in the presence of different concentrations of it. Putting Eqn. (25) into logarithmic form, we obtain

$$\log(K_{d_0}/K_d - 1) = n\log[A] + \log\beta_n. \quad (26)$$

A graphical plot of relationship (26) enables n to be determined from the slope of the curve relative to the abscissa; the stability constant of the complex is calculated from Eqn. (25).

Fronaeus' method[59,65] is used to study systems in which several complexes are formed, including positively charged complexes which are absorbed by a cation exchanger. An indication of the formation of several complexes over a given range of ligand concentrations is a non-linearity for the relationship $1/K_d = f([A^{y-}])$.

For a reaction between a central ion M^{q+} and a ligand A^{y-} to form the complexes $MA^{(q-y)+}$, $MA_2^{(q-2y)}$, and $MA_3^{(q-3y)}$, of which the first is markedly absorbed by the cation exchanger, the stability constants are calculated from the following equations:

$$\varphi = \frac{K_{d_0}/K_d - 1}{[A]} = \frac{\beta_1 - l + \beta_2[A] + \beta_3[A]^2}{1 + l[A]}, \quad (27)$$

$$f = \frac{K_{d_0}/K_d\{(\beta_1 - l)[A] - 1\} + 1}{[A]^2} = \beta_1\varphi - x, \quad (28)$$

$$x = \beta_2 + \beta_3[A], \quad (29)$$

$$\frac{\Delta f}{\Delta[A]} = \beta_1\frac{\Delta\varphi}{\Delta[A]} - \beta_3. \quad (30)$$

In these equations K_{d_0} and K_d are the distribution coefficients of the element under investigation between the cation exchanger and the solution in the absence and presence of the ligand respectively, [A] is the equilibrium ligand concentration, β_n are the cumulative stability constants of the complexes, l is a quantity which takes account of the absorption of the complex $MA^{(q-y)+}$, φ and f are the Fronaeous functions, $\Delta\varphi = \varphi - \varphi_0$, $\Delta f = f - f_0$. Experimentally one determines the values of K_d and K_{d_0}‡ for a constant ionic strength of the solution observing the condition $[M]_{total} \ll [A^{y-}]$§.

It follows from Eqn. (27) that

$$\lim_{[A]\to 0}\varphi = \beta_1 - l = \varphi_0.$$

Substituting the value of β_1-l obtained in formula (28) enables the function f to be calculated at different ligand concentrations. The value of f_0 is found graphically by extrapolating relationship (28) to zero ligand concentration. By having a number of values of φ and f for different ligand concentrations, β_1 and β_3 can be determined from Eqn. (30):

$$\lim_{\frac{\Delta\varphi}{\Delta[A]}\to 0}\frac{\Delta f}{\Delta[A]} = -\beta_3, \qquad \frac{\Delta f}{\Delta[A]}\Big/\frac{\Delta\varphi}{\Delta[A]} = \beta_1.$$

β_2 is calculated from Eqns. (28) and (29).

It is also possible to use the Fronaeus method for calculating stability constants in the more complicated case where four complexes are formed in the system concerned. An example of such a calculation may be found in a paper dealing with the chloro-complexes of Zr^{IV}.[11]

Paramonova's absorption curve method[66] provides for the use of both cation and anion exchangers for studying complex formation processes, the method leading to a way of expressing the experimental results which enables data obtained for both types of resin to be compared. In this method one studies the absorption of micro- or semimicro-concentrations of an element by cation and anion exchangers from solutions having constant ionic strength and constant salt composition, but differing from each other in ligand concentration. The experimental results are expressed in relative units of absorption of the element by the cation exchanger $\gamma_+ = g_M/g_M^\circ$ and the anion exchanger $\gamma_- = g_{MA}/g_{MA}^\circ$, where g_M° is the maximal absorption of the element M by the cation exchanger in the absence of ligand A, g_M is the absorption of M by the cation exchanger in the presence of A, g_{MA} is the absorption of M by the anion exchanger from the solution under investigation, and g_{MA}° is the absorption of M by the anion exchanger from a solution in which the concentration of A is so high that the further addition of ligand does not lead to an increase in the absorption of M, since it is already present completely in the form of a coordinatively saturated anionic complex.

‡ K_{d_0} can be determined graphically by extrapolating the relationship $K_d = f([A^{y-}])$ to zero ligand concentration.

§ The total molar concentration of M in the equilibrium solution should not exceed 1–2% of the total molar concentration of $[A^{y-}]$. Furthermore, the concentration of the element under investigation should be considerably less than the concentration of the exchanging ions.

The latter circumstance somewhat limits the range of application of anionic exchange. For low-stability complexes the anionic species are formed only at appreciable ligand concentrations, in which case the ligand may displace anionic complexes of the element under investigation from the anionic exchanger, thus making it difficult to determine γ_-. In this case, for approximate calculations, the maximum absorption of M attained by the anion exchanger on increasing the concentration of A may be used for g°_{MA}.

If the concentration of the element under investigation is considerably lower than the concentration of the exchanging ion then it can be shown that γ_+ and γ_- express the fraction of cationic and complex anion species of the element in a given solution. The fraction of the element present in solution in the form of an electrically neutral complex is equal to:

$$\gamma_0 = 1 - \gamma_+ - \gamma_-.$$

When working under static conditions γ_+ and γ_- are calculated from the formula

$$\gamma = \frac{(C_{init} - C)\, C_0}{(C_{init} - C_0)\, C}.$$

Here C_{init} is the concentration of the initial solution, C is the total concentration of M in the equilibrium solution in the presence of the ligand, C_0 in the calculation of γ_+ is the total concentration of M in the solution in equilibrium with the cation exchanger in the absence of the ligand; C_0, when calculating γ_-, is the total concentration of M in the solution in equilibrium with the anion exchanger at that ligand concentration at which all of the element is combined in anionic complexes (or a maximal absorption of M by the anion exchanger is observed).

As an example we present for the simplest cases the formulae for calculating the stability constants of complexes from the experimentally found γ_+ and γ_-.

(a) Complex formation taking place according to the equation $M^{z+} + A^{y-} \rightleftharpoons MA^0$. In this case

$$\beta = \frac{[MA^0]}{[M^{z+}][A^{y-}]} = \frac{1-\gamma_+}{\gamma_+ [A^{y-}]}. \qquad (31)$$

It follows from Eqn. (31) that the stability constant is numerically equal to $1/[A^{y-}]$ at $\gamma_+ = 0.5$.

(b) Complex formation proceeding according to the scheme $M^{z+} + Ay^- \rightleftharpoons MA^{x-}$ $(y > z)$. In this case

$$\beta = \frac{[MA^{x-}]}{[M^{z+}][A^{y-}]} = \frac{\gamma_-}{\gamma_+ [A^{y-}]}. \qquad (32)$$

It follows from Eqn. (32) that $\beta = 1/[A^{y-}]$ at $\gamma_- = \gamma_+$.

(c) Two complexes being formed according to the scheme $M^{z+} + A^{y-} \rightleftharpoons MA^0$, $MA^0 + A^{y-} \rightleftharpoons MA_2^{y-}$. For this system β_1 is found as in case (a) at those ligand concentrations where there is no anionic complex. The overall stability constant is calculated from the formula

$$\beta_2 = \frac{[MA_2^{y-}]}{[M^{z+}][A^{y-}]^2} = \frac{\gamma_-}{\gamma_+ [A^{y-}]^2}. \qquad (33)$$

It follows from Eqn. (33) that $\beta_2 = 1/[A^{y-}]^2$ at $\gamma_- = \gamma_+$.

The methods described above enable the stability constants to be determined for cases where the state of the central ion M^{q+} and the ligand A^{y-} does not change during the complex formation, that is, the reaction between them takes place according to the scheme

$$M^{q+} + nA^{y-} \rightleftarrows MA_n^{(q-yn)}.$$

For complex formation in which hydrolysed cations $M(OH)_x^{(q-x)+}$ participate, the state of the latter may change during complex formation

$$M(OH)_x^{(q-x)+} + nA^{y-} \leftrightarrows M(OH)_{x-n}A_n^{(q+n-yn)} + nOH^-.$$

In this case the above methods only make it possible to determine the equilibrium constants at a given pH.

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Arising from certain specific properties of ion exchangers (equivalence of ion exchange, swelling, the diffusion kinetics of exchange) the ion-exchange method can be successfully applied to studying the states of high-valency ions in solution. At the present time ion exchange is the only method which enables the magnitude of the charge on ions in solution to be determined directly by experiment. Ion exchange enables us to study the polymerisation of inorganic compounds in solution in addition to other methods available. In conjunction with other methods ion exchange is a powerful means of studying the complexes of high-valency elements and it enables us to determine the quantitative characteristics of complex formation processes in solution.

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Institute of General
and Inorganic Chemistry,
Academy of Sciences
of the Ukrainian SSR,
Kiev