1. L. A. Chugaev, Z. anorg. Chem., 46, 144 (1905).
2. H. Grossmann and B. Schück, Ber., 39, 3356 (1906).
3. O. Baudisch, Chem.-Ztg., 33, 1298 (1909).
4. M. Il'inskii and F. Knorre, Ber., 18, 699 (1885).
5. S. Chaberek and A. Martell, "Organic Sequestering Agents" New York, John Wiley and Sons, 1959.
6. F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions", New York, John Wiley and Sons, 1958.
7. F. Hein, "Chemische Koordinationslehre", Leipzig, 1950.
8. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", Copenhagen, 1941.
9. A. K. Babko, Zavod. Lab., 4, 518 (1935); Trudy Kiev. Industr. Inst., 283 (1937); Nauch. Zap. Kiev. Gos. Univ., 4, 81 (1939); "Fiziko-khimicheskii Analiz Kompleksnykh Soedinenii v Rastvorakh" (Physicochemical Analysis of Complex Compounds in Solution), Kiev, 1955.
10. I. Leden, Z. phys. Chem., 188A, 160 (1941).
11. S. Fronaeus, Komplex system Hos Koppar, Lund, 1948.
12. J. Sullivan and J. Hindman, J. Amer. Chem. Soc., 74, 6091 (1952).
13. A. A. Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Moscow–Leningrad, 1951.
14. L. Orgel, "An Introduction to Transition Metal Chemistry and Ligand-Field Theory", London, Methuen, 1960.
15. K. B. Yatsimirskii, Zhur. Neorg. Khim., 3, 2244 (1958).
16. A. Werner, "New Ideas in Inorganic Chemistry" (Translated into Russian), Leningrad, 1936.
17. L. G. Sillén, Quart. Rev., 13, 146 (1959).
18. A. A. Grinberg and G. A. Shagisultanova, Zhur. Neorg. Khim., 5, 280 (1960); 1895 (1960) [Russ. J. Inorg. Chem., 134, 920 (1960)].
19. A. A. Grinberg and M. I. Gel'man, Dokl. Akad. Nauk SSSR, 133, 1081 (1960).
20. A. D. Gel'man and E. F. Karandasheva, Dokl. Akad. Nauk SSSR, 87, 597 (1952).
21. O. E. Zvyagintsev and E. F. Karandasheva, Dokl. Akad. Nauk SSSR, 101, 93 (1955); 108, 477 (1956).
22. A. A. Grinberg, Chem. Zvesti, 13, 201 (1959); Zhur. Neorg. Khim., 4, 1517 (1959) [Russ. J. Inorg. Chem., 683 (1959)].
23. D. Banerjea, F. Basolo, and R. Pearson, J. Amer. Chem. Soc., 79, 4055 (1957).
24. L. Grantham, P. Elleman, and D. Martin, J. Amer. Chem. Soc., 77, 2965 (1955).
25. P. Elleman, J. Reishus, and D. Martin, J. Amer. Chem. Soc., 80, 536 (1958).
26. H. Taube, "Progress in Inorganic Chemistry and Radiochemistry", Vol. 1, New York, 1959, p. 1.
27. B. Jezowska-Trzebiatowska, XVI Congres International de Chimie Pure et Appliquee, Paris, 1957.
28. A. A. Grinberg and Kh. I. Gil'dengershel', Zhur. Prikl. Khim., 22, 1059 (1949).
29. A. A. Grinberg and E. N. In'kova, Zhur. Neorg. Khim., 3, 1315 (1958).
30. A. A. Grinberg and Yu. N. Kukushkin, Dokl. Akad. Nauk SSSR, 132, 1071 (1960).
31. R. Rich and H. Taube, J. Amer. Chem. Soc., 76, 2608 (1954).
32. R. Dreyer, Inaugural Dissertation, Berlin, 1958.
33. A. A. Grinberg and L. E. Nikol'skaya, Zhur. Prikl. Khim., 22, 542 (1949); 24, 893 (1951).
34. A. A. Grinberg, Chem. Zvesti, 13, 201 (1959).
35. H. Brown, S. Fallab, and H. Erlenmeyer, Helv. Chim. Acta, 39, 1486 (1956).
36. I. I. Chernyaev, Izv. Inst. po Izuch. Platiny, 4, 243 (1926).
37. I. I. Chernyaev, Izv. Inst. po Izuch. Platiny, 5, 156 (1927).
38. A. A. Grinberg and D. I. Ryabchikov, Acta Physicochim. U.R.S.S., 3, 55 (1935).
39. A. A. Grinberg, Acta Physicochim. U.R.S.S., 3, 573 (1935).
40. K. A. Jensen, Z. anorg. Chem., 242, 87 (1939).
41. J. Bjerrum and S. Rasmussen, Acta Chem. Scand., 6, 1265 (1952).
42. F. Woldbye, quoted in ref. 6.
43. V. G. Tronev and V. N. Chulkov, Dokl. Akad. Nauk SSSR, 63, 545 (1948).
44. G. B. Bokii and S. S. Batsanov, Dokl. Akad. Nauk SSSR, 95, 1205 (1954).
45. G. B. Bokii and G. A. Kukina, Kristallografiya, 2, 400 (1957).
46. J. Chatt, J. Duncanson, and L. Venanzi, J. Chem. Soc., 4456 (1955).
47. H. Cardwell, Chem. and Ind., 422 (1955).
48. L. Orgel, J. Inorg. Nuclear Chem., 2, 137 (1956).
49. A. A. Grinberg, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 350 (1943).
50. I. I. Chernyaev and A. Ganiev, Zhur. Neorg. Khim., 2, 765 (1957).
51. A. V. Ablov and N. I. Lobanov, Zhur. Neorg. Khim., 2, 2570 (1957).
52. N. M. Samus', "Dioksiminy Trekhvalentnogo Kobalta" [Cobalt(III) Dioxime Complexes], Thesis, Kishinev, 1959.
53. I. I. Chernyaev and O. N. Adrianova, Izv. Sektora po Izuch. Platiny, 23, 9 (1949); 24, 79 (1949); Zhur. Neorg. Khim., 2, 204 (1953).
54. I. I. Chernyaev and G. S. Muraveiskaya, Izv. Sektora po Izuch. Platiny, 25, 35 (1950).
55. I. I. Chernyaev, Uspekhi Khim., 26, 1230 (1957).
56. E. Corey and J. Bailar, J. Amer. Chem. Soc., 81, 2620 (1959).
57. A. A. Grinberg, B. V. Ptitsyn, and V. N. Lavrent'ev, Zhur. Fiz. Khim., 10, 661 (1937).
58. A. A. Grinberg and B. Z. Orlova, Zhur. Prikl. Khim., 21, 1083 (1948); 22, 441 (1949).
59. Ya. D. Fridman, Zhur. Neorg. Khim., 3, 1865 (1958).
60. Ya. D. Fridman and D. S. Sarbaev, Zhur. Neorg. Khim., 4, 1849 (1959).
61. J. Chatt, L. Duncanson, and B. Shaw, Proc. Chem. Soc., 343 (1957).
62. F. Dwyer and F. Lions, J. Amer. Chem. Soc., 72, 1545 (1950); 74, 4188 (1952).
63. J. Majer, J. Dvořak, and M. Strugar, "Summary of Reports to the 3rd National Conference on Inorganic Chemistry" (Translated into Russian), Bratislava, 1959.
64. Ya. K. Syrkin, Uspekhi Khim., 28, 904 (1959).

Khlopin Radium Institute,
the USSR Academy of Sciences

SORPTION AND ION EXCHANGE ON AMPHOTERIC OXIDES AND HYDROXIDES

G. M. Zhabrova and E. V. Egorov

CONTENTS

1. Applications of amphoteric oxides and hydroxides as inorganic ion exchangers and sorbents. 339

2. Sorptive properties of various oxides and hydroxides 339
A. Aluminium oxide and hydroxide 339
B. Ferric oxide and hydroxide 340
C. Titanium dioxide 341
D. Zirconium oxide and hydroxide and derived ion exchangers 341
E. Zinc oxide and hydroxide 342
F. Stannic hydroxide; oxides and hydroxides of some other metals 343
3. Some features of the mechanism of ion exchange on oxides and hydroxides 343

1. APPLICATIONS OF AMPHOTERIC OXIDES AND HYDROXIDES AS INORGANIC ION EXCHANGERS AND SORBENTS

The study of the sorption of electrolytes on oxides and hydroxides is of considerable importance in various fields of science: ion exchange, radiochemistry, chromatography, catalysis, inorganic chemistry, geochemistry, and soil science. The majority of amphoteric oxides and hydroxides are amphoteric ion exchangers (ampholytes) exhibiting both cation- and anion-exchange properties. The oxides and hydroxides of aluminium, iron, zirconium, tin, uranium, and other metals have been extensively used as ion exchangers and sorbents.

Considerable interest has recently been shown in the problems of sorption on amphoteric oxides and hydroxides in connection with study of the behaviour of fission fragments[1], isolation of radioactive isotopes[2], deactivation of effluents from radiochemical plants[3-6], studies in radiochromatography[7-8], and concentration of microquantities of radioelements[9].

Inorganic ion exchangers have a number of advantages over synthetic resins. In most cases the latter are decomposed in solution at temperatures over 150° and their capacity, selectivity, and rate of exchange are affected by high doses of ionising radiation (over 10^8 r [10-12]), whereas inorganic ion exchangers, particularly amphoteric oxides and hydroxides, are in most cases stable to high temperatures and ionising radiations[13].

Synthesis of inorganic ion exchangers of the amphoteric oxide and hydroxide type is extremely simple[14-16] and the cost per unit of capacity is in most cases much lower than that for organic resins. When inorganic ion exchangers are used to purify and deactivate various industrial solutions and effluents, regeneration of the ion exchanger is often unnecessary and it is effective when used once only. Some inorganic ion exchangers, such as zirconium and uranium hydroxides and zirconium phosphate, have high selectivity[7] and make possible a sharp separation of elements in the same group of the Periodic System on a column only a few centimetres long.

In addition to ion-exchange sorption, amphoteric oxides and hydroxides can be used for chemical[17-19] and molecular[20] sorption. The properties of ampholytes are also shown by some oxides and hydroxides which normally do not exhibit amphoteric properties, for example nickel oxide[21].

The chief disadvantage of these ion exchangers is that in most cases their capacity is lower than that of synthetic resins. Also, many amphoteric oxides and hydroxides dissolve in concentrated solutions of acid or alkali, making it impossible to use them when there is a marked change in hydrogen ion concentration. If, however, the ion exchanger is a polymer with a network structure, it is practically stable over any pH range[22].

Other possible uses of the sorptive and ion-exchange properties of amphoteric oxides and hydroxides should be mentioned. The ion-exchange sorption of cations and anions and also chemisorption on amphoteric oxides and hydroxides can be used as methods for changing the microchemical composition of the surface of oxide catalysts and for controlling catalytic properties. Zhabrova, Vladimirova, and Egorov[23] established that Na^+ and Cl^- ions introduced into zinc oxide by ion exchange increased the activity of the zinc oxide catalyst in the dehydrogenation of isopropyl alcohol. The sorption of zinc sulphate on zinc oxide, however, considerably decreased the rate of dehydrogenation and increased the rate of dehydration of the alcohol. Boreskov, Dzis'ko, and Borisova[24] found a decrease in the rate of dehydration of ethyl alcohol on aluminium oxide after sorption of sodium hydroxide. This is attributed to displacement, by sodium ions, of hydrogen atoms of the hydroxide groups on the catalyst surface.

The influence of sodium ions sorbed by the surface of oxide catalysts of more complex composition has been considered by many workers, but we shall refer to only a few examples. Bitepazh[25] showed that the aluminosilicate catalyst used for cracking is poisoned by sodium and other alkali metal ions sorbed by cation exchange on the catalyst surface. Topchieva[26] showed that it is possible to alter the activity of aluminosilicate catalysts (for various reactions) by means of sodium ions, introduced either from sodium chloride or acetate solutions or from sodium hydroxide solution.

The use of ion exchange to prepare sorbents with different sorptive properties, for example silica gels in which the exchanger hydroxide ions are replaced by fluoride ions[27], has also been proposed. It appears that by the rational use of the anion- and cation-exchange properties of oxides and hydroxides from which catalysts and sorbents are prepared, it is possible to introduce controlled quantities of impurities on to the surface; this is of considerable importance for controlling catalytic activity and sorptive properties. The irreversible chemisorption of electrolytes can be used as an effective method for controlling the microchemical composition of the surface of many amphoteric hydroxides used for the preparation of catalysts and sorbents.

2. SORPTIVE PROPERTIES OF VARIOUS OXIDES AND HYDROXIDES

A. Aluminium Oxide and Hydroxide

Aluminium oxide and hydroxide have been studied by many workers[28-32]. Nikol'skii[33] showed that the hydroxide ions or protons of aluminium hydroxide are replaced by anions or cations from the solution. This exchange is due to dissociation of $Al(OH)_3$ in two ways:

$$Al(OH)_3 \rightleftharpoons Al(OH)_2^+ + OH^-,$$
$$Al(OH)_3 \rightleftharpoons Al(OH)_2O^- + H^+.$$

Thus aluminium hydroxide may be either a cation exchanger (in alkaline medium) or an anion exchanger (in acid medium),

and within a certain pH range can act as an amphoteric ion exchanger.

Various chromatographic processes on aluminium oxide have been studied[34-39], and cations and anions have been arranged[40-41] in order of their sorbability on aluminium oxide standardised by Brokmann's method[42]. The same has been done by Gapon and Shuvaeva[43]. The authors regard exchange on aluminate aluminium oxide as one of cations with Na^+ and exchange on acidic aluminium oxide as one of anions with NO_3^-. In aluminium oxide cation-exchanger the functional groups are the Na^+ groups in $(Al_2O_3)_x.AlO_2^-.Na^+$; when the aluminium oxide cation-exchanger is washed with nitric acid the product is aluminium oxide anion-exchanger whose exchange groups are the NO_3^- groups in $(Al_2O_3)_x.AlO^+.NO_3^-$.

The interesting phenomenon of the combined sorption of anions with highly-charged cations and of cations with highly-charged anions, established by Schwab[28-29], was attributed by Gapon and Shuvaeva[43] to a change in the sign of the surface charge. The sorption of anions with singly-charged cations and of cations with singly-charged anions was not observed by the authors.

Fischer[44] and Umland[45] classified the sorption of electrolytes on aluminium oxide as equivalent or nonequivalent†.

In the first case more cations than anions are sorbed (from $CuCl_2$ solution) and the solution becomes acidic. Equivalent quantities of cations and anions are readily washed off with water but an excess of sorbed cations cannot be washed off. This excess was attributed to exchange with aluminium ions or sodium ions present as an impurity in the Al_2O_3, being equivalent to the quantity of Na^+ or Al^{3+} passing into solution. The replacement of Al^{3+} by H^+ in the surface layer by treating the Al_2O_3 with 0.1*N* hydrochloric acid solution decreases the sorption and makes it equivalent. This phenomenon is related to the order of the cations in Schwab's series. In the second case more anions than cations are sorbed; this is attributed to exchange of anions with NO_3^- or OH^- ions, and has been observed for $NiCl_2$ and KCl. Excess sorption of anions or cations is attributed to a relatively strong bond (the sorbability) between cation or anion and the ion exchanger. Umland[45] and Hayek *et al.*[46] point out, however, that in many cases the separation of ions cannot be due entirely to processes of ion exchange or molecular sorption. The observed deviations from equivalence and the non-reproducibility of the series may be due to precipitation of sparingly soluble bases and basic salts.

Fischer[44] and Umland[45] observed sorption of anions and cations on pure aluminium oxide although Gapon[43] considers that it does not exhibit ion-exchange properties. Sorption was attributed to production on the surface of the oxide of H^+ and OH^- groups capable of exchange.

Voznesenskii *et al.*[18], using radioactive caesium, strontium, cerium, and ruthenium, showed that sorption of cerium and ruthenium takes place at a positively charged aluminium oxide surface by exchange with the potential-determining aluminium ions in the primary layer, while sorption of strontium takes place at a negatively charged surface as a result of the formation of aluminate at high pH values (Fig. 1). Almost no caesium is sorbed.

The structure and sorptive properties of aluminium oxide and hydroxide are greatly influenced by the conditions of their preparation. At the moment of formation aluminium hydroxide consists of amorphous particles and is an extremely active sorbent. During aging the gel becomes more compact and crystallises, with a decrease in active surface area and sorptive capacity[47-50]. By varying the conditions of preparation it is possible to obtain aluminium oxide with cation- or anion-exchange and also amphoteric ion-exchange properties[14,15,42,43].

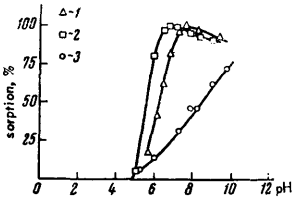


Fig. 1. Sorption isotherms for strontium, ruthenium, and cerium on aluminium hydroxide[18]: 1) Ce; 2) Ru; 3) Sr.

B. Ferric Oxide and Hydroxide

Much has been done on the sorption of ions on ferric oxide and hydroxide, and the work of Kurbatov and co-workers[51-61] must be mentioned first. From their results, they attempt a quantitative estimation of the sorption of doubly-charged cations. They consider that ferric hydroxide acts as a chemisorbent towards strontium, calcium, and barium, and assume that the process is reversible and obeys the law of mass action, but the regular features they observed can hardly express the general rules of sorption on hydroxides[62].

Ratner[63,64] established that the sorption of cobalt, zinc, and radium on ferric hydroxide exhibits the characteristics of secondary exchange (ion exchange in the outer layer of the electrical double layer). Sorption is negligible at low pH values but increases sharply at pH 7.

According to the data of Voznesenskii *et al.*[3], the nature and mechanism of the sorption of highly-charged ions on ferric hydroxide differ from those for alkali and alkaline-earth metal ions. Sorption of highly-charged cations (yttrium, cerium, promethium and ruthenium) takes place to a considerable extent throughout the whole volume of the precipitate (internal sorption), whereas alkali and alkaline-earth metal ions (strontium and calcium) are sorbed only on the surface of the precipitate (adsorption). Desorption of alkaline-earth elements from ferric hydroxide is comparatively easy, but desorption of polyvalent elements is difficult. Highly-charged cations can

† The term "nonequivalent sorption" denotes sorption of the cations and anions from an electrolyte solution in nonequivalent quantities. Electrical neutrality of the solution and sorbent is maintained by sorption or desorption of foreign ions.

be regarded as sorbed in the internal micro-cracks and micro-capillaries[65], or it is possible that solid solutions are formed. It is difficult to establish the nature and type of sorption on ferric hydroxide, however, since the structure of the sorbent itself is still disputed. The conditions of its precipitation and preparation have a decisive influence on its structure and sorptive capacity[47,66-69]. According to Krause[70], the ferric hydroxide particles initially have the structure

$$Fe(OH)_2-O-Fe(OH)-O-Fe(OH)-Fe=O.$$

Polymerisation of these molecules yields complexes containing 40–50 iron atoms. These amorphous spherical particles of ferric hydroxide subsequently pack together and crystallise[47].

Pushkarev[19], in a study of the sorption of radioactive caesium, strontium, cerium, and ruthenium on ferric hydroxide, showed that the sorption of ruthenium and cerium is maximal at pH 3–6.5 and takes place at a positively charged surface by exchange with the potential-determining iron ions in the primary layer. The sorption of strontium takes place at fairly high pH values on a negatively charged surface with the formation of ferrites. Almost no cerium is sorbed. The shape of the sorption isotherms is similar to that for aluminium hydroxide (Fig. 1). Although this mechanism of the sorption of ruthenium and cerium (exchange with the potential-determining iron ions) is probably correct, there are some experimental data which made Pushkarev's conclusions doubtful. A negative charge may appear[71] on ferric hydroxide at pH > 3 and sorption of ruthenium and cerium as potential-determining ions becomes improbable. It is also necessary to take account of the state (ionic or colloidal) of the microquantities of radioelements which were used in the work[72]. Moreover, the nature of the potential-determining ions in ferric hydroxide is still disputed; different authors have assumed them to be Fe^{3+}, FeO^+ [73-75], or hydrogen ions[76,77].

Kargin *et al.*[76,78] studied the processes taking place when an Fe_2O_3 sol is treated with electrolytes and established that they involve complete or partial replacement of the peptising acid (HCl) by the acid (H_2SO_4) formed in the reaction between HCl and the added salt (Na_2SO_4). It was also found that the sorbed acids do not react with Fe_2O_3 to form iron salts down to pH 3. At low initial HCl concentration, the sorption of SO_4^{2-} and the displacement of Cl^- are approximately equivalent. With increase in the concentration of one or other of the acids, deviation from equivalent exchange takes place. The deviation is greater, the lower the equilibrium pH values.

Others have studied the sorption of cations on ferric hydroxide[79-82]. The results show that ferric oxide and hydroxide may exhibit either cation- or anion-exchange properties, depending on the presence of various impurities, the concentration of electrolyte, and the pH of the solution.

C. Titanium Dioxide

Titanium dioxide has been shown to exhibit amphoteric ion-exchange properties. According to Amphlett *et al.*[83], titanium dioxide exhibits anion-exchange properties in acid and neutral solutions, and cation-exchange properties in alkaline solutions. Amphlett attributes the amphoteric ion-exchange properties of titanium dioxide to hydrolysis of the oxide with formation of a surface layer of hydroxide and dissociation of the latter in two ways to form H^+ and OH^- functional groups capable of exchange, *i.e.*, the mechanism proposed by Nikol'skii for aluminium oxide[33].

Kargin[84] regards colloidal titanium dioxide as a sorbent capable of molecular sorption of salts and acids, and points out that sorption of neutral salts is negligible compared with the sorption of acids. It was found that with a mixture of sulphuric and hydrochloric acids, sorption of sulphuric acid predominates. At a fairly high equilibrium concentration of Na_2SO_4 (sulphuric acid is formed by reaction between HCl in the sol and the Na_2SO_4 added), the relation between sorption of SO_4^{2-} ions and solution pH is linear. Sorption of SO_4^{2-} stops almost completely at pH 6.5–7.

According to Maidanovskaya[85], titanium dioxide exhibits cation-exchange properties. It hydrolyses in water according to

$$TiO_2 + 2H_2O \rightleftharpoons TiO_2(OH)_2^{2-} + 2H^+.$$

The H^+ ions are functional groups capable of cation exchange.

D. Zirconium Oxide and Hydroxide and Derived Ion Exchangers

Ion exchangers based on zirconium are of particular interest. They have a high capacity, of the order of one milligramme-equivalent per gramme, corresponding to two milligramme-equivalents per cubic centimetre of dry material. They exhibit exceptional selective sorption, which makes it possible to separate elements in the same group of the Periodic System on a column only a few centimetres long. These ion exchangers have a three-dimensional polymeric network structure and are in most cases stable to acids, alkalies, high temperatures, and radiation. Much work has been done on them recently.

Zirconium oxide and hydroxide dissociate, in aqueous solution, as a weak base or weak acid[83]. The H^+ and OH^- functional groups produced on dissociation are capable of exchanging with cations and anions of the solution. In neutral and acid media, pure zirconium hydroxide acts chiefly as an anion exchanger. In alkaline solution, zirconium oxide and hydroxide are capable of exhibiting cation exchange[86]. Typical ion-exchange curves for zirconium hydroxide are given in Fig. 2

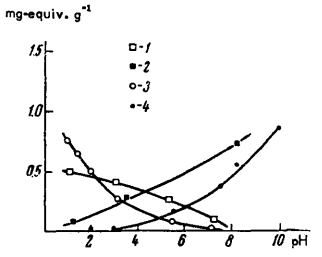
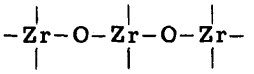


Fig. 2. Dependence of ion-exchange capacity of zirconium and stannic hydroxides on hydrogen ion concentration in solution[7,86]:
1) and 2) $Zr(OH)_4$; 3) and 4) $SnO_2 \cdot 2H_2O$.

The cation-exchange capacity of zirconium hydroxide is increased when the sorbent is treated with phosphoric acid[13, 87, 88]. This is shown in Fig. 3, which also gives the dependence of the cation-exchange sorption by zirconyl chromate on the pH of the solution [89]. Zirconium phosphate possesses a strongly acidic ionogenic group. The ion-exchange properties of the sorbent remain unchanged at 200° and it is extremely selective towards singly-charged ions. For example, rubidium and caesium ions are readily separated using zirconium phosphate.

Polymeric chains of the type



have been shown to exist in zirconyl perchlorate solutions. When such a solution is treated with a polybasic acid or its salt, the polymeric chains are linked by acid anionic bridges, and part of the acid or salt, by attaching itself to the free valencies, forms functional groups capable of exchange [89]. If the acid is strong, the products are strong ion exchangers; if the acid is weakly dissociated, titration of zirconium ion exchangers containing this acid as functional group shows that the ion-exchange sorption is very dependent on the pH of the solution. This dependence is similar to that for weakly acidic carboxylic or phenolic organic ion exchangers.

There are two viewpoints on the nature of ion exchange on zirconium exchangers. Bresler [89] considers that it takes place throughout the whole volume of the ion exchanger and is, within limits, independent of the particle size. The capacity of the ion exchanger will thus be directly proportional to its weight, but in contrast to a synthetic resin, the swelling is negligible. On the other hand, Kraus [7, 90, 91] suggests that exchange on zirconium ion exchangers takes place at the surface of the sorbent and the exceptional selectivity is attributed to differences in accessibility of the pores of the sorbent to different ions. Increase in the temperature of drying and ignition leads to partial sintering of the pores and to a decrease in the working surface and ion-exchange capacity of the sorbents.

Two possible mechanism of ion exchange on pure zirconium oxide and hydroxide may be put forward. According to the first, exchange is due to dissociation of zirconium hydroxide as an acid or base [83]. According to the second, reaction takes place in acid medium between the acid and the hydroxide [7], leading to formation of water from the proton of the acid and the hydroxide ion. According to Kraus and coworkers, this water remains fixed in the lattice or on its surface. The zirconium hydroxide lattice is positively charged, and the anion of the acid is attracted to it, so that both sorbent and solution attain electrical neutrality. If the anion of the acid does not diffuse into the depth of the lattice but remains on the surface, it can exchange with other ions of the solution and thus determine the ion-exchange capacity of the zirconium hydroxide. A similar phenomenon is shown in alkaline solution, but then the lattice is negatively charged and cations sorbed on the surface are responsible for the cation-exchange capacity. These schemes can be represented as follows:

$$Zr(OH)_4 + HCl \rightleftharpoons [Zr(OH)_3H_2O]^+ Cl^-$$

$$Zr(OH)_4 + NaOH \rightleftharpoons [Zr(OH)_3(O)H_2O]^- Na^+.$$

With lower pH, there is a higher positive charge on the lattice and greater anion-exchange capacity; with higher pH, higher negative charge on the lattice and greater cation-exchange capacity. Within a certain range of hydrogen ion concentration, both reactions are possible.

The frontal method has been used with zirconium ion exchangers to separate cations, and fairly high enrichment coefficients have been obtained [89]; the elution method has been used to separate alkali and alkaline-earth elements and to carry out separations within each group of the Periodic System. Zirconium oxide, hydroxide, tungstate, molybdate, and phosphate have been used for this purpose [13].

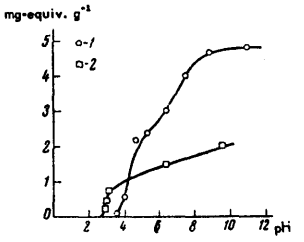


Fig. 3. Dependence of cation-exchange capacity of zirconium ion-exchangers on hydrogen ion concentration in solution [13, 89].
1) zirconyl phosphate; 2) zirconyl chromate.

E. Zinc Oxide and Hydroxide

Less work has been done on ion exchange and sorption on zinc oxide and hydroxide than on typical inorganic sorbents and ion exchangers such as the hydroxides of iron, aluminium, zirconium. This is due firstly to the low ion-exchange capacity of zinc oxide and hydroxide and secondly to the solubility of zinc oxide sorbents in both acid and alkali solutions. Maidanovskaya [85] has shown that zinc oxide sorbs potassium and barium cations from neutral, weakly acidic, and weakly alkaline solutions, the sorption being of the electrochemical type. Sorption of anions from solution was not observed.

Tewari [92] studied sorption of hydroxide ions and protons on zinc hydroxide. The zinc hydroxide was prepared by reaction of a zinc salt ($ZnCl_2$) with alkali (NaOH), and its sorptive properties were found to depend on the presence of excess of one or other of these components. When prepared with excess NaOH it sorbed H^+ ions most strongly, and with excess zinc salt OH^- ions most strongly. Zhabrova and coworkers [17, 23] established that zinc oxide is an amphoteric ion exchanger with functional groups of the weak acid type in alkaline solution and of the weak base type in acid solution (Fig. 4). In the neutral range, zinc oxide may exhibit both cation- and anion-exchange properties. Ion exchange on zinc oxide is limited to the narrow pH range 6.5–9.5. At pH $\geq$9.5 various zincates are formed, and in the acid range (pH $\leq$ 6.5) basic salts of varying composition may exist. Molecular sorption from fairly concentrated solutions of neutral salts, for example zinc sulphate [23], has been observed.

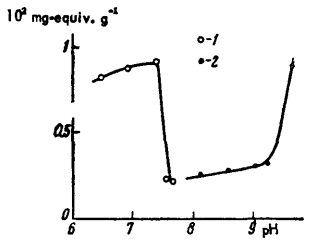


Fig. 4. Dependence of cation- and anion-exchange capacities of zinc oxide on hydrogen ion concentration in solution:
1) anionic exchange (Cl^-); 2) cationic exchange (Na^+).[17, 23]

F. Stannic Hydroxide; Oxides and Hydroxides of Some Other Metals

According to Merz, stannic hydroxide exhibits anion-exchange properties in acid media[86]. Stannic hydroxide contains mobile hydroxide ions which are replaced by an equivalent quantity of anions from the solution. At pH > 7, stannic hydroxide exhibits chiefly cation-exchange properties (Fig. 2). Kraus *et al.*[7] consider that stannic hydroxide starts to operate as a cation exchanger at pH > 3 (Fig. 2). The ion-exchange properties of uranium oxide and hydroxide, thorium and tungsten oxides, and various other oxides and hydroxides have also been described[7, 88].

3. SOME FEATURES OF THE MECHANISM OF ION EXCHANGE ON OXIDES AND HYDROXIDES

The ion-exchange properties of amphoteric oxides and hydroxides are as a rule determined by two factors. Firstly, they depend on the composition and structure of the sorbent. The presence of impurities may produce a sharp change in the capacity and selectivity of the ion exchanger. The structure of the sorbent may also have a marked influence on the selectivity of sorption. Thus crystalline sorbents are more selective than amorphous sorbents. Secondly, the ion-exchange properties of amphoteric oxides and hydroxides depend on the solution conditions, especially the hydrogen ion concentration. Since most of the ion exchangers we have considered are weak bases and weak acids, this dependence is particularly marked.

The regular features of ion exchange on hydroxides and oxides can be explained qualitatively in terms of two possible ion exchange mechanisms. According to the first, the functional groups capable of exchange are H^+ and OH^- groups on the surface or in the bulk of the oxide and hydroxide[17, 33, 88]. As a rule, the exchange sorption is markedly dependent on the pH of the solution. Whether dissociation is acidic or basic, with transfer of protons or hydroxide ions to the outer layer of the electrical double layer, is determined primarily by the pH.

The second mechanism of ion exchange is applicable to oxides and hydroxides with a high capacity for impurities[43-45], which may be introduced beforehand or on contact between the sorbent and solution. The amphoteric oxide or hydroxide acts as a rigid insoluble or sparingly soluble skeleton (often a three-dimensional polymeric network) on which functional groups capable of exchange are situated. These sorbents may be weak or strong ion exchangers, depending on the nature of the functional groups. In a number of cases these ion exchangers have a capacity greater than that of the pure oxides and hydroxides. When the functional groups are highly dissociated, the quantity of sorbed ions depends only to a slight extent on the pH of the solution.

Although the theory of ion exchange on oxides and hydroxides satisfactorily explains and confirms the experimental results qualitatively, there is as yet no clear quantitative theory of ion exchange on these sorbents. The isolated attempts to develop such a theory for individual sorbents can hardly reflect the general relationship[62].

The lack of a theory of ion exchange on oxides and hydroxides is due chiefly to the difficulty of systematising the experimental material and separating ion exchange distinctly from other sorption processes (this is not always possible). Molecular and chemical sorption may take place on these sorbents in addition to ion-exchange processes.

The results obtained by different authors for the same oxides and hydroxides and the same range of pH and electrolyte concentration often differ considerably. This is evidently due to differences in the conditions of preparation of the sorbents, uptake of impurities, etc. Data for ion exchange on stannic hydroxide and the hydroxides of zirconium, zinc, and other metals are given in the Table.

TABLE. Cation- and anion-exchange capacities of amphoteric oxides and hydroxides.

Sorbent	Cation exchange (capacity in mg-equiv. g^{-1})							Anion exchange (capacity in mg-equiv. g^{-1})							Reference
	pH 1	pH 3	pH 5	pH 7	pH 9	pH 11	pH 13	pH 1	pH 3	pH 5	pH 7	pH 9	pH 11	pH 13	
$Zr(OH)_4$	0	0.25	0.4	0.6	0.9	—	—	1	0.9	0.8	0.6	0	0	0	86
$Zr(OH)_4$	0	0	0.03	0.1	0.25	0.5	—	1	0.8	0.4	0.1	0	0	0	7
ZrO_2	—	—	—	—	—	—	—	1.15	0.8	0.6	0.4	0.2	0.1	0	88
$SnO_2 \cdot 2H_2O$	0	0	0.15	0.3	0.65	—	—	0.8	0.25	0.1	0.05	0	0	0	7
$SnO_2 \cdot 2H_2O$	0.05	0.35	0.5	0.7	0.8	—	—	0.5	0.4	0.3	0.2	0	0	0	86
ThO_2	—	—	—	—	—	—	—	—	1	0.75	0.5	0.15	0	0	88
$Fe(OH)_3$	—	—	—	—	—	—	—	—	—	0.07	0.13	pH 9.4 0.077	—	—	93
$Zn(OH)_2$	0	0	0	pH 8 $2.5 \cdot 10^{-3}$	pH 9.55 $2.7 \cdot 10^{-3}$	—	—	—	—	—	$8 \cdot 10^{-3}$	pH 7.75 $2 \cdot 10^{-3}$	0	0	17

For a quantitative consideration of ion exchange on amphoteric oxides and hydroxides, the following points must be noted. The ion-exchange capacity of the pure sorbent is determined chiefly by the degree of its acidic or basic dissociation. Let us assume that α_1 and α_2 are the degrees of acidic or basic dissociation of the hydroxide at the hydroxide–solution boundary. The functional H^+ or OH^- groups responsible for the ion-exchange properties lie in the outer layer of the electrical double layer. The degree of dissociation α_1 or α_2 is a function of the solution pH, concentration of ions, the ionic strength, nature of the solvent, temperature, etc. If exchange takes place only at the surface of the sorbent, the total ion-exchange capacity under a given set of conditions (pH, concentration of ions, temperature, etc.) will be

$$\Gamma = \alpha NS \qquad (1)$$

where Γ is the exchange capacity of 1 g of sorbent, α the degree of dissociation, N the number of hydroxide molecules per unit surface area, and S the specific surface of the sorbent.

If exchange takes place throughout the whole volume of the sorbent, Eqn. (1) becomes

$$\Gamma = \alpha MV \qquad (2)$$

where M is the number of hydroxide molecules in unit volume and V the specific volume of the sorbent.

When dealing with Eqns. (1) and (2) it is assumed that the volume of sorbent, the number of molecules of hydroxide per unit volume or specific surface, and the actual specific surface and specific volume are constant quantities independent of the pH of the solution, concentration of ions, ionic strength, temperature, etc. The variable α in Eqns. (1) and (2) which is a function of many parameters cannot at present be calculated.

It appears possible to determine the degree of dissociation experimentally by measuring the capacity of the electrical double layer under various initial conditions. Although the capacity of the double layer and the degree of dissociation are not related unambiguously to one another, to a first approximation this method may give useful results for moderate values of electrolyte concentration and pH close to 7.

Ion exchange on amphoteric oxides and hydroxides exhibits the features of a heterogeneous chemical reaction at the boundary of the electrical double layer, and Nikol'skii, on the basis of the law of mass action, put forward an equation for the exchange of two ions of equal valency [94, 95]

$$\frac{f'^{1/z_1}_{M_1} \cdot g^{1/z_1}_{M_1}}{f'^{1/z_2}_{M_2} \cdot g^{1/z_2}_{M_2}} = K \frac{f^{1/z}_{M_1} \cdot c^{1/z_1}_{M_1}}{f^{1/z_2}_{M_2} \cdot c^{1/z_2}_{M_2}}, \qquad (3)$$

where g is the concentration of the ion in the solid phase, c the concentration of the ion in solution, f' the activity coefficient of the ion in the solid phase, f the activity coefficient of the ion in solution, z the valency of the ion, M its index, and K the ion-exchange constant. Experiment has shown [96] that K is constant over a wide range of concentration of the sorbed ions.

Determination of the activity coefficients of ions in the solid phase is not at present possible. For ion exchangers such as pure oxides and hydroxides, however, the concentration of ions in the solid phase is generally small and the activity coefficients can, to a first approximation, be taken as unity.

The participation of H^+ and OH^- ions in an ion-exchange process often makes it difficult to treat the experimental results by means of any ion-exchange equation. The energy of the bond formed by a proton and a hydroxide ion with the sorbent is very much greater than that of bonds formed by other ions. The proton and hydroxide ion penetrate into the depth of the sorbent and may be held very strongly [97]. Moreover, when a proton or hydroxide ion takes part in ion exchange, there is a change in the pH of the solution before and after exchange, leading to a change in the constant in ion-exchange equations [for example K in Eqn. (3)].

Published data indicate that the following sorption processes are possible on amphoteric oxides and hydroxides: (1) ion exchange in the primary layer with potential-determining ions (cationic in acid, anionic in alkaline medium); (2) ion exchange in the outer (secondary) layer (anionic in acid, cationic in alkaline medium); (3) combined anionic and cationic exchange in the outer layer (close to the isoelectric point); (4) chemical sorption in acid medium with formation of basic salts and other surface compounds; (5) chemical sorption in alkaline medium with formation of aluminates, ferrites, zincates, and other compounds; (6) molecular sorption at high electrolyte concentrations and pH close to 7; (7) exchange between cations and anions in molecules sorbed by molecular sorption and cations and anions in solution; (8) combined sorption of anions with polyvalent cations and of cations with polyvalent anions, associated with a change in the sign of the surface charge.

1. An. N. Nesmeyanov, N. P. Rudenko, and A. V. Lapitskii, "Polucheniye Radioaktivnykh Izotopov" (The Preparation of Radioactive Isotopes), Goskhimizdat, 1954.
2. I. A. Korshunov and A. I. Shafiev, Zhur. Neorg. Khim., 3, 100 (1958).
3. S. A. Voznesenskii, G. A. Sereda, P. F. Dolgikh, and L. I. Baskov, "Vtoraya Mezhdunarodnaya Konferentsiya po Mirnomu Ispol'zovaniyu Atomnoi Energii, Zheneva, Doklady Sovetskikh Uchenykh" (Reports of Soviet Scientists to the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva), Vol. 4, 1958, p. 189.
4. K. A. Bol'shakov, A. R. Avdonin, V. T. Borshchev, F. V. Rauzen, *et al.*, *ibid.*, p. 195.
5. C. P. Straub and W. J. Lacy, "International Conference on the Peaceful Uses of Atomic Energy", 1958, p. 311.
6. R. I. Morton and C. P. Straub, "Reactor Operational Problems", Vol. 11, Pergamon Press, New York, 1957, pp. 1–9. [These references appear to be in error (Ed. of Translation)].
7. K. A. Kraus, H. O. Phillips, T. A. Carlson, and K. S. Johnson, "Vtoraya Mezhdunarodnaya Konferentsiya po Mirnomu Ispol'zovaniyu Atomnoi Energii, Zheneva, Doklady Inostrannykh Uchenykh" (Reports of Non-Soviet Scientists to the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva), Vol. 5, 1958, p. 252.
8. E. N. Gapon and V. V. Rachinskii, "Sbornik, Issledovaniya v Oblasti Khromatografii" (Collection, Studies in Chromatography), Izd. Akad. Nauk SSSR, Moscow, 1952, p. 30.
9. K. F. Lazarev and S. M. Grashchenko, Radiokhimiya, 1, 4, 493 (1953).
10. J. C. Bresee, J. R. Flanary, J. H. Goode, C. D. Watson, and J. S. Watson, Nucleonics, 14, 9, 75 (1956).
11. G. I. Cathers, "Radiation Damage to Radiochemical Processing Reagents" Paper 548, First International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955.

12. G. I. Cathers, Report No. 743, First International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955.
13. C. Amphlett, "Vtoraya Mezhdunarodnaya Konferentsiya po Mirnomu Ispol'zovaniyu Atomnoi Energii, Zheneva, Doklady Inostrannykh Uchenykh" (Reports of Non-Soviet Scientists to the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva), Vol. 5, 1958, p. 241.
14. V. V. Rachinskii and T. B. Gapon, "Khromatografiya v Biologii" (Chromatography in Biology), Izd. Akad. Nauk SSSR, Moscow, 1950, p. 31.
15. N. A. Fuks, Zavod. Lab., 8, 878 (1950).
16. K. A. Kraus and H. O. Phillips, J. Amer. Chem. Soc., 77, 4508 (1955).
17. G. M. Zhabrova and E. V. Egorov, Radiokhimiya, 1, 5, 538 (1959).
18. S. N. Voznesenskii, V. V. Pushkarev, and V. F. Bagretsov, Zhur. Neorg. Khim., 3, 235 (1958).
19. V. V. Pushkarev, Zhur. Neorg. Khim., 1, 178 (1956).
20. V. A. Kargin, Uspekhi Khim., 8, 298 (1939).
21. N. G. Klyukina, Kolloid. Zhur., 21, 292 (1959).
22. E. B. Trostyanskaya, "Sbornik, Ionnyi Obmen i Ego Primenenie" (Collection, Ion Exchange and Its Application), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 17.
23. G. M. Zhabrova, Uspekhi Khim., 24, 598 (1955); G. M. Zhabrova, V. I. Vladimirova, and E. V. Egorov, Zhur. Fiz. Khim., 33, 2442 (1959) [Rus. J. Phys. Chem., 467 (1959)].
24. G. K. Boreskov, V. A. Dzis'ko, and M. S. Borisova, Zhur. Fiz. Khim., 27, 1172 (1953).
25. Yu. A. Bitepazh, Zhur. Obshch. Khim., 17, 199 (1947).
26. K. V. Topchieva, Uch. Zap. Moskov. Gos. Univ., 174, 75 (1955).
27. I. E. Neimark, R. Yu. Sheinfain, and L. G. Svintsova, "Sbornik, Metody Issledovaniya Struktury Vysokodispersnykh i Poristykh Tel" (Collection, Methods of Studying the Structure of Highly-Dispersed and Porous Solids), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 128.
28. G. M. Schwab, Dattler, Angew. Chem., 50, 691 (1937).
29. G. M. Schwab and A. N. Ghosh, Angew. Chem., 52, 666 (1939).
30. L. Sacconi, Discuss. Faraday Soc., 7, 173 (1949).
31. I. A. Dean, Analyt. Chem., 23, 202 (1951).
32. P. N. Kovalenko, Uch. Zap. Rostov. Gos. Univ., 40, 23 (1958).
33. B. P. Nikol'skii, Zhur. Fiz. Khim., 5, 266 (1934).
34. O. Erämestä, Th. G. Saham, and V. Kanula, Ann. Acad. Sci. Fennicae, 57, Paper 3 (1940).
35. K. Lindner, Z. Electrochem., 54, 421 (1950).
36. F. Nydahl and L. A. Gustafsson, Acta Chem. Scand., 7, 143 (1953).
37. S. N. Tewaris and S. Ghosh, Kolloid. Zhur., 130, 167 (1953).
38. W. Noddack and E. Bankman, Z. Elektrochem., 58, 725 (1954).
39. K. R. Kar, J. Sci. Ind. Res., India, BC17, No. 5, 175 (1958).
40. G. M. Schwab and K. Jockers, Angew. Chem., 50, 546 (1937).
41. H. Kubli, Helv. Chim. Acta, 30, 435 (1947).
42. H. Brokmann and H. Scholder, Ber., 74, 73 (1941).
43. E. N. Gapon and G. M. Shuvaeva, "Sbornik, Issledovaniya v Oblasti Khromatografii" (Collection, Studies in Chromatography), Izd. Akad. Nauk SSSR, Moscow, 1952, p. 41.
44. W. Fischer and A. Kulling, Z. Elektrochem., 60, 680 (1956).
45. F. Umland and C. Engel, Z. Elektrochem., 63, 510 (1959).
46. E. Hayek, F. Lorenz, H. Schimann, and H. Ude, Monatsh., 90, 1, 49 (1959).
47. S. A. Levina and N. F. Ermolenko, Izv. Akad. Nauk Beloruss. SSR, 1, 407 (1954); Kolloid. Zhur., 17, 4, 287 (1955).
48. M. A. Piontkovskaya, Ya. V. Zhigailo, L. A. Eremenko, and I. E. Neimark, Kolloid. Zhur., 21, 347 (1959).
49. I. V. Krotov, Dokl. Akad. Nauk SSSR, 108, 263 (1956).
50. P. V. Rufimskii, Kolloid. Zhur., 21, 351 (1959).
51. M. H. Kurbatov, J. Phys. Chem., 36, 1241 (1932).
52. I. D. Kurbatov and M. H. Kurbatov, Phys. Rev., 69, 60 (1945).
53. M. H. Kurbatov and I. D. Kurbatov, Phys. Rev., 71, 466 (1947).
54. M. H. Kurbatov, I. D. Kurbatov, and Fu Chum-Gu, J. Chem. Phys., 16, 87 (1948).
55. M. H. Kurbatov and I. D. Kurbatov, J. Amer. Chem. Soc., 71, 1923 (1949).
56. M. H. Kurbatov and I. D. Kurbatov, J. Amer. Chem. Soc., 71, 858 (1949).
57. M. H. Kurbatov, I. D. Kurbatov, and G. B. Wood, J. Chem. Phys., 19, 258 (1951).
58. M. H. Kurbatov and I. D. Kurbatov, J. Phys. Chem., 55, 1171 (1951).
59. M. H. Kurbatov, I. D. Kurbatov, and G. B. Wood, J. Phys. Chem., 56, 698 (1952).
60. M. H. Kurbatov and I. D. Kurbatov, J. Amer. Chem. Soc., 69, 438 (1947).
61. I. D. Kurbatov, J. Amer. Chem. Soc., 67, 1923 (1945).
62. I. E. Starik, "Sbornik, Izotopy i Izlucheniya v Khimii" (Collection, Isotopes and Radiation in Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 382.
63. A. P. Ratner, Doctorate Thesis (D. Sc. Equivalent), Radium Institute, USSR Academy of Sciences, Leningrad, 1948.
64. A. P. Ratner and Z. N. Simonyak, "Sbornik Rabot po Radiokhimii" (Collected Papers on Radiochemistry), Izd. Leningrad. Gos. Univ., 1955, p. 17.
65. S. E. Bresler, "Radioaktivnye Elementy" (Radioactive Elements), Tekhteorizdat, Moscow, 1957, p. 111.
66. I. E. Neimark and I. B. Sinyakova, Kolloid. Zhur., 21, 340 (1959).
67. I. E. Neimark, Uspekhi Khim., 25, 748 (1956).
68. I. E. Neimark and R. Yu. Sheinfain, Kolloid. Zhur., 15, 145 (1953).
69. Yu. M. Glazman, D. N. Strazhesko, and N. A. Biskalova, Zhur. Neorg. Khim., 3, 115 (1958).
70. S. Krause, Z. anorg. Chem., 204, 20 (1932).
71. I. E. Starik, F. E. Starik, and A. I. Apollonova, Zhur. Neorg. Khim., 3, 121 (1958).
72. I. E. Starik, "Osnovy Radiokhimii" (Fundamentals of Radiochemistry), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1959, p. 366.
73. H. Freundlich, Kapillarchemie, 13, 2, 94 (1932).
74. V. N. Krestinskaya and Z. V. Khakimov, Zhur. Obshch. Khim., 14, 70 (1944).
75. H. R. Kruyt, "Colloid Science" (Translated into Russian), ONTI, Leningrad, 1936, p. 95.
76. V. A. Kargin and V. V. Kiseleva, Zhur. Fiz. Khim., 12, 461 (1938).
77. V. F. Ust'-Kachkantsev, Kolloid. Zhur., 15, 394 (1953).
78. V. A. Kargin and G. V. Klimovitskaya, Zhur. Fiz. Khim., 12, 467 (1938).
79. V. N. Krestinskaya and Z. V. Khakimov, Zhur. Obshch. Khim., 13, 780 (1943).
80. V. N. Krestinskaya and Z. V. Khakimov, Zhur. Obshch. Khim., 14, 70 (1944).
81. O. I. Dmitrienko, V. A. Kargin, and A. A. Ryabinina, Kolloid. Zhur., 13, 31 (1951.
82. Yu. M. Glazman, D. N. Strazhesko, and B. E. Tartakovskaya, Kolloid. Zhur., 15, 161 (1953).
83. C. Amphlett, L. McDonald, and M. Redman, J. Inorg. Nuclear Chem., 6, 220 (1958).
84. V. A. Kargin and P. S. Tolstaya, Zhur. Fiz. Khim., 13, 211 (1939).
85. L. G. Maidanovskaya, V. V. Sokolov, and F. K. Bolynets, Trudy TGU, 126, 171 (1954).
86. E. Merz, Z. Elektrochem., 63, 288 (1959).
87. K. A. Kraus and H. O. Phillips, J. Amer. Chem. Soc., 78, 3, 694 (1956).
88. C. Amphlett, L. McDonald, and M. Redman, J. Inorg. Nuclear Chem., 6, 220 (1958).
89. S. E. Bresler, Yu. D. Sinochkin, A. I. Egorov, and D. A. Perunov, Radiokhimiya, 1, 507 (1959).

90. K. A. Kraus and H. O. Phillips, J. Amer. Chem. Soc., 78, 249 (1956).
91. K. A. Kraus, T. A. Carlson, and K. S. Johnson, Nature, 177, 1128 (1956).
92. S. N. Tewari, Kolloid Z., 149, 2–3, 65 (1956).
93. S. A. Durov and N. I. Perova, Izv. Vys. Ucheb. Zaved. (Ivanovo), Khim. i Khim. Tekhnol., 2, 64 (1959).
94. B. P. Nikol'skii, Pochvovedenie, 29, 180 (1934).
95. B. P. Nikol'skii and V. I. Paramonova, Uspekhi Khim., 8, 1535 (1939).
96. K. M. Saldaze, "Sbornik, Issledovaniya v Oblasti Ionoobmennoi Khromatografii" (Collection, Studies in Ion-Exchange Chromatography), Moscow, Izd. Akad. Nauk SSSR, 1957, p. 38.
97. B. P. Nikol'skii, Zhur. Neorg. Khim., 3, 59 (1958).

Institute of Physical Chemistry and
Institute of Chemical Physics, the
USSR Academy of Sciences