U.D.C. 541.183.24 : 661.183

Thermal Stability of Cation-exchange Resins

N.G.Polyanskii and P.E.Tulupov

Experimental work on the thermal stability of cation-exchange resins in air, water, certain aqueous solutions, and also organic media is summarised for the first time. Conclusions are reached about the effect of various factors on the thrmal stability and about the nature of the processes responsible for the decrease in exchange capacity. Special attention is paid to the existence of an inherent relation between the thermal stability and the catalytic activity of ion-exchange materials. A list of 235 references is included.

CONTENTS

1. Introduction 1030
2. Methods for the study of the stability of ion-exchange materials 1030
3. Thermal stability of cation-exchange resins in gases and vapours 1032
4. Thermal stability of cation exchangers in water and aqueous solutions 1034
5. Thermal stability of sulphonated cation-exchange resins in organic media 1038

1. INTRODUCTION

The action of heat[1,2], radiation[3], and oxidants[4] on carbon-chain polymers often causes irreversible chemical changes in their macromolecules owing to rupture of the carbon–carbon single bond and the occurrence of degradation processes. Ion-exchange materials (resins and membranes) contain also the far less stable bonds between functional groups and the polymer matrix (carbon–nitrogen, carbon–sulphur, carbon–phosphorus, etc.). For this reason the main problem of the thermal, chemical, and radiation stability of ion-exchange materials is the behaviour of the functional groups, which are responsible for the ion-exchange and electrochemical properties under certain conditions.

The importance of this problem arises entirely from the inevitable heat-treatment of exchanger resins and membranes during their preparation and examination of their physicochemical properties. In several actual cases of practical exploitation, exchangers are subject simultaneously to thermal, chemical, and radiation effects.

At the high temperature of the polycondensation of hydroxybenzenesulphonic acid with formaldehyde the exchange capacity of the sulphonated cation-exchange resin may be diminished by desulphonation[5], the formation of sulphones, and the interaction of sulpho-groups with formaldehyde[6], and the three-dimensional structure of the polymer may undergo partial breakdown with oxidation of the degradation products by sulphuric acid[7]. In the preparation of sulphonated cation-exchange resins based on polystyrene and formaldehyde[8] or vinyl polymers[9] an excessive rise in temperature results in a decrease in the exchange capacity.

The drying of exchange resins, which is usually conducted at a high temperature (at or above 100°C) in order to determine their physicochemical properties[10,11], and their preparation for chromatographic separations[12-17] and for the production of heterogeneous membranes[18] may be accompanied by a diminution in the exchange capacity[10,18,19] and by irreversible changes in the structure of the three-dimensional network[20].

Many analytical separations by ion-exchange chromatography are conducted at high temperatures[21-29]. While utilising the kinetic and thermodynamic advantages which this confers, we must reduce to a minimum the chemical changes in the exchange resins that are inevitable with an incorrect choice of temperature conditions for the separation. The regeneration of spent exchangers is often accomplished by means of heated solutions[30-32], the consumption of which decreases with rise in temperature.

Exchangers are often used at high temperatures under industrial conditions, e.g. in the deionisation of industrial waters[33], the purification of radioactive solutions[34], and many catalytic reactions of organic compounds[35]. The correct choice of exchanger, necessarily taking into account its thermal, chemical, and radiation stability, will govern its useful life, and often the successful accomplishment of the desired processes. Thus practical interests demand a comprehensive investigation and survey of data on the thermal, chemical, and radiation stability of ion-exchange materials in all the typical media in which they are used. Results for the radiation stability of ion-exchange materials have been reported in detail in a monograph[36], but data on their thermal and chemical stability are now summarised for the first time.

2. METHODS FOR THE STUDY OF THE STABILITY OF ION-EXCHANGE MATERIALS

Ion-exchange materials are not individual compounds. Their composition and properties depend on the purity of the original monomers and the conditions for synthesis of the polymer, the content of low-molecular-weight compounds in the final product, and its pretreatment. The physicochemical properties are therefore determined on exchanger fractions of definite particle-size distribution, freed from impurities by acid[37-39] or alkali–acid[40-45] treatment, and in individual cases also by washing with organic solvents[46,47]. Ion-exchange membranes are usually prepared by similar methods[48,49], but the possibility of destroying the reinforcing fabric must be borne in mind[49].

Several physicochemical properties—exchange capacity, moisture capacity, relative swelling, density, etc.—must be studied for a complete description of exchangers and their stability, and with membranes the electrical conductivity, selectivity, permeability to water, mechanical strength, and elasticity must also be examined.

The most important physicochemical characteristic of ion-exchange materials is the total exchange capacity. In the case of polyfunctional exchangers and membranes the exchange capacity is also determined with respect to individual functional groups. However, by no means all methods described in the literature for estimating exchange capacity can be used to study the stability of exchangers and membranes. Many authors recommend statistical methods for determining the total exchange capacity of mono- and poly-functional exchangers in the hydrogen or the hydroxide form; these involve treating a weighed portion of the resin with excess of a standard solution of alkali [40,45] or acid [40,50,51] in a closed flask for a definite time. Sometimes a neutral salt is added to the solution to accelerate the exchange of mobile ions [39]. Total exchange capacity is not a happy choice to represent the stability of a polyfunctional exchanger, since different types of functional groups usually split off at different rates, and furthermore carboxylic and phenolic groups may be formed on irradiation or by the action of oxidants.

The most reliable measure of the resistance of an exchanger to a given factor is the capacity which is retained with respect to individual active groups (expressed in mg-equiv. g^{-1} initial resin or as a percentage of its original exchange capacity), determined potentiometrically [40,52-55], conductometrically [56,57], or titrimetrically [40,41]. Potentiometric methods require a large amount of time, and are advisable only for studying reaction mechanisms and the formation of new functional groups. In series of experiments it is more useful to apply rapid methods for the separate determination of the exchange capacity of cation-exchange resins in the hydrogen form [58,59] (direct titration of the resin in the presence of a neutral salt), for whose development much credit is due to Vasil'ev and his coworkers [60-66]. The considerable difficulties involved in the separate determination of the active groups of different strengths in phosphoric-acid cation-exchange resins [67] have not yet been overcome.

Complexometric methods [41,68], which do not require conversion of the exchanger into the hydrogen form, have undoubted advantages in estimating the exchange capacity of the salt forms of cation exchangers.

In laboratory practice, and sometimes also in studies of the stability of ion-exchange materials, use is quite often made of the static exchange capacity [40,49,69,70], which is determined by titrating a solution of a neutral salt, an acid, or an alkali in equilibrium with the test polyelectrolyte. The static exchange capacity depends on many factors—the concentration of the solution, the temperature, the degree of cross-linking of the exchanger, etc.—and therefore cannot serve as a criterion of its stability.

In the determination of the exchange capacity of an exchanger under dynamic conditions an electrolyte solution is filtered through a layer of the resin, and the ions displaced from the active groups are subsequently titrated in the filtrate [38,40,41,67,71]. This method is considerably more complicated than the static method, and requires a large consumption of reagents, but it gives valuable information on the dynamics of ion-exchange processes and on the properties of the exchangers.

Values obtained by the above methods for the exchange capacity may differ from those calculated from the formula of the structural unit, owing to incomplete sulphonation and phosphorylation or the occurrence of secondary processes which convert some of the functional groups into an "inactive" state [72-75]. The content of "inactive" sulphur or phosphorus is determined from the difference between the results of elementary analysis [76] and titration.

Exchange capacity is usually expressed in mg-equiv. g^{-1} dry material. This quantity is to some extent arbitrary, since it is evidently impracticable to obtain "absolutely" anhydrous exchangers without changing their chemical nature. Yet in several cases it is necessary to use dehydrated exchangers.

Conditions of dehydration must be chosen for each type of ion-exchange resin or membrane. It must be remembered that part of the bound water remains in the exchangers, and is capable of exerting a decisive effect on their behaviour towards radiation, heat, and reagents. It is interesting that the cation exchanger KU-2, after being dried at 100°C to constant weight, contains monohydrates of the sulpho-groups or ~ 9% water [77].

Many methods have been described for removing water from cation-exchange resins: these reduce to drying in a thermostat at 90°, [78] 95–100°, [79] 100 ± 50°, [40] 105 ± 2°, [80] 105–110°, [10,11,39,42,81,82] 110–115°, [83] 110–120°, [84] or 120°C [85], distilling off the water azeotropically with an organic solvent [86], or evacuating in the presence of a drying agent [20,45,52,87-94].

Cation exchangers having a polystyrene–divinylbenzene matrix can be dehydrated without danger of destruction by any of the above methods, but the most convenient treatment in practice is to heat in an air thermostat at 110–115°C to constant weight. The less thermostable sulphophenol–formaldehyde and sulphostyrene–butadiene (SBS resin) cation-exchange resins are appreciably desulphonated under these conditions: it is advisable to dry them over phosphorus pentoxide or magnesium perchlorate at a residual pressure of 5–10 mmHg in a vacuum desiccator.

The equilibrium moisture content of an exchanger is measured by the moisture capacity, expressed as the number of grams or millimoles of water retained by 1 g of the resin or 1 mg-equiv. of functional groups in the state of maximum swelling [87,94]. Determined under rigorously standardised conditions, this quantity is of great value for indicating changes in structure of the matrix on heat-treatment, although it must be accepted with the same reservations as the concept of an "absolutely dry" exchanger. The most reliable method for determining the moisture capacity is to remove adherent water from the fully swollen exchanger by centrifuging [45,94-98] (or by squeezing between sheets of filter paper in the case of membranes [99]), and then dehydrating.

The moisture capacity is closely connected with one of the most important characteristics of exchangers—the relative swellability—that govern their mechanical, kinetic, and catalytic properties. The relative swellability is defined as the percentage increase in volume of the resin in the hydrated state with respect to the volume of the dry resin. Most known methods give only apparent values of this quantity. In particular, the simplest method, involving measuring the volume of the anhydrous and the swollen resin in a cylinder [37,40,100] or in a calibrated column [96], gives values which depend on the granularity of the exchanger. Methods based on measurement of the volume [101,102] or the weight [103] of bound solvent yield in effect the moisture capacity, owing to the breakdown of additivity [94]. The true value of the relative swellability can be determined by measuring the specific volumes [94] or from the increase in volume of a pyknometric liquid in a microburette on the introduction of weighed portions of the resin [41]. Quite reliable values of the relative swellability can be obtained by measuring individual resin particles photographically [104], microscopically [96,105,106], or pyknometrically [40,94,107]. A simple pyknometric method [108]

makes it possible to determine simultaneously density, relative swellability, and moisture capacity, which are interrelated functionally. An interesting method has been described[109] for determining the true density of ion-exchange materials in binary solvent mixtures.

The change in the rate constant for the racemisation of (+)-α-isobutyldeoxybenzoin has recently been used[110] as an indication of the thermal stability of the resin Amberlite-15 when heated in inert media. This approach embodies the idea of a close connection between thermal stability and catalytic activity in ion-exchange materials, which has been expressed repeatedly by the Reviewers in a series of publications.

Since direct methods for recording changes in the structure of exchanger macromolecules have not been discussed in the literature, indirect methods (moisture capacity, relative swellability, sorption properties, etc.) are used. The spectrophotometric method gives interesting details of the chemical structure of a resin macromolecule[77,111-116]. Nuclear magnetic resonance[117-120], electron spin resonance[121,122], and the Mössbauer effect[123,124] are undoubtedly of interest for studying the internal structure, in particular the bonding of water in the resin macromolecule. These methods should find wide application for investigating the thermal stability of exchangers. The application of diverse methods for investigating the properties of exchangers in organic media and in the gas phase[112,125] will provide valuable information on the mechanism of the changes which occur.

The complete characterisation of ion-exchange membranes requires also a knowledge of the changes in selectivity[126-130], electrical conductivity[127,131-136], water permeability[128,131,137], mechanical strength, and specific elongation under tension[138]. It must be remarked that publications very seldom give a complete description of the properties of membranes (or of ion-exchange resins), and this lessens the value of the published results. Authors usually determine only the most important electrochemical properties of membranes, such as the conductivity and the selectivity: a more complete description of the physicochemical properties of membranes will be found in only a few papers[127,128,131].

3. THERMAL STABILITY OF CATION-EXCHANGE RESINS IN GASES AND VAPOURS

The systematic study of the thermal stability of exchangers in air was initiated by the work of Saldadze[139,140]. Using a thermographic method, he observed an endothermic change, probably corresponding to dehydration and occurring in the range 100–130°C depending on the nature of the exchanger. Further heating to 400°C was not accompanied by thermal effects which could be recorded, and this was interpreted[139] as evidence of great thermal stability in the exchangers. Somewhat later Evlanov and his coworkers[141] employed chemical and thermographic methods of analysis to show the presence, on the thermogram of the cation-exchange resin KU-1, of a second endothermic effect at 260–270°C, which was ascribed to the detachment of sulpho-groups. Nevertheless, the titrimetric method employed[141], which gave the total exchange capacity (including phenolic hydroxyls), was insufficiently sensitive to detect small losses of sulpho-groups, and led to the erroneous conclusion that the exchanger had high thermal stability at the temperature of the first endothermic effect (105–115°C). For the same reason no change in concentration of sulpho-groups was noticed[139] at 150°C, and the exchange capacity was judged to be constant from the potentiometric titration curve before and after the heat-treatment of sulphonated phenol–formaldehyde cation-exchange resins. By the use of more delicate methods, involving measurement of the exchange capacity with respect to sulpho-groups alone[8,142] or the loss thereof using the acidity of aqueous extracts, Vasil'ev[8], Polyanskii[142-145], and Jacubovic[20] showed that these exchangers underwent desulphonation at 100°C.

The sulphonated copolymer of styrene and divinylbenzene (KU-2 resin) was considerably more heat-resistant, its exchange capacity remaining unchanged even after 2 months' storage in sealed ampoules at 70°C.[139] When the temperature was raised to 150°C, however, losses in capacity of up to 3% were detected analytically after only 1 day[142].

The loss in weight by the sulphonated cation-exchange resins KU-1 and KU-2 at 110°C is due to the removal of water. The only other substance liberated is sulphuric acid, always in equimolecular proportion to the decrease in exchange capacity at sulpho-groups, independently of the duration of heating[88]. Hence under these conditions desulphonation is due to thermal hydrolysis

$$RSO_3H + H_2O \rightleftharpoons RH + H_2SO_4 \qquad (1)$$

involving residual water in the exchanger. The sulphuric acid which accumulates in the resin absorbs some water from the air, and therefore the weight of the cation exchanger passes through a minimum with continued heating[146].

Raising the temperature to 150° and 185°C leads to the accumulation not only of sulphuric but also of sulphurous acid, their total quantity being molecularly equivalent to the losses in capacity at sulpho-groups, and the proportion of sulphurous acid increases with increased duration of the experiment (in a closed ampoule)[147]. The formation of sulphurous acid is explained by redox reactions of the type

$$Red + H_2SO_4 \rightleftharpoons Ox + H_2O + SO_2, \qquad (2)$$

where Red represents a molecule or an atomic grouping having reducing properties and present in the exchanger[61,148-151], and Ox the corresponding oxidised form.

One of the Reviewers has shown[146,147] that the particle-size distribution of different cation-exchange resins has little effect on the relative losses in exchange capacity. Hence thermal desulphonation can be regarded, not as a topochemical process taking place at the surface of the solid phase in contact with air, but as a chemical reaction occurring throughout the exchanger grain.

The structure of the hydrocarbon skeleton of the matrix, the position of the sulpho-group, and the presence of other substituents in the aromatic ring greatly influence the relative loss of exchange capacity. The maximum thermal stability of the cation-exchange resin KU-2 may be due to an especially stable matrix[1,148], which has a saturated hydrocarbon chain structure. The cation-exchange resin SBS, although an addition polymer, exhibits far lower thermal stability, probably owing to the presence of unsaturated bonds in its matrix. At 185°C its stability is comparable with that of sulphophenol–formaldehyde resins[146]. The latter resins, containing phenolic hydroxyls in the aromatic ring, are unstable even at low temperatures (110°C), their rate of desulphonation increasing with the exchange capacity[143]. On comparing the relative losses in capacity[143] of the cation exchangers KU-1 and Wofatit P, we cannot agree with Naumann's statement[152]

that resins containing sulpho-groups in the side-chain should be more stable. The sulphonaphthalene–formaldehyde resin KU-5, which is monofunctional, is more stable when heated in air than is the cation-exchange resin KU-1G, which has a similar exchange capacity, but is considerably inferior to the resin KU-2.

Decreasing the residual water content in cation exchangers (by raising the temperature of the preliminary drying) slows down the thermal hydrolysis (1). Thus specimens of KU-2 which had been dried at 110° and 130°C lost 37.7% and 17.5% respectively of their exchange capacity after being heated in sealed ampoules at 185°C for 24 h.[146] When heated in open weighing bottles at 185°C for 24 h the exchanger KU-2 loses only 14.5% of its exchange capacity. The reason for these differences in rate of desulphonation is that, when experiments are conducted in sealed ampoules, not only the residual water but also the water formed in the redox reaction (2) takes part in the hydrolysis. The rate of the redox reaction is determined by the structure of the macromolecule and decreases in the sequence KU-1 > SBS > KU-2. Thus in experiments with the cation-exchange resin KU-1 in sealed ampoules at 195°C the proportions of the sulphuric acid formed by hydrolysis that take part in reaction (2) after 1, 6, and 24 h are respectively 46%, 90%, and 100%, but in experiments with KU-2 only 5%, 12%, and 31% respectively[147].

Heating a cation exchanger based on phenoxyethanesulphonic acid and formaldehyde in air for 8 h at 100°, 120°, 130°, 140°, and 150°C produces a change in exchange capacity[153] from 4.30 to 4.40, 4.35, 4.10, 3.80, and 3.75 mg-equiv. g^{-1}. Sulphuric acid is detected in aqueous extracts obtained after the resin has been heated at 130° and 140°C. Oligomers pass into the aqueous extract when the experimental temperature is raised to 150°C.

Thus the quantity of sulphur dioxide evolved cannot be the sole criterion of the thermal stability of a resin. It is not fortuitous that the sequence of thermal stability of sulphonated cation exchangers according to Griesbach[154] varies with the temperature: at 150°C Amberlite IR-100 < Wofatit KS < Wofatit P < Dowex 50 < polynaphthalenesulphonic exchanger = Amberlite IR-120 = Wofatit KPS-20; at 200°C Wofatit P < Amberlite IR-100 < polynaphthalenesulphonic exchanger < Wofatit KS < Dowex 50 < Wofatit KPS 200 < Amberlite IR-120. The thermal stability of the benzylsilane exchanger[154], which is desulphonated above 300°C, is especially noteworthy.

A kinetic interpretation of the experimental results is undoubtedly made difficult by the complicated effect of the redox reaction (2) on the thermal hydrolysis (1). In spite of the large quantity of data which have accumulated on the thermal stability of ion-exchange resins, only the first steps have so far been made in examining the kinetics of the decrease in exchange capacity.

During the initial period of heating in open weighing bottles all the cation exchangers investigated show fairly high rates of desulphonation[144,145,155] (see Table 1), after which the process slows down. Application of first-order and second-order kinetic equations did not reveal a law describing desulphonation for all heating times[145]. This may be a consequence not only of variation in the water content of the resin[146], which should ultimately become constant for a given temperature and relative atmospheric humidity, but also of the presence of energetically non-equivalent sulpho-groups in the exchangers.

Observations[156,157] on the effect of heat-treatment in air on the selectivity and the kinetic properties of sulphonated cation exchangers, which is especially marked in the resin KU-1, are of undoubted theoretical and practical interest. In the absence of heat-treatment, KU-1 absorbs potassium, magnesium, and quinine cations quantitatively from solutions of their salts until breakthrough occurs. Both cations are absorbed from binary mixtures of a solution of quinine sulphate with a salt of one of the above elements in variable quantities. After KU-1 has been heated in air at 150°C, however, none of the organic cations nor magnesium is absorbed from mixtures of potassium or magnesium with quinine, salsoline, or ephedrine, whereas potassium is extracted quantitatively from a comparatively large volume of the filtering solution. Since formation of magnesium complexes of the alkaloids is excluded (absorption proceeds normally on the resin KU-1 before heat-treatment), the observed effect is explained by blocking of the surface of the grain by the large organic cations and loss by the sorbent of the capacity for the bulk absorption of strongly hydrated multivalent ions. In the case of the cation-exchange resin KU-2 preliminary heat-treatment in air at 150° and 185°C is apparent only in a slowing down of ion exchange[156–158] and is accompanied by an increase in the exchange volume capacity.

Table 1. Kinetics of the variation in exchange capacity of cation exchangers in open weighing bottles at 185°C.[144,145,155]

Duration, h	Exchange capacity after heat-treatment, mg-equiv. g^{-1} original resin			Relative loss in capacity, %		
	KU-1	KU-2	KU-5	KU-1	KU-2	KU-5
0	2.01	4.75	3.37	0	0	0
1	1.75	4.64	3.00	12.9	2.8	11.0
3	1.66	4.52	2.72	17.4	4.8	19.3
6	1.35	4.42	2.46	32.9	7.0	27.0
12	1.30	4.26	2.26	35.4	10.3	33.0
24	1.18	4.06	1.98	41.2	14.5	41.3
144	0.59	3.00	1.44	70.7	36.8	57.4
312	0.58	2.40	1.27	71.2	49.3	62.4

The change in the kinetic properties of sulphonated cation-exchange resins and their assumption of the properties of ionic sieves, as a result of heat-treatment in air, can reasonably be attributed to contraction of the three-dimensional structure of the macromolecule. This is supported by the decrease in the equivalent moisture capacity[88,143,156,158].

Treatment of KU-2 with superheated steam produces a decrease in exchange capacity and an increase in the selectivity of the Ag^+–H^+ exchange, which is also explained by structural changes in the resin[159]. Heat-treatment of the sulphonated cation-exchanger SBS in a current of superheated steam at 200°C leads to a slowing down of the van der Waals sorption of phenol, nitrobenzoic acid, and other organic compounds[160], doubtless because of the change in the structure of the sorbent.

The mechanism of the contraction of the three-dimensional network has not been finally elucidated, but it is obvious that preliminary heat-treatment in air may become a method for controlling the kinetic properties of ion-exchange materials.

Heat-treatment of sulphonated cation-exchange resins in air is accompanied also by changes in the relative swellability and in the density in dry and swollen states[155,158].

A possible cause of the decrease in the sorption capacity of sulphonated cation exchangers might have been the formation of weakly acidic groups[55]. However, no new groups of this type are formed in KU-1 and KU-2 on heat-treatment at temperatures up to 185°C.[146] This may be evidence of the insignificant part played up to 200°C by oxidative degradation of the macromolecule. Oxidative degradation of the polymer matrix occurs vigorously at around 400°C and is accompanied by the accumulation of carboxy-groups[161].

The application of the modern methods of thermographic, differential thermographic, thermal, and differential thermal analysis to the investigation of ion-exchange resins has undoubtedly given interesting results[161-165]. With sulphonated cation-exchange resins the last of these methods has revealed[161-163] three endothermic changes, at 100–210°, 270–310°, and above 430°C, which were attributed respectively to dehydration, desulphonation, and oxidative degradation of the matrix. An exothermic effect at 370°C is ascribed to depolymerisation of the copolymer[161]. The elementary composition of the exchangers after heat-treatment is assumed[161,162,164] to indicate partial conversion of sulpho-groups into sulphones and the formation of additional cross-links. Among possible modes of formation of sulphones Soldatov et al.[162] assume direct reaction between sulpho-groups and the matrix:

$$RSO_3H + RH = RSO_2R + H_2O. \qquad (3)$$

At 430°C almost all the sulphur in the resin is already in an inactive state (as sulphones)[161]. Further rise in temperature[161,165] produces intense degradation of the macromolecule with breakdown of the sulphones and formation of sulphur dioxide as the chief sulphur-containing product. Ehlers et al.[165] assume the evolution of this gas to be a consequence of the reaction

$$RSO_2R \rightarrow R\dot{S}O_2 + \dot{R} \rightarrow SO_2 + R{-}R \qquad (4)$$

which occurs by a radical mechanism.

Examination of a single property may lead to erroneous conclusions concerning the behaviour of an exchanger when heated. Thus the existence of two forms of bond between water and functional groups in carboxylated and sulphonated cation-exchange resins (KB-4P and KU-2) was assumed[166] from the number of endothermic effects (at 100–110° and 150–180°C), but this conclusion has not been confirmed by later workers[161-163]. There is also insufficient basis for the conclusion, reached from the results of elementary analysis, that the hydrogen form of the exchanger KU-2, dried at 200°C, contains $1\frac{1}{2}$ molecule of water for every sulpho-group[163]. In view of the partial conversion of sulpho-groups into sulphones[161,162], elementary analysis must be supplemented in this case by alkalimetric titration in order to determine the content of mobile hydrogen ions.

Dependence of the form of thermogravimetric and differential thermal analysis curves on the water content of the original exchanger[162] emphasises the importance of using resins in the same initial state of hydration. The resin dried at 100°C to constant weight, and containing one water molecule for every sulpho-group, may serve as such a state[77].

Desulphonation of the cation exchanger SBR-4 when heated in a current of superheated steam at 200–250°C is accompanied by the formation of volatile products (sulphur dioxide, hydrogen sulphide) and additional cross-links of sulphonyl character with a corresponding contraction of the three-dimensional network and diminution of the moisture capacity[164]. Unfortunately, this interesting investigation[164] was conducted on a non-standard exchanger, which makes it impossible to compare the thermal stability in air with that in superheated steam.

The conversion of sulphonated cation-exchange resins from the hydrogen form into a salt form is accompanied by a significant improvement in their thermal stability in air[140,161,164,167-169]. However, investigation of the behaviour of salt forms of sulphonated cation exchangers is only in its initial stages, and the mechanism of the reactions involved is still obscure.

The behaviour of carboxylated cation exchangers when heated in air has been studied in far less detail than that of sulphonated exchangers, while phosphoric-acid resins have remained almost uninvestigated. From the results of thermographic and chemical examination, together with an analysis of the infrared spectrum, Peryshkina et al.[170] have established that the carboxylated cation-exchange resin KB-4 is stable in the hydrogen form to prolonged heating at up to 120°C. At 200°C the resin loses only water—initially water of hydration, and then water evolved by the condensation of neighbouring carboxyls in the chain:

$$-R-\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}}-R_1- \rightarrow H_2O + -R-\underset{\underset{O=C-O-C=O}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{|}{\overset{\overset{CH_3}{|}}{C}}-R_1- \quad . \qquad (5)$$

Between 200° and 260°C small amounts of carbon dioxide are evolved together with water, as a consequence of decarboxylation[170]. Similar conclusions were reached by Chapiro et al.[171] in a study of the thermal stability of homogeneous membranes based on carboxy-containing monomers. These workers note[171] that reaction (5) slows down when the membranes are heated in a vacuum. Hence atmospheric oxygen plays a definite part in this reaction. The salt forms of carboxylic cation exchangers are more resistant to heating in air than is the hydrogen form[172], as in the case of sulphonic exchangers. The behaviour of the ammonium form of the cation-exchange resin KB-4 is somewhat unusual, for the thermal stability is intermediate between those of the hydrogen and the salt forms[172]. Myagkoi and Suslina's conclusion[172] concerning the energetic non-equivalence of the water of hydration in the exchanger KB-4, which is based on a study of the equilibrium changes in weight of the resin at 100°, 150°, and 200°C, appears to be unsound. The weight of the resin inevitably becomes constant at each temperature, owing to the establishment of sorption–desorption equilibrium between the exchanger and air, provided that decarboxylation and the formation of anhydrides make no significant contribution to the total weight losses.

4. THERMAL STABILITY OF CATION EXCHANGERS IN WATER AND AQUEOUS SOLUTIONS

One of the first papers on the chromatographic separation of rare-earth elements by high-temperature elution[173] mentions the decomposition of the sulphonated phenol–formaldehyde resin IR-1 above 60°C, and Dickel et al.[174] assume that sulpho-groups split off from cation exchangers even during storage of the resins. Calmon and Kressman consider[168] that resins containing cyclic sulpho-groups cannot be used above 40°C, since they undergo hydrolysis with liberation of sulphuric acid. Osborn[175] does not recommend working with ion-exchange resins at temperatures above 70–80°C. Sulphonated cation-exchange resins whose active groups are linked to the aromatic ring through methylene bridges are less liable to hydrolysis[168],

and can be used above 80–90°C. All the authors note that polycondensed sulphonated cation-exchange resins have the greater thermal stability, as when heated in air. According to Lindsay et al.[176] the polymerised cation exchanger Dowex-50 is stable when heated in water up to 105–115°C.

By heating a sulphonated polystyrene cation exchanger in water at 180–210°C Boyd et al.[177] prepared a series of sorbents differing in exchange capacity, in which the quantity of sulphur present in active groups corresponded precisely to that found by elementary analysis. The equivalent moisture capacity of specimens obtained by partial desulphonation passed through a maximum (corresponding to the loss of 50% of the sulpho-groups), its variation showing loosening of the three-dimensional network. The structural changes in sulphonated cation exchangers resulting from their heat-treatment are clearly confirmed by the differences in the coefficients of self-diffusion of ions[177,178] in desulphonated specimens and in the selectivity of ion exchange[91]. The self-diffusion coefficients of Na^+, Ag^+, Zn^{2+}, Y^{3+}, and La^{3+} first increase with decrease in the exchange capacity, pass through a maximum, and then decrease[178]. The equivalent moisture capacity shows a similar variation.

Table 2. Variation in exchange capacity of sulphonated cation-exchange resins when heated in water[146].

Type of exchanger	Temp., °C	Exchange capacity (mg-equiv. g^{-1} initial resin) after heating for			Relative loss in capacity (%) after heating for	
		0	6 h	24 h	6 h	24 h
KU-1	110	2.01	1.84	1.72	8.5	14.4
KU-1	175	2.01	0.17	0.08	91.5	96.1
KU-5	175	1.99	1.77	1.50	11.0	24.6
SBS-3	175	0.91	0.57	0.48	36.7	47.6
KU-2 × 1.5	170	0.87	0.86	0.81	1.3	6.6
KU-2 × 5	170	2.00	1.81	1.61	10.3	19.4
KU-2 × 20	170	1.51	1.21	1.08	19.7	28.3
KU-23 × 3	170	1.17	1.15	1.10	2.0	6.1
KU-23 × 6	170	1.56	1.52	1.47	2.0	5.5
KU-23 × 15	170	1.35	1.25	1.15	7.2	14.9
KU-23 × 20	170	1.40	1.11	0.88	20.6	37.0
KU-2 × 12PS	170	1.87	1.71	1.46	8.8	22.0

The most thorough studies of the thermal stability of sulphonated cation-exchange resins in water have been reported in Refs. 48, 87, 179, and 180. Table 2 gives as illustration the exchange capacity and the relative loss in capacity of specimens when heated in water. The exchange capacity of KU-1 is based on the dehydrated material; in other cases it refers to the state of limiting swelling. The exchange capacity of all the sulphonated resins decreases with rise in temperature and increased duration of heating in water. Owing to the presence of a permanent excess of water, the rate of decrease in the exchange capacity varies more slowly with the duration of heating than in experiments in air. With the same heating time, therefore, the relative loss of exchange capacity is greater in water with some exchangers, and greater in air with others.

Certain conclusions concerning thermal hydrolysis as a cause of the desulphonation of cation-exchange resins in water can be drawn from a comparison of the absolute losses of exchange capacity with the sulphuric-acid content of the aqueous extracts. If thermal hydrolysis is not complicated by redox processes involving the sulphuric acid formed or by the detachment of oligomers containing sulpho-groups, the content of H^+ and SO_4^{2-} ions is double (in number of milliequivalents) the absolute losses of capacity by the exchangers. Table 3 shows that such a correlation has been established, within the limits of experimental error, for the cation exchangers KU-1, KU-2 × 4, and KU-2 × 12PS. In individual cases, e.g. in experiments with KU-5, KU-23 × 15, and especially SBS-3, agreement between losses of capacity calculated from titration of the resin and of aqueous extracts breaks down[146] (Table 3), which may be due not only to redox processes leading to the formation of sulphur dioxide (KU-1 and KU-2) or hydrogen sulphide (SBS) but also to the separation of sulphonic acids of low molecular weight[146,179].

Table 3. Relative loss of exchange capacity after heating for 24 h from titration of resin and of aqueous extracts[146].

Type of exchanger	Temp., °C	Relative loss of capacity (%) from titration of		
		resin	H^+ in extract	SO_4^{2-} in extract
KU-1	175	96.1	95.8	98.5
KU-2 × 4	175	19.5	18.2	19.8
KU-5	175	24.6	23.6	22.2
SBS-3	170	47.6	37.3	—
KU-23 × 15	170	14.8	17.4	17.1
KU-2 × 12PS	170	22.5	23.1	22.3

Table 2 shows that the thermal stability of the sulphonated cation-exchange resins in water diminishes in the sequence—KU-23 × 15 > KU-2 > KU-5 > SBS > KU-1—as in air. In this sequence the condensation polymers KU-32–KU-40 based on aromatic fused-ring systems (anthracene, phenanthrene, pyrene), and the addition polymer KU-3A based on 1-vinylnaphthalene, are probably intermediate in thermal stability[181] between the resins SBS and KU-1. The relative losses of capacity by the exchangers in water depend substantially on the type of exchanger, the chemical structure of its macromolecule, the porosity of the grain (which usually improves stability), and the purity of the initial monomers. Replacement of technical divinylbenzene by the pure *meta*- and *para*-isomers produces some improvement in the stability of the resin, presumably owing to the greater regularity of structure of the macromolecule[182]. Infrared spectroscopy has shown that sulphonation involves partial entry of sulpho-groups into *m*-divinylbenzene[182]. The relative losses of capacity increase with increased quantity of cross-linking agent in gel-like[43] and macroporous[179] samples of the cation exchangers. This rule has been explained hitherto[43,179] by the diminished strength of bonding of sulpho-groups with the matrix due to the increased mutual repulsion between ions as the swelling of the polymer decreases. However, an alternative is to regard the hydrolysis of sulphonated cation-exchange resins as a process catalysed by the hydrogen ions of the sulpho-groups and of the sulphuric acid which is formed. Such a view has been developed in connection with sulphonic acids of low molecular weight[183]. Increase in the degree of cross-linking leads to a decrease in the water content in the exchanger phase, an increased concentration of hydrogen ions relative to water in the vicinity of sulpho-groups, and a consequent increase in the rate of hydrolysis. No direct

connection between degree of cross-linking and the water content of the resin phase exists in macroporous cation exchangers[179]. Their water must be regarded as bound (forming part of hydrate sheaths) and free (filling the pores). Whereas in the desulphonation of gel-like cation-exchange resins[146] the equivalent moisture capacity varies insignificantly, in macroporous specimens it increases continually[179], since the content of free water remains practically unchanged with decrease in the exchange capacity. Moreover, the volume of bound water probably decreases with increase in the content of cross-linking agent even in macroporous exchangers, so that the hydrogen-ion concentration near functional groups and the rate of hydrolysis of the latter also increase.

Many attempts have been made at a kinetic interpretation of experimental results on the hydrolysis of sulphonated cation-exchange resins when heated in water[87,91,146,179,184], but none of them can be regarded as successful, since regularities concerned individual types of exchangers and a limited time interval. Thus a linear relation was found[87] between the logarithms of the loss of capacity and of the duration of heating for the exchangers KU-1 and KU-2, but this rule is by no means always followed by the exchanger KU-5[145] and macroporous specimens[179] based on styrene and divinylbenzene. The relative loss of capacity $\Delta E/E_0$ was found[184] to vary linearly with the duration of heating at 40–90°C with extremely low degrees of desulphonation, and from this the incorrect conclusion was drawn that hydrolysis of the sulpho-groups in the cation exchangers KU-1, KU-11, sulphonated coal, Zeocarb-215, Wofatit P, KU-21, KU-5, and KU-6G conforms to a first-order rate law.

The logarithm of the mean rate of desulphonation of the cation exchanger Dowex-50 × 12 was shown[91] to vary linearly with the reciprocal of the absolute temperature, which indicated that the hydrolysis of sulphonated cation-exchange resins obeys the Arrhenius equation.

In none of the above investigations was the formation of weakly acidic groups detected when sulphonated cation-exchange resins were heated in water. Therefore the conclusions[185] that such groups appear when the sodium form of the cation exchanger Ankalit KT-3 is heated in water at 90–100°C for 100 h, and that some of the sulpho-groups are converted into sulphonyl groups, are somewhat unexpected. In our opinion the basis for these conclusions is insufficient.

Heating sulphonated cation exchangers in water is accompanied not only by a decrease in exchange capacity but also by changes in swelling and moisture capacity. The increase in the swelling of KU-1 and KU-2 as a result of being heated in water at 100°C is accompanied by an increase in their electrical conductivity[186].

Boyd et al.[177] attribute the slight increase in the equivalent moisture capacity of gel-like cation exchangers to a decrease in the number of cross-links in the matrix on heating in water. However, it was shown later[87] that the changes in equivalent moisture capacity are reversible, and level out after drying followed by swelling in water.

The same effects occur when heat-treated KU-2 and KU-1 are regenerated with alkali and acid with complete (KU-2) or partial (KU-1) restoration of the electrical conductivity[186]. In view of the reversible character of the changes in moisture capacity on heat-treatment, one of the Reviewers has attributed them to temporary deformation of the three-dimensional network under the influence of immobilised water[87].

Heating macroporous cation exchangers in water produces a redistribution of pore size, while the total porosity remains unchanged[179]. This observation opens up methods for controlling the properties of ion-exchange materials.

The salt forms of cation exchangers[168] (KU-1[87], MSF[140], polystyrenesulphonate[177], polycyclohexadiene[187]) show considerably better thermal stability than the hydrogen form when heated in water, as in air. At 175°C appreciable desulphonation effects are observed only with KU-1 resin[87]. The thermal stability of sulphonated cation-exchange resins depends on the nature of the gegenion, and diminishes in the sequence of ionic forms $Mg^{2+} > Ca^{2+} > Na^{+} \gg H^{+}$.[180] Thus when KU-1 was heated in these ionic forms at 150°C for 1 day, the corresponding losses in exchange capacity were 21.6%, 25.2%, 29.6%, and 81.2%.[180] The rule found for the series of salt forms can reasonably be explained by desulphonation by the reaction[87,180]

$$RSO_3M + H_2O = RH + MHSO_4 . \quad (6)$$

The hydrogen ions liberated by the hydrolysis (6) undergo ion exchange

$$RSO_3M + MHSO_4 = RSO_3H + M_2SO_4 \quad (7)$$

replacing some of the metal ions in the sulpho-groups and lowering the thermal stability of the exchangers.

The abnormally low thermal stability of the hydrogen form of KU-1 in comparison with other cationic forms was explained by hydration of the hydrogen ion in the resin and by its special polarisation and quantum-mechanical properties[180]. However, if hydrolysis of the sulpho-groups is considered in terms of acid catalysis, the above experimental results find an unequivocal explanation. In fact, heating KU-1 under conditions excluding access of hydrogen ions to the resin phase (in a carbonate buffer)[188] does not result in desulphonation at 150°C. From the above discussion, it is easy to understand why the sodium form is less stable than the magnesium and calcium forms: in conformity with the charge and radius of the hydrated ion, sodium is most easily replaced by the hydrogen ion in the resin phase. However, the magnesium form is more stable than the calcium form, although according to the exchange constants the magnesium ion should be replaced more easily by the hydrogen ion in the resin phase. This apparent discrepancy is eliminated by assuming that the equilibrium

$$(RSO_3)_2Ca + H_2SO_4 \rightleftarrows CaSO_4 + 2RSO_3H \quad (8)$$

shifts to the right because the calcium ions in the liquid phase are bound as the relatively sparingly soluble sulphate[180]. A more general view may be to assume that the equilibrium is reversed at high temperatures owing to variation in the molar volumes of the hydrated exchangeable ions[189], as follows from the Gregor–Glückauf equation[190].

Thus the thermal stability of the salt form of a resin in an unbuffered medium can be discussed only arbitrarily, with the realisation that actually it is determined by the proportion of sulpho-groups present in the hydrogen form.

The changes in other physicochemical properties (density, swelling, moisture capacity, etc.) which occur when the salt forms of sulphonated cation-exchange resins are heated in water are essentially the same as those observed with the hydrogen form[87,88].

Published assessments of the stability of sulphonated cation-exchange resins in alkaline and acidic media are contradictory. The suggested[148] low resistance of sulphophenol–formaldehyde exchangers to the action of alkalis is partly confirmed by experiment. Thus the exchange capacity of Wofatit P is diminished by prolonged (> 40

min) boiling with 0.1–1.0 *N* potassium hydroxide solutions, but is unaffected by shorter treatment[140]. Another phenolsulphonic exchanger, Dowex 30, loses its exchange capacity when heated in 1 *N* caustic soda above 100°C, but the observed losses are nevertheless smaller than with the hydrogen form of the exchanger under the same conditions. At high pH-values the polymer structure breaks down with separation of an organic compound even at moderate temperatures. Nevertheless, according to Lindsay et al.[176] the properties of the addition polymer Dowex-50 are unaffected by brief heating in solutions of pH 10.5 and in 1 *N* caustic soda up to 168°C. In weakly alkaline media sulphophenol–formaldehyde cation exchangers[191] and the condensation polymers KU-5 and KU-6 are completely stable both in the cold and on heating[78,192]. The decrease in exchange capacity observed in some cases when phenol–formaldehyde cation exchangers are heated in alkaline media[140,148] is probably due, not to hydrolytic elimination of sulpho-groups, but to degradation of the macromolecule and separation of sulphonates of low molecular weight.

Heating in dilute non-oxidising acids also produces larger losses in capacity of sulphonated phenol–formaldehyde resins than of polystyrene resins. A monograph[193] mentioned the possibility of using sulphonated polystyrene cation exchangers in acid media at temperatures up to 120°C. Other results[139] indicate breakdown of sulphonated phenol–formaldehyde resins on prolonged boiling in dilute hydrochloric and sulphuric acid, but no definite conclusions can be drawn owing to the absence of a comparison between the action of these media and that of water. The loss in capacity of KU-1 at 100°C has been found[194] to diminish with increase in the concentration of sulphuric acid, being 92%, 72%, and 48% after 6 h in the 0.1 *N*, 0.5 *N*, and 1.0 *N* acid respectively. This was explained[194] by suppression of hydrolysis of the sulpho-groups in sulphuric-acid media, but this contradicts other conclusions[147].

Homogeneous sulphonated cation-exchange resin membranes based on polyethylene[195] are not very stable in alkaline media. After being kept in 10 *N* potassium hydroxide solution at room temperature their electrical resistance has fallen from 0.51 to 0.26 ohm cm^2.

Membranes based on fluorinated polymers are probably the most promising with regard to thermal stability and chemical resistance. According to Chapiro and Seidler[171] graft membranes based on tetrafluoroethylene and acrylic acid are stable at room temperature in 6 *N* caustic potash, water, and concentrated solutions of hydrochloric acid, sulphuric acid, and potassium carbonate, but undergo decarboxylation and dehydration with conversion of the carboxyls into anhydrides when heated to 200°C. The polytetrafluoroethylene matrix remains unchanged for 140 h at 200°C.

According to Munari and his coworkers[196,197], sulphonated cation-exchange membranes based on styrene grafted to tetrafluoroethylene can function for a long time in water at 180°C (in the hydrogen form) and at 280°C (in the salt forms), but in concentrated solutions of sodium hydroxide, sulphuric, hydrochloric, and nitric acids, and a mixture of hydrochloric and nitric acids at temperatures above 100°C. Unfortunately, these conclusions were not supported by experimental results.

In oxidising acids the hydrolytic elimination of sulpho-groups is accompanied by degradation and oxidation of the matrix. Thus the addition of potassium chromate to dilute sulphuric acid greatly diminishes the stability of the cation exchanger KU-1 owing to simultaneous desulphonation and redox processes[194]. Kazantsev et al.[198,199] showed by means of infrared spectroscopy that the desulphonation of KU-1 in dilute nitric acid is accompanied by the entry of nitro- and carboxy-groups into the aromatic rings of the matrix. Losses of capacity by KU-1 in 3 *N* nitric acid are enormous even in the cold, reaching 50% after 24 h. Under the same conditions KU-2 loses up to 25% of its capacity. The exchanger SDV-3 is completely desulphonated after being heated in the presence of 1 *N* nitric acid at 90°C for 30 days. Investigation by several independent methods of the behaviour of KU-2 at 20° and 80°C in solutions of potassium bromate and dichromate, hydrogen peroxide, and nitric acid indicated[200] fundamental structural changes in the resin and the occurrence of a variety of reactions.

A study[201] of the stability of the sulphonated cation-exchange resins KU-2, KU-2 × 8chs, KU-2P, and KU-22 in 6 *N* sodium hydroxide solution and in 3 *N* nitric acid at 75°C indicated that KU-2 was the most stable with respect to change in weight. However, variation in weight cannot be regarded as an unambiguous criterion of the stability of exchangers. In nitric acid the exchange capacity of the resins even increases. Atroshchenko et al.[202] observed no changes in capacity or signs of breakdown of the macromolecule when KU-2 was regenerated in the cold with 13–26% nitric acid. However, the exchanger broke down with the evolution of oxides of nitrogen when boiled in 40% nitric acid for 2 h. The working exchange capacity of a filter bed of this resin was 5% less than that of a layer which had been subjected to 16 cycles of treatment with 15% nitric acid in the cold and to 19 cycles with 40% nitric acid. After this the capacity of the resin remained unchanged during normal operation[202].

Cation exchangers containing sulpho-groups in the side-chain (Wofatit P, Stacionit F) are more stable in solutions of various oxidising agents (hydrogen peroxide, potassium permanganate, chromic acid) than are resins having sulpho-groups in the ring (KU-1G)[149]. In our opinion the statement that Wofatit P is more stable than the sulphonated polystyrene cation-exchange resin in permanganic acid and hydrogen peroxide containing iron(III) salts[149] requires verification. Additions of tervalent iron and other ions which accelerate the decomposition of hydrogen peroxide greatly intensify the breakdown of the sulphonated polystyrene cation exchanger Permutit Q in 50% hydrogen peroxide at 60°C, with rupture of cross-links and ultimately complete dissolution of the resin[203]. These processes most probably involve the intermediate formation of hydroperoxides, which are converted into sulphonic acids of low molecular weight. According to Wiley and Reich[204] the stability of sulphonated copolymers of styrene with 8% of divinylbenzene in 3% hydrogen peroxide in the presence of iron(II) sulphate at 75°C is strongly dependent on the purity of the monomers and the nature of the divinylbenzene isomer. The rate of desulphonation is highest with the technical cation exchanger Dowex-50 × 8, and decreases in the series of resins containing *p*-divinylbenzene, technical divinylbenzene, and *m*-divinylbenzene. Complete breakdown of the exchangers is observed after 270–300 min.

Raising the temperature accelerates the changes in capacity, density, and especially swelling of the exchanger KU-2 on treatment with oxidising agents[205]. Correct procedures were used in this work[205] to prove the formation of carboxylic, ketonic, and alcoholic groups when the oxidants attacked C–H bonds in methylene groups and at tertiary carbon atoms. Mixtures of nitric acid with potassium bromate and with potassium dichromate possessed greater oxidising power than these oxidants alone,

hydrogen peroxide, or ammonium peroxodisulphate[205]. The sulphonated cation exchanger and membranes based on $\alpha\beta\beta$-trifluorostyrene[206] show no change in properties when heated with 3% hydrogen peroxide in the presence of Fe^{3+} ions at 70°C for 24 h. Under these conditions the loss in weight of a phenol–formaldehyde exchanger is 97%, and those of sulphonated styrene–divinylbenzene cation exchangers containing 1%, 2%, 4%, 8%, and 12% of divinylbenzene are respectively 62%, 46%, 26%, 11%, and 6%. The great stability of the new exchanger towards oxidants was explained[206] by the greater strength of the C–F bond than of the C–H bonds (103 and 77 kcal $mole^{-1}$).

Many authors assign great importance to elementary oxygen as a sensitiser of the aging of resins[58,84,140,207] by the rupture of cross-links. Industrial establishments, therefore, undertake the deaeration of water or add reducing agents (e.g. sodium sulphite), in this way increasing the useful life of the exchangers to many years[207]. It must be remarked, however, that the important question of the role of oxygen in determining the thermal stability of ion-exchange resins has not yet found due recognition in laboratory investigations, and needs to be studied systematically.

Very little study has been made of the stability of phosphoric-acid cation exchangers towards thermal hydrolysis[208,209]. Published information enables only a few general conclusions to be drawn: with the same structure of hydrocarbon network in the macromolecule the phosphoric-acid exchangers (KF-1, KF-11,[209] and SF [208]) are more stable than the sulphonated exchangers (KU-2), but the stability also falls with increase in the divinylbenzene content. The difference in behaviour between salt forms and the hydrogen form is far smaller than with the sulphonated exchangers[208]. In contrast to the latter, porous specimens of phosphoric-acid resins possess lower thermal stability than the gel-like resins[209]. Changes in exchange capacity after heating in water are larger at the less thermostable strongly acidic groups than at the weakly acidic groups[209]. However, this interpretation cannot be accepted, since the exchangers investigated contained $-PO(OH)_2$ groups, which dissociate in two stages. In our opinion the observed effects are more plausibly explained by variation in the proton-donor power of the active groups resulting from heat-treatment of the exchangers.

5. THERMAL STABILITY OF SULPHONATED CATION-EXCHANGE RESINS IN ORGANIC MEDIA

The use of sulphonated cation-exchange resins as catalysts in various organic syntheses[35] stimulated interest in the study of their behaviour in organic media. Before the appearance of experimental results it seemed to many authors[210,211] that such exchangers should exhibit great thermal stability in organic media. Thus Astle[211] was sure that they could be used in organic media up to 180°C, but expected rapid breakdown under more severe conditions. Saldadze et al.[210] consider that they can be used in hydrocarbon media at 150–170°C.

However, the very first experimental results showed that assumptions of great thermal stability were too optimistic. Thus Andreas[212] used a sulphonated phenol–formaldehyde exchanger as catalyst for the esterification of acetic acid by ethanol and by butanol, and of adipic acid by methanol, and found that the resin was not wholly stable to heating above 120°C. He observed that Wofatit P decomposed with the evolution of sulphur dioxide and formaldehyde at temperatures above 180°C. Losev and Trostyanskaya[213], who used the exchangers MSF and SBS as catalysts for the preparation of butyl butyrate, found that the catalytic activity and the acidity (a measure of exchange capacity) of both resins fell rapidly with increased number of cycles. In view of the poor stability of the exchangers, these workers[213] recommend that they should not be employed above 120°C.

According to Menyailo et al.[214] the exchangers KU-2 and SBS show poor stability when used to catalyse the hydration of propene at 160–170°C. Naumann[152] found the polycondensation exchangers Wofatits P and F to be inferior in stability to the polyaddition resin Wofatit KRS-200. Solubility data indicate that all the resins are more stable in non-polar than in polar solvents.

Systematic investigation of the behaviour of sulphonated cation-exchange resins in various organic media was begun by the present Reviewers[42,47,112,215–217].

The relative losses of exchange capacity found by titrating the resin and the aqueous extracts (R_k and R_a), which are compared in Table 4, indicate that KU-1 is less stable than KU-2 in hydrocarbon media, as when heated in water and in air. The losses in exchange capacity by KU-1 are almost the same in hydrocarbons and in air[215,217]. The thermal stability of KU-2 resin, on the other hand, is lower in hydrocarbon media[42,216,217]. At 100°C, however, the effects of different media even out[42,215].

Table 4. Relative losses in capacity (%) of cation-exchange resins after being heated in various media.

Expt. No.	Temp., °C	Duration, h	Air		Isopentane		Isopentenes		Ref.
			R_k	R_a	R_k	R_a	R_k	R_a	
KU-1 cation exchanger									
1	100	10	11.3	10.9	—	—	12.8	10.9	215
2		120	24.6	23.7	—	—	26.0	23.7	
3		240	25.6	25.1	—	—	30.3	24.1	
4	125	10	17.5	18.5	—	—	14.7	15.2	
5		120	31.4	22.6	34.0	—	37.8	23.5	
6		240	39.7	29.4	42.0	—	43.7	34.3	
KU-2 cation exchanger									
7	150	10	6.7	6.5	5.7	4.6	7.8	4.8	46
8		24	6.6	6.5	7.7	5.6	13.1	5.0	
9		120	10.1	8.5	11.0	5.4	37.0	3.4	
10	200	2	12.0	9.7	15.0	7.5	36.0	5.4	
11		10	26	12	41	5.4	65	1.7	
12		24	54	15	62	6.1	75	2.6	

The diminished stability of KU-2 in alkenes[42,216,217] is explained by a weakening of the R–SO_3H bond as a consequence of the formation of a carbonium ion from the alkene and the hydrogen ion of the sulpho-group[215], and also by redox reactions the products of which (H_2O) either take part in or promote thermal hydrolysis. Formation of carbonium ions and redox interaction are less marked with saturated than with unsaturated hydrocarbons, and therefore KU-2 resin is more stable in the former. However, KU-2 is less stable in isopentane[42,216] and benzene[217] than in straight-chain alkanes and in air. Benzene and alkanes containing a tertiary carbon atom probably form π-complexes and carbonium ions with the gegenions of the active groups[218]; they undergo redox interaction with sulphuric acid.

The lack of effect of the medium on the thermal stability of the exchanger KU-1, like the low rate of polymerisation of alkenes in its presence, is explained[215] by steric hindrance to the formation of carbonium ions. It is interesting that the catalytic activity of KU-1 in the polymerisation of alkenes is enhanced by grinding or by pretreatment with methanol in a Soxhlet extractor[219]. However, the activation of the exchanger is only temporary, and disappears after heating at 150°C for a short time[219].

Comparison of the values of R_k and R_a (Table 4) shows that the nature of the medium affects the course of the redox reactions. Identical values of R_a and R_k indicate the transfer of sulpho-groups to degradation products as sulphuric acid owing to hydrolysis (1) involving the residual water in the exchanger. With rise in temperature and increase in duration of heating, sulphuric acid accumulates in the reaction products until it reaches a concentration at which redox reactions involving molecules of the resin and of the medium can occur. The reducing properties are, of course, more pronounced for alkenes than with alkanes[42,216,217]. Reducing activity increases in the series of resins—KU-2, KU-1, SBS.[220]

An empirical linear relation[42] $\lg E = f(\lg \tau)$ describes the kinetics of the variation in the exchange capacity of KU-2 in air, isopentane, and isopentenes, as in water. The slope of the straight line serves as a qualitative indication of the effect of the medium on the rate of desulphonation. The temperature dependence of the loss of capacity in KU-2 obeys the Arrhenius equation[217].

The breaks between the linear portions of the $\lg E - \lg \tau$ graphs probably indicate acceleration of hydrolysis of the sulpho-groups in the exchangers by the redox reaction (2) and its products. The correctness of such an interpretation is supported by the agreement between the abscissa for the break and the start of the redox reactions[42].

The rate of desulphonation is unaffected by the grain-size of the exchanger KU-2, contamination with traces of sulphonic acids of low molecular weight, or the relative proportion of resin and isopentenes[47]. This confirms the fact established previously, that the desulphonation of cation-exchange resins is controlled by an actual chemical reaction (hydrolysis) occurring throughout the resin[146,147].

Increasing the divinylbenzene content from 3% to 7% does not affect the thermal stability of the cation exchanger KU-2, but further increase in the degree of cross-linking (to 17% of divinylbenzene) is accompanied by a decrease in thermal stability. It is interesting that the ratio of the losses in capacity by a strongly and by a weakly cross-linked specimen of the exchanger decreases with rise in temperature and increase in duration of heating. Thus when resins containing 17% and 7% of divinylbenzene are heat-treated for 10, 24, and 48 h the ratio $R_k^{(17)}/R_k^{(7)}$ is respectively 1.94, 1.52, and 0.91.[47] Similar relations have been established in the heat-treatment in water of KU-2 containing 24% and 12% of divinylbenzene[43] for which the ratio of the losses in capacity $R_k^{(24)}/R_k^{(12)}$ after heating at 150°C for 6, 24, and 120 h is respectively 1.94, 1.69, and 1.25. This levelling of the rate of elimination of sulpho-groups from specimens having different contents of divinylbenzene was explained[47] by an equalisation of the electrostatic interaction between functional groups. However, such an explanation is equivocal. An alternative view relates the change in thermal stability to the existence of energetically non-equivalent sulpho-groups, the number of which should increase with increase in the degree of cross-linking in the resin. When the resin is heated in any medium, weakly bound sulpho-groups (e.g. those occupying the *ortho*-position in styrene-2,4-disulphonic acid) should be the first to split off; but when equivalent sulpho-groups remain (occupying the *para*-position), the effect of the degree of cross-linking should level out.

A comparative study of the behaviour of various cation exchangers when heated in air and in isopentenes showed that, as in aqueous media, the thermal stability increased in the sequence KU-1G < KU-1 < SBS < KU-2[146,220]. Addition polymers in the above series are more stable when heated than are polycondensation exchangers. Experiments with KU-1 and KU-2 revealed that polymerisation of the alkenes inevitably led to acceleration of the loss of exchange capacity. Different results were obtained with the resins SBS and KU-1G: the polymerisation of isopentenes is catalysed by SBS, although its thermal stability is the same in air and in isopentenes; yet KU-1G is almost without catalytic effect on this reaction, although its thermal stability in isopentenes is less than in air. This anomaly has not yet been explained satisfactorily, and requires further study.

A detailed chemical, potentiometric, and spectrophotometric (infrared) investigation of the cation exchanger KU-2 established[112] that, under all conditions of heat-treatment in air up to 200°C, all the sulphur is present in sulpho-groups. When KU-2 is heated in isopentane, a small portion of the sulphur passes into an "inactive" state. A considerably larger quantity of "inactive" sulphur is present after the resin has been heated in isopentenes. Successive treatment of the resin with alkali and acid converts part of the "inactive" sulphur into a state which is active with respect to ion exchange, and is included in the determination of sulpho-groups. This "inactive" sulphur is assumed[112] to be present as *S*-esters of thiosulpho-groups $R.SO_2.SR'$, where R and R′ are organic radicals of the resin and of a thiol. The infrared spectra show that severe heat-treatment of KU-2 in air and in isopentane can cause sulpho-groups to migrate from the *para*- to the *meta*-position, and polyphenyl bonds may be formed, with a decrease in the equivalent moisture capacity[112].

Table 5. Effect of content of water in KU-2 resin on its thermal stability at 150°C.[216]

Expt. No.	Water in resin, %	Relative loss in exchange capacity, %							
		in air after				in isopentenes after			
		1 day		2 days		1 day		2 days	
		R_k	R_a	R_k	R_a	R_k	R_a	R_k	R_a
1	*	2.4	1.8	2.8	2.0	4.0	2.4	7.1	2.4
2	**	6.6	6.5	7.5	8.2	13.1	5.0	25.8	2.8
3	24.2	12.2	14.0	18.0	19.5	8.6	6.6	14.4	6.2
4	48.4	9.6	9.2	10.0	10.0	9.6	8.2	9.0	11.2
5	57.3	6.2	6.8	8.2	9.0	4.8	6.8	8.6	8.8

* Exchanger dehydrated at 150°C
** At 110°C.

Bound water is involved in the hydrolysis of sulphonated cation exchangers, and has a great influence on the occurrence of reactions (1) and (2)[216] (Table 5). With increased water content the relative loss in capacity passes through a maximum, whose position and height depend on the nature of the medium. In air the maximum losses of capacity occur in a resin containing 24% of water.

The increase in the rate of hydrolysis of sulpho-groups as the water content of the resin increases to 24% is probably due, not only to the autocatalytic action of the sulphuric acid[216], but also to the easier transport of H_3O^+ ions to the hydrolysable C–S bond. Further increase in the water content of the resin inevitably dilutes the sulphuric acid in the exchanger phase and diminishes its catalytic activity.

In contact with isopentenes the losses in capacity are largest with a specimen of the resin which has been dehydrated at 110°C. Developing the earlier views[216] we must suggest that direct reduction of sulpho-groups by the alkenes with the formation of sulphur-containing compounds is probable, as is redox interaction between sulphuric acid and reducing groups in the resin or the medium. According to Table 5 use of a resin which has been dehydrated at 150°C is most favourable for the occurrence of such processes.

If the choice of catalyst for organic synthesis is guided solely by considerations of thermal stability, well dehydrated exchangers are to be preferred. However, the removal of water may hinder dissociation of the active groups, and thereby have an adverse effect on the catalytic activity of the exchanger. The resin KU-2 in a state of limiting swelling at 150°C catalyses the isomerisation of 3-methylbut-1-ene into 2-methylbut-2-ene and 2-methylbut-1-ene[121], the hydration of isopentenes to t-pentyl alcohol, and the polymerisation of alkenes[216]. In the presence of an exchanger containing up to 24% of water no hydration of isopentenes occurs, only polymerisation. The inability of hydrate water in KU-2 of moisture content 24.2% (or 3.5 mmoles H_2O mg-equiv.$^{-1}$ sulpho-groups) to effect hydration is probably due to its very strong bonding to the sulpho-groups. This is supported by data[222] indicating that absorption of the first three molecules of water on each sulpho-group in the resin is accompanied by a large heat release. The exchanger KU-2 which has been dehydrated at 110°C exhibits the maximum catalytic activity for the polymerisation of isopentenes: further dehydration at 150° and 175°C lowers the activity[216].

The infrared spectra show that catalysis yields sulphur-containing compounds and small amounts of aromatic compounds—degradation products of the polymeric matrix—as well as polymers. Chemical, potentiometric, and polarographic analyses have established the presence of elementary sulphur, thiols, and alkyl sulphides among the products of catalysis[112]. The difference between the total sulphur content found by elementary analysis and the aggregate quantity present as the above compounds was attributed to polysulphides and sulphoxides[112].

Sulphur dioxide and hydrogen sulphide were detected in the gas phase[125]. With experiments in isopentane and in air, the gas phase contained only sulphur dioxide, but the aqueous extracts contained both sulphuric and sulphurous acids[125].

The whole range of reactions which occur when the cation-exchange resin KU-2 is heated in hydrocarbons[112,146], discussed above, can be summarised as indicated below.

Resin Phase

The fall in the exchange capacity is governed by hydrolysis of sulpho-groups involving residual water (reaction 1). This is accompanied by redox interaction of the resulting sulphuric acid with reducing groups of the macromolecule (reaction 2). In media which undergo no chemical reactions, the changes undergone by cation exchangers are confined to these two reactions. In alkenes sulphones may be formed:

$$RSO_3H + C_5H_{10} = RSO_2{-}C_5H_9 + H_2O \qquad (9)$$

and also *S*-esters of thiosulphonic acids:

$$RSO_3H + C_5H_9SH = RSO_2{-}SC_5H_9 + H_2O. \qquad (10)$$

It is quite probable that sulphuric acid may take part in the formation of polyphenyl cross-links:

$$-CH_2{-}\underset{|}{CH}{-}C_6H_5 + -CH_2{-}\underset{|}{CH}{-}C_6H_5 + H_2SO_4 = 2H_2O + SO_2 + \\ + -CH_2\underset{|}{CH}{-}C_6H_4{-}\underset{\diagdown\,CH_2}{\overset{/}{C}}{-}C_6H_5 \,. \qquad (11)$$

Liquid Phase

The following changes are possible in the liquid phase.

1. Processes involving isopentenes and catalysed by hydrogen ions from the resin: (*a*) isomerisation of alkenes[112,221]

$$CH_3{-}\underset{|}{CH}{-}CH{=}CH_2 \xrightarrow{H^+} \begin{cases} \rightarrow CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3 \\ \rightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}CH_3 \end{cases} \qquad (12)$$

(*b*) polymerisation of isopentenes

$$n\,C_5H_{10} \xrightarrow{H^+} (C_5H_{10})_n \qquad (13)$$

(*c*) hydration of isopentenes

$$C_5H_{10} + H_2O \xrightarrow{H^+} C_5H_{11}OH \,. \qquad (14)$$

2. Reactions between alkenes and desulphonation products: (*a*) formation of sulphonates

$$C_5H_{10} + H_2SO_4 \rightarrow C_5H_{11}{-}OSO_3H \qquad (15)$$

$$2\,C_5H_{10} + H_2SO_4 \rightarrow C_5H_{11}{-}OSO_2O{-}C_5H_{11} + 2\,H_2O \qquad (16)$$

(*b*) formation of sulphoxides[223]

$$2\,C_5H_{10} + SO_2 \rightarrow C_5H_9{-}SO{-}C_5H_9 + H_2O \qquad (17)$$

(*c*) formation of thiols

$$C_5H_{10} + H_2S \rightarrow C_5H_{11}SH \qquad (18)$$

(*d*) formation of polysulphides

$$x\,C_5H_{10} + y\,S \rightarrow (C_5H_{10})_xS_y \,. \qquad (19)$$

The sulphur consumed in reaction (19) has been formed by the interaction of sulphur dioxide and hydrogen sulphide: $2H_2S + SO_2 \rightarrow 3S + 2H_2O$.

3. Reactions of derivatives of alkenes: (*a*) disproportionation of sulphoxides into sulphones and sulphides

$$2\,C_5H_9{-}SO{-}C_5H_9 \xrightarrow{H^+} C_5H_9{-}S{-}C_5H_9 + C_5H_9{-}SO_2{-}C_5H_9 \qquad (20)$$

(*b*) formation of aldehydes and thiols from sulphoxides

$$C_5H_9{-}SO{-}C_5H_9 \xrightarrow{H_2O} C_5H_9SH + C_4H_7C\overset{O}{\diagdown\!\!\diagup H} \qquad (21)$$

(*c*) formation of dialkyl disulphides in the presence of atmospheric oxygen

$$4\,C_5H_9SH + O_2 \rightarrow 2\,C_5H_9{-}S{-}S{-}C_5H_9 + 2\,H_2O \qquad (22)$$

(*d*) reaction between dialkyl disulphides and water

$$C_5H_9{-}S{-}S{-}C_5H_9 + H_2O \rightarrow C_5H_9SH + C_4H_7C\overset{O}{\diagdown\!\!\diagup H} + H_2S \qquad (23)$$

(*e*) formation of sulphides

$$C_5H_{11}SH + C_5H_{10} \rightarrow C_5H_{11}{-}S{-}C_5H_{11} \,. \qquad (24)$$

This whole complicated system of changes, including catalytic reactions, has a decisive effect on the thermal stability of the cation exchanger KU-2 in tertiary pentenes and determines the composition of the products.

The existence of a connection between the thermal stability of cation exchangers and catalytic reactions of the medium is confirmed by analogous investigations of resins in alcohols[217,224], phenol[225], and acetone[225]. Table 6 shows that the thermal stability of the cation exchangers KU-1 and KU-2 depends on the nature of the alcohol. Losses in capacity by KU-2 increase, whereas those of KU-1 decrease, as the alcohol molecules become larger. At 150°C the exchanger KU-1 is almost completely desulphonated after 24 h. At 125°C losses in capacity by KU-1 are almost the same in ethanol, n-pentanol, and isopentanol, but considerably greater than in t-pentyl alcohol or decanol. At 100°C the effect of the nature of the alcohol on the thermal stability of KU-1 levels off, and the losses in capacity after 24 and 120 h in ethanol are 16.6% and 36%, compared with 12.2% and 38.8% in decanol[224].

Table 6. Thermal stability of sulphonated cation-exchange resins in alcohols[217,224].

Temp., °C	Duration, h	Loss in capacity of resin, %									
		ethanol		n-pentanol		isopentanol		t-pentyl alcohol		decanol	
		R_k	R_a	R_k	R_a	R_k	R_a	R_k	R_a	R_k	R_a
KU-1 cation exchanger											
125	24	55.2	22.5	62.2	18.7	59.3	15.3	43.1	38.8	26.8	22.5
150	24	92.9	73.5	100	80.4	96.5	69.5	96.1	70.0	39.2	20.0
KU-2 cation exchanger											
150	10	3.0	2.6	7.1	5.5	3.6	5.0	7.4	6.6	10.0	4.8
	24	7.0	5.8	12.0	12.0	9.4	8.6	12.4	11.4	15.6	6.2
	48	8.2	6.8	15.2	11.6	17.2	13.2	14.4	12.2	18.5	1.6

The discrepancy observed between R_k and R_a cannot be explained by redox reactions of type (2), since alcohols are dehydrated to ethers and alkenes

$$2\,C_5H_{11}OH \xrightarrow{H^+} C_5H_{11}OC_5H_{11} + H_2O \quad (25)$$

$$C_5H_{11}O{-}C_5H_{11} \xrightarrow{H^+} 2\,C_5H_{10} + H_2O \quad (26)$$

in the presence of sulphonated cation exchangers[35], and the water that is formed dilutes the sulphuric acid, whose redox potential is lowered. Since no sulphur-containing compounds were present in the gas phase, the discrepancy was explained by the assumed formation of esters of the alcohols with sulphuric acid and with sulpho-groups of the resin[217,224]

$$C_5H_{11}OH + H_2SO_4 \xrightarrow{H^+} C_5H_{11}{-}O{-}SO_3H + H_2O \quad (27)$$

$$C_5H_{11}OH + RSO_3H \rightarrow RSO_2O{-}C_5H_{11} + H_2O\,. \quad (28)$$

As the alcohol molecules become larger, the relative solvation of the KU-2 falls, and the corresponding increase in concentration of active groups accelerates esterification[224]. These factors tend to accelerate the thermal hydrolysis of cation exchangers in alcohols in comparison with the rate of this process in water[224].

Examination of the thermal stability of KU-2 in phenol and in acetone[225] reveals an apparent breakdown in the usual type of relation between catalytic reactions of the medium and the stability of cation-exchange resins. In the presence of KU-2 phenol does not undergo any chemical change other than oxidation by air. Acetone gives various condensation products and water even in the cold. It would appear that KU-2 should be less thermostable in acetone than in phenol. However, experiment indicates that the thermal stability of the resin decreases on passing from acetone to its mixtures with phenol and to phenol itself[225]. This "anomaly" is explained by formation of a large quantity of water on the condensation of acetone; this water is sorbed by the resin and tends to increase its thermal stability[216].

The condensation products of acetone accumulate in the "pores" of the exchanger, shield the sulpho-groups, and may lead to a loss of catalytic activity by the resin even in the absence of thermal hydrolysis. The process of shielding must be distinguished from blocking of the sulpho-groups by their direct interaction with molecules of the medium to form such compounds as esters (with alcohols).

Thus the investigations give an idea of the specific character of the processes occurring in exchanger macromolecules in organic media. First, a correlation between thermal stability and catalytic activity is clearly revealed in cation exchangers. Secondly, the thermal hydrolysis of cation exchangers in organic media is not the only cause of the diminution in exchange capacity, for its competes with blocking and screening of the ion-exchange groups. Thirdly, the relative loss of capacity in organic media is determined by the composition and the properties of the reaction system as a whole (including reaction products), not only by the added liquid reagent. Unfortunately, the question of the effect on thermal stability of the distribution of components between liquid phase and resin has not yet been raised.

---o0o---

Experimental results which have accumulated show that the main reason for the decrease in exchange capacity of ion-exchange materials when heated and subjected to corrosive media is the detachment of functional groups, in most cases by hydrolysis. Among the numerous factors influencing the strength of bonding between active groups and the matrix, and therefore the thermal hydrolysis of the exchangers, the nature of the heat-treatment medium, the chemical structure of the exchanger macromolecule, and the nature of the functional group and its gegenion are especially important.

The medium in which the exchanger is heated affects the decrease in exchange capacity in four cases: (1) the medium or its reaction products interact with the functional groups; (2) the medium undergoes catalytic reactions involving the gegenion of the functional group (polymerisation of hydrocarbons, esterification of alcohols, condensation of ketones, etc.); (3) the molecules of the medium form unstable addition products, including π-complexes, with the functional groups; or (4) the "pores" of the resin grains are filled with reaction products of the medium that shield the functional groups (products of the condensation of acetone, the polymerisation of alkenes, etc.). Hence it follows that the necessity of considering the thermal stability and the catalytic activity of ion-exchange materials together with their reactions is dictated not only by the requirements of a right choice of catalysts but also by considerations of the causal relation between these properties in molecular terms.

Some interesting relations between the chemical structure and the thermal stability of the exchangers have been revealed. As in the lower sulphonic acids, the electron-donor phenolic hydroxyls in sulphonated phenol–formaldehyde cation exchangers facilitate electrophilic substitutions. Therefore all phenolsulphonic acids of high molecular weight undergo hydrolysis more easily than, and are inferior in thermal stability in the media investigated to, sulphonated cation exchangers having a polystyrene–divinylbenzene matrix. The cation exchanger SBS is inferior to KU-2 resin in thermal stability, perhaps because butadiene groups have a stronger polarising action than have divinylbenzene groups on the C–S bond. Increase in the degree of cross-linking of sulphonated polystyrene exchangers is accompanied by an increase in the rate of hydrolysis of the sulpho-groups. Thus variation in the chemical structure of the matrix may be an effective means for the planned synthesis of thermostable cation exchangers.

With matrices of the same structure the liability of cation exchangers to undergo thermal hydrolysis and other processes leading to a change in exchange capacity depends on the nature of the active group. This aspect needs to be studied thoroughly, but it can already be stated that sulphonated exchangers are less stable than resins containing phosphate and carboxylate groups. The hydrogen forms of the exchangers, like the ordinary oxy-acids, are less stable than the corresponding salts. On the other hand, it must be emphasised that very few investigations have been made on the thermal stability of the salt forms, despite their importance; this gap must be filled in the near future.

However, the main task in investigating the thermal and chemical stability of ion-exchange materials is, in our opinion, to study the elementary processes occurring in exchangers and leading to deterioration in their operational properties, and also to establish the kinetics of these processes. Progress in this field will undoubtedly contribute to the development of methods for the planned synthesis of ion-exchange materials having specified properties and satisfying the demands of modern science and technology.

---o0o---

While the manuscript has been awaiting publication, several papers have appeared which have deepened our knowledge of the thermal stability of cation-exchange resins. They include detailed thermographic investigations[226-228], and new generalisations on the thermo-oxidative degradation of carboxylated exchangers[229].

Individual papers[230,231] have raised the question of the useful life of cation-exchange resins as catalysts of organic reactions under industrial conditions at 130–150°C. Experience indicates[230] that, after use as an alkylation catalyst for 40–45 days, KU-2 loses its activity and cannot be regenerated. In our view the development of methods for the regeneration of cation exchangers requires the closest attention, and is urgently required for their practical employment in several catalytic reactions conducted at high temperatures.

The work of Paushkin and his pupils[232-235] on the preparation of thermostable cation exchangers containing a system of aromatic rings in the conjugated chain is worthy of special mention. However, a direct study of thermal stability in various media is required to assess the prospects for new cation exchangers.

REFERENCES

1. S. L. Madorsky, Polymer Reviews, Vol. 7, "Thermal Degradation of Organic Polymers" (Translated into Russian), Mir, Moscow, 1967.
2. V. V. Korshak and S. V. Vinogradova, Uspekhi Khim., 37, 2024 (1968) [Russ. Chem. Rev., No. 11 (1968)].
3. A. Charlesby, "Atomic Radiation and Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1962.
4. N. Grassie, "Chemistry of High Polymer Degradation Processes" (Translated into Russian), Inostr. Lit., Moscow, 1959.
5. I. P. Losev, A. S. Tevlina, and E. B. Trostyanskaya, in "Teoriya i Praktika Primeneniya Ionoobmennykh Materialov" (Theory and Practical Application of Ion-exchange Materials), Izd. Akad. Nauk SSSR, Moscow, 1955, p. 35.
6. A. A. Vasil'ev, in "Issledovaniya v Oblasti Ionoobmennoi Khromatografii" (Researches on Ion-exchange Chromatography), Izd. Akad. Nauk SSSR, Moscow, 1957, p. 89.
7. E. B. Trostyanskaya, I. P. Losev, and A. S. Tevlina, Uspekhi Khim., 24, 69 (1955).
8. A. A. Vasil'ev and A. A. Vansheidt, Zhur. Prikl. Khim., 31, 1692 (1958).
9. A. A. Vasil'ev and A. A. Vansheidt, Zhur. Prikl. Khim., 32, 150 (1959).
10. A. A. Vasil'ev, Zhur. Prikl. Khim., 30, 1022 (1957).
11. R. Kunin and R. Mayers, "Ion-exchange Resins" (Translated into Russian), Inostr. Lit., Moscow, 1952, p. 151.
12. A. M. Phipps and D. N. Hume, Analyt. Chem., 39, 1755 (1967).
13. K. Govindaraju, Analyt. Chem., 40, 24 (1968).
14. F. W. E. Strelow, C. J. Libenberg, and C. N. Notle, J. S. African Chem. Inst., 21, 93 (1968).
15. L. Wodkiewicz and R. Dybczynski, J. Chromatog., 32, 394 (1968).
16. F. W. E. Strelow, W. J. Louw, and C. H. Weinhert, Analyt. Chem., 40, 2021 (1968).
17. J. Pauwels and K. Louer, Z. analyt. Chem., 240, 225 (1968).
18. P. E. Tulupov, M. A. Zhukov, A. B. Pashkov, and B. Ya. Kel'man, in "Ionoobmennye Membrany v Elektrodialize" (Ion-exchange Membranes in Electrodialysis), Khimiya, Leningrad, 1970, p. 33.
19. N. G. Polyanskii and M. A. Shaburov, Zhur. Prikl. Khim., 38, 1072 (1965).
20. A. O. Jacubovic, J. Chem. Soc., 4820 (1960).
21. B. K. Preobrazhenskii, A. V. Kalyamin, and O. M. Lilova, Zhur. Neorg. Khim., 2, 1164 (1957).
22. G. Brunisholz and R. Roulet, Helv. Chim. Acta, 53, 126 (1970).
23. B. K. Preobrazhenskii, O. M. Lilova, A. N. Dobronravova, and E. D. Teterin, Zhur. Neorg. Khim., 1, 2294 (1956).
24. C. Schoumacher, E. Merciny, and G. Duyckaerts, J. Chromatog., 31, 510 (1967).
25. D. O. Campbell and S. R. Buxton, Ind. Eng. Chem. (Process Design), 9, 89 (1970).
26. K. B. Lebedev and S. A. Ageev, Izv. Akad. Nauk Kazakh. SSR, No. 2, 5 (1967).
27. J. E. Powell and H. R. Burkholder, J. Chromatog., 29, 210 (1967).
28. G. Brunisholz and R. Roulet, Chimia, 21, 188 (1967).
29. V. Kopras and N. Fojtik, Chem. Zvesti, 22, 333 (1968).

30. Yu. I. Usatenko and L. I. Gureeva, Zavod. Lab., 22, 781 (1956).
31. D. E. Weiss, B. A. Bolto, R. McNeill, A. S. Macpherson, R. Siudak, E. A. Swinton, and D. Willis, Austral. J. Chem., 19, 589 (1966).
32. D. E. Weiss, B. A. Bolto, R. McNeill, A. S. Macpherson, R. Siudak, and D. Willis, Austral. J. Chem., 19, 791 (1966).
33. Anon., Bull. Amer. Railway Assoc., 55, 361 (1953).
34. Yu. V. Kuznetsov, V. N. Shchebetkovskii, and A. G. Trusov, "Osnovy Dezaktivatsii Vody" (Principles of the Demineralisation of Water), Atomizdat, Moscow, 1968, p. 131.
35. N. G. Polyanskii, Uspekhi Khim., 31, 1046 (1962) [Russ. Chem. Rev., No. 9 (1962)]; 39, 504 (1970) [Russ. Chem. Rev., No. 3 (1970)].
36. E. V. Egorov and P. D. Novikov, "Deistvie Ioniziruyushchikh Izluchenii na Ionoobmennye Materialy" (Action of Ionising Radiations on Ion-exchange Materials), Atomizdat, Moscow, 1965.
37. G. W. Bodamer and R. Kunin, Ind. Eng. Chem., 45, 2577 (1953).
38. C. Pulido, Acta Chem. Scand., 10, 49 (1956).
39. S. Fischer and R. Kunin, Analyt. Chem., 27, 1191 (1955).
40. K. M. Saldadze, A. B. Pashkov, and V. S. Titov, "Ionoobmennye Vysokomolekulyarnye Soedineniya" (Macromolecular Ion-exchange Compounds), Goskhimizdat, Moscow, 1960.
41. N. G. Polyanskii, Zhur. Prikl. Khim., 33, 1108 (1960).
42. N. G. Polyanskii and P. E. Tulupov, Zhur. Prikl. Khim., 35, 2281 (1962).
43. K. M. Saldadze, N. G. Polyanskii, and A. B. Pashkov, in "Khromatografiya, ee Teoriya i Primenenie" (Chromatography—Theory and Applications), Izd. Akad. Nauk SSSR, Moscow, 1960, p. 77.
44. H. P. Gregor, J. Belle, and R. A. Markus, J. Amer. Chem. Soc., 76, 1984 (1954).
45. G. Scatchard and N. J. Anderson, J. Phys. Chem., 65, 1536 (1961).
46. W. P. Arnold, New England J. Med., 145, 331 (1951).
47. P. E. Tulupov, Zhur. Prikl. Khim., 39, 1661 (1966).
48. P. E. Tulupov, V. P. Greben', and A. I. Kasperovich, Khim. Vysok. Energii, 3, 274 (1969).
49. G. D. Bazikova, Z. V. Klimova, and K. M. Saldadze, in "Khimicheski Aktivnye Polimery i Ikh Primenenie" (Chemically Reactive Polymers and Their Applications), Khimiya, Leningrad, 1969, p. 200.
50. E. B. Trostyanskaya, in "Ionnyi Obmen i Ego Primenenie" (Ion Exchange and Its Applications), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 11.
51. G. Sundvist, Acta Chem. Scand., 15, 1485 (1961).
52. N. E. Topp and K. W. Pepper, J. Chem. Soc., 3299 (1949).
53. K. M. Saldadze and E. A. Bozhevol'nikov, in "Sbornik Trudov Instituta Khimicheskikh Reaktivov" (Transactions of the Institute of Chemical Reagents), 1951, Vol. 20, p. 125.
54. J. R. Kirby and A. J. Baldwin, Analyt. Chem., 40, 689 (1968).
55. E. B. Trostyanskaya, I. P. Losev, and A. S. Tevlina, Zhur. Anal. Khim., 11, 578 (1956).
56. T. Sasaci and A. Inaba, Bull. Chem. Soc. Japan, 24, 1 (1951).
57. G. Günther and H. Staude, Z. phys. Chem. (Leipzig), 206, 126 (1957).
58. W. C. Baumann, J. R. Skidmore, and R. H. Osmun, Ind. Eng. Chem., 40, 1350 (1948).
59. J. Ungar, Analyt. Chem., 34, 413 (1962).
60. A. A. Vansheidt, A. A. Vasil'ev, O. I. Okhrimenko, and G. A. Petrova, in "Khromatografiya" (Chromatography), Izd. Leningrad. Gos. Univ., Leningrad, 1956, p. 51.
61. A. M. Vasil'ev, L. A. Vasil'eva, and A. A. Vasil'ev, in "Sbornik Trudov Kazanskogo Khimiko-tekhnologicheskogo Instituta" (Transactions of the Kazan Institute of Chemical Technology), 1957, Vol. 22, p. 33.
62. A. A. Vansheidt, A. A. Vasil'ev, and O. I. Okhrimenko, see Ref. 5, p. 110.
63. A. A. Vasil'ev and V. S. Matrosova, Zhur. Prikl. Khim., 37, 2493 (1964).
64. A. A. Vasil'ev, Zhur. Prikl. Khim., 40, 1101 (1967).
65. A. A. Vasil'ev and T. S. Tsygankova, Zhur. Prikl. Khim., 41, 2261 (1968).
66. A. M. Vasil'ev, L. A. Vasil'eva, and A. A. Vasil'ev, see Ref. 61, p. 42.
67. P. E. Tulupov, Zhur. Prikl. Khim., 42, 78 (1969).
68. N. G. Polyanskii, V. I. Vishnevskaya, and A. P. Podionova, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 3, 96 (1960).
69. O. Samuelson, "Ion-exchange Separations in Analytical Chemistry" (Translated into Russian), Khimiya, Moscow–Leningrad, 1966, p. 35.
70. K. M. Saldadze, V. B. Kargman, and N. B. Galitskaya, in "Khimicheski Aktivnye Polymery" (Chemically Reactive Polymers), Nauka, Leningrad, 1969, p. 193.
71. A. A. Vasil'ev, Zhur. Prikl. Khim., 32, 297 (1959).
72. A. A. Vasil'ev and A. A. Vansheidt, Zhur. Prikl. Khim., 31, 1273 (1958).
73. A. A. Vasil'ev, V. A. Orestova, and N. A. Nikolaeva, Zhur. Prikl. Khim., 32, 2650 (1959).
74. M. N. Tsypkina, G. I. Makhnovetskaya, and V. V. Sergeeva, Zhur. Prikl. Khim., 35, 2440 (1962).
75. A. A. Vasil'ev and A. A. Vansheidt, Zhur. Prikl. Khim., 31, 1527 (1958).
76. N. V. Sokolova, V. A. Orestova, and N. A. Nikolaeva, Zhur. Anal. Khim., 14, 472 (1959).
77. N. A. Slovokhotova, V. A. Nikashina, and M. M. Senyavin, Zhur. Fiz. Khim., 35, 2387 (1961) [Russ. J. Phys. Chem., No. 10 (1961)].
78. N. I. Sudarikova, Candidate's Thesis, Joint Council of the Institutes of Physical Organic Chemistry, General and Inorganic Chemistry, and Peat of the Belorussian SSR Academy of Sciences, Minsk, 1970.
79. D. I. Ryabchikov, M. M. Senyavin, and K. V. Filippova, Zhur. Anal. Khim., 8, 220 (1953).
80. H. A. Shah and S. L. Bafna, J. Indian Chem. Soc., 29, 187 (1952).
81. T. Westermark, Acta Chem. Scand., 14, 1858 (1960).
82. R. Cole and H. L. Shulman, Ind. Eng. Chem., 52, 859 (1960).
83. O. D. Bonner and J. C. Moorefield, J. Phys. Chem., 58, 555 (1954).
84. E. R. Tompkins, J. Chem. Educ., 26, 32 (1949).
85. T. R. E. Kressman and J. A. Kitchener, J. Chem. Soc., 1190 (1949).
86. V. I. Isagulyants and E. V. Panidi, Zhur. Prikl. Khim., 34, 1578 (1961).
87. N. G. Polyanskii, Zhur. Prikl. Khim., 32, 735 (1959).
88. N. G. Polyanskii, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 152 (1958).
89. H. P. Gregor and J. I. Bregman, J. Amer. Chem. Soc., 70, 2370 (1948).
90. M. Mattison and O. Samuelson, Acta Chem. Scand., 12, 1395 (1958).

91. K. A. Kraus and R. J. Raridon, J. Phys. Chem., 63, 1901 (1959).
92. V. L. Bogatyrev, "Ionity v Smeshannom Sloe" (Ion-exchange Resins in Fluidised Beds), Khimiya, Leningrad, 1968, p. 14.
93. G. A. Razuvaev, V. A. Shushunov, and V. A. Yablokov, Dokl. Akad. Nauk SSSR, 139, 1128 (1961).
94. K. W. Pepper, D. Reichenberg, and D. K. Hale, J. Chem. Soc., 3129 (1952).
95. H. P. Gregor, K. M. Held, and J. Bellin, Analyt. Chem., 23, 620 (1951).
96. G. M. Panchenkov and V. I. Gorshkov, Vysokomol. Soed., 3, 177 (1961).
97. K. W. Pepper, J. Appl. Chem., 1, 124 (1951).
98. V. I. Gorshkov, O. N. Vorontsova, and M. S. Safonov, in "Termodinamika Ionnogo Obmena" (Thermodynamics of Ion Exchange), Nauka i Tekhnika, Minsk, 1968, p. 99.
99. P. E. Tulupov and V. P. Greben', Khim. Vysok. Energii, 4, 275 (1970).
100. S. A. Bernhard and L. P. Hammett, J. Amer. Chem. Soc., 75, 1798 (1953).
101. B. A. Dogadkin, K. Pechkovskaya, and L. Chernikina, Kolloid. Zhur., 8, 31 (1946).
102. V. I. Gorshkov, V. I. Slovetskii, and G. M. Panchenkov, Kolloid. Zhur., 23, 345 (1961).
103. B. A. Dogadkin and A. A. Dontsov, Kolloid. Zhur., 23, 346 (1961).
104. D. H. Freeman, in "Ion Exchange" (Translated into Russian), Mir, Moscow, 1968, p. 332.
105. V. I. Gorshkov, Candidate's Thesis, Moscow State University, Moscow, 1958.
106. V. P. Meleshko and O. N. Myagkoi, Kolloid. Zhur., 19, 684 (1957).
107. F. Helfferich, "Ionenaustauscher" (Translated into Russian), Inostr. Lit., Moscow, 1962, p. 219.
108. N. G. Polyanskii, P. E. Tulupov, and V. S. Markevich, Kolloid. Zhur., 25, 209 (1963).
109. V. L. Bogatyrev, A. I. Vulikh, and S. I. Sokolova, Zhur. Prikl. Khim., 39, 1760 (1966).
110. F. T. Fang, Proc. 3rd Internat. Congr. Catalysis, Amsterdam, 2, 90 (1964).
111. G. K. Salovskaya, V. A. Nikashina, N. A. Slovokhotova, and M. M. Senyavin in "Radiatsionnaya Khimiya Polimerov" (Radiation Chemistry of Polymers), Nauka, Moscow, 1966, p. 396.
112. N. G. Polyanskii, P. E. Tulupov, G. K. Sadovskaya, and N. A. Slovokhotova, Zhur. Prikl. Khim., 38, 910 (1965).
113. B. N. Laskorin et al., Zavod. Lab., 34, 966 (1968).
114. A. A. Vasil'ev and K. K. Kalnin'sh, in "Sintez i Svoistva Ionoobmennykh Materialov" (Preparation and Properties of Ion-exchange Materials), Nauka, Moscow, 1968, p. 79.
115. V. I. Paramonova, G. P. Nikitina, and G. A. Akopov, Radiokhimiya, 10, 638 (1968).
116. V. I. Paramonova, G. P. Nikitina, and G. A. Akopov, Radiokhimiya, 10, 646 (1968).
117. J. E. Gordon, Chem. and Ind., 267 (1962).
118. S. Kinastowski and Z. Pajak, Compt. rend., 252, 1774 (1961).
119. R. H. Dinius and G. R. Choppin, J. Phys. Chem., 68, 425 (1964).
120. J. P. Villiers and J. R. Parrish, J. Polymer Sci., A2, 1331 (1964).
121. D. N. Stamires and J. Turkevich, J. Amer. Chem. Soc., 86, 757 (1964).
122. N. I. Nikolaev, V. I. Muromtsev, G. G. Chuvileva, M. D. Kalinina, and A. D. Naumov, Kinetika i Kataliz, 8, 1120 (1968).
123. J. L. Mackey and R. L. Collins, J. Inorg. Nuclear Chem., 29, 655 (1967).
124. I. P. Suzdalev, A. S. Plachinda, E. F. Makarov, and V. A. Dolgopolov, Zhur. Fiz. Khim., 41, 2831 (1967) [Russ. J. Phys. Chem., No. 11 (1967)].
125. N. G. Polyanskii and P. E. Tulupov, in "Issledovanie Svoistv Ionoobmennykh Materialov" (Investigation of the Properties of Ion-exchange Materials), Nauka, Moscow, 1964, p. 145.
126. L. V. Nidrak and V. T. Grabb, in "Toplivnye Elementy" (Fuel Cells), Sudostroenie, Leningrad, 1966, p. 225.
127. "Demineralizatsiya Metodom Elektrodializa" (Demineralization by Electrodialysis), Atomizdat, Moscow, 1963.
128. B. N. Laskorin and N. M. Smirnova, "Ionoobmennye Sorbenty v Promyshlennosti" (Ion-exchange Sorbents in Industry), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 71.
129. T. R. E. Kressman and F. L. Tye, Discuss. Faraday Soc., 185 (1956).
130. P. E. Tulupov and V. P. Greben', Elektrokhimiya, 5, 563 (1969).
131. B. N. Laskorin, N. M. Smirnova, and M. N. Gantman, "Ionoobmennye Membrany i Ikh Primenenie" (Ion-exchange Membranes and Their Applications), Atomizdat, Moscow, 1961.
132. F. L. Tye, Discuss. Faraday Soc., 200 (1956).
133. R. Schlogl and B. Stein, Z. Elektrochem., 62, 340 (1958).
134. J. T. Clarke, J. A. Marinsky, W. Juda, N. W. Rosenberg, and S. Alexander, J. Phys. Chem., 56, 100 (1952).
135. W. Juda, N. W. Rosenberg, J. A. Marinsky, and A. A. Kasper, J. Amer. Chem. Soc., 74, 3736 (1952).
136. N. I. Isaev and V. A. Shaposhnik, Zavod. Lab., 31, 1213 (1965).
137. V. D. Vaganov, N. Ya. Lyubman, F. T. Shostak, and K. Zh. Kulumbetova, in "Sintez i Issledovanie Vysokomolekulyarnykh Soedinenii" (Preparation and Investigation of Macromolecular Compounds), Izd. Akad. Nauk Kazakh. SSR, Alma-Ata, 1964, p. 176.
138. A. P. Rudakov and N. A. Semenov, Mekhanika Polimerov, 155 (1965).
139. K. M. Saldadze, in "Issledovanie v Oblasti Khromatografii" (Research on Chromatography), Izd. Akad. Nauk SSSR, Moscow, 1952, p. 114.
140. K. M. Saldadze and Z. G. Demonterik, see Ref. 6, p. 106.
141. G. A. Evlanov and N. E. Saf'yanova, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 6, 341 (1963).
142. N. G. Polyanskii, Priroda, No. 9, 102 (1957).
143. N. G. Polyanskii, Uch. Zap. Daugavpilssk. Gos. Ped. Inst., 2, 121 (1959).
144. N. G. Polyanskii, see Ref. 43, p. 72.
145. N. G. Polyanskii, V. I. Vishnevskaya, and Yu. M. Mizh-Mishin, Vysokomol. Soed., 8, 1249 (1959).
146. N. G. Polyanskii, Doctoral Thesis, Leningrad State University, Leningrad, 1969.
147. N. G. Polyanskii, in "Kataliz v Vysshei Shkole" (Catalysis in College), Moscow State University, Moscow, 1962, Vol. 2, p. 242.
148. A. A. Vasil'ev, see Ref. 6, p. 89.
149. K. Dušek and R. Chromeček, Chem. průmysl, 10, 267 (1960).
150. A. S. Konishcheva, N. M. Morozova, and K. M. Ol'shanova, see Ref. 114, p. 115.

151. Z. P. Suranova, A. A. Morozov, and O. Ya. Grabchuk, see Ref. 125, p. 133.
152. G. Naumann, Chem. Tech. (Berlin), 11, 18 (1959).
153. N. N. Kuznetsova, A. A. Vansheidt, K. P. Papukova, and T. N. Komyakova, Zhur. Prikl. Khim., 37, 1624 (1964).
154. R. Griesbach, "Theorie und Praxis des Ionenaustausches" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 488.
155. N. G. Polyanskii, Izv. Akad. Nauk Latv. SSR, No. 12, 163 (1957).
156. N. G. Polyanskii and G. L. Shik, Uch. Zap. Daugavpilssk. Pedinst., 2, 133 (1959).
157. N. G. Polyanskii and G. L. Shik, Vestnik Tekh. Ekon. Inf., No. 3, 43 (1960).
158. N. G. Polyanskii, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 276 (1960).
159. V. S. Soldatov, A. I. Tsukurova, and A. I. Pokrovskaya, Zhur. Fiz. Khim., 42, 428 (1968) [Russ. J. Phys. Chem., No. 2 (1968)].
160. O. R. Skorokhod, M. L. Tabulo, and L. I. Dorofeeva, Kolloid. Zhur., 26, 100 (1964).
161. Yu. A. Leikin, A. V. Smirnov, A. B. Dabankov, and V. V. Korshak, Vysokomol. Soed., A10, 157 (1968).
162. V. S. Soldatov, A. I. Pokrovskaya, and L. I. Tsukurova, Zhur. Fiz. Khim., 42, 1258 (1968) [Russ. J. Phys. Chem., No. 5 (1968)].
163. O. N. Karpov, V. V. Klimov, and V. I. Volkov, Zhur. Fiz. Khim., 42, 2295 (1968) [Russ. J. Phys. Chem., No. 9 (1968)].
164. G. L. Starobinets, M. P. Sednev, A. I. Pokrovskaya, and G. S. Martinchik, in "Sbornik Nauchnykh Rabot" (Scientific Papers), Minsk, 1960, Vol. 1, p. 214.
165. G. F. L. Ehlers, K. R. Fisch, and W. R. Powell, J. Polymer Sci., 7, A-1, 2955 (1969).
166. Yu. M. Marchevskaya and O. D. Kurilenko, Zhur. Fiz. Khim., 39, 2849 (1965) [Russ. J. Phys. Chem., No. 11 (1965)].
167. J. Inczedy, "Analytische Anwendungen von Ionenaustauschern", Budapest, 1964, p. 36.
168. C. Calmon and T. R. E. Kressman, "Ion Exchangers In Organic and Biochemistry", New York, 1957.
169. G. L. Starobinets, L. I. Sevost'yanova, and G. N. Bulatskaya, Zhur. Prikl. Khim., 33, 690 (1960).
170. N. G. Peryshkina, N. I. Sudarikova, and V. S. Soldatov, Vestnik Akad. Nauk Beroruss. SSR, Ser. Khim., No. 1, 20 (1965).
171. A. Chapiro and P. Seidler, European Polymer J., 1, 189 (1965).
172. O. N. Myagkoi and T. G. Suslina, in "Teoriya i Praktika Sorbtsionnykh Protsessov" (Theory and Practice of Sorption Processes), Izd. Voronezhsk. Gos. Univ., Voronezh, 1968, Vol. 2, p. 33.
173. B. H. Ketelle and G. E. Boyd, in "Chromatographic Separation of Ions" (Translated into Russian), Inostr. Lit., Moscow, 1949, p. 159.
174. G. Dickel and L. Nieciecki, Z. Elektrochem., 59, 913 (1955).
175. G. H. Osborn, "Synthetic Ion Exchangers" (Translated into Russian), Mir, Moscow, 1964, p. 30.
176. F. K. Lindsay, L. F. Wirth, and A. M. Durinski, Ind. Eng. Chem., 43, 1062 (1951).
177. G. E. Boyd, B. A. Soldano, and O. D. Bonner, J. Phys. Chem., 58, 456 (1954).
178. B. A. Soldano, Ann. New York Acad. Sci., 57, 117 (1953).
179. N. G. Polyanskii, N. L. Polyanskaya, E. I. Lyustgarten, and A. I. Nikitina, in "Ionnyi Obmen i Ionity" (Ion Exchange and Ion Exchangers), Nauka, Leningrad, 1970, p. 146.
180. N. G. Polyanskii, see Ref. 114, p. 109.
181. P. E. Tulupov and A. I. Kasperovich, see Ref. 179, p. 75.
182. P. E. Tulupov, S. I. Bel'fer, and K. M. Saldadze, see Ref. 179, p. 53.
183. E. E. Gilbert, "Sulphonation and Related Reactions" (Translated into Russian), Khimiya, Moscow, 1969, p. 370.
184. K. M. Saldadze and N. L. Luk'yanova, see Ref. 49, p. 211.
185. K. D. Dzhandosova, I. N. Azerbaev, and F. T. Shostak, Izv. Akad. Nauk Kazakh. SSR, Ser. Khim., No. 1, 62 (1969).
186. V. A. Makarova, M. V. Pevnitskaya, and V. D. Grebonyuk, Izv. Sibirsk. Otd. Akad. Nauk SSSR, 6, No. 14, 118 (1969).
187. B. V. Erofeev, S. F. Naumova, and M. I. Makovetskii, Izv. Akad. Nauk Beloruss. SSR, No. 4, 48 (1964).
188. N. G. Polyanskii, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 164 (1958).
189. A. T. Davydov and G. M. Lisovina, see Ref. 43, p. 122.
190. N. N. Matorina and A. N. Popov, Zhur. Fiz. Khim., 32, 2557 (1958).
191. W. C. Baumann, Ind. Eng. Chem., 38, 46 (1946).
192. V. A. Klyachko and A. A. Kastal'skii, "Ochistka Vody dlya Promyshlennykh Vodoprovodov" (Purification of Water for Industrial Supplies), Stroiizdat, Moscow, 1951, p. 198.
193. F. C. Nachod and J. Schubert (Editors), "Ion-exchange Technology" (Translated into Russian), Metallurgizdat, Moscow, 1959.
194. M. A. Potapova, N. I. Petrova, K. M. Ol'shanova, and K. M. Saldadze, in "Sintez i Svoistva Ionoobmennykh Materialov" (Preparation and Properties of Ion-exchange Materials), Nauka, Moscow, 1968, p. 113.
195. A. A. Vasil'ev, M. B. Gershman, and T. A. Vasil'eva, Zhur. Prikl. Khim., 35, 2288 (1962).
196. S. Munari, F. Vigo, G. Tealdo, and C. Rossi, J. Appl. Polymer Sci., 11, 1563 (1967).
197. S. Munari, F. Vigo, G. Tealdo, and C. Rossi, J. Polymer Sci., B4, 547 (1966).
198. E. I. Kazantsev, M. V. Vinogradov, Yu. A. Makeev, N. V. Sapogov, and L. I. Grofimova, see Ref. 114, p. 102.
199. E. I. Kazantsev, N. V. Sapogov, and V. M. Vinogradov, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 780 (1968).
200. E. I. Kazantsev and V. M. Vinogradov, in "Tezisy Dokladov 2-i Nauchno-tekhnicheskoi Konferentsii Ural'skogo Politekhnicheskogo Instituta" (Abstracts of Papers at the Second Scientific and Technical Conference of the Ural Polytechnic Institute), Sverdlovsk, 1969.
201. V. V. Alekseeva, Yu. I. Ostroushko, L. I. Vodolazov, Yu. N. Fedulov, G. S. Pakhomova, and T. A. Tirman, Zhur. Prikl. Khim., 42, 396 (1969).
202. V. I. Atroshchenko, Ya. I. Asnin, and Z. A. Nikitskaya, Khim. Prom., 7, 551 (1960).
203. W. Wood, J. Phys. Chem., 61, 832 (1951).
204. R. Wiley and E. Reich, J. Polymer Sci., A1, 6, 3174 (1968).
205. E. I. Kazantsev and V. M. Vinogradov, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 13, 54 (1970).

206. R. B. Hodgdon, J. Polymer Sci., **A1**, 6, 171 (1968).
207. L. F. Wirth, C. A. Feldt, and K. Odland, Ind. Eng. Chem., **53**, 638 (1961).
208. N. D. Talanov and G. V. Astakhova, Zhur. Prikl. Khim., **39**, 1907 (1966).
209. T. V. Mekvabishvili, K. M. Saldadze, and B. Ya. Kel'man, see Ref. 49, p. 205.
210. See Ref. 40, p. 113.
211. See Ref. 168, p. 658.
212. F. Andreas, Chem. Tech. (Berlin), **11**, 24 (1959).
213. I. P. Losev and E. B. Trostyanskaya, see Ref. 139, p. 188.
214. A. T. Menyailo, M. Ya. Klimenko, Z. N. Verkhovskaya, and M. M. Afanas'ev, Khim. Prom., **7**, 544 (1960).
215. N. G. Polyanskii and P. E. Tulupov, Zhur. Prikl. Khim., **37**, 2686 (1964).
216. N. G. Polyanskii and P. E. Tulupov, Zhur. Prikl. Khim., **36**, 2244 (1963).
217. N. G. Polyanskii, P. E. Tulupov, and M. A. Shaburov, see Ref. 125, p. 137.
218. D. S. Bystrov, Dokl. Akad. Nauk SSSR, **154**, 407 (1964).
219. N. G. Polyanskii and P. E. Tulupov, Neftekhimiya, **4**, 860 (1964).
220. P. E. Tulupov, Zhur. Fiz. Khim., **39**, 2708 (1965) [Russ. J. Phys. Chem., No. 11 (1965)].
221. N. G. Polyanskii and P. E. Tulupov, USSR P. 172 308; Byull. Izobret., No. 13 (1965).
222. L. K. Arkhangel'skii and E. A. Materova, in "Fiziko-khimicheskie Svoistva Rastvorov" (Physicochemical Properties of Solutions), Leningrad. Gos. Univ., Leningrad, 1964, p. 163.
223. H. Szmant, in "Organic Sulphur Compounds" (Edited by N. Kharasch), Pergamon Press, 1961, Chapter 16.
224. P. E. Tulupov, Zhur. Prikl. Khim., **39**, 2434 (1966).
225. P. E. Tulupov and Yu. I. Belonogova, Zhur. Prikl. Khim., **39**, 2535 (1966).
226. I. F. Gleim, V. A. Moichenko, and V. S. Soldatov, in "Ionnyi Obmen i Ionity" (Ion Exchange and Ion Exchangers), Nauka, Moscow, 1970, p. 58.
227. V. S. Soldatov, Z. R. Pavlovskaya, and I. F. Gleim, in "Ionnyi Obmen i Ionity" (Ion Exchange and Ion Exchangers), Nauka, Moscow, 1970, p. 64.
228. Z. N. Eirish, M. V. Eirish, and M. V. Vittikh, Izv. Akad. Nauk Kazakh. SSR, Ser. Khim., **20**, 32 (1970).
229. I. N. Lyapunov, E. I. Kazantsev, and V. M. Kosarev, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., **13**, 1606 (1970).
230. P. S. Belov, I. E. Libinshtein, and N. M. Egorov, Khim. Tekhnol. Topliv Masel, No. 4, 17 (1970).
231. B. S. Konovalov and P. S. Belov, Khim. Prom., 732 (1969).
232. Ya. M. Paushkin, S. V. Meshcheryakov, and S. A. Mangasarov, in "Ionoobmennye Materialy v Nauke i Tekhnike, Materialy Seminara v Moskovskom Dome Nauchno-tekhnicheskoi Propagandy im. F. E. Dzerzhinskogo" (Ion-exchange Materials in Science and Technology—Proceedings of a Seminar in the Dzerzhinskii Moscow House for the Popularisation of Science and Technology), Moscow, 1969, p. 29.
233. Ya. M. Paushkin, O. Yu. Omarov, S. A. Mangasarov, and L. P. Golubovskaya, Zhur. Prikl. Khim., **43**, 2258 (1970).
234. Ya. M. Paushkin and S. V. Logashin, Plastmassy, No. 2, 10 (1971).
235. S. V. Logashin, Candidate's Thesis, Institute of the Petrochemical and Gas Industry, Moscow, 1970.

Tambov Institute of Chemical Engineering

Karpov Physicochemical Scientific
Research Institute, Moscow