U.D.C. 541.183.12

Thermal Stability of Anion-exchange Resins

P.E.Tulupov and N.G.Polyanskii

This paper is a logical continuation of the previous review by the authors[1] and reflects the present state of studies on the thermal stability of anion-exchange materials. It deals with the principal methods for the investigation of the thermal stability of anion-exchange resins and presents rational formulae for the recalculation of exchange capacities which facilitate comparison of the experimental data of different investigators. Attention has been concentrated on a general description of data on the thermal stability of different anion-exchange resins in air, in water and aqueous solutions, and in organic and mixed media. A new mechanism is proposed for processes involving changes in ion-exchange resins in the above media. Rigorous kinetic equations describing the decrease of the exchange capacity with respect to highly basic groups, deamination, and degradation of the amino-groups in anion-exchange resins have been obtained on its basis and agree satisfactorily with the experimental data. Further aims of studies on the thermal stability of ion-exchange resins have been outlined.
The bibliography includes 112 references.

CONTENTS

I.	Introduction	754
II.	Methods for investigating the thermal stability of anion-exchange resins	754
III.	The stability of anion-exchange resins on heating in air	757
IV.	Thermal stability of anion-exchange resins in water and aqueous solutions	758
V.	Thermal stability of anion-exchange resins in organic and mixed media	761
VI.	The mechanism and kinetics of processes occurring on heating anion-exchange resins in water and aqueous organic and organic media	762

I. INTRODUCTION

Anion-exchange resins, like cation-exchange resins, are in practice frequently subjected to heat treatment. In many cases heating accompanies even the preliminary preparation of the anion exchangers for experiments in order to remove as far as possible trapped water or another solvent. Some investigators dry anion-exchange resins in air[2], others *in vacuo* at 64°C, and yet another group use a thermostat at 100°C.[3,4] Regardless of the drying conditions, strongly basic anion-exchange resins undergo far-reaching chemical changes[5].

Anion-exchange resins are frequently employed at an elevated temperature for the analytical separation of multicomponent mixtures[6] but for the usual single employment of the sorbent the problems of durability have of course not been considered.

On the other hand, in catalysis by ion-exchange resins[7] durability is of prime importance, determining the possibility of reusing the catalyst and frequently deciding whether its employment is economical.

Water treatment undertakings are the largest consumers of anion-exchange resins (together with cation-exchange resins) and for these purposes the thermal stability of these high-polymer electrolytes determines not only whether or not the technological processes are economical but also the quality of the deionised water[8,9].

Despite the enormous theoretical and practical importance of this problem,the number of studies on the thermal stability of anion-exchange resins is not very great, and with few exceptions their standard is lower than in the corresponding field of research on cation-exchange resins[1].

The lag in studies on the thermal stability of anion-exchange resins is due to the inadequate systematic approach to the problem, the competitive reactions which frequently occur simultaneously, and to a certain extent the smaller availability of the specimens for study than in the case of cation-exchange resins.

Systematic studies on the thermal stability of anion-exchange resins began only after the development of reliable methods for the separate determination of their exchange capacities with respect to active groups of different basicity. Further development of studies in this field depends largely on the validity of the methods employed by investigators.

As in the original reports, attention is concentrated on AV-17 anion-exchange resin and its analogues which have been most widely used under industrial conditions.

II. METHODS FOR INVESTIGATING THE THERMAL STABILITY OF ANION-EXCHANGE RESINS

This section deals with methods which are of specific importance for anion-exchange resins. Technical anion-exchange resins are first freed from impurities by prolonged treatment in a column or on a filter with 3 N hydrochloric acid and then washed with water and converted into the hydroxide-form by passage of 1 N aqueous KOH solution. To condition the resins, the above operations are repeated twice and the last washing with water is terminated as soon as the consumption of 0.01 N hydrochloric acid in the titration of 100 ml of wash liquid falls to 0.3 ml.

When necessary, the anion exchanger is converted into a salt-form by passing through the column a 0.5 N solution of the corresponding acid until its concentration in the filtrate remains constant. To avoid hydrolytic scission of counterions, weakly basic anion exchangers are washed free of the electrolyte with 96% ethanol until the filtrate gives a neutral response.

Anion-exchange resins are heat-treated in air in weighing bottles or in other vessels suitable for weighing[5] and, when an aqueous or organic medium is employed, the heat treatment is in an open or sealed tube[10]. The devices recommended by the authors of this review[11] are very convenient for the investigation of gaseous nitrogen-containing compounds formed on heat treatment of anion-exchange resins.

After the specified duration of heat treatment has elapsed, the anion exchanger is repeatedly washed with deionised water until a neutral response is obtained with respect to phenolphthalein and the phases are investigated separately.

In the simplest case, the total content of basic substances is determined in the liquid phase (called the aqueous extract) by titration with hydrochloric acid [5]. In more complex cases, the substances passing to the aqueous extract and representing the resin degradation products are identified by general chemical [3,12,13], potentiometric [12], and spectrophotometric [12] methods. Finally, many investigators [14-17] disregard the aqueous extract, confining themselves to a more or less detailed study of the anion exchangers themselves before and after their thermochemical [14-16] or radiation [17] treatment. In the study of the mechanism of the changes occurring in anion-exchange resins, as in the determination of small losses of exchange capacity which are not revealed by the direct investigation of the solid phase, such limitation of the research technique used is completely unjustified.

An example of the most complete investigation of an ion-exchange resin after thermochemical treatment is that of Vinogradov and Kazantsev [14]. The authors determined the exchange capacity of the anion-exchange resin with respect to strongly and weakly basic groups, the total nitrogen content, and the physicochemical characteristics of the resin, such as absorption in the infrared spectrum, density, and the coefficieint of the moisture absorption capacity. Among the above properties, all the investigators attribute the greatest importance to the exchange capacity, for the determination of which a wide variety of methods have been developed, but these require a rigorous and critical approach.

A compilation of methods for the determination of the exchange capacity of anion-exchange resins and the relevant recipes may be found in monographs [18-20] and in an All-Union Standard [21]. All the methods for the determination of the static exchange capacity (SEC) taking into account without discrimination a proportion of the active groups which depends on the specific conditions of the analysis should be ignored. We believe that best results in the study of the thermal stability of anion-exchange resins can be obtained by the following method for the determination of the exchange capacity.

A differential determination of the strongly and weakly basic groups is provided for in Kunin's method [22], which was perfected in studies by English [23,24] and Czech [25] investigators. According to the evidence of Polak and Wyroba [26], Kunin's original method gives somewhat high values for the content of weakly basic groups. More reliable results were obtained using Stamberg's version [25]. With certain additional modifications, the method has been used to determine the exchange capacities of anion-exchange resins mixed with cation-exchange resins [27].

A direct determination of groups with different basicities without a preliminary conversion of the anion-exchange resins into a salt-form is achieved in the method of Polyanskii and Shaburov [28].

Studies of Kopylova and coworkers [29,30] on the use of non-aqueous media for the separate determination of primary, secondary, and tertiary amino-groups in anion-exchange resins are of great practical importance.

The methods of Fischer and Kunin [22] and Polyanskii et al. [31] yield the best results in the determination of the exchange capacities of anion-exchange resins in the Cl-form. In the method of Fischer and Kunin [22], it is recommended that the resin be washed in a column with 4% aqueous K_2SO_4 solution with subsequent titration of chloride ions in the filtrate by Mohr's method. Polyanskii and Shaburov [31] proposed a simpler static version of the method based on the titration of the Cl^- ions evolved on interaction of the anion-exchange resin with 10% aqueous K_2SO_4 solution without the separation of the phases.

Since strongly and weakly basic groups present in polyfunctional anion-exchange resins exhibit different thermal stabilities, the state of the anion-exchange resin can be fully characterised only by the separate determination of these groups; the method of expressing their concentrations is then important.

The majority of investigators assess the thermal stabilities of anion-exchange resins on the basis of the time variation of the exchange capacity or from the relative loss of exchange capacity R:

$$R = \frac{E_0 - E_t}{E_0} \cdot 100\% \ , \qquad (1)$$

where E_t and E_0 are the exchange capacities after and before this treatment. It is noteworthy that these criteria, in particular for polyfunctional anion-exchange resins, are only of relative value, since for a first-order reaction R is independent of the initial exchange capacity [32]. In studies on thermal stability, the exchange capacity of anion-exchange resins is referred to 1 g of dry (E^d) or swollen (E^h) resin and sometimes is expressed in fractions of the conversion of the functional groups [33,34]. One should note that all these quantities depend on many variables (the amount of bound water, the weight of functional groups, the type of counterions) and therefore they are unsuitable for the kinetic treatment of the experimental data when the ion-exchange resins are heated or irradiated.

As a rule, the most stable component of the resin is the matrix. Therefore in kinetic studies the exchange capacity is referred to 1 g of the matrix (E^M) without functional groups, counterions, and sorbed water.

The wide variety of existing methods for expressing the exchange capacities of ion-exchange resins hinder the comparison of the experimental data obtained by different investigators and require the derivation of conversion formulae in each case. Such recalculations are facilitated by the relations presented in Table 1 and in Eqns. (2)–(6), which are valid for all types of ion-exchange materials.

Table 1 may be supplemented by formulae for the calculation of exchange capacity when the ionic form changes from B to A, which can be written as follows for the dry and swollen resins [32]:

$$E_A^d = \frac{E_B^d}{1 + E_B^d(\epsilon_A - \epsilon_B)} \ , \qquad (2)$$

$$E_A^h = \frac{(1 + K_B)E_B^h}{(1 + K_A)[1 + E_B^h(1 + K_B)(\epsilon_A - \epsilon_B)]} \ . \qquad (3)$$

In the corresponding change of the ionic form of only one type (i) of functional groups in a polyfunctional resin [32], we have

$$E_{i,A}^d = \frac{E_{i,B}^d}{1 + E_{i,B}^d(\epsilon_{i,A} - \epsilon_{i,B})} \ , \qquad (4)$$

$$E_{i,A}^h = \frac{(1 + K_B)E_{i,B}^h}{(1 + K_{i,A})[(1 + K_B)E_{i,B}^h(\epsilon_{i,A} - \epsilon_{i,B}) + 1]} \ , \qquad (5)$$

where K is the coefficient of moisture absorption capacity in g H_2O/g dry resin, E the exchange capacity in mequiv. g^{-1}, ϵ the equivalent weight of the functional groups with counterions A or B, $K_{i,A}$ the coefficient of

Table 1. Formulae for the recalculation of the exchange capacities of ion-exchange resins.

Resin exchange capacity	E^h	E^d	E^M	N^h	N^d	N_c^h	N_c^d
$E^h = \frac{\text{mequiv.}}{\text{g swollen resin}}$	E^h	$\frac{E^d}{1+K}$	$\frac{E^M}{(1+\sum_{i=1}^{n} E_i^M \epsilon_i)(1+K)}$	$\frac{N^h}{d^h}$	$\frac{N^d}{(1+K)d^d}$	$\frac{N_c^h}{d^h\epsilon^h}$	$\frac{N_c}{(1+K)\epsilon^d d^d}$
$E^d = \frac{\text{mequiv.}}{\text{g dry resin}}$	$E^h(1+K)$	E^d	$\frac{E^M}{1+\sum_{i=1}^{n} E_i^M \epsilon_i}$	$\frac{N^h(1+K)}{d^h}$	$\frac{N^d}{d^d}$	$\frac{N_c^h(1+K)}{d^h\epsilon^h}$	$\frac{N_c^d}{\epsilon^d d^d}$
$E^M = \frac{\text{mequiv.}}{\text{g resin matrix}}$	$\frac{E^h}{\frac{1}{1+K}-\sum_{i=1}^{n} E_i^h\epsilon_i}$	$\frac{E^d}{1-\sum_{i=1}^{n} E_i^d\epsilon_i}$	E^M	$\frac{N^h}{\frac{d^h}{1+K}-\sum_{i=1}^{n} N_i^h\epsilon_c}$	$\frac{N^d}{d^d-\sum_{i=1}^{n} N_i^d\epsilon_i}$	$\frac{N_c^h}{\frac{d^h\epsilon^h}{1+K}-\sum_{i=1}^{n} N_{ki}^h\epsilon_i}$	$\frac{N_c^d}{d^d\epsilon^d-\sum_{i=1}^{n}\Sigma_{ki}^d\epsilon_i}$
$N^h = \frac{\text{mequiv.}}{\text{ml swollen resin}}$	$E^h d^h$	$\frac{E^d d^h}{1+K}$	$\frac{E^M d^h}{(1+K)(1+\sum_{i=1}^{n} E_i^M \epsilon_i}$	N^h	$\frac{N^d d^h}{(1+K)d}$	$\frac{N_c^h}{\epsilon^h}$	$\frac{N_c^d d^h}{(1+K)\epsilon^d d^d}$
$N^d = \frac{\text{mequiv.}}{\text{ml dry resin}}$	$E^h(1+L)d^d$	$E^d d^d$	$\frac{E^M d^d}{1+\sum_{i=1}^{n} E_i^M \epsilon_i}$	$\frac{N^h(1+K)d^d}{d^h}$	N^d	$\frac{N_c^h(1+K)d^d}{\epsilon^h d^h}$	$\frac{N_c^d}{\epsilon^d}$
$N_c^h = \frac{\text{mequiv.}}{\text{ml swollen resin in column}}$	$E^h d^h \epsilon^h$	$\frac{E^d d^h \epsilon^h}{1+K}$	$\frac{E^M d^h \epsilon^h}{(1+K)(1+\sum_{i=1}^{n} E_i^M \epsilon_i)}$	$N^h\epsilon^h$	$\frac{N^d d^h \epsilon^h}{(1+K)d^d}$	N_c^h	$\frac{N_c^d d^h \epsilon^h}{(1+K)d^d\epsilon^d}$
$N_c^d = \frac{\text{mequiv.}}{\text{ml dry resin in column}}$	$E^h(1+K)\epsilon^d d^d$	$E^d d^d \epsilon^d$	$\frac{E^M d^d \epsilon^d}{1+\sum_{i=1}^{n} E_i^M \cdot \epsilon_i}$	$\frac{N^h(1+K)\epsilon^d d^d}{d^h}$	$N^d\epsilon^d$	$\frac{N_c^h(1+K)\epsilon^d d^d}{E^h d^h}$	N_c^d

moisture absorption capacity of the resin in which the groups i are in the A-form and the rest are in the B-form, and d is the density of the resin in g ml^{-1}.

When the ionic forms of all the functional groups change the exchange capacity with respect to one of them designated as the first is given by the following formula for the simplest case of the coexistence of two different functional groups [32]:

$$E_{1,A}^d = \frac{E_{1,B}^d(1+E_2^M \cdot \epsilon_{2,B})}{1+E_2^M \cdot \epsilon_{2,A}+E_{1,B}^d(\epsilon_{1,A}-\epsilon_{1,B})+E_{1,B}^d \cdot E_2^M(\epsilon_{1,A} \cdot \epsilon_{2,B}-\epsilon_{1,B} \cdot \epsilon_{2A})} \cdot \quad (6)$$

where the subscripts $1,A$ and $2,B$ imply that the capacity or the equivalent weight refers to the first type of functional groups in the ionic form A or to the second type of groups in the ionic form B.

In order to be able to employ the above formulae, it is necessary to know the densities d of the dry and swollen resins, the coefficient of moisture absorption capacity, and the degree of filling of the columns ϵ. The derivation of these quantities was considered in the preceding review [1]. However, in the measurement of the coefficient of moisture absorption capacity for strongly basic anion-exchange resins in the OH-form, one cannot employ the trivial method, since in the dehydration stage not only water but also nitrogen-containing compounds volatilise [5].

A compromise solution was proposed by Greben' [32], who employed the relatively high thermal stability of the salt-forms of ion-exchange resins. He derived a formula for the calculation of the coefficient of moisture absorption capacity K_A of the ionic forms A which decompose on drying, in terms of the weight of the swollen resin p in forms A and B, the corresponding equivalent weights of the functional groups, the exchange capacity, and the coefficient of moisture absorption capacity K_B of the thermostable form B:

$$K_A = \frac{(1+K_B)\,p_{A/p_B}^h}{1-(1+K_B)E_B^h(\epsilon_B-\epsilon_A)} - 1 \cdot \quad (7)$$

A decrease in the content of the functional groups is accompanied by a decrease in the weight of the resin, which is given by the following formula in the absence of degradation of the matrix to soluble oligomers:

$$W_{exp} = \frac{p_0^d - p_t^d}{p_0^d} \cdot 100\,\% = \left[1 - \frac{p_t^h(1+K_0)}{p_0^h(1+K_t)}\right] \cdot 100\,\% \cdot \quad (8)$$

The experimental weight losses can be usefully compared with the calculated values W_{calc}, which are given by the following expression when the condition mentioned above is fulfilled:

$$W_{calc} = (1+K_0)\sum_{i=1}^{n}\left(E_{0,i}^h - E_{t,i}^h \frac{p_t^h}{p_0^h}\right)\epsilon_i \cdot 100\,\% =$$

$$= \sum_{i=1}^{n}\left(E_{0,i}^d - E_{t,i}^d \frac{p_t^d}{p_0^d}\right)\epsilon_i \cdot 100\,\% = \frac{\sum_{i=1}^{n}(E_{0,i}^M - E_{t,i}^M)\,\epsilon_i}{1+\sum_{i=1}^{n} E_{0,i}^M\,\epsilon_i} \cdot 100\,\% \cdot \quad (9)$$

The satisfactory agreement between W_{exp} and W_{calc}, established in a study of the thermal stability of AV-17 anion-exchange resin [35] demonstrates the absence of degradation of the matrix to soluble oligomers under the experimental conditions.

To characterise the processes involved in the loosening or contraction of the three-dimensional network but not the breakdown of the matrix, it is useful to employ the equivalent coefficient of moisture absorption capacity K^e:

$$K^e = \frac{K}{0{,}018\,E^d} = \frac{K}{0{,}018\,(1+K)\,E^h} \cdot \quad (10)$$

Eqn. (10) shows that the equivalent coefficient of moisture absorption capacity defines a number of millimoles of water per milliequivalent of functional groups provided the entire trapped liquid is in a bound state and does not merely fill pores, cracks, etc. and that the hydration shells of adjacent groups do not overlap [36,37].

In certain cases, the formation of cracks leads to an increase of the equivalent coefficient of moisture absorption capacity[37], which is in no way related to the expansion of the three-dimensional network. The decrease of this quantity for the usual gel cation-exchange resins may indicate a contraction of the three-dimensional network while for macroporous resins it may be evidence of a decrease of the overall porosity. In the literature on ion exchange, publications have already appeared in which the effect of heat treatment on the porometric characteristics of cation-exchange resins is considered[38,39]. Similar studies have not so far been made on anion-exchange resins.

Infrared spectroscopic methods are particularly important for the investigation of the changes in the chemical structure of anion-exchange resins on heat treatment and irradiation. The basic aspects of the application of infrared spectroscopy to anion-exchange resins have already been considered[14,140]; in addition, interesting experimental results have been presented in other publications[41-44].

In many cases, comparison of the results of different workers is difficult owing to the absence in the reports of a detailed description of the resins investigated (the degree of their cross-linking, capacity with respect to different active groups, and the coefficient of moisture absorption capacity) and sometimes due to an unduly concise description of the experimental technique. For example, such details as the proportions of the resin and solution phases are undeservedly regarded as unimportant and are usually not mentioned. Nevertheless, in cases where there is a direct interaction of the medium with the functional groups[44], when the products of the reaction affect its rate[27], and for reversible changes in resins, the kinetics of the decrease of exchange capacity depend on the quantitative proportions of the phases. Naturally, there are no grounds for being dogmatic about these relations, but it is important that each investigator base his treatment on something concrete.

III. THE STABILITY OF ANION-EXCHANGE RESINS ON HEATING IN AIR

The study of the thermal stability of anion-exchange resins in air was begun in 1952 [45] and was confined to the observation of an endothermic effect associated with the evolution of water and an exothermic effect associated with the combustion of the resin. In another, more sophisticated study[46], the thermal stability of an anion-exchange resin based on methylvinylpyridine and divinylbenzene was investigated but in this case the change in the content of acid groups was not determined by chemical analysis.

Two endothermic effects observed on the thermogram for AV-17 anion-exchange resin in the OH-form have been interpreted[47]: the first (at 120–150°C) was attributed to the desorption of water and the elimination of active groups and the second (at 190–280°C), to the thermal degradation of the resin itself. Together with the decrease of exchange capacity, heat treatment results in a decreased capacity of the anion-exchanger for hydration, but it is not surprising that below 140°C these effects are not observed.

Comparative thermographic data for the stability of anion-exchange resins of different basicities have been published[48,49]. In studies on EDE-10P, Dowex-1 × 4 and Dowex-2 × 4 resins, differences between the stabilities of strongly and weakly basic active groups have been clearly demonstrated: a decrease of exchange capacity is observed mainly in relation to strongly basic groups. EDE-10P anion-exchange resin in the OH-form is stable in air up to 150°C, but in the range 160–200°C strongly basic groups are converted into weakly basic groups without loss of the total exchange capacity[48]. Strongly basic polymerisation anion-exchange resins lose thier active groups completely after heating for 3 h at 220°C.[49]

As shown by one of the present authors and Shaburov[5], even simple drying of AV-17 anion-exchange resin at room temperature entails an appreciable decrease of the total exchange capacity with a simultaneous accumulation of weakly basic groups. Following Dybczynski[50], the authors explained these changes by deamination:

$$R{-}CH_2{-}N(CH_3)_3OH + H_2O \rightarrow R{-}CH_2OH + NH(CH_3)_3OH \qquad (11)$$

and degradation

$$R{-}CH_2{-}N(CH_3)_3OH + H_2O \rightarrow R{-}CH_2{-}NH(CH_3)_2OH + CH_3OH\ . \qquad (12)$$

However, one cannot rule out the possibility that reactions (11) and (12) are of subsidiary importance and that the main cause of the changes in the capacity of AV-17 anion-exchange resin is interaction of two active groups with formation of a tetramethylammonium base and of two polymeric molecules, one of which should be a weakly basic anion exchanger:

$$\begin{matrix} R{-}CH_2{-}N(CH_3)_3OH \\ R{-}CH_2{-}N(CH_3)_3OH \end{matrix} + H_2O \rightarrow \begin{matrix} R{-}CH_2{-}NH(CH_3)_2OH \\ R{-}CH_2OH \end{matrix} + N(CH_3)_4OH\ . \qquad (13)$$

Mechanism (13) is supported primarily by the fairly high basicity of the aqueous extracts from AV-17 anion-exchange resin dried *in vacuo*, which may be attributed to the tetramethylammonium base the volatility of which is known[51] to be low in aqueous solutions. Furthermore, mechanism (13) is confirmed by the finding that the rates of deamination and degradation of anion-exchange resins depend little on the method of drying[5].

Thus AV-17 × 2 anion-exchange resins dried at room temperature *in vacuo*, at room temperature in the presence of $CaCl_2$ and Anhydrone, and at 110°C to constant weight lost 1.69, 1.57, and 1.96 milliequivalents of strongly basic groups per gramme of dry resin as a result of deamination and 1.42, 1.15, and 1.89 mequiv. g^{-1} as a result of degradation. Under the same drying conditions, AV-17 × 16 resin lost 0.44, 0.37, and 0.68 mequiv. g^{-1} as a result of deamination and 0.39, 0.39, and 0.56 mequiv. g^{-1} as a result of degradation. All these findings make it possible to regard the deamination and degradation of the OH-form of AV-17 anion-exchange resin as coupled and not as independent processes.

Bearing in mind the comparatively low volatility of the conversion product of AV-17 anion-exchange resin according to mechanism (13), it is easy to explain the finding of Soldatov et al.[52] that its exchange capacity remains unchanged when dried at 60°C. Indeed, this constancy is only an apparent consequence of the equivalent relations between the number of strongly basic groups eliminated and the tetramethylammonium base formed and remaining in the resin phase under mild drying conditions. If the analysis of liquid extracts is neglected it is thus possible to arrive at completely incorrect ideas about the stability of the anion-exchange resin.

In AV-27 anion-exchange resins, the ethanol group is linked to the nitrogen atom less strongly than the methyl groups[13] and therefore the main cause of the changes in the

resin is degradation with elimination of ethylene glycol according to the equation

$$\begin{array}{l}RCH_2N(CH_3)_2OH\\ \quad\quad|\\ \quad CH_2CH_2OH\end{array} + H_2O \rightarrow \begin{array}{l}RCH_2N(CH_3)_2OH\\ \quad\quad|\\ \quad\quad H\end{array} + HO{-}CH_2CH_2{-}OH\ . \quad (14)$$

Shaburov and Saldadze's studies[53] on the behaviour of the polyfunctional AV-16 anion-exchange resin in the OH-form involving a large scale employment of chemical-analytical methods showed that at 110°C the capacity decreases mainly in relation to the strongly basic pyridinium groups, which the authors believe to undergo tautomeric transformations. The changes in exchange capacity during the drying process lead to a marked contraction of the three-dimensional network and to a decrease of swellability almost by a factor of two.

The salt-forms of AV-17 anion-exchange resin[44,49,54-56] and of anion exchangers based on polyallylamine and epoxide ethers[57] are in general more resistant to heat treatment in air than the corresponding resins in the hydroxide-form. The salt-forms derived from acids with non-oxidisable anions can be arranged in the following sequence in terms of the decrease of thermal stability: $RCl > R_2SO_4 > R_3BO_3$. The relative thermal stability of the nitrate-form depends on temperature[49,58]. At 140°C it is more resistant to heating than the hydroxide-form, while at 160–200°C it undergoes pyrolytic decomposition and self-ignition. The self-inflammation temperature decreases with increased degree of cross-linking of Dowex-1 anion-exchange resin and with the concentration of the nitric acid employed for its regeneration. Barghusen and Jonke[58] do not recommend the employment of the nitrate-form of the resin above 60°C and note that, other conditions being equal, the thermal stability of anion-exchange resins in this form decreases in the series Dowex 2 > Permutit SK > Amberlite IRA-401.

Anion-exchange resins of type AV-17 in the Cl-form are entirely stable on heating in air up to 70°C [55] and, according to Shaburov[54], up to 100°C; they even withstand brief heating at 160°C.[35]

On prolonged heating at a temperature as low as 130°C, active groups of different basicities are split off, tentatively[55] in accordance with the mechanisms

$$RCH_2N(CH_3)_3Cl \rightarrow RCH_2Cl + N(CH_3)_3\ , \quad (15)$$

$$RCH_2NH(CH_3)_2Cl \rightarrow RCH_2Cl + HN(CH_3)_2\ . \quad (16)$$

A further increase of temperature from 130° to 180°C leads to a sharp fall of exchange capacity in relation to strongly basic groups with a possible accumulation of weakly basic groups owing to degradation:

$$RCH_2N(CH_3)_3Cl \rightarrow RCH_2N(CH_3)_2 + CH_3Cl\ . \quad (17)$$

It has been shown[35,44] that the number of weakly basic groups formed on heating AV-17 resin in a mixed Cl–OH-form to 150–170°C is smaller by a factor of two than the number of strongly basic groups split off under these conditions and it has been established that the scission of these groups is not due to the reactions (15)–(17) but is a result of hydrolysis involving the residual water. In the presence of a high water content, one amino-group is involved in the hydrolysis:

$$RCH_2N(CH_3)_3Cl + H_2O \rightarrow RCH_2OH + HN(CH_3)_3Cl\ , \quad (18)$$

and in the presence of a deficiency of water two amino-groups are involved:

$$\begin{array}{l}RCH_2N(CH_3)_3Cl\\ RCH_2N(CH_3)_3Cl\end{array} + H_2O \rightarrow \begin{array}{l}RCH_2OH\\ RCH_2NH(CH_3)_2Cl\end{array} + N(CH_3)_4Cl\ . \quad (19)$$

If the anion-exchange resin is dried *in vacuo* at 100°C, reaction (18) altogether fails to take place owing to the insufficiency of water and hydrolysis via mechanism (19) probably involves the interaction of two amino-groups via the following mechanism:

$$\begin{array}{l}RCH_2N(CH_3)_3Cl\\ RCH_2N(CH_3)_3Cl\end{array} \rightarrow \begin{array}{l}RCH_2\\ RCH_2\end{array}\!\!>\!N(CH_3)_2Cl + N(CH_3)_4Cl\ . \quad (20)$$

When AV-17 anion-exchange resins in the Cl-form are heated in open tubes to 150–180°C, partial decomposition of tetramethylammonium chloride is possible[44]. An increase of temperature to 270°C leads to the total loss of exchange capacity and to the appearance of inactive nitrogen[55], possibly owing to the oxidation of the amino-groups by atmospheric oxygen to nitro-groups.

EDE-10P anion-exchange resin in the Cl-form is less resistant to heating than in the mixed Cl–OH-form[35], since the HCl evolved in the hydrolysis of the weakly basic groups decomposes the anion-exchanger macromolecule. Condensation anion-exchange resins of type AT are more stable than EDE-10P resin[57], the increase of stability in the series AT-7 < AT-8 < AT-6 being explained (without convincing evidence) by different relative contents of primary, secondary, and tertiary amino-groups. The above anion exchangers were investigated by the thermographic method[57], which showed the presence of an endothermic effect in the range 160–200°C corresponding to the degradation of the functional groups. The differential thermal (DTA) curves for a number of strongly basic anion exchangers in salt-forms are quoted in a number of publications[48,49,52].

The resistance of anion-exchange resins in salt- and hydroxide-forms to frost has been investigated[59,60] and it has been established that the main result of the action of low temperatures is disruption of some of the polymeric chains, the cracking of grains, and deamination; degradation was not observed[59].

The thermal stability of anion-exchange resins with phosphonium and sulphonium groups[61] is appreciably lower than that of quaternary ammonium bases with an analogous matrix structure.

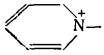
IV. THERMAL STABILITY OF ANION-EXCHANGE RESINS IN WATER AND AQUEOUS SOLUTIONS

Isolated data for the thermal stabilities of anion-exchange resins in water were obtained incidentally by the authors of the first studies of the properties[62,63] and behaviour of anion-exchange resins under the conditions of their industrial employment[64-68]. A general characteristic of these investigations is the random choice of the objects of study, the inadequate reliability of the experimental methods employed, and the formal nature of the results, which do not always yield a consistent picture of the main phenomenon during heat treatment—the decrease of the exchange capacity of the anion-exchange resin.

Systematic studies on the thermal stability of a wide range of different types of anion-exchange resins were undertaken by Pashkov et al.[3] On the basis of extensive experimental data, the authors showed that the thermal stability of anion-exchange resins depends on the matrix structure and on the nature of the active groups and the counterion. Thus weakly basic resins proved to be more stable than strongly basic resins and their salt-forms proved to be more stable than the hydroxide-forms. Other conditions being equal, polymerisation anion-exchange resins are more stable than condensation resins, although

individual examples of the latter, for instance EDE-10P resin [3] and particularly AT-6 resin [69], exhibit a high stability. Unfortunately all the experiments were carried out by Pashkov et al. [3] only at a single temperature (100°C) and for a single duration of heating (60 h) and the chosen criterion of thermal stability was the static exchange capacity, which is known [70] to depend on the conditions of its determination.

Table 2. Thermal stabilities of a series of anion-exchange resins in the OH-form

Type of anion-exchange resin	Active groups	Temp., °C	Time, h	Relative change in exchange capacity, %			References
				total	w.r.t. strongly basic groups	w.r.t. weakly basic groups	
AV-17	$-\overset{+}{N}(CH_3)_3$	100	48	+33	+18	+60	73
		100	120	+36	+29	+48	73
		100	120	+12	+19	−6	74,75
		100	240	+33	+35	+29	73
		100	240	+16	+23	−5	75
AV-27	$-\overset{+}{N}(CH_2-CH_2OH)(CH_3CH_3)$	100	48	+17	+52	−54	73
		100	120	+28	+63	−44	73
		100	120	+13	+80	−63	75
		100	240	+18	+87	−67	75
		120	48	+36	+93	−81	73
		120	120	+44	+95	−59	73
AN-22	$-NH_2$, >NH	120	120	+2	—	—	73
AV-16	>N, >NH,	150	120	+26	+86	—	75
		150	240	+27	+86	—	75
EDE-10P	>N, >NH, $>\overset{+}{N}<$	150	48	+10	+71	2	73
		150	120	+11	+75	2	73
AN-2F	N<	150	24	—	—	90	71

Additional information about the thermal stability of various anion-exchange resins in the OH-form can be found for a wider temperature range in studies by Ol'shanova and coworkers [71-73]. The most important results obtained in the above investigations are presented in Table 2, where the plus sign before the value of the relative change in exchange capacity of the anion-exchange resin as a result of its heat treatment corresponds to a decrease and the minus sign to an increase of exchange capacity.

Comparison of the results in Table 2 reveals primarily a poor agreement between the values of exchange capacity losses established by different workers. This is most probably due to the non-equivalence of the resins investigated, which might have differed in the degree of cross-linking and in the composition of the samples used. For example, 6% of the exchange capacity corresponded to the contribution by the weakly basic groups of AV-17 resins in the study by Shaburov et al. [74], while in the study by Petrova and Potakova [73] the corresponding percentage was 36. The divinylbenzene content of the AV-17 anion-exchange resins has been indicated only by Shaburov et al. [74] and is not mentioned in the other investigations. This significant omission vitiates the experimental results no less than the use of faulty research techniques.

Bearing in mind the above inconsistency, it is necessary to compare the results of the determination of the losses of capacity obtained in the same laboratory. In this connection, the data in Table 2 lead to the conclusion that the stabilities of polymerisation and condensation anion-exchange resins with weakly basic groups are different. For anion-exchange resins with strongly basic groups, these differences become blurred, since, owing to the $-I$-effect in quaternary ammonium bases [76], the linkage with $C-\overset{+}{N}$ is so highly polarised that the structure of the framework becomes of secondary importance as a factor in thermal stability. Moreover, this levelling is favoured by the poor choice by the authors of the above studies of the relative change in capacity as a criterion of the thermal stability of anion-exchange resins known to have different contents of active groups.

The decrease of the exchange capacity of anion-exchange resins in the OH-form in relation to strongly basic groups has been shown [10,12,13,77] to take place owing to the deamination and degradation processes examined above, which are usually identified with the familiar Hofmann degradation [78]. The methanol and trimethylamine formed on heat treatment of AV-17 anion-exchange resins were identified; according to Shaburov and Saldadze [12] and Roginskaya et al. [77], their amounts corresponded to changes in exchange capacity with respect to strongly and weakly basic groups. However, the data in Roginskaya's disseration [79] and in the study of Minto et al. [112] contradict this assertion.

The relative contribution by the deamination and degradation of AV-17 anion-exchange resins depends on the duration of heat treatment and on the content of divinylbenzene (DVB) in the test object [74]. In the first, rapid stage involving the decrease of exchange capacity, the ratio of the rates of these reactions changes with increase of the degree of cross-linking in favour of deamination, which has been explained [74] by a weakening of the protective effect of the hydration shells of the active groups as the swellability of the resin decreases. Generalising such data [71,72,80,84,112], we may note that in the majority of cases an increase of the content of the cross-linking agent entails a decrease of the thermal stability of strongly basic anion exchangers in the OH-form.

Not only the variation of the degree of cross-linking but also an increase in the specified purity of the starting material employed in the synthesis and the introduction of active groups into mixed aliphatic-aromatic [81] or even aliphatic [82] structures give rise to some possibility of controlling the thermal stability. For example, it has been established that [80] the anion-exchange resin based on styrene and *p*-divinylbenzene has a higher resistance to heating than the specimen synthesised from technical DVB, the impurities of which cause the formation of defects in the macromolecule. An improved thermal stability of strongly basic anion-exchange resins in which the active group is separated from the aromatic ring by the isobutyl group has been predicted [81].

AV-27 anion-exchange resin, which occupies an intermediate position as regards thermal stability, and its analogue Amberlite IRA-410, readily split off the CH_2CH_2OH group with formation of ethylene glycol and a high-molecular-weight tertiary amine (degradation) [13]. This process is faster than the overall deamination and degradation of AV-17 resin and is responsible for the higher rate of decrease of the exchange capacity of AV-27 resin in relation to strongly basic groups.

An interesting study on the thermal stability of the vinylpyridine anion-exchange resin VP-IAP in water and certain aqueous solutions has recently been made by Kiseleva et al.[43] On the basis of a large-scale experiment by the infrared spectroscopic method, they showed that heating the anion-exchanger in water at 200–230°C for 10–60 h leads not only to the usual losses of exchange capacity but also to the oxidation of the methyl groups of the ring to aldehyde and carboxy-groups and to the formation of hydroxypyridines. In alkaline solutions, the formation of a stable form of pyridones accompanied by the loss of exchange capacity is observed. If the heat treatment of the anion exchanger was carried out at 70°C, the pyridones formed were protonated to hydroxypyridines with restoration of exchange capacity on subsequent heating of the anion exchanger in water or nitric acid solutions at 200°C.

The resistance of strongly basic anion-exchange resins and model low-molecular-weight quaternary ammonium bases to heating in alkaline media has been investigated[82-87] and it has been established that resins of the phenyl type, like the corresponding low-molecular-weight bases with aromatic substituents, undergo mainly deamination (to the extent of 60–70%). Anion exchangers of the benzyl type and quaternary ammonium bases with benzyl substituents largely undergo the Hofmann degradation, its rate being higher than for aliphatic alkyltrimethylammonium bases[82]. Hence it follows that the synthesis of anion-exchange resins with aliphatic structures constitutes a likely pathway to the creation of thermostable polyme. with anion-exchange properties.

In a later study[87], it was shown that at 40–100°C macroporous ion-exchange resins are more stable in 2–10 *N* solutions of alkali than gel ion exchangers; similar observations were made in studies on the thermal stability of macroporous sulphonic acid cation-exchange resins[39]. Studies in this field should be continued and require theoretical consideration.

Data for the stability of anion exchangers in solutions of alkalis and non-oxidising acids, which are of interest for practical purposes, have been published[15,87,89]. The studies of Laskorin et al.[15] led to the establishment of a norm for the prolonged employment of a number of USSR-produced anion-exchange resins, which are listed in Table 3.

All the inorganic reagents investigated can be arranged in the following sequence in terms of their influence on the rate of decrease of the exchange capacity of anion-exchange resins: $NaOH > NH_4OH > Na_2CO_3 > HNO_3 > H_2SO_4$. Thus the disrupting capacity of alkalis is greater than that of acids (even the oxidising nitric acid). In nitric acid solutions at a concentration up to 6 *N*, AM and AMP anion-exchange resins can be used only at room temperature, while VP-IA resin can be used up to 80°C. According to other data, the exchange capacity of the anion-exchange resins AN-23, AN-25, AN-27, AN-35, AN-40, and AN-42 based on vinylpyridine is hardly altered after heating for 90 h in 5 *N* HNO_3 at 100°C.[88]

The salt-forms of strongly basic anion-exchange resins are more stable than the hydroxide-forms not only on heating in an aqueous medium[3,54,71,90,91] but also on treatment with corrosive agents such as free chlorine[62].

In hydrogen peroxide solutions at concentrations up to 1 M, the stability of AM-6, AMP, and VP-IA anion-exchange resins decreases in the order in which they have been stated. The addition of 0.2 *N* KOH to hydrogen peroxide enhances its oxidising activity and the addition of 0.2 *N* H_2SO_4 reduces it. The anion-exchange resins exhibit a particularly low stability in calcium hypochlorite solutions.

Disdar[92] and Bychkov et al.[93] made the most interesting and complete investigation of the behaviour of AV-17 anion-exchange resins in hydrogen peroxide solutions. It was shown[93] that AV-17 anion-exchange resins absorb selectively hydrogen peroxide as a result of the displacement of water and the exchange sorption of the HO_2^- ion. Hydrogen peroxide then undergoes catalytic decomposition and the anion exchanger undergoes deamination and degradation; the catalytic activity of the anion exchanger in the decomposition of hydrogen peroxide decreases faster than the exchange capacity in relation to strongly basic groups. An increase of the concentration of the oxidant leads to an increase of the loss of exchange capacity by the anion exchanger and an increase of the amount of carbon dioxide given off. Owing to their partial oxidation, the amount of amines determined is somewhat lower than the value calculated from the loss of the exchange capacity of the resin. Strongly basic anion-exchange resins in the Cl-form and weakly basic anion exchangers in the OH-form decompose to a lesser extent[93].

Table 3. The limiting permissible operational standards for anion-exchange resins in solutions of acids and alkalis.

Reagent	Standards for stable operation of anion-exchange resins					
	AM		AMP		VP-IA	
	normality of reagent	temp., °C	normality of reagent	temp., °C	normality of reagent	temp., °C
H_2SO_4	0.1—17	20—80	0.1—17	20—80	0.1—17	20—80
HNO_3	up to 6	not more than 20	up to 6	not more than 20	0.1—6	20—80
HNO_3	less than 1	20—80	less than 1	up to 80		
NaOH	0.1—3	20—80	less than 0.01	20	0.1	not more than 20
NH_4OH	—	—	less than 0.1	up to 20	up to 3	20—80
Na_2CO_3	—	—	up to 3	30	up to 3	50

Vinogradov's dissertation[94] has made a significant contribution to the elucidation of the mechanism of the action of oxidants on anion-exchange resins. He showed that the ionogenic groups are involved in reactions of three types: deamination, degradation, and inactivation. Oxidants mainly induce inactivation, i.e. the loss of the capacity of the functional groups to participate in ion exchange. Moreover, oxidants act on the matrix, causing the formation of new functional groups containing a C=O double bond. With increase of the divinylbenzene content in the anion-exchange resin, the number of these groups also increases; there is a simultaneous intensification of degradation and a decrease of the contribution by deamination. Anion-exchange resins containing pyridine or quinoline groups are the most resistant to the action of oxygen. In all the oxidants investigated, except solutions of ammonium persulphate, they withstand heating to 80°C. Weakly basic anion-exchange resins in oxidant solutions are less stable than strongly basic resins, although in pure water the opposite behaviour was observed. The change in the composition of the medium probably alters the mechanism of the processes occurring.

V. THERMAL STABILITY OF ANION-EXCHANGE RESINS IN ORGANIC AND MIXED MEDIA

Studies in this field were begun 10 years ago by one of the present authors and Shaburov[10] and were then continued by Shaburov and Saldadze[12,53,54,95,96]. The principal results of the studies on the thermal stability of anion-exchange resins in mixed and organic media are compiled in Table 4. For comparison, it also includes data characterising the thermal stability of anion-exchange resins in water.

Table 4. Thermal stabilities of anion-exchange resins in mixed and organic media.

Type of anion-exchange resin	Ionic form	DVB content, %	Medium	Temp., °C	Duration of experiment, h	Loss of capacity w.r.t. strongly basic groups, %		References
						by deamination	by degradation	
AV-17	OH	2	H_2O	100	120	6	4	74
ditto	OH	2	CH_3OH	100	120	42	14	74
»	OH	2	C_2H_5OH	100	120	33	9	74
»	OH	6	H_2O	100	120	14	17	10
»	OH	6	50 % CH_3OH	100	120	33	10	10
»	OH	6	75 % CH_3OH	100	120	56	13	10
»	OH	6	CH_3OH	100	120	54	20	12
»	OH	6	C_2H_5OH	100	120	46	18	12
»	OH	16	H_2O	100	120	17	20	74
»	OH	16	CH_3OH	100	120	46	13	74
»	OH	16	C_2H_5OH	100	120	37	16	74
»	Cl	8	H_2O	150	120	29	0	54
»	Cl	8	H_2O	100	120	2	0	54
»	Cl	8	CH_3OH	150	120	62	0	54
»	Cl	8	C_2H_5OH	150	120	70	0	54
»	Cl	8	C_3H_7OH	150	120	76	0	54
»	Cl	8	$C_5H_{11}OH$	150	120	75	0	54
»	Cl	8	$C_{10}H_{21}OH$	150	120	61	0	54
»	OH	6	CH_3COCH_3	100	120	51	23	95
AV-27	OH	8	H_2O	75	120	7	13	13
ditto	OH	8	CH_3OH	75	120	17	29	13
»	OH	8	C_3H_7OH	75	120	11	33	13
AV-16	OH	—	H_2O	150	120	14	72	53
ditto	OH	—	CH_3OH	150	120	10	78	53

The data in Table 4 show that all anion-exchange resins in the OH-form undergo both deamination and degradation, the relative losses of exchange capacity increasing with the concentration of the organic component in the mixed media. In absolute alcohol and acetone, the losses of the exchange capacity of AV-17 anion-exchange resins are much greater than in water. The comparatively low thermal stability of AV-17 anion-exchange resin in alcohols is easily explained by the formation of association complexes of the alcohols with the amino-groups[10,13,54] and in acetone by the polarisation of the C—N bond owing to the participation of the amino-groups in catalysis of the aldol condensation of acetone[95]; all these factors facilitate the elimination of trimethylamine from the matrix. However, the lower thermal stability of the OH- and Cl-forms of the anion-exchange resins in alcohols than in water[13,44,54] is presumably due to the direct chemical interaction between the alcohol molecules and the amino-groups of the anion exchanger catalysed by hydroxide ions. Such interaction with the anion exchanger in the Cl-form leads to deamination via the mechanism[44]

$$RCH_2N(CH_3)_3Cl + R_1OH \rightarrow RCH_2OH + R_1N(CH_3)_3Cl, \quad (21)$$

$$RCH_2N(CH_3)_3Cl + R_1OH \rightarrow RCH_2OR_1 + HN(CH_3)_3Cl. \quad (22)$$

The real composition of the mixture of nitrogen-containing compounds formed as a result of the deamination of AV-17 × 8(Cl) anion-exchange resin in various alcohols at 180°C is presented in Table 5, which shows that the proportion of alkyltrimethylammonium chloride increases with the dimensions of the alcohol molecule, i.e. in parallel with the increased steric hindrance to the formation of ordered solvation shells around the counterions of the functional groups.

Table 5. Composition of the deamination products of AV-17 anion-exchange resin in the Cl-form[97].

Alcohol	Duration of experiment, h	Content, mequiv. g^{-1}		Fraction of alkyltrimethylammonium chloride, %	Loss of capacity, %
		trimethylammonium chloride	alkyltrimethylammonium chloride		
CH_3OH	4	0.84	0.15	15	31
CH_3OH	6	1.00	0.22	18	38
C_2H_5OH	4	0.65	0.12	16	24
C_2H_5OH	6	0.85	0.26	23	35
n-C_3H_7OH	4	0.65	0.23	26	28
n-C_3H_7OH	6	0.75	0.33	30	34
i-C_3H_7OH	6	0.77	0.34	30	34
n-C_4H_9OH	4	0.77	0.32	29	34
n-C_4H_9OH	6	1.11	0.51	32	51
n-$C_5H_{11}OH$	4	0.69	0.37	35	33
n-$C_5H_{11}OH$	6	0.82	0.49	37	41

Deamination of AV-17 anion-exchange resins in the OH-form on interaction with methanol takes place via mechanism (23), as shown by infrared spectroscopy[12]:

$$RCH_2N(CH_3)_3OH + CH_3OH \rightarrow RCH_2OCH_3 + HN(CH_3)_3OH. \quad (23)$$

With increase of the size of the organic group of the alcohol, its reactivity also increases, which leads to a decrease of the thermal stability of AV-17 and AV-27 anion-exchange resins. This correlation, which is in fact between the thermal stability and the positive inductive effect of the aliphatic groups[98], persists only until steric hindrance to the penetration of alcohol molecules into the resin phase appears. When this happens the deamination reactions become more difficult and the thermal stability of anion-exchange resins in alcohols increases after having passed through a minimum[44,54]. A similar relation governs the changes in the losses of exchange capacity as a function of the degree of cross-linking of AV-17 anion-exchange resin. However, in this case it is also necessary to bear in mind the internal concentration of OH^- ions in the resin phase in relation to the sorbed alcohol, which determines (as for cation-exchange resins[99]) the rate of interaction. In particular, the decrease of the thermal stability of the resin with increased content of the cross-linking agent from 2 to 6% is related to this factor[74]. A further increase of the degree of cross-linking to 16% leads to a sharp lowering of the swellability of the resin in alcohols, which causes a corresponding decrease in the concentration of one of the reactants. As a result, the rate of deamination falls despite the increased concentration of OH^- ions relative to the sorbed alcohol. All these factors lead to a higher thermal stability of the anion-exchange resin with 16% DVB compared with less cross-linked specimens.

The relative losses of the capacity of AV-17 anion-exchange resin with respect to the strongly basic groups

in water in the range of cross-linking agent contents investigated (2–16%) are a continuous increasing function of the degree of cross-linking. The difference between this relation and that which has just been discussed for thermal stability in alcohols is undoubtedly due to the higher swellability of the anion-exchange resin in water. As a result, the rate of deamination is determined only by the concentration of the catalytically active OH^- ions in the resin in relation to the bound water, the concentration increasing with the degree of cross-linking.

The electrostatic factors discussed by Shaburov et al.[74] are probably of subsidiary importance.

Degradation involving the residual water [via reaction (12)] is always observed together with deamination when the OH-form of AV-17 anion-exchange resin is heated in alcohols[75]. The absolute decrease of the total exchange capacity of AV-16 and AV-17 anion-exchange resins as a result of their heat treatment in methanol or ethanol exceeds the amount of tertiary amine eliminated[12,13], which indicates the conversion of part of the nitrogen into an inactive state. The mechanism of the reactions occurring under these conditions still requires elucidation.

VI. THE MECHANISM AND KINETICS OF PROCESSES OCCURRING ON HEATING ANION-EXCHANGE RESINS IN WATER AND AQUEOUS ORGANIC AND ORGANIC MEDIA

Earlier it was already stated that the deamination and degradation of the amino-groups of the OH-form of type AV-17 anion-exchange resins are regarded by all investigators as the Hofmann degradation of the quaternary ammonium bases. However, the data in Roginskaya's dissertation[79] and those of other investigators[112], which unfortunately have not been interpreted in sufficient detail, are inconsistent with these ideas and throw doubt on the mechanism adopted for the deamination and degradation of the amino-groups and anion-exchange resins. The following facts are inconsistent with the Hofmann decomposition mechanism.

1. The relative contribution of deamination with a loss of capacity as strongly basic groups on heating the anion-exchange resin in sealed tubes with water falls with increased duration of the experiment, while in a mixed bed and under dynamic conditions it remains unchanged[27,77,79,96].
2. The deamination process terminates long before the strongly basic groups are completely exhausted[27,77].
3. Methanol is evolved in appreciably smaller amounts than that of the weakly basic groups formed[79,112].
4. The content of trimethylamine in the aqueous extract is lower than that of OH^- ions and the deaminated amino-groups formed[79].
5. The unsatisfactory description of the kinetics of the deamination and degradation of the amino-groups by first-order rate equations[75,77,79].
6. The presence of secondary amines among the decomposition products of the anion-exchange resin in the OH-form at 150°C.[77]

We regard the deamination and degradation processes of the amino-groups[100,101] as complex parallel-consecutive reactions involving the nucleophilic substitution of the trialkylamino-group in tetra-alkylammonium by a nucleophilic residue of the molecule of the solvent or the solute, which may consist of products split off from the anion-exchange resin. In these reactions OH^- ions exhibit a catalytic activity[102] and therefore the rate of deamination and degradation of the amino-groups in the OH-form of the anion-exchange resin is much higher than in the Cl-form.

The role of OH^- consists in the activation of the nucleophilic agent as a result of interaction with it. When anion-exchange resins in the OH-form are heated in alcohol, acetone, water, and aqueous solutions of amines the nucleophilic agents are anions (R_1O^-, $CH_3C\lesssim^{CO^-}_{CH_2}$), carbanions ($CH_3COCH_2^-$), hydrated hydroxide ions ($H_2O.OH^-$), and neutral ($R_1-\underset{R_2}{\underset{|}{N}}-R_3$) or hydrated molecules $[(R_1-\underset{R_2}{\underset{|}{NH}}-R_3)OH]$.

In order to understand the chemical reactions of the amino-groups of anion-exchange resins when these are heated in various media, one must take into account the polarisation of the bonds in the amino-group and the resulting induced charges. In the quaternary ammonium groups of AV-17 and AV-27 resins, an induced positive charge arises at the carbon atoms linked to nitrogen as a result of a powerful negative inductive effect[78]. Owing to the influence of the alcoholic hydroxyl, the positive charge induced on the carbon atom of the ethanol group in AV-27 anion-exchange resin is higher than on the other carbon atoms. The presence of an induced positive charge facilitates attack on the carbon atoms by the nucleophilic agent. Each of the carbon atoms linked to nitrogen and the second carbon atom of the ethanol group of AV-27 anion-exchange resin is subject to nucleophilic attack.

Taking into account the foregoing factors, one possible mechanism for the deamination and degradation of the amino-groups of AV-17 anion-exchange resin on heating in sealed tubes with water can be represented schematically by the following reactions[101]:

$$RCH_2\overset{+}{N}(CH_3)_3 + OH^- \rightleftarrows RCH_2N(CH_3)_3OH\ , \qquad (24)$$

$$RCH_2N(CH_3)_3OH + H_2O\cdot HO^- \nearrow RCH_2OH + HN(CH_3)_3OH + OH^-\ , \qquad (25)$$

$$\searrow RCH_2NH(CH_3)_2OH + CH_3OH + OH^-\ . \qquad (26)$$

The trimethyl- and benzyldimethyl-ammonium hydroxides evolved are readily dehydrated and converted into tertiary amines:

$$HN(CH_3)_3OH \rightleftarrows H_2O + N(CH_3)_3\ , \qquad (27)$$

$$RCH_2NH(CH_3)_2OH \rightleftarrows RCH_2N(CH_3)_2 + H_2O\ . \qquad (28)$$

Part of the trimethylamine formed dissolves in the aqueous phase and, after Donnan sorption, can participate in the nucleophilic substitution reaction:

$$RCH_2N(CH_3)_3OH + N(CH_3)_3 \rightarrow RCH_2N(CH_3)_2 + N(CH_3)_4OH\ . \qquad (29)$$

When the OH-form of the anion-exchange resin is heated in trialkylamine, the formation of trialkylmethylammonium hydroxide via a reaction of type (29) is probably accompanied also by the substitution of the amino-group of the resin:

$$RCH_2N(CH_3)_3OH + R_1-N\lesssim^{R_3}_{R_2} \rightarrow \left(RCH_2N\lesssim^{R_1}_{R_3}R_2\right)OH + N(CH_3)_3\ . \qquad (30)$$

The above reactions explain some of the contradictions noted above which do not fit within the framework of the old hypotheses. Thus the formation of tetramethylammonium hydroxide via reaction (29) should lead to an increased contribution of the degradation process to the overall loss of capacity by the anion exchanger with increase of the duration of heating and to the appearance of a deficiency of methanol and trimethylamine compared with the content of the weakly basic groups accumulating in the resin and of

OH^- ions in solution. Naturally the deficiency should correspond to the amount of tetramethylammonium hydroxide formed. The cessation of the deamination of strongly basic groups on heating can be explained by postulating that an equilibrium is established between the deamination and amination processes. The amination of the polymeric alcohol produced in reaction (25) by trimethylamine can be represented thus:

$$RCH_2OH + N(CH_3)_3 \rightarrow RCH_2N(CH_3)_3OH\ . \qquad (31)$$

When AV-17 anion-exchange resin is heated in alcohols [101], the following reactions probably occur together with reaction (24):

$$RCH_2N(CH_3)_3OH + R_1O^- \rightarrow RCH_2OR_1 + N(CH_3)_3 + OH^-\ , \qquad (32)$$

$$RCH_2N(CH_3)_3OH + R_1O^- \rightarrow RCH_2N(CH_3)_2 + CH_3OR_1 + OH^-\ . \qquad (33)$$

The involvement of trimethylamine in reactions of types (29) and (31) is in this case less likely than in water owing to its binding by the alcohol molecules into complexes [105].

The heating of AV-17 anion-exchange resins in water under dynamic conditions is accompanied by the removal from the reaction zone of all the products of the conversion of the amino-groups and the processes should be restricted to reactions (25) and (26). In a mixed bed, only trimethylammonium ions are removed, and methanol, which remains partly in the anion-exchanger phase, participates in reactions of types (32) and (33).

The deamination and degradation of AV-17 anion-exchange resin on heating in acetone are due primarily to the interaction of the amino-groups with the solvent and not with the water evolved in the Aldol condensation or contained in the resin. This is confirmed by the much greater losses of capacity by the anion exchanger in acetone than in water. The changes in AV-17 anion-exchange resin in acetone can be represented schematically as follows:

$$CH_3C(O^-)(CH_3)CH_2 \rightarrow RCH_2OC(CH_3)=CH_2 + N(CH_3)_3 + OH^-\ , \qquad (34)$$

$$RCH_2N(CH_3)_3OH + CH_3COCH_2^- \rightarrow RCH_2N(CH_3)_2 + CH_3COC_2H_5 + OH^-\ , \qquad (35)$$

$$RCH_2N(CH_3)_3OH + CH_3COCH_2^- \rightarrow RCH_2CH_2COCH_3 + N(CH_3)_3 + OH^-\ . \qquad (36)$$

When AV-27 anion-exchange resin is heated in water and alcohols the following reactions are likely, disregarding secondary processes involving the products (for example under dynamic conditions):

$$RCH_2N(CH_3)_2OH + H_2O \cdot OH^- \rightarrow RCH_2NH(CH_3)_2OH + HOCH_2CH_2OH + OH^-\ , \qquad (37)$$

$$RCH_2N(CH_3)_2OH + H_2O \cdot OH^- \rightarrow RCH_2OH + HN(CH_3)_2OH + OH^-\ , \qquad (38)$$

$$RCH_2N(CH_3)_2OH + H_2O \cdot OH^- \rightarrow RCH_2N(CH_3)_3OH + H_2CO + OH^-\ , \qquad (39)$$

$$RCH_2N(CH_3)_2OH + H_2O \cdot OH^- \rightarrow RCH_2NH(CH_3)OH + CH_3OH + OH^-\ , \qquad (40)$$

$$RCH_2N(CH_3)_2OH + R_1O^- \rightarrow RCH_2OR_1 + N(CH_3)_2 + OH^-\ , \qquad (41)$$

$$RCH_2N(CH_3)_2OH + R_1O^- \rightarrow RCH_2N(CH_3)_2 + R_1OCH_2CH_2OH + OH^+\ , \qquad (42)$$

$$RCH_2N(CH_3)_2OH + R_1O^- \rightarrow RCH_2N(CH_3) + CH_3OR_1 + OH^-\ . \qquad (43)$$

The first attempts at a kinetic treatment of the experimental decrease of the exchange capacity with respect to strongly basic groups on heating AV-17 and AV-27 anion-exchange resins in the OH-form in water and organic media reduced to the derivation of formal empirical relations of the type $\lg E^{SBG} - f(\lg\tau)$ [13] or to the application of the equation for first-order reactions [75,77,79,106]. We must emphasise that in almost all cases the kinetic curves were found to consist of two sections with different linear slopes. The presence of two stages were explained [10,106] by the energy non-equivalence of the bonds between the amino-groups and the anion-exchanger matrix, while other workers [13,17] suggested that the reaction is inhibited by the deamination product—trimethylamine.

According to Bauman's data [106], the second, slower stage in the decrease of the exchange capacity of Amberlite IRA-400 anion-exchange resin in water is described satisfactorily by a first-order rate law with a 50% conversion time equal to 43 days at 90°C. The authors of later investigations [77,79] adopted the first-order equation for the entire range of deamination and degradation processes involving AV-17 anion-exchange resin in water, but the resulting scatter of the observed rate constants about the mean was unduly great (±60%) and therefore one can hardly regard this attempt as successful.

The change in AV-17 and AV-27 anion-exchange resins in the OH-form on heating in water and ethanol is described satisfactorily by a linear relation between $\lg E^{SBG}$ and $\lg\tau$. [13] However, in acetone the relation becomes more complicated and, when the anion exchanger is re-used, the rate of change of the exchange capacity falls. This feature of the properties of the anion-exchange resin was attributed [95] to its catalytic activity and reactions of the medium.

It follows from the foregoing that the above kinetic equations for the description of the processes involved in the decrease of the exchange capacity of anion-exchange resins are approximate and apply to special cases only.

In recent years a new promising trend appeared in studies on the kinetics of the elimination of functional groups from ion-exchange resins, the principles of which were laid down in a number of investigations [36,37,97,107,108]. The main idea of these studies is that the molecules of the solvent (water or organic liquid) in the solvation shells in the resin phase participate in the process involving the removal of the functional groups. The total amount of solvent in the solvation shells is proportional to the exchange capacity throughout the experiment, since during the heat treatment part of the solvation shell of the functional group split off is removed with it from the resin phase.

The above principles were used in a general treatment of the kinetic data for the deamination of AV-17 anion-exchange resin in the Cl-form, which is the only factor in the decrease of its exchange capacity [54]. Taking into account the foregoing, the rate of deamination in water is defined by the equation

$$-dE/d\tau = k'\,E\,\bar{C}_{H_2O}\ . \qquad (44)$$

Since

$$\bar{C}_{H_2O} = nE\ , \qquad (45)$$

Eqn.(44) is converted into the equation for a reaction which is second-order with respect to the concentration of the functional groups:

$$-dE/d\tau = k'E^2 n = k\,E^2, \qquad (46)$$

where n is the solvation number of the functional group (mmoles H_2O mequiv.$^{-1}$). Under the initial conditions ($\tau = 0$, $E = E_0$),

$$E = E_0/(1 + k\,E_0\,\tau). \qquad (47)$$

The agreement between the experimental data for the deamination of AV-17 anion-exchange resin in the Cl-form

and the values calculated by Eqn.(47) has been demonstrated convincingly[107]. The temperature variations of the apparent rate constant for the deamination reaction obeys the Arrhenius equation quite satisfactorily with a pre-exponential factor of $(4.3 \pm 0.1) \times 10^{17}$ kg matrix mole^{-1} h^{-1} and an activation energy of 40.2 ± 0.2 kcal mole^{-1}.

The mechanism[44] and kinetics of the processes occurring[107] change with decrease of the water content of the anion-exchange resin, deamination being supplemented by degradation.

A detailed study of the kinetics of the deamination of AV-17 anion-exchange resin in the Cl-form in alcohols has been made[97]. It might have been expected that in alcohols, as in water, the deamination of the Cl-form of the resin could be described by the equation for second-order reactions. This is indeed the case for all the alcohols except methanol[97]. The kinetics of the deamination of AV-17 anion-exchange resin in methanol obey a first-order rate law. Evidently in this case the effect of the high affinity of methanol for the active groups operates, as a result of which the nucleophilic substitution reaction involves the same mechanism as under homogeneous conditions. The amount of trimethylammonium chloride[97] varies with time according to a curve with a maximum, which indicates its consecutive transformation via the reaction

$$HN(CH_3)_3Cl + CH_3OH \rightarrow N(CH_3)_4Cl + H_2O \ . \qquad (48)$$

This concept is fully consistent with the correspondence of the overall content of nitrogen-containing compounds in the resin decomposition products both to the loss of exchange capacity and to the total amount of Cl^- ions in the liquid phase. Bearing in mind that the kinetics of reaction (48) are described by a first-order equation[109] the decrease of the exchange capacity of AV-17 anion-exchange resin (E) in methanol via reactions (21) and (22) and of the accumulation of trimethylammonium (C_1) and tetramethylammonium (C_2) chlorides is described[97] by the equations

$$-dE/d\varepsilon = (k_1 + k_2)E \ , \qquad (49)$$

$$dC_1/d\tau = \frac{k_1^2}{k_1 + k_2} \cdot E - k_3 C_3 \ , \qquad (50)$$

$$dC_2/d\tau = \frac{k_2}{k_1 + k_2} \cdot E + k_3 C_1 \ , \qquad (51)$$

where k_1, k_2, and k_3 are the apparent rate constants for reactions (22), (21), and (48). For the initial conditions ($\tau = 0$, $E = E_0$, $C_1 = 0$, and $C_2 = 0$), the solution of Eqns. (49)–(51) is

$$E = E_0 \cdot \exp[-(k_1 + k_2)\tau] \ , \qquad (52)$$

$$C_1 = \frac{k_1^2 E_0}{(k_1 + k_2)(k_1 + k_2 - k_3)} \{\exp(-k_3\tau) - \exp[-(k_1 + k_2)\tau]\} \ , \qquad (53)$$

$$C_2 = \frac{E_0}{(k_1 + k_2)} \left\{ \frac{k_1^2}{(k_1 + k_2 - k_3)} [1 - \exp(-k_3\tau)] - \left[\frac{k_1^2 \cdot k_3}{(k_1 + k_2)(k_1 + k_2 - k_3)} + \frac{k_2^2}{(k_1 + k_2)} \right] [1 - \exp[-(k_1 + k_2)\tau]] \right\} \cdot \qquad (54)$$

The apparent rate constants for the above reactions at different temperatures and the results of calculations using the Arrhenius equationare presented in Table 6.[97]

The subscripts 1, 2, and 3 to the symbols k, ΔU, and A show that they refer to reactions (22), (21), and (48) respectively.

More complete information about the process kinetics on heating anion-exchange resins in the OH-form may be obtained taking into account the mechanism proposed[101] and the characteristics of the behaviour of the swollen resin. The resin is then regarded[111] as a pseudohomogeneous system consisting of the hydrocarbon matrix, fixed ions, counterions, hydration (solvation) shells, and the molecules sorbed from the external solution. During the heat treatment, the ions and molecules sorbed by the resin phase (by the hydration shells) are expelled from it by the elastic forces of the matrix together with the functional groups eliminated and the hydration shells. Thus during the heat treatment of the resin, the content of all the components, except the weight of the matrix, changes. Hence it follows that, in calculations on the kinetics of the elimination of functional groups from resins, the method of expressing the concentrations of the remaining components per litre of the solvent, which is generally adopted in physical chemistry, is inapplicable and the method proposed previously[37] in which they are referred to 1 g (1 kg) of the matrix treated formally as a "solvent" is the most reliable. The dilution of the mobile counterions and sorbed molecules by the solvent in the resin phase is then taken into account by the molality $\bar{m} = \bar{C}d_S/\bar{C}_S\epsilon_S$, where $\bar{C}$ and $\bar{C}_S$ are the concentrations of the dissolved component and the solvent in the resin phase [mequiv. (mmole)/g matrix] and d_S and ϵ_S are the density and the molecular weight of the solvent.

Table 6. Kinetic parameters of reactions (22), (21), and (48) in methanol[97].

Temp., °C	Reaction rate constant, h^{-1}			Activation energy, kcal mole^{-1}	Pre-exponential factor in Arrhenius equation, h^{-1}
	10^2k_1	10^2k_2	10^2k_3		
160	3.66±0.08	0.79±0.06	2.70±0.06	$\Delta U_1 = 35$	$A_1 = 1.2 \cdot 10^{16}$
170	7.6 ±0.2	2.14±0.14	5.45±0.17	$\Delta U_2 = 40$	$A_2 = 6.0 \cdot 10^{17}$
180	20.0 ±1.4	6.3 ±0.5	10.7 ±0.8	$\Delta U_3 = 26$	$A_3 = 4.1 \cdot 10^{11}$

Taking into account reactions (24)–(27), (29), and (31) and the analogies with the treatment of Tulupov and Shaburov[101], the kinetics of the processes involving the decrease of the exchange capacity with respect to strongly basic groups (E^{SBG}), deamination (q_1), and degradation (q_2) of AV-17 anion-exchange resin on heating with water in sealed tubes are described by the following equations:

$$-dE^{SBG}/d\tau = (k'_{25} + k'_{26})\bar{C}_b\bar{C}_a/\bar{C}_{H_2O} + k'_{29}\bar{C}_b\bar{C}_e/\bar{C}_{H_2O} - k'_{31}\bar{C}_f\bar{C}_e/\bar{C}_{H_2O}, \qquad (55)$$

$$dq_1/d\varepsilon = k'_{25}k'_{25}\bar{C}_b\bar{C}_a/\bar{C}_{H_2O}(k'_{25} + k'_{26}) - k'_{31}\bar{C}_f\bar{C}_e/\bar{C}_{H_2O} \ , \qquad (56)$$

$$dq_2/d\tau = k'_{26}k'_{26}\bar{C}_b\bar{C}_a/\bar{C}_{H_2O} + k'_{29}\bar{C}_b\bar{C}_e/\bar{C}_{H_2O} \ . \qquad (57)$$

The material balance equation is

$$E_0^{SBG} = E^{SBG} + q_1 + q_2 \ . \qquad (58)$$

Assuming that the strongly basic groups of the anion-exchanger are fully dissociated, like alkalis of the NaOH type, and that $\bar{C}_{RCH_2\dot{N}(CH_3)_3} = E^{SEG}$, Eqns.(55)–(57) can be reduced to the following form by simple rearrangements:

$$-dE^{SBG}/d\tau = (k''_{25} + k''_{26})(E^{SBG})^2(1 + \alpha)\bar{m}_{OH^-} + k''_{29}E^{SBG}\bar{m}_e\bar{m}_{OH^-} - k''_{31}(E^{SBG})^2 \cdot \bar{m}_{OH^-}\bar{m}_e \ , \qquad (59)$$

$$dq_1/d\tau = \frac{k''_{25} \cdot k''_{26}}{k''_{25} + k''_{26}}(E^{SBG})^2(1 + \alpha)\bar{m}_{OH^-} - k''_{31}(E^{SBG})^2\bar{m}_e\bar{m}_{OH^-}(1 + \alpha) \ , \qquad (60)$$

$$dq_2/d\tau = \frac{k''_{26} \cdot k''_{26}}{k''_{25} + k''_{26}}(E^{SBG})^2(1 + \alpha)\bar{m}_{OH^-} + k''_{29}(E^{SBG})\bar{m}_e\bar{m}_{OH^-} \ . \qquad (61)$$

The following notation is employed: $a = H_2O.OH^-$; $b = RCH_2N(CH_3)_3OH$; $e = N(CH_3)_3$; $f = RCH_2OH$; $g = RCH_2\overset{+}{N}(CH_3)_3$; α = content (mmole mequiv.$^{-1}$) [108] of tetramethylammonium hydroxide in the hydration shell of the functional group sorbed by the Donnan mechanism;

$$k''_{25} = k'_{25}K_{24}K_e \cdot 55{,}5\,\bar{\gamma}_g\bar{\gamma}^0_{OH^-}/\bar{\gamma}_a\bar{\gamma}_b;\ k''_{26} = k'_{26}k''_{25}/k'_{25},$$
$$k''_{29} = k'_{29}K_{24} \cdot 55{,}5^2\bar{\gamma}_g\gamma_{OH^-}/\gamma_{H_2O}\bar{\gamma}_b;\ k''_{31} = k'_{31}k'_{25}k''_{25}/(k'_{25} + k'_{26}).$$

The numerical subscript to the rate constant k or the equilibrium constant K corresponds to the number of the reaction, K_e is the equilibrium constant for the hydration of hydroxide ions, γ is the activity coefficient, and a bar over a symbol implies that it refers to the resin phase.

The solution of Eqns. (59)–(61) involves considerable difficulties, since the molalities of the hydroxide ions and trimethylamine in the resin phase vary continuously as the deamination and degradation of the anion-exchange resin proceed.

The molality of trimethylamine in the resin phase found from the Donnan equilibrium [110] depends on the proportions of the external solution and the resin in the experiment and on the solubility of trimethylamine in the external solution:

$$\bar{m}_e = \frac{-0.018E^{SBG}}{2\bar{C}_{H_2O}} + \sqrt{\left(\frac{0.018E^{SBG}}{2\bar{C}_{H_2O}}\right)^2 + \beta\frac{0.018C_e}{C_{H_2O}}} \quad (62)$$

As the limiting solubility of triethylamine in the external solution is approached, its molality in the resin phase will tend to a constant value. The molality of OH^- ions in the anion-exchange phase is determined by the capacity for hydration of the strongly basic amino-groups† and tetramethylammonium hydroxide sorbed as a result of the Donnan distribution:

$$\bar{m}_{OH^-} = \frac{0.018E^{SBG}}{2\bar{C}_{H_2O}} + \sqrt{\left(\frac{0.018E^{SBG}}{2\bar{C}_{H_2O}}\right)^2 + \beta_1\frac{0.018C_{N(CH_3)_4OH}}{C_{H_2O}}}, \quad (63)$$

where β and β_1 are the ratios of the activity coefficients of trimethylamine and tetramethylammonium hydroxide in the resin phase and in the external solution.

As tetramethylammonium hydroxide accumulates, the molality of OH^- ions in the resin phase and the rates of the deamination and degradation processes should increase. However, in the presence of a large excess of "external" water and also on heating the anion-exchange resin under dynamic conditions and in a mixed bed, the Donnan sorption of trimethylamine and tetramethylammonium hydroxide may be neglected. In such experiments the contribution of reactions (29) and (31) to the decrease of the exchange capacity of the anion exchanger will be reduced to a minimum and Eqns. (59) to (61) simplify to

$$-dE^{SBG}/d\tau = (k'_{25} + k'_{26})(E^{SBG})^2\bar{m}_{OH^-}, \quad (64)$$

$$dq_1/d\tau = \frac{(k'_{25})^2}{(k'_{25} + k'_{26})} \cdot (E^{SBG})^2\bar{m}_{OH^-}, \quad (65)$$

$$dq_2/d\tau = (k'_{26})^2(E^{SBG})^2\bar{m}_{OH^-}/(k'_{25} + k'_{26}). \quad (66)$$

The change in the molality of OH^- ions in the anion-exchanger phase during the experiment may be neglected (as in experiments with cation exchange resins [111]) and, having assumed that the activity coefficient ratio in the resin is constant, we obtain the following solution of Eqns. (64)–(66) for the initial conditions ($\tau = 0$, $E^{SBG} = E^{SBG}_0$, $q_1 = q_2 = 0$):

$$E^{SBG} = E^{SBG}_0/[1 + (k_{25} + k_{26}) \cdot E^{SBG}_0 \cdot \tau], \quad (67)$$

$$q_1 = k_{25} \cdot E^{SBG}_0/[k_{25} + k_{26} + 1/\tau \cdot E^{SBG}_0], \quad (68)$$

$$q_2 = k_{26} \cdot E^{SBG}_0/[k_{25} + k_{26}) + 1/\tau \cdot E^{SBG}_0], \quad (69)$$

where $k_{25} = k'_{25}\bar{m}_{OH^-}$ and $k_{26} = k'_{26}\bar{m}_{OH^-}$ are the apparent rate constants for the deamination and degradation of the anion exchanger amino-groups.

One must note that Eqns. (67)–(69) make it possible to carry out calculations on the process kinetics even when there are difficulties in the determination of the molality of OH^- ions (macroporous and condensation resins) or in the interpretation of published experimental data containing insufficient information about the capacity of the functional groups for hydration. In such cases one can find the constant k, which includes the molality of hydroxide ions.

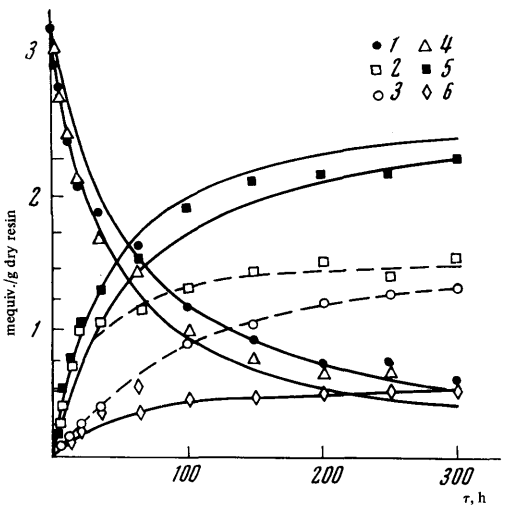


Figure 1. Decrease of E^{SBG} (*1* and *4*), deamination (*2* and *5*), and degradation (*3* and *6*) of the amino-groups of AV-17 anion-exchange resin in the OH-form at 125°C in water (*1*–*3*) and in a mixed bed (*4*–*6*). The continuous curves have been calculated by Eqns. (67)–(69) and the dashed curves have been drawn on the basis of the experimental data; points *1*–*6* have been taken from Roginskaya' et al. [27]

Thus interpretation of the experimental results obtained on heating AV-17 anion-exchange resin under dynamic conditions [96] and in a mixed bed [27] demonstrated the satisfactory applicability of Eqns. (67)–(69). The discrepancy between the experimental and calculated data for high degrees of decomposition of the amino-groups of AV-17 anion-exchange resin in a mixed bed is due to the conversion of the functional groups from the OH-form into the sulphate-form as a result of the neutralisation of the sulphuric acid evolved on desulphonation of KU-2 cation-exchange resin [27]. Reactions (29)–(31) have a compensating effect on the decrease of E^{SBG} and therefore, even when the anion-exchange resin is heated with water in sealed tubes, there is a satisfactory agreement between the experimental data and the values calculated by Eqn. (67) (Fig. 1).

† The dissociation of the weakly basic groups is neglected.

The deamination and degradation curves calculated by Eqns.(68) and (69) did not then of course coincide with the experimental curves, since the contributions of the second terms in Eqns.(56) and (57) cannot be neglected. The contribution of reactions (29) and (31) to the deamination and degradation processes increases with the duration of heating and also with decrease of the degree of cross-linking of the matrix and of the ratio of the volumes of the external solution and the resin in the experiment. In studies by Shaburov and coworkers [13,74,75], the relative content of water was probably significantly higher than in the work of Roginskaya and coworkers [27] and therefore in the first case even deamination and degradation of amino-groups are frequently described satisfactorily by Eqns.(68) and (69). This can be illustrated by the data in Fig. 2.

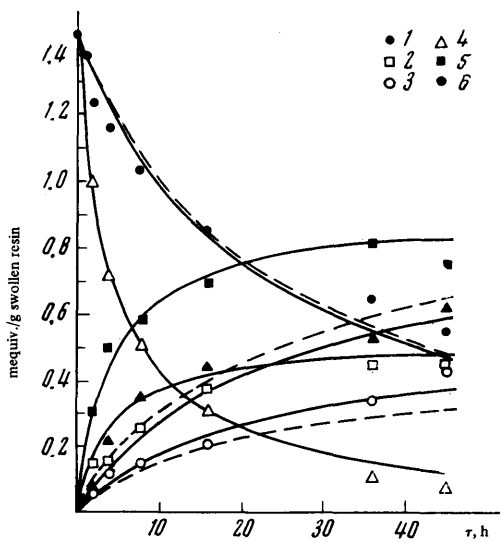


Figure 2. Decrease of E^{SBG} (*1* and *4*), deamination (*2* and *5*), and degradation (*3* and *6*) of the amino-groups of AV-17 × 6 anion-exchange resin in the OH-form on heating in water at 135°C (*1–3*) and 150°C (*4–6*). The continuous and dashed curves have been calculated by Eqns.(67)–(69) and (67)–(71) respectively. The experimental points have been taken from Shaburov [75].

The sum of the apparent rate constants $k_{25} + k_{26}$ was found from the relation $1/E^{SBG} - 1/E_0^{SBG} = (k_{25} + k_{26})\tau$. The constants k_{25} and k_{26} were found from the sum of the constants and the contributions of the deamination and degradation processes under the initial conditions when reactions (29) and (31) may be neglected. The rate constants calculated by this method, the ranges of variation of the exchange capacity at different temperatures, and the calculated exchange capacities E_0^{SBG} (in mequiv./g matrix) (from the formulae in Table 1) are listed in Table 7.

The data in Table 7 show that the deviations from the mean values of the apparent rate constants for the deamination and degradation of the amino-groups found with the aid of the equations proposed amount to 10–25% and are appreciably smaller than those found using the equations for first-order reactions (±60%). [77,79] This finding is undoubtedly evidence in support of the new principles underlying the treatment of the thermal stability of the functional groups of ion-exchange resins.

One must note that in the kinetic treatment of published data about 13% of amino-groups, which were split off in water and alcohols at an appreciably higher rate than the remaining groups, were detected only for the anion-exchanger specimen with 16% DVB.

Table 7. Apparent rate constants for the deamination (k_{25}) and degradation (k_{26}) of the amino-groups of anion-exchange resins on heating in water.

Type of anion-exchange resin	Temp., °C	Exchange capacity, mequiv. g^{-1} in text E_0^{SBG}	in text E_f^{SBG}	$E_d^{M,SBG}$, mequiv. /g matrix	Rate constants, kg matrix $mole^{-1}$ h^{-1} 10^3k_{25}	10^4k_{26}	References
AV-17 × 6[a] (OH)	85	4.03	3.24	5.90	7.8 ±1.3	0.16±0.03	79
	103		2.62		0.24±0.04	0.7 ±0.12	79
	118		0.42		2.7 ±0.2	11.0 ±0.9	79
	140		0.08		8 ±2	55.0 ±13	79
AV-17 × 8[a] (OH)	90	3.26	1.80	4.38	0.21±0.02	1.1±0.1	77
	110		0.67		1.04±0.1	6.2±0.6	77
	116		0.83		1.9 ±0.3	8 ±1	79
	125		0.26		7.1 ±0.9	44 ±5	79
	116[d]		0.84		2.8 ±0.3	13 ±2	27
	125[d]		0.52		3.9 ±0.5	18 ±2	27
AV-17 × 2[b] (OH)	100	1.10	0.97	5.67	0.1 ±0.02	0.7±0.2	74
AV-17 × 6[b] (OH)	75	1.44	1.32	5.00	0.016±0.003	0.13±0.03	75
	100		1.09		0.22±0.05	1.5±0.3	13
	120		0.69		1.07±0.03	7.7±0.2	75
	135		0.56		5.0 ±1.0	40 ±7	75
	150[c]		0.07		277 ±10	2000±70	75
	75[e]		1.15		0.33±0.002	0.9±0.01	96
	90[e]		1.09		0.46±0.1	1.16±.024	96
AV-17[a] (Cl)	150	3.72	2.41	5.65	0.50±0.07		74
	160	3.20	0.77	4.57	2.2 ±0.2		97
	170		0.98		6.1 ±0.2		97
	180	2.96	1.11	4.23	16.6 ±0.8		97
AV-17 × 16[b] (OH)	100	1.56	0.98	2.97	0.44 ±0.01	2.8±0.1	74
AV-27[b] (OH)	75	1.57	0.93	5.50	0.215±0.003	3.1±0.03	13
	100		0.17		3.2 ±0.5	57 ±9	13

[a]The exchange capacity was quoted in the original paper in mequiv./g dry resin. [b]The exchange capacity in the original paper was quoted in mequiv./g swollen resin. [c]These constants in the Arrhenius equation correspond to $t = 190°C$. [d]The resin was heated in a mixed bed with KU-2 cation-exchange resin in the H-form. [e]The resin was heated under dynamic conditions.

The kinetic parameters in the Arrhenius equation obtained for the experiments in water on the basis of the data of Shaburov and coworkers [75] and Roginskaya and coworkers [77] are virtually identical. Thus the deamination of AV-17 × 6 (Shaburov [75]) and AV-17 × 8 (Roginskaya et al. [77]) anion-exchange resins in water is characterised by activation energies of 27 ± 2 and 26 ± 3 kcal $mole^{-1}$ and pre-exponential factors of (3.9 ± 2.5) × 10^{12} and (1.2 ± 0.2) × 10^{12} kg matrix $mole^{-1}$ h^{-1}; the corresponding parameters for their degradation are 26 ± 6 and 25 ± 3 kcal $mole^{-1}$ and (8.5 ± 6.3) × 10^{11} and (9.9 ± 3.6) × 10^{11} kg matrix $mole^{-1}$ h^{-1} respectively.

Eqns. (67)–(69) can be successfully extended to other media. Thus their use yielded satisfactory results for experiments in which AV-17 anion-exchange resin was heated not only in alcohol but also in aqueous alcoholic media and in acetone, as shown by the slight scatter of the apparent rate constants about the mean (Table 8) and the satisfactory agreement between the calculated and experimental kinetic curves (Fig. 3).

Table 8. Apparent rate constants and the contribution of deamination to the loss of capacity of anion-exchange resins in the OH-form at 100°C in organic media and aqueous methanol.

Anion-exchange resin	Medium	Deamination, %	Rate constant, 10^4 kg matrix mole^{-1} h^{-1}		References
			deamination k_{32}	degradation k_{23}	
AV-17 × 2	CH_3OH	74±4	11±1	6.5±0.5	74
AV-17 × 6	50 % CH_3OH	76±1	11±8	6.5±4.7	75
AV-17 × 6	75 % CH_3OH	78±2	16±3	8.4±1.3	75
AV-17 × 6	CH_3OH	75±3	27±2	16 ±1	75
AV-17 × 6	C_3H_7OH	86±3	11±2	4.4±1	13
AV-17 × 6	$C_5H_{11}OH$	69±1	26±5	17 ±3	13
AV-17 × 6	CH_3COCH_3	70±9	5±1*	3.6±0.8**	95
AV-17 × 16	CH_3OH	76±3	29±4	17 ±2	74
AV-27	CH_3OH	38±1	180±30	220 ±40	13
AV-27	CH_3COCH_3	27±1	53±19*	87 ±31**	94

Note. In acetone, the deamination (*) and degradation (**) constants are $k_{34} + k_{36} + k_{35}$ respectively.

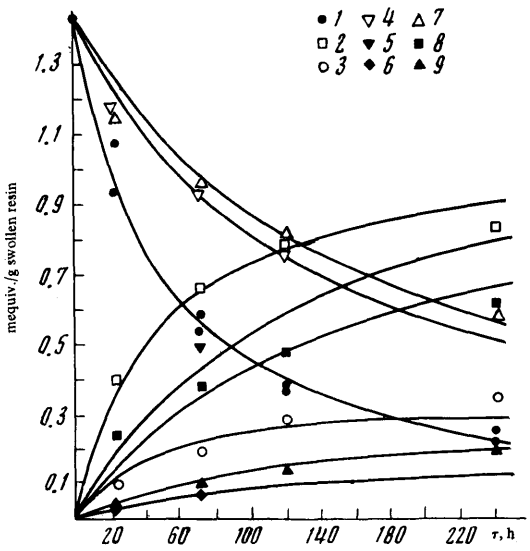


Figure 3. Decrease of E^{SBG} (*1*, *4*, and *7*), deamination (*2*, *5*, and *8*), and degradation (*3*, *6*, and *9*) of the amino-groups of AV-17 × 6 anion-exchange resin in the OH-form at 100°C in methanol (*1–3*), pentanol (*4–6*), and 50% aqueous methanol (*7–9*). The curves have been calculated by Eqns. (67)–(69); the experimental points *1–9* have been taken from Shaburov and coworkers [13,75].

According to Shaburov [75], in ethanol the deamination process has an activation energy of 28 ± 2 kcal mole^{-1} and a pre-exponential factor of (5.2 ± 0.6) × 10^{13} kg matrix mole^{-1} h^{-1}; the corresponding parameters for its degradation are 28 ± 3 kcal mole^{-1} and (2.6 ± 0.4) × 10^{13} kg matrix mole^{-1} h^{-1}.

Despite the expected wide variety of reactions on heating AV-27 anion-exchange resin, the overall processes involving a decrease of E^{SBG}, deamination, and degradation are satisfactorily described by Eqns. (67)–(69) in all the media investigated, as shown by the small deviations of the rate constants from the mean values (Tables 7 and 8) and by the satisfactory agreement between the experimental points and the calculated kinetic curves (Figs. 4 and 5).

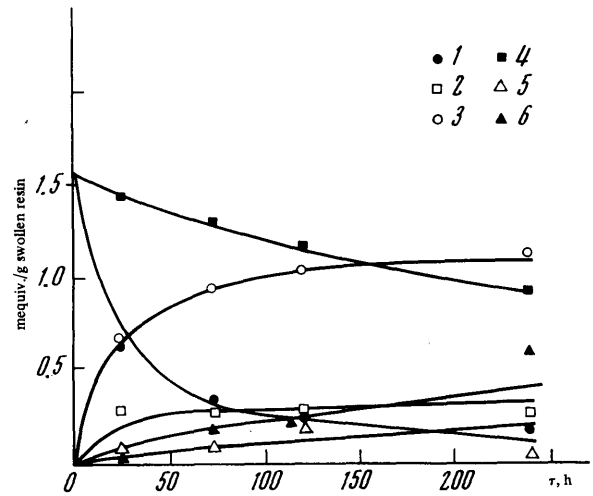


Figure 4. Decrease of E^{SBG} (*1* and *4*), deamination (*2* and *5*), and degradation (*3* and *6*) of the amino-groups of AV-27 anion-exchange resin in the OH-form in water at 100°C (*1–3*) and 75°C (*4–6*). The curves have been calculated by Eqns. (67)–(69); the experimental points *1–6* have been taken from Shaburov and Saldadze [13].

Eqns. (67)–(69) show that there should be a direct proportionality between the apparent rate constants for deamination and degradation and the molality of OH^- ions in the anion-exchanger phase in relation to the sorbed solution for resins with different contents of the cross-linking agent. The molalities of hydroxide ions in AV-17 resin specimens with 2.6 and 16% DVB calculated from the initial equivalent coefficients of moisture absorption capacity quoted by Shaburov et al. [74] are 1.52, 2.41, and 4.34 equiv.OH^-/litre water.

The linear relation between the constants k_{25} and k_{26} and the pre-exponential factors in the Arrhenius equation on the one hand and the molality of the hydroxide ion in the anion-exchanger phase on the other (Fig. 6) leads to a realistic method for the theoretical calculation of the thermal stability of the resins in water at any temperature. A similar relation was found earlier also for sulphonic acid cation-exchange resins [111].

The apparent rate constants for the deamination and degradation of the amino-groups may be calculated from equations which follow from Fig. 6:

$$k_{25} = (3.51 \cdot \bar{m}_{OH^-} - 2.50) \cdot 10^{12} \cdot \exp(-28 \cdot 10^3/RT) , \quad (70)$$

$$k_{26} = (1.36 \cdot \bar{m}_{OH^-} - 0.40) \cdot 10^{12} \cdot \exp(-28 \cdot 10^3/RT) . \quad (71)$$

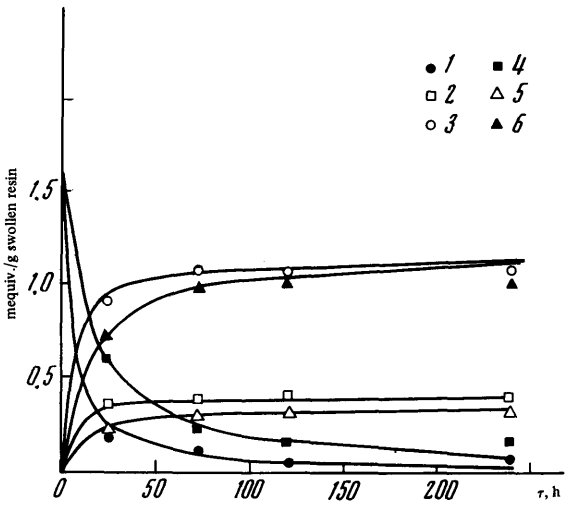


Figure 5. Decrease of E^{SBG} (*1* and *4*), deamination (*2* and *5*), and degradation (*3* and *6*) of the amino-groups of AV-27 anion-exchange resin in the OH-form at 100°C in ethanol (*1*–*3*) and pentanol (*4*–*6*). The curves have been calculated by Eqns. (67)–(69); the experimental points *1*–*6* have been taken from Shaburov and Saldadze [13].

The applicability of Eqns. (70) and (71) combined with Eqns. (67)–(69) for the calculation of the curves describing the decrease of E^{SBG}, deamination, and degradation may be illustrated by the data presented in Fig. 2 for experiments in which AV-17 anion-exchange resins were heated in water at 135°C.

The present stage in the development of studies on the thermal stability of anion-exchange resins is characterised by an endeavour on the part of investigators to extend the range of instrumental methods for the solution of many problems concerning not only the fate of the functional groups but also the changes in the matrix itself; they will provide a key to the creation of mechanically stable ion-exchange resins.

Another characteristic feature of such studies is an endeavour to unify and standardise the research techniques. Unfortunately little has yet been done in this important field.

A third and most important feature of the present stage in the development of studies on the thermal stability of resins is the concentration of the efforts of investigators on the elucidation of the mechanisms of processes involving the elimination of functional groups. The results presented in this review have demonstrated quite clearly the effect of the medium and its capacity to undergo changes under the influence of the anion-exchange counterions on the stability of the functional groups of the resin itself. This view concerning the relation between the catalytic activity and thermal stability of sulpho-groups was formulated in the previous review [1] and in this review has been developed further and given a more clear-cut theoretical basis.

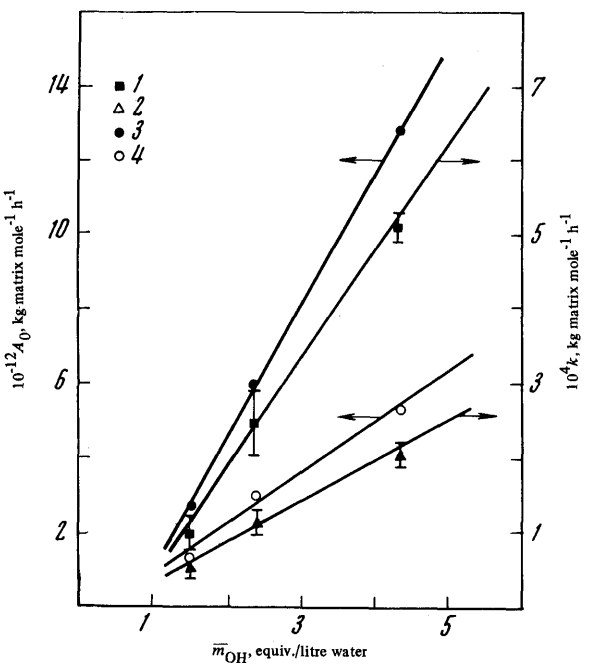


Figure 6. Variation of the apparent rate constants k at 100°C (*1* and *2*) and the pre-exponential factors A_0 in the Arrhenius equation (*3* and *4*) for the deamination (*1* and *3*) and degradation (*2* and *4*) of the amino-groups of AV-17 anion-exchange resin in water as a function of the molality of OH^- ions in the resin phase (points *1*–*4* have been obtained from the data of Shaburov et al. [74]).

The endeavour by investigators to give a mathematical description of the conversion of functional groups on the basis of a kinetic approach we believe to deserve all possible encouragement and further development.

The new ideas about the mechanisms of the deamination and degradation of anion-exchange resins in which the bond polarisation in the unit cell and the involvement of OH^- ions as reaction catalysts in the formation of intermediates are taken into account may not correspond to the true situation in all details and in this sense remain controversial. However, the fruitfulness of this approach is evident. With its aid, kinetic equations have been obtained giving a satisfactory description of earlier experimental data and allowing theoretical calculations, based on the known exchange capacities and molalities of the counterions in the resin phase, on the kinetics of the decrease of the content of strongly basic groups, deamination, and degradation of anion-exchange resins at any temperature. There is no doubt that further development

of studies in the field of the thermal stability of ion-exchange materials and (as model substances) of their low-molecular-weight analogues will create firm foundations for the synthesis of such materials in which the structural elements will be correctly combined and new resins with satisfactory operational properties will be created.

REFERENCES

1. N.G. Polyanskii and P.E. Tulupov, Uspekhi Khim., 40, 2250 (1971) [Russ. Chem. Rev., No. 12 (1971)].
2. J. Kressin and G.R. Wateraury, Analyt. Chem., 34, 1958 (1962).
3. A.B. Pashkov, M.I. Itkina, N.V. Vatenina, and E.I. Lyustgarten, Plast. Massy, No. 5, 20 (1961).
4. J.P. Faris and J.W. Warton, Analyt. Chem., 34, 1077 (1962).
5. N.G. Polyanskii and M.A. Shaburov, Zhur. Prikl. Khim., 38, 1072 (1965).
6. O. Samuelson, "Ion Exchange Separations in Analytical Chemistry", New York–London, 1963.
7. N.G. Polyanskii, Uspekhi Khim., 39, 504 (1970) [Russ. Chem. Rev., No. 3 (1970)].
8. A.A. Khonikevich, "Dezaktivatsiya Sbrosnykh Vod" (Deactivation of Waste Water), Atomizdat, Moscow, 1966, p. 161.
9. V.L. Bogatyrev, "Ionity v Smeshannom Sloe" (Mixed-Bed Resins), Izd. Khimiya, Leningrad, 1968.
10. N.G. Polyanskii and M.A. Shaburov, Zhur. Prikl. Khim., 38, 115 (1965).
11. N.G. Polyanskii and P.E. Tulupov, Symposium, "Issledovanie Svoistv Ionoobmennykh Materialov" (The Properties of Ion-Exchange Materials), Izd. Nauka, Moscow, 1964, p. 145.
12. M.A. Shaburov and K.M. Saldadze, Zhur. Prikl. Khim., 39, 106 (1966).
13. M.A. Shaburov and K.M. Saldadze, Zhur. Fiz. Khim., 40, 561 (1966) [Russ. J. Phys. Chem., No. 3 (1966)].
14. V.M. Vinogradov and E.I. Kazantsev, Izv. Vys. Ucheb. Zaved., Ser. Khim. i Khim. Tekhnol., 13, 1294 (1970).
15. B.N. Laskorin, L.I. Vodolazov, and L.M. Stepanova, Zhur. Prikl. Khim., 42, 529 (1969).
16. B.N. Laskorin, L.I. Vodolazov, and L.M. Stepanova, Zhur. Prikl. Khim., 42, 1034 (1969).
17. E.D. Kiseleva and K.V. Chmutov, Zhur. Fiz. Khim., 44, 2545 (1970) [Russ. J. Phys. Chem., No. 10 (1970)].
18. K.M. Saldadze, A.B. Pashkov, and V.S. Titov, "Ionoobmennye Vysokomolekulyarnye Soedineniya" (High-Molecular-Weight Ion-Exchange Compounds), GKhI, Moscow, 1960.
19. S. Fischer and R. Kunin, Symposium, "Analiticheskaya Khimiya Polimerov" (Analytical Chemistry of Polymers) (Translated into Russian), Inostr. Lit., Moscow, 1963, Vol. I, p. 488.
20. E.I. Kazantsev, V.S. Pakholkov, Z.Yu. Kokoshko, and O.N. Shupakhin, "Ionoobmennye Materialy, Ikh Sintez i Svoistva" (Ion-Exchange Materials, Their Synthesis and Properties), Izd. UPI, Sverdlovsk, 1969.
21. GOST 10 897–64.
22. S. Fischer and R. Kunin, Anal. Chem., 27, 1191 (1955).
23. A.L. Wilson, J. Appl. Chem., 9, 466 (1959).
24. A.L. Wilson, J. Appl. Chem., 11, 151 (1961).
25. J. Stamberg and F. Juračka, Zhur. Prikl. Khim., 35, 2295 (1962).
26. F. Polak and A. Wyroba, Zesz. nauk. univ. Jagieleonskiego, Prace chem. 191–209, 162, No. 12, 191 (1967).
27. B.S. Roginskaya, N.V. Bychkov, and A.I. Kasperovich, Symposium, "Ionnyi Obmen i Ionity" (Ion Exchange and Ion-Exchange Resins), Izd. Nauka, Leningrad, 1970, p. 71.
28. N.G. Polyanskii and M.A. Shaburov, Zhur. Anal. Khim., 18, 304 (1963).
29. V.D. Kopylova, G.D. Asambadze, and K.M. Saldadze, Zavod. Lab., 1180 (1969).
30. V.D. Kopylova, K.M. Saldadze, and G.D. Asambadze, Zhur. Anal. Khim., 24, 1727 (1969).
31. N.G. Polyanskii, M.A. Shaburov, and A.A. Efimov, Zhur. Anal. Khim., 19, 1192 (1962).
32. V.P. Greben', Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1972.
33. E.V. Egorov and P.D. Novikov, "Deistvie Ioniziruyushchikh Izluchenii na Ionoobmennye Materialy" (The Effect of Ionising Radiation on Ion-Exchange Materials), Atomizdat, Moscow, 1965.
34. P.E. Tulupov and A.I. Kasperovich, Khim. Vys. Energii, 3, 157 (1969).
35. P.E. Tulupov, M.A. Zhukov, A.B. Pashkov, and B.Ya. Kel'man, Symposium, "Ionoobmennye Membrany v Elektrodialize" (Ion-Exchange Membranes in Electrodialysis), Izd. Khimiya, Leningrad, 1970, p. 33.
36. P.E. Tulupov, Zhur. Fiz. Khim., 45, 1205 (1971) [Russ. J. Phys. Chem., No. 5 (1971)].
37. P.E. Tulupov and V.P. Greben', Zhur. Fiz. Khim., 45, 2275 (1971) [Russ. J. Phys. Chem., No. 9 (1971)].
38. N.G. Polyanskii, Doctoral Thesis, Leningrad State University, 1969.
39. N.G. Polyanskii, N.L. Polyanskaya, and V.N. Mazin, Zhur. Fiz. Khim., 45, 2858 (1971) [Russ. J. Phys. Chem., No. 11 (1971)].
40. D. Whittington and I.R. Millar, J. Appl. Chem., 18, 122 (1968).
41. E.D. Kiseleva, V.M. Khasanova, and K.V. Chmutov, Zhur. Fiz. Khim., 45, 1196 (1971) [Russ. J. Phys. Chem., No. 5 (1971)].
42. E.D. Kiseleva and K.V. Chmutov, Zhur. Fiz. Khim., 45, 1509 (1971) [Russ. J. Phys. Chem., No. 6 (1971)].
43. E.D. Kiseleva, V.M. Khasanova, T.D. Semenovskaya, and K.V. Chmutov, Zhur. Fiz. Khim., 45, 2862 (1971) [Russ. J. Phys. Chem., No. 11 (1971)].
44. P.E. Tulupov and V.P. Greben', Symposium, "Ionnyi Obmen i Ionity" (Ion Exchange and Ion-Exchange Resins), Izd. Nauka, Leningrad, 1970, p. 83
45. K.M. Saldadze, Symposium, "Issledovaniya v Oblasti Khromatografii" (Studies in Chromatography), Izd. Akad. Nauk SSSR, Moscow, 1952, p. 114.
46. Yu.A. Leikin, A.V. Smirnov, A.B. Davankov, and V.V. Korshak, Vysokomol. Soed., 10A, 157 (1968).
47. Z.N. Eirish, M.V. Eirish, and M.V. Vittikh, Izv. Akad. Nauk Kazakh. SSR, No. 5, 32 (1970).
48. I.B. Yanovich, I.F. Gleim, and V.S. Soldatov, Vestnik Akad. Nauk Beloruss. SSR, Ser. Khim. Nauk, 4, 29 (1968).
49. I.B. Yanovich, I.F. Gleim, and V.S. Soldatov, Vestnik Akad. Nauk Beloruss. SSR, Ser. Khim. Nauk, 1, 112 (1969).
50. R. Dybczynski, Przemysl Chem., 38, 216 (1959).
51. Houben-Weyl, "Die Methoden der organischen Chemie, analytische" (Translated into Russian), GKhI, Moscow, 1963, p. 664.

52. V. S. Soldatov, Z. R. Pavlovskaya, and I. F. Gleim, Symposium, "Ionnyi Obmen i Ionity" (Ion Exchange and Ion-Exchange Resins), Izd. Nauka, Leningrad, 1970, p. 64.
53. M. A. Shaburov and K. M. Saldadze, Zhur. Prikl. Khim., 39, 2803 (1966).
54. M. A. Shaburov, Zhur. Prikl. Khim., 38, 2666 (1965).
55. O. N. Myagkoi, T. G. Suslina, and V. I. Tyagunova, Symposium, "Teoriya i Praktika Sorbtsionnykh Protsessov" (Theory and Practice of Sorption Processes), Izd. Voronezh. Gos. Univ., Voronezh, 1966, No. 1, p. 170.
56. P. E. Tulupov, Symposium, "Ionnyi Obmen i Khromatografiya" (Ion Exchange and Chromatography), Izd. Voronezh. Gos. Univ., Voronezh, 1971, Part 2, p. 7.
57. V. V. Zykova, Candidate's Thesis, Alma-Ata, 1969.
58. J. J. Barghusen and A. A. Jonke, Power Technology and Reactor Fuel Processing, 10, 2, 170 (1967).
59. K. M. Ol'shanova, M. A. Potapova, N. I. Petrova, N. I. Chebotareva, and L. E. Tsupak, see Ref. 6, Voronezh, Part 2, p. 56.
60. R. Angeles, M. Aldridge, D. Freeman, and L. Wall, J. Polymer Sci., B7, 609 (1969).
61. E. B. Trostyanskaya and S. B. Makarova, Zhur. Prikl. Khim., 39, 1754 (1966).
62. R. M. Wheaton and W. C. Bauman, Ind. Eng. Chem., 43, 1088 (1951).
63. M. Gilwood, C. Calmon, and A. Greer, "12-th Annual Water Conference Proceedings", 1951, p. 119.
64. F. K. Lindsay and J. S. D'Amico, Ind. Eng. Chem., 43, 1085 (1951).
65. N. Frisch et al., Symposium, "Vodopodgotovka i Vodnyi Rezhim Kotlov na Teplovykh Elektrostantsiyakh" (The Preparation of the Water and the Water Regime in Steam Power Station Boilers), Gosenergoizdat, Moscow, 1958, Nos. 7 and 8.
66. L. D. Virt, Symposium, "Vodopodgotovka i Vodnyi Rezhim Kotlov na Teplovykh Elektrostantsiyakh" (The Preparation of the Water and the Water Regime in Steam Power Station Boilers), Gosenergoizdat, Moscow, 1957, Nos. 3 and 46.
67. T. Griesbach, "Theorie und Praxis des Ionenaustausches" (Translated into Russian), Inostr. Lit., Moscow, 1963.
68. M. Fodor, E. Szabo, and Z. Poko, Acta Chim. Acad. Sci. Hung., 29, 1 (1961).
69. V. V. Zykova, M. V. Vittikh, and L. D. Mareeva, Symposium, "Sintez i Issledovanie Vysokomolekulyarnykh Soedinenii" (The Synthesis and Study of High-Molecular-Weight Compounds), Izd. Akad. Nauk Kazakh. SSR, Alma-Ata, 1964, p. 89.
70. A. A. Vasil'ev and T. S. Tsygankova, Zhur. Prikl. Khim., 41, 2261 (1968).
71. M. A. Potapova, M. N. Kuznetsova, K. M. Saldadze, and K. M. Ol'shanova, Symposium, "Ionoobmennye Sorbenty v Promyshlennosti" (Ion-Exchange Sorbents in Industry), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 60.
72. M. A. Potapova, K. M. Ol'shanova, K. M. Saldadze, and N. I. Petrova, Symposium, "Issledovanie Svoistv Ionoobmennykh Materialov" (The Properties of Ion-Exchange Materials), Izd. Nauka, Moscow, 1964, p. 158.
73. N. I. Petrova and M. A. Potapova, Symposium, "Sintez i Svoistva Ionoobmennykh Materialov" (The Synthesis and Properties of Ion-Exchange Materials), Izd. Nauka, Moscow, 1968, p. 120.
74. M. A. Shaburov, L. G. Myasnikova, and Yu. I. Belonogova, Plast. Massy, No. 5, 54 (1965).
75. M. A. Shaburov, Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1965.
76. J. Mathieu and A. Allais, "Principes de Synthèse Organique" (Translated into Russian), Inostr. Lit., Moscow, 1962, p. 68.
77. B. S. Roginskaya, A. I. Kasperovich, and N. V. Bychkov, "Sintes i Svoistva Ionoobmennykh Materialov" (The Synthesis and Properties of Ion-Exchange Materials), Izd. Nauka, Moscow, 1968, p. 140.
78. A. R. Surrey, "Name Reactions in Organic Chemistry" (Translated into Russian), GKhI, Moscow, 1962, p. 96.
79. B. S. Roginskaya, Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1970, p. 93.
80. Ts. S. Tsurtskhaliya and K. M. Saldadze, Symposium, "Khimicheski Aktivnye Polimery i Ikh Primenenie" (Chemically Active Polymers and Their Applications), Izd. Khimiya, Leningrad, 1969, p. 208.
81. M. J. Hatch and W. D. Lloyd, J. Appl. Polym. Sci., 8, 1659 (1964).
82. J. Petrariu and J. Štamberg, Coll. Czech. Chem. Comm., 32, 798 (1967).
83. Z. Vašiček and J. Štamberg, "Kunstharz Ionenaustauscher", Berlin, 1970, p. 272.
84. Z. Vašiček, J. Štamberg, and O. Dufka, Coll. Czech. Chem. Comm., 36, 1817 (1971).
85. Z. Vašiček, J. Klaban, and J. Štamberg, Coll. Czech. Chem. Comm., 36, 1825 (1971).
86. J. Rahm and J. Štamberg, Coll. Czech. Chem. Comm., 36, 2698 (1971).
87. J. Petrariu, O. Petreus, A. Carpov, C. Luca, and M. Dima, Rev. Chim. (Roumania), 22, 177 (1971).
88. K. M. Saldadze, V. B. Kargman, and N. B. Galitskaya, Symposium, "Khimicheski Aktivnye Polimery i Ikh Primenenie" (Chemically Active Polymers and Their Applications), Izd. Khimiya, Leningrad, 1969, p. 193.
89. I. V. Samborskii and M. K. Saldadze, Symposium, "Khimicheski Aktivnye Polimery i Ikh Primenenie" (Chemically Active Polymers and Their Applications), Izd. Khimiya, Leningrad, 1969, p. 230.
90. J. Lindeman, "Mezhdunarodnyi Simposium po Makromolekulyarnoi Khimii, Moskva, Sektsiya 3" (International Symposium on Macromolecular Chemistry, Moscow, Section 3), 1960, p. 146.
91. A. I. Vulikh, "Ionoobmennyi Sintez" (Ion-Exchange Synthesis), Izd. Khimiya, Moscow, 1973, p. 26.
92. Z. J. Disdar, Bull. Inst. Nuclear Sci., 8, 157 (1958).
93. N. V. Bychkov, A. I. Kasperovich, and B. S. Roginskaya, Zhur. Fiz. Khim., 43, 2522 (1969) [Russ. J. Phys. Chem., No. 10 (1969)].
94. V. M. Vinogradov, Candidate's Thesis, The Urals Polytechnic Institute, Sverdlovsk, 1971.
95. M. A. Shaburov and K. M. Saldadze, Zhur. Prikl. Khim., 41, 593 (1968).
96. M. A. Shaburov and K. M. Saldadze, Zhur. Prikl. Khim., 41, 2179 (1968).
97. P. E. Tulupov, Zhur. Fiz. Khim., 45, 431 (1971) [Russ. J. Phys. Chem., No. 2 (1971)].
98. O. A. Reutov, "Teoreticheskie Osnovy Organicheskoi Khimii" (Theoretical Principles of Organic Chemistry), Izd. Moskov. Gos. Univ., Moscow, 1964, p. 81.
99. P. E. Tulupov, Zhur. Prikl. Khim., 39, 2434 (1966).
100. P. E. Tulupov, Symposium, "Tezisy Dokladov Vsesoyuznoi Konferentsii po Primeneniyu Ionitov v

Narodnom Khozyaistve" (Abstracts of Reports at the All-Union Conference on the Application of Ion-Exchange Resins in the Nation Economy), Moscow, 1973 (in the press).
101. P. E. Tulupov and M. A. Shaburov, Zhur. Fiz. Khim. (in the press).
102. See Ref. 76, p. 578.
103. See Ref. 76, p. 531.
104. A. N. Nesmeyanov and N. A. Nesmeyanov, "Nachala Organicheskoi Khimii" (The Principles of Organic Chemistry), Izd. Khimiya, Moscow, 1969, Book I, pp. 103, 145.
105. S. Hatem, J. Chim. Phys., 48, 407 (1951).
106. E. W. Bauman, J. Chem. Eng. Data, 5, 376 (1960).
107. P. E. Tulupov, Zhur. Fiz. Khim., 45, 665 (1971) [Russ. J. Phys. Chem., No. 3 (1971)].
108. P. E. Tulupov and V. P. Greben', Plast. Massy, No. 10, 53 (1971).
109. K. J. Laidler, "Kinetics of Organic Reactions" (Translated into Russian), Izd. Mir, Moscow, 1966, p. 306.
110. Yu. A. Kokotov and V. A. Pasechnik, "Ravnovesie i Kinetika Ionnogo Obmena" (Equilibria and Kinetics of Ion Exchange), Izd. Khimiya, Leningrad, 1970, p. 57.
111. P. E. Tulupov, V. P. Greben', and A. M. Butaev, Dokl. Akad. Nauk SSSR, 210, 1392 (1973).
112. M. A. Minto, G. J. Moody, and J. D. R. Thomas, Lab. Pract., 21, 797 (1972).

Karpov Physicochemical Institute, Moscow

Tambov Institute of Chemical Machine Engineering