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New Advances in Catalysis by Ion-exchange Resins

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Current research on the general problems, methods and theory of catalysis by ion-exchange resins as well as new advances in its application in hydrolytic, hydration, and dehydration reactions, the synthesis of esters, alkylation, polymerisation, isomerisation, and condensation are surveyed.
The bibliography includes 276 references.

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This review is a continuation and logical development of previous publications by one of the authors[1,2], which appeared in 1962 and 1970. Reviews on the applications of ion-exchange resins as catalysts of various organic reactions[3-5] and narrowly specialist review articles on hydration[6], condensation[7,8], and esterification[9] reactions were published somewhat later; the literature references cover publications mainly after 1970. This review surveys the literature on catalysis by ion-exchange resins up to February 1976.

I. GENERAL PROBLEMS OF CATALYSIS BY ION-EXCHANGE RESINS

The catalytic functions of ion-exchange resins and other similar substances reduce to the formation of reactive intermediate complexes either by the addition of the mobile ions (counterions) of the polymers to the molecules of one of the reactants or by the protonation of the electron-donating atoms of the active groups. Since there is no ion exchange either at this or subsequent reaction stages up to the formation of the final product, it is desirable to replace the established term "ion-exchange catalysis"[2,10] by "catalysis by ion-exchangers"[11].

Recent development of catalysis by ion exchangers in the stage under consideration, which includes the period 1969–1975, has led to numerous confirmations of their advantages as catalysts for chemical reactions involving organic substances over soluble acids and bases, which have been used for a long time in acid–base catalysis.

The simplicity of separation of the ion exchangers from the reaction products opens new effective pathways to the solution of the global problem — the protection of nature from chemical pollution by eliminating or greatly reducing the amount of waste water and harmful gases produced in various branches of chemical industry manufacturing alkylphenols[12], phenols[13], epoxy-compounds[14], and other products. In many cases this advantage confers also additional benefits such as reduction of the risk of fire and explosion in the manufacturing process, the facilitation of continuous technological processes, the simplification of the use of heat-exchange apparatus, etc. Since cation and anion exchangers constitute different phases and are immiscible with the reaction mass, the methods of catalysis by ion-exchangers makes it possible to carry out in a single stage reactions proceeding via a cationic or anionic mechanism, for example the synthesis of aminoaldehyde resin and its esterification by butanol[15]. It is noteworthy, that, as a result of the application of ion exchangers, new advances have been made in the synthesis of aminoresins with a high purity and their practical properties have been thereby improved.

In very many cases ion exchangers surpass soluble acids and bases as regards the specificity of catalytic action and this leads to a decrease in the amount of reactants wasted on side processes and improves the yield of the desired product (for example in the esterification of propylene glycol by stearic acid[16] and in the decomposition of isopropylphenyl hydroperoxides[13,17]).

Naturally, the specificity of ion exchangers as catalysts of organic reactions must not be overestimated. As an illustration, we may quote a number of reactions of different types where at least one, and sometimes a whole series, of side products are formed together with the main product. Such reactions include the thiolysis of 1,3-dioxepan by ethanethiol[18], the alkylation of cresol by indene[19], as well as numerous condensation reactions catalysed by cation exchangers (those of bicyclopentadiene[20], 4-vinylcyclohexene[21], and α-methylstyrene[22] with formaldehyde and of methylallyl alcohol with phenol[23]) or anion exchangers (the condensation of n-butylraldehyde with formaldehyde[24]). One of the main problems of catalysis by ion exchangers is the reduction to a minimum of side reactions and the possible acceleration of the main reaction, which is achieved by the selection of the optimum ion exchanger, solvent, molar reactant ratio, and experimental temperature.

Ion exchangers are milder catalysts than soluble acids and bases, which makes it possible to prevent undesirable reactions, for example the opening of the epoxide ring on epoxidation[14] and permits the extremely delicate synthesis of fructose-1,6-diphosphate by the condensation of triosephosphates[25], which was previously achieved only by enzymatic catalysis. This feature of the catalytic action of ion exchangers will undoubtedly find many further useful applications in biochemical and fine organic syntheses.

However, one should note that such reactions catalysed by the protons of soluble acids are either not accelerated by the so called standard or gel ion exchangers or give rise to the useful products in insignificant yields. Even a brief list of such reactions, including the interaction of

acetic acid with benzyl alcohol[26], the reaction of dodecyl alcohol with sorbic acid[27] (which hardly occurs in the presence of the usual KU-2 × 8 cation-exchange resin), the reaction of t-butyl hydroperoxide with aliphatic acids[28], and the reaction of benzene with propene[29], shows that the negative result is due to steric causes, namely the inability of the large molecules of the reactants or products to penetrate the resin micropores and enter or leave the gel phase.

In very many instances, these difficulties can be overcome by means of ion exchangers with an artificially created heterogeneity, usually synthesised from macroporous styrene–divinylbenzene copolymers. Such ion exchangers have been particularly effective as catalysts of reactions in non-solvating non-aqueous media: in the absence of swelling of high-molecular-weight polyelectrolytes, the access of the reactant molecules to the active groups is assured by the large internal surface area.

Table 1 lists the most important properties of typical porous sulphonated cation exchangers synthesised from the copolymers of styrene with different amounts of divinylbenzene.

Table 1. Certain properties of porous sulphonated cation-exchange resins[30] with different contents of divinylbenzene (DVB).

DVB, %	10	15	25	50	70
Volume capacity, mequiv. g^{-1}	5.34	5.28	3.43	2.68	2.22
Specific surface, $m^2 g^{-1}$	0.1	43.0	77.5	263.2	266.3
True density, g cm^{-3}	1.44	1.43	1.40	1.33	1.31
Apparent density, g cm^{-3}	1.38	0.96	0.86	0.49	0.48
Total porosity, ml ml^{-1}	0.04	0.329	0.386	0.632	0.634
Average pore radius, Å	—	148	147	101	77
Calculated pore wall thickness, Å	—	110	89	26	19

The most striking feature noted when the data in Table 1 are inspected is the enormous specific surface of cation exchangers containing ≥ 15% of divinylbenzene and the considerable differences between the true and apparent densities, indicating the porous nature of the ion-exchange copolymers investigated. The average pore radius in the cation-exchange resin synthesised varies in the range 77–148 Å. Depending on the conditions of synthesis of the copolymers and ion exchangers, the pores can be larger or smaller (see pp. 54 and 55 in Polyanskii's monograph[11]), but in most instances their equivalent radius amounts to hundreds of angstroms. According to Dubinin's classification[31], such sorbents should be regarded as mesoporous, but the term "macroporous ion exchangers" has become firmly established in the literature on ion exchange; to avoid confusion, this term will be used henceforth in the present text. We may point out for comparison that gel ion exchangers contain cavities with molecular dimensions, varying in the range from 8 to 20 Å for the SBS cation-exchange resin and from 7 to 13 Å for the KU-2 cation-exchange resins with different degrees of cross linking (see p. 55 in Polyanskii's monograph[11]).

A study of the polymerisation of dimethylcyclosiloxanes has shown[32] that the catalytic activity of macroporous ion exchangers can be predicted on the basis of the overall porosity of the resins, which can be determined by simpler methods than the specific surface or pore radius. In the above reaction, the maximum catalytic activity was shown by sulphonic acid cation-exchange resins with an overall porosity of 0.8 $cm^3 g^{-1}$, a specific surface not less than 60–70 m^2, and a pore radius not greater than 300 Å. Naturally, these characteristics are not of general significance, but depend on the chemical structure of the reactants and products. It is also clear that the optimum ion exchanger should have a fairly high porosity and not unduly small pores; for macroporous ion-exchange polymers, these conditions are usually fulfilled in the presence of 20–30% of divinylbenzene (DVB). Ion exchangers with this degree of cross linking retain their porosity after many repeated swelling and drying operations and do not lose it as a result of conversion from one ionic form to another either. On the other hand, cation exchangers with 10% DVB lose their porosity entirely and become gel resins when they are kept in water or another solvating liquid[30]. Such changes can have a decisive influence on the catalytic properties of ion exchangers.

When macroporous ion exchangers began to be used, it was possible to achieve reactions which did not occur in the presence of gel resins[27,29], to accelerate other reactions with reduction or elimination of the induction period[33], and in certain cases to raise the yield of the desired product[13]. At the same time, reactions have also been described (alkylation of phenol by isobutyl alcohol) in which the macroporous cation exchanger employed did not have kinetic or other advantages over gel resins[34]. In aqueous or mixed media, the reactions can actually take place faster in the presence of gel cation exchangers (for example the inversion of sucrose[35] or the hydrolysis of esters[36]) if the molecules of the reacting substances do not penetrate into the pore walls of macroporous ion-exchange polymers, which have a dense three-dimensional network in the presence of a high DVB content, but do penetrate into the gel phase of cation exchangers with moderate degree of cross linking. Some authors[37] do not recommend at all the use of macroporous resins for the acceleration of the Prins reaction, since these ion exchangers sorb the reaction mass with cracking of the grains, which hinders both the repeated use of the catalyst and the filtration of the reaction mass through the latter. However, one should note that this conclusion cannot be regarded as general, since the authors[37] tested only one cation-exchanger specimen and did not determine its porosity. There is no doubt that the porometric characteristics of the ion exchangers influence not only their catalytic activity but also the effects due to the blocking of the active centres by the components of the reaction mixture (see pp. 505 and 506 in Polyanskii's review[2]) on which the stability of the operation of the catalyst depends.

Both macroporous and gel ion exchangers have been used not only in hydrogen- or hydroxide-forms, but also in salt-forms, functioning as Lewis acids or bases. These catalysts are as a rule more thermostable[38,39] and in some cases surpass cation exchangers in the H-forms and anion exchangers in the OH-forms as regards the specificity of their action. The use of carboxylic cation exchangers in the Zn-forms in the condensation of urea with formaldehyde[40] and of the Zn-forms of sulphonic acid cation exchangers in the alkylation of phenol[41] has been described. A gel sulphopolystyrene resin in the Fe-form has been used as the catalyst of the conversion of *para*-hydrogen[42] and the macroporous Amberlyst 15 cation exchanger, containing Na^+ counterions and those of *d* (or *f*) elements, proved to be an effective catalyst of the isomerisation of but-1-ene[43]. The activity and stereo-selectivity of the catalyst depend on the electronegativity of the counterions, i.e. on their strength as Lewis acids.

Metallised cation exchangers, obtained by the reduction of the corresponding ionic forms to the free metal, have been tested as substitutes for certain catalysts used in heterogeneous catalysis[44,45]. This interesting field undoubtedly requires further development. There are no data on the use of metallised anion exchangers, but the salt-forms of these polyelectrolytes have been used successfully in a few cases. In this connection mention should be made of the use of Cu^{2+} or Co^{2+} complexes with bifunctional anion exchangers as catalysts of the reaction of 2- or 4-vinylalkylpyridines with amines to form N-substituted aminoethylalkylpyridines[46,47] and also of the employment of a strongly basic anion exchanger in the chloroplatinate-form in a very interesting reaction involving the hydrosilylation of alkenes, alkynes, and unsaturated acid esters[48].

Together with the modification of ion exchangers with the aim of imparting catalytic functions to them, investigators have resorted to different procedures for the promotion or stabilisation of catalysts. It has been shown[49] that treatment of the AV-17 anion-exchange resins with aqueous suspensions of calcium and magnesium oxides, forming complexes with hydroxy-compounds, accelerates the reaction between formaldehyde and ethyl methyl ketone, increasing thereby the yield of the main reaction product—3-hydroxymethylbutan-2-one. Another modification procedure, based on the esterification of the sulphogroups by mercaptoethanol, increases the stability of the Dowex-50 W cation-exchange resin and the duration of its operation without a significant decrease of activity[50].

The problems of the stability of catalysts in the course of their operation and the causes and prevention of the changes in catalytic properties as well as regeneration procedures constitute a set of inter-related problems. It has been shown[51] that their solution is possible only by a joint consideration of the thermal stability of ion exchangers, in a broad sense of this term, and of their catalytic activity.

The first possible cause of the decrease of the catalytic activity of ion exchangers is the decrease of their exchange capacity owing to reactions involving the electrolytic or nucleophilic substitution of the active groups as a result of the interaction with the components of the reaction mixture, including the moisture present initially in the catalyst itself. This concerns the desulphonation of strongly acidic cation exchangers or the deamination of anion exchangers, which determine the position of the upper temperature limit of the prolonged use of ion-exchange resins: 150° and 300°C for sulphonated styrene–divinylbenzene copolymers in the hydrogen- and salt-forms respectively; 60–70° and 100–110° for highly basic anion exchangers in the OH- and salt-forms.

Under milder conditions, excluding desulphonation or deamination, the second cause of the decrease of catalytic activity operates—the blocking of the ion-exchange groups. This phenomenon is most typical in the presence of substances reacting with the active groups (for example, as a result of the esterification of the sulpho-group by alcohols[52]) and also on formation of polymeric or crystalline products of different types, shielding the counterions from interaction with the reactant molecules (for example, the blocking of cation exchangers in condensation[53,54], thiolysis[55], and alkylation[56] reactions and of anion exchangers in the hydrosilylation reaction[48]).

The third cause of the decrease of the activity and of the duration of the useful life of ion exchangers is the possible substitution of the H^+ and OH^- counterions by other ions with formation of salt-forms which do not catalyse the reaction under the experimental conditions. The source of the substituting ions may be impurities in the reactants or the products of the corrosion of the reactor material. By passing the reactants through an ion-exchange column, the impurities are removed and the useful life of the catalyst is greatly increased[53].

The fourth cause of the decrease of the useful life of ion-exchanger catalysts is the limited osmotic stability of the latter, i.e. the disruption of their grains following changes in swellability in different media; the resulting fine particles offer a greater resistance to the flow of reactants and the process stops. For this reason, it was necessary to abandon the KU-2 cation-exchange resin as the catalyst of the condensation of mesityl oxide with methanol and preference had to be given to the less thermostable sulphophenolformaldehyde cation-exchange resin, the grains of which did not fragment; the mild reaction conditions (20–30°C) make this change feasible[57].

The changes in ion exchangers described above frequently influence the kinetics of the reactions which they catalyse (see Polyanskii[11], pp. 20 and 21 and Fig. 2, as well as the paper of Reikhsfel'd et al.[48]), are responsible for the decreased yield of the desired products and the enhanced formation of side products[58,59], and alter the selectivity of the catalytic action in reactions involving multicomponent mixtures of related substances and the composition of the reaction mass[60].

The intensity of the changes enumerated above, leading to a decrease of the useful life of the catalysts, depends on the nature of the ion exchanger, solvent, and reaction mixture, reaction temperature, the purity of the starting materials, and the corrosion resistance of the reactor material. In various syntheses, these parameters change over a wide range and it is therefore not surprising that investigators quote extremely different useful lives of resin catalysts. Without regeneration, catalysts of the KU-type in the H-form have been used in the synthesis of peracids (150 h),[14] in the dehydration of ethylene glycol to dioxan (200 h),[61] in the alkylation of *p*-cresol by isobutene (500 h),[62] and in the decomposition of isopropylphenyl hydroperoxide (1400 h).[17] The activity of the AV-17 anion-exchange resin in the chloroplatinate-form as the catalyst of the hydrosilylation of alkenes decreased sharply, owing to their partial polymerisation, after 20–30 h. However, when the polymers are periodically dissolved in hexane, the catalyst can be employed twenty times in the course of 180 h.[48]

The examples quoted show that an increase of the lifetime of the catalysts may be achieved only on the basis of a combined approach involving a comprehensive study of all the causes of the decrease of catalytic activity; the synthesis of new thermostable ion exchangers, on which investigators have been working persistently and not without success, constitutes only part of the general problem.

Despite the difficulties enumerated above, a considerable expansion of the fields of application of ion exchanger catalysis has occurred in the last few years. The synthesis of a wide variety of compounds is no longer its only field of application. The catalytic properties of ion exchangers are used to convert isomers with very similar properties into substances capable of subsequent separation by distillation[63], for the elimination of whole series of impurities from phenol[64], and for the selective extraction of isobutene from mixtures with n-butenes, which remain unchanged under the reaction conditions[12]. Ion exchanger catalysis is finding increasing applications in biochemical synthesis[65–67] and in analysis[68]. There is a continuous growth of interest in ion exchangers as catalysts in scientific disciplines related to chemistry.

II. EXPERIMENTAL METHODS

Granulated ion exchangers are usually employed as catalysts, but in special cases, when the kinetic studies are performed to investigate the reaction mechanism and spectroscopic measurements have to be made, film or membranes are used[69,70]. The method of preparation of ion-exchange films has been described in a paper[70] and in a monograph[71].

Before use in catalysis, technical ion exchangers must be conditioned—the three-dimensional network has to be purified and conditioned in order to stabilise its structure. The best conditioning procedure is believed to involve the treatment of cation exchangers with 1–2 *N* NaCl or NaOH solutions, water, 1–2 *N* HCl solution, and again water, while anion exchangers are treated with 1–2 *N* NaCl or HCl solutions, 1–2 *N* NaOH solution, and again water. The treatment in the Na–H or Cl–OH exchange cycles lasts approximately 12 h in each case and is repeated three–four times. Cation and anion exchangers which are weak electrolytes are conditioned with NaOH or HCl respectively instead of NaCl, since otherwise the preparation of their salt-forms requires enormous volumes of reagents. There are almost no data concerning the influence of conditioning on the catalytic properties of ion exchangers, apart from a study[50] where it was noted that there is no change in sulphonated cation exchangers based on the styrene–divinylbenzene copolymer, used as catalysts of the condensation of phenol and acetone, after alternate treatment with NaOH and HNO_3 solutions. More extensive systematic studies are needed in order to reach final conclusions on this problem.

The elimination of low-molecular-weight organic impurities from ion exchangers is achieved by treatment with alcohols, benzene, an alcohol–benzene mixture, or acetone in Soxhlet apparatus. Methanol has been used successfully to regenerate the spent ion exchangers by removing polar blocking impurities[53] and a sulphonated cation exchanger of the polycondensation type, used as the catalyst of the hydration of isobutene, has been regenerated by treatment with concentrated sulphuric acid at 105°C for 2 h.[72]

Ion exchangers are converted into the required ionic form by passing through them a 1–2 M solution of the appropriate reagent (a strong acid, usually hydrochloric acid, in order to obtain cation exchangers in the H-form, alkali to produce anion exchangers in the OH-form, chlorides or other soluble salts in order to obtain salt-forms) until its concentration in the filtrate is constant, or preferably until the test for the displaced ion is negative. In the preparation of salt-forms of ion exchangers, one must bear in mind that hydrolysed ions may be absorbed from salt solutions. To avoid the displacement of the hydrolytic equilibrium in such cases and also in the preparation of any salt-forms of weakly acidic cation exchangers or weakly basic anion exchangers, they must be washed with 95% ethanol and not water. A high degree of substitution of counterions is sometimes achieved in the preparation of one salt-form from another and not from the H-form of the cation exchanger or the OH-form of the anion exchanger. Such a case has been described[73], the authors having used an anion exchanger in the tetrachloropalladate(II)-form as the catalyst of the hydrogenation of olefins and allyl alcohol[74]. A high degree of substitution of counterions can be achieved by displacing the equilibrium associated with the formation of a relatively undissociated compound. This principle has been used by Reikhsfel'd et al.,[48] who obtained the AV-17 anion-exchange resin with the $PtCl_6^{2-}$ counterion by passing an aqueous solution of H_2PtCl_6 through the resin in the OH-form. The mechanically sorbed acid was extracted with water by treating the hydrosilylation catalyst obtained in a Soxhlet apparatus.

Metallised cation exchangers have been obtained[75] from the macroporous Amberlyst 15 resin in the Na-form, through which aqueous solutions of $Pt(NH_3)_4Cl_2$, $Pd(NH_3)_4 \cdot Cl_2$, $NiCl_2$ in the presence of an excess of NH_4OH, or $AgNO_3$ in the presence of an excess of NH_4OH were passed. The cation exchanger was then washed with water and alcohol, dried in air and then *in vacuo* at 107°C, and the ions reduced to the free metal in a stream of hydrogen or by treatment with an aqueous hydrazine solution which had been made alkaline; the resulting catalyst was used to accelerate the oxidation of ethanol under very mild conditions.

Ion exchangers designed to accelerate reactions in non-aqueous media are usually employed in the dehydrated state. In preparative studies, they normally are dried when the water in the ion exchanger can cause undesirable reactions of the components of the reaction mixture, for example the hydrolysis of esters in transesterification reactions[76]. In kinetic studies, it is necessary to bear in mind the influence of water on the rate of the catalysed reaction (see below) and one must therefore standardise rigorously the moisture content of the resin. In some cases, the nature of the reaction occurring depends on the resin moisture content (see p. 511 in Polyanskii's review[2]).

The behaviour of various cation and anion exchangers on drying by heat has been examined in detail[38,39]. The drying is carried out at atmospheric pressure in air, in a stream of hydrogen or helium, or *in vacuo*. Unfortunately, the recommended conditions are extremely varied even for ion exchangers of the same type and in most cases have been inadequately described and by no means always justified. In addition to the procedures described in the reviews quoted above, we shall list the most characteristic conditions used in the drying of sulphonated cation exchangers based on styrene–divinylbenzene copolymers and used as catalysts of various organic reactions: at 90°C and 14 mmHg;[77] at 90°C and 10^{-6} mmHg;[42] at 120°C[29,43] (residual pressure not indicated); at 120°C in a stream of helium dried at the temperature of liquid nitrogen[78] and having a partial water vapour pressure of 10^{-6} mmHg. Some workers use two-stage drying methods—initially at the usual pressure and then *in vacuo*. Thus the Zeocarb-225 cation-exchange resin is initially dried in a thermostat at 110°C for 48 h and then for 2 h at 150°C and a residual pressure of 10^{-2} mmHg. The additional weight loss in the second stage amounted to 10%.[79] The same cation exchanger has been dried[80] in a thermostat at 130°C (time not indicated) and in a vacuum of 10^{-2} mmHg at 120°C for 2 h. As in the previous case, the additional weight loss in the second stage amounted to 10%. Within the limits of the sensitivity of infrared spectroscopy, the cation exchanger dried under the above conditions in a stream of helium did not contain water. In the remaining cases, no data are quoted for the water content in the dried cation-exchange resins.

Some workers store the dried cation exchangers in a desiccator over P_2O_5 (sometimes in sealed tubes), while others proceed more correctly, drying the required amount of the cation exchanger directly before each experiment. It is noteworthy that, before introducing the sample into the reactor, it is desirable to test for soluble desulphonation products, which are formed during drying as a result of thermal hydrolysis or decomposition of the matrix[38]. For this purpose, it is sufficient to introduce approxi-

mately 200 mg of the resin into 5–10 ml of water, separate the liquid after stirring for 10 min, and titrate with 0.01 *N* hydrochloric acid using Methyl Orange; the amount of titrant used should not exceed 3–4 ml.

We believe that two-stage drying is the most effective and convenient method for routine work. Before drying *in vacuo*, it is desirable to separate the resin into fractions in order to isolate grains having a specified size and eliminate the fine particles, which increase the resistance of the resin to the flow of liquid.

It is desirable to fractionate the dehydrated resins by dry screening, which may be accelerated by means of a special apparatus[81] with an electric motor and an articulated transmission. A small amount of grains of similar size, suitable for accurate kinetic studies, can be obtained by using a Kapron [Russian nylon] brush to remove the grains caught in the mesh of each sieve. The authors of this review succeeded in obtaining by this procedure fairly homogeneous fractions of a carboxylic acid cation-exchange resin with grain sizes of 0.504 ± 0.021, 0.403 ± 0.016, and 0.262 ± 0.012 mm. In view of the possible inhomogeneity of the resins, the isolated fractions must be tested in terms of fundamental physicochemical properties.

Unfortunately, one should note that, even in modern studies on catalysis by ion exchangers, the catalysts employed are frequently not characterised in terms of their fundamental physicochemical parameters. Kinetic studies are thereby made almost completely valueless. The description of any ion exchanger used as the catalyst must include the characteristics of its thermal stability in the reaction mass, exchange capacity, and the coefficient of moisture absorption capacity. In kinetic studies on reactions occurring in the resin phase, it is also necessary to quote the partition coefficients of the reactant λ, to which the resin efficiency is related (see p. 505 in Polyanskii's review[2]). Methods for the determination of these parameters have been examined in Polyanskii's monograph[11] and in reviews[38,39]. In connection with recent studies, certain additional comments must be made concerning the partition coefficient.

According to Helfferich[82], this quantity is expressed in one of two ways:

$$\lambda' \equiv \bar{c}_i/c_i, \quad (1)$$

$$\lambda \equiv \bar{m}_i/m_i, \quad (2)$$

where c and m are respectively the molar and molal concentrations, $\bar{c}_i$ and $\bar{m}_i$ refer to the resin phase, $\bar{c}_i$ being expressed in terms of the number of moles of the given substance retained per unit volume of the swollen resin and $\bar{m}_i$ referring to the unit mass of the absorbed solvent. For reactions in aqueous solutions, $\bar{m}_i$ is found from the degree of sorption of the reacting substance by the resin and its water content. The concentrations of the substance in aqueous solution c_i and m_i have the corresponding significance.

It has been suggested[35] that the partition coefficient be defined as the ratio of the mass of the sorbate to the volume of the resin divided by the content of the same substance per unit volume of the solution. This definition is most convenient for the description of the partition of the reactants between resins and non-aqueous systems.

An approximate quantitative estimate of the partition coefficient is possible by means of the familiar relation

$$q = \lambda\bar{k}/k, \quad (3)$$

where q is the relative efficiency (see p. 1046 in Polyanskii's review[1]) and $\bar{k}$ and k are the rate constants for the reaction catalysed by ion exchangers and solutions of acids or bases respectively at the equivalent concentration of the catalyst ions. If $\bar{k} = k$, the efficiency of the resin may be inferred from the partition coefficient and conversely. Wolf[83], who suggested this principle, made the additional assumption that the active groups are present in the reaction volume (which was calculated from the exchange capacity and the weight of the resin sample) in the form of a 0.1 *N* solution. The efficiencies of three different Wofatits as catalysts of the hydrolysis of methyl acetate, ethyl acetate, and n-butyl acetate were calculated from the rate constants, measured in the presence of the resin and the equivalent amount of 0.1 *N* HCl, and are compared in Table 2 with the experimental partition coefficients of various substances which remain unchanged in the presence of Brønsted acids.

Table 2. The efficiencies of cation-exchange resins as catalysts of the hydrolysis of methyl acetate (q) and ethyl acetate (q') at 20°C and their comparison with the partition coefficients λ between ion-exchange resins and 2% solutions of certain organic substances[83].

System	q	q'	λ (C_6H_5OH)	λ (CH_3COOH)	λ (C_6H_6OH)	λ (n-C_3H_7OH)	λ (n-C_4H_9OH)
Wofatit	1.90	2.12	5.0	2.2	1.9	2.0	2.5
Wofatit P	2.44	3.17	19.6	4.3	2.2	2.2	3.0
Wofatit KPS × 8 KPS×8	1.31	1.48	3.3	1.2	1.5	1.5	1.3

Table 2 shows that there is an approximate correspondence between the resin efficiency and the partition coefficient of an indifferent substance with the same number of carbon atoms as in the ester whose hydrolysis is investigated. Similar relations have been observed in the hydrolysis of esters catalysed by macroporous ion exchangers[84]. It has been shown[84] that the partition coefficients of alcohols and ketones are almost independent of the overall porosity, but decrease rapidly with increase of the divinylbenzene content in the cation exchanger. Data concerning the effect of the degree of cross linking on the partition coefficient of 1-butanol and benzoic acid between their mixtures and the Dowex-50 W gel cation-exchange resin have been published[85].

In studies of vapour-phase processes, it is necessary to measure the sorption of vapours by ion exchangers. This problem is solved by means of the classical sorption technique based on the use of the McBain balance[86] and its modifications[30]. With macroporous resins, these methods yield the overall sorption due to adsorption and capillary condensation in the mesopores, the macropores remaining unfilled under these conditions.

On the other hand, in contact with non-solvating organic liquids, open pores of any size are completely filled, which has been used by one of the present authors and Gorbunov to determine the overall porosities of macroporous ion exchangers[87]. For this purpose, 200–300 mg of the resin dried at 120°C for 8 h was placed in a dry test tube and covered with anhydrous solvents. After 2 h, the pores were completely filled, after which the samples were transferred quantitatively to dry weighed polyethylene test tubes with holes in the bottom, closed by lids, and centrifuged: for 1 min at 130*g* in the case of n-heptane and iso-octane, and for 5 min at 1200*g* in the presence of other more viscous and less volatile liquids, for example

n-decane. The test tubes were then reweighed and the weight increment was divided by the density of the corresponding liquid at the experimental temperature and by the weight of the initial sample of the dry resin, the overall porosity being calculated in cm^3 per gram of the sorbent. The method described provides a simple experimental solution of the problem of the determination of porosity and yields more accurate results than the densimetric methods usually employed for this purpose[88]. As stated above, the overall porosity is an important characteristic of the catalytic properties of macroporous ion exchangers and must therefore be determined in kinetic studies.

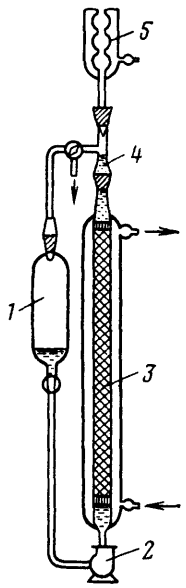


Figure 1. Apparatus for a catalytic process[32]: 1) collector; 2) metering micropump; 3) catalytic column; 4) packing; 5) reflux condenser.

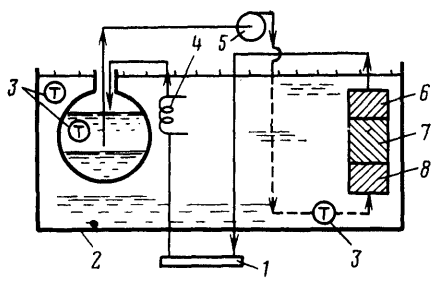


Figure 2. Reactor with circulation[35]: 1) polarimeter; 2) thermostat; 3) control devices; 4) heater; 5) pump; 6) glass beads or a weakly basic anion-exchange resin; 7) catalyst; 8) glass beads or a weakly acidic cation-exchange resin.

The reactions in the presence of ion exchanger catalysts are carried out in glass or metallic tubes (see pp. 81 and 82 in Polyanskii's monograph[11]), in reactors with mechanical[89] or pneumatic[90] stirring, and in various columns through which a stream of the test liquid is passed. In order to accelerate the reactions and the displacement of the equilibrium, one of the products, usually water, is removed, by separating its azeotrope with a suitable component of the reaction mixture[89] or a specially added indifferent solvent[91], for example toluene. The condensed reaction mixture is separated in a Dean–Stark trap, the organic layer being returned to the reactor. On the other hand, if the products must be separated by fractionation, the chemical reaction is carried out in an apparatus of the fractionating column type, which is filled above and below with glass packing and the resin is placed in the intervening gap. Chebotarev et al.[92] successfully carried out the hydrolysis of butyl butyrate on apparatus of this type using as the catalyst a sulphonated cation exchanger combined with a thermoplastic material and moulded in the shape of Raschig rings. Some investigators[93] recommend that a mixture of the resin and glass beads be introduced into the column in order to improve heat exchange.

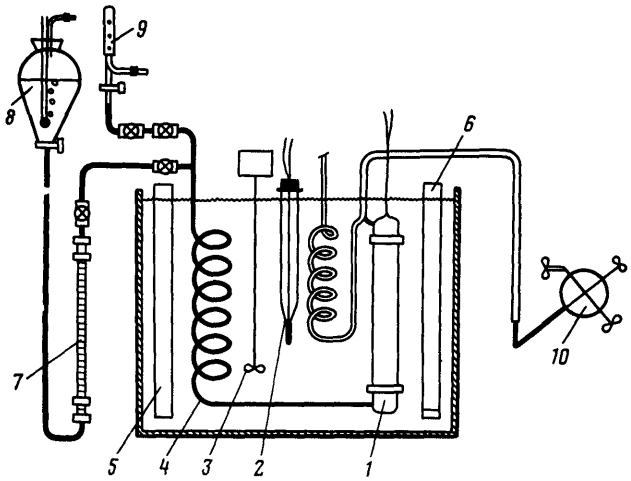


Figure 3. Apparatus with a tubular reactor[94]: 1) reactor; 2) thermoregulator; 3) stirrer; 4) evaporator; 5) and 6) heaters; 7) flow meter; 8) reservoir; 9) burette; 10) valve for the removal of gas.

All the above reactors are suitable for the investigation of kinetics, provided that conditions have been created in the system such that the reaction proceeds in the kinetic region, which is achieved by vigorous stirring or rapid circulation of the reactants in order to eliminate the effects of transport or film diffusion. Naturally such measurements are made with rigorous temperature control of the reaction volume and measurement of the temperature in the reactor itself.

Without going into details, Figs. 1–4 illustrate schematically several of the most interesting types of apparatus used to investigate the kinetics of liquid-phase[32,35] and vapour-phase[70,94] reactions. In the scheme shown in Fig. 2, provision is made for the continuous polarimetric monitoring of the reaction kinetics, while in the scheme illustrated in Fig. 3 the reaction kinetics are followed by a chromatographic method. Fig. 4 illustrates schematically a flow-type reactor with a membrane as the catalyst, which

combines the functions of a cell for the recording of infrared spectra. A reactor designed for the simultaneous investigation of reaction kinetics and the sorption of reactant vapour by the catalyst (from the increase in the length of a quartz coil) has been described[95].

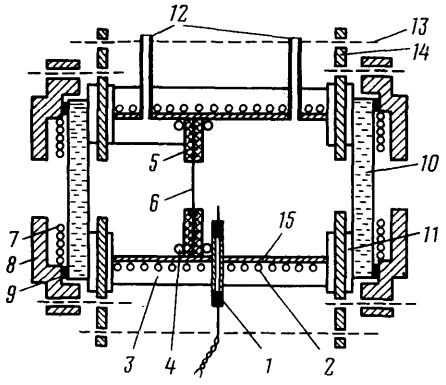


Figure 4. Flow-type cuvette for the investigation of dehydration[70]: 1) thermocouple; 2) heater; 3) insulation; 4) spring; 5) Teflon frame of the membrane; 6) catalytic membrane; 7) window heater; 8) brass window frame; 9) paper washer; 10) NaCl window; 11) silicone rubber seal; 12) tubes for the introduction and removal of solution; 13) supporting bolts; 14) stainless steel plates; 15) stainless steel shell.

The results of the study of the kinetics of different reactions will be examined in the next Section.

III. KINETICS OF REACTIONS CATALYSED BY ION-EXCHANGE RESINS

During the period under consideration, the kinetics of reactions catalysed by ion exchangers have been studied at a rate higher than for research in other fields. The extensive experimental data obtained confirmed the validity of the general treatment of reactions in the presence of resins, in which Polyanskii[11] and Helfferich[82] saw the features of both homogeneous and heterogeneous catalysis.

Reactions occurring throughout the bulk of the swollen resin grain can be legitimately regarded as homophase processes, since there is no interface between the reaction mass and the catalyst itself. The kinetics of such reactions (and sometimes also the nature of the product formed) depend on the composition of the reaction mass in the catalyst pores, which is in its turn determined by the partition coefficient of each component between the resin and the external solution [see pp. 504 and 505 in Polyanskii's review[2] and Eqn. (3) in the present paper].

It is important to find the partition coefficients over a wide range of concentrations of the reactants if a different analytical expression describes the sorption isotherm of each. The isotherms can be described by the Langmuir equation for some substances and by the Freundlich equation for others, while a third group can give rise to complex saddle-shaped curves[96]. In such cases the enhancement of the absorption of one substance by the resin influences the degrees of sorption of the other components of the reaction mixture, which in its turn affects the reaction rate.

The fruitfulness of the combined study of the sorption of the reaction components by resins and of the kinetics of the catalysed reaction has been strikingly demonstrated[97,98]. According to the data of Reikhsfel'd et al.,[97] the effective rate constants for the transesterification of ethyl acrylate by butyl alcohol in the presence of different cation-exchange resins show an excellent correlation with the degrees of sorption of butanol from real reaction mixtures. The rate of this (and the reverse) reaction depends on the concentration of the intermediate complex ROH_2^+ formed as a result of the interaction of the alcohol molecules with the cation exchanger counterions. Naturally, there is no correlation of this kind if the intermediate complex, formed by the given reaction component (for example ethyl acetate in the study of Reikhsfel'd et al.[97]), is not reactive.

The true rate constants k_{true} can be found from the sorbability by the resin of the component which forms a reactive complex and from the experimentally determined effective rate constants k_{eff}, using the relation

$$k_{eff} = k_{true}(\alpha_i^{rs} - \alpha_i^0), \qquad (4)$$

where α_i^{rs} is the sorbability of the above component calculated as the ratio of the number of moles of this substance in the catalyst phase to its overall amount in moles and α_i^0 is the sorbability of the same component in the inactive form, determined by extrapolating the linear function $k_{eff} = f(\alpha_i^{rs})$ to the abscissa axis. In contrast to k_{eff}, which increases steadily and appreciably with the sorbability of the component forming the reactive complex, k_{true} changes only slightly. The equilibrium constant depends on the sorbabilities of both components of the transesterification reaction; it can be easily calculated by means of the equation quoted by Reikhsfel'd et al.[98]

The difference between the compositions of the reaction mass in the resin phase and in solution is an important specific feature of catalysis by ion exchangers compared with homogeneous acid–base catalysis. A second characteristic of catalysis by ion exchangers, in terms of which it resembles heterogeneous catalysis, is that the reaction kinetics are frequently determined by adsorption processes. In such cases, the rate of reaction depends on the probability that the reactant molecules encounter fixed active centres. With increase in the concentration of the sorbed reactant, it rises initially, but reaches a limit as soon as all the active centres have been filled. This situation has been demonstrated, for example, in a study of the kinetics of the propylation of benzene in n-heptane on Amberlyst 15, the results being illustrated in Fig. 5 by a plot of the reaction rate against the concentration of the reactants. Evidently the behaviour of propene is described by the Langmuir–Hinshelwood model of an ideal adsorbed layer. The rate-limiting stage of the reaction is the electrophilic interaction of the chemisorbed propene with the benzene which has penetrated into the resin phase together with n-heptane. Since the concentrations of benzene in the inner and outer solutions vary in parallel, the rate of reaction increases continuously with increased concentration in the solution. The non-linearity of the curve describing the variation of the reaction rate with benzene concentration[29] indicates the inhibition of the reaction by n-heptane, which competes with the aromatic hydrocarbon in the swelling of the resin matrix.

The Langmuir–Hinshelwood model has been tested in studies of many other reactions catalysed by resins, for example esterification[99], transesterification[100], and

dehydration[101-104]. The authors of the above studies suggested that account be taken of the competition between the starting materials and reaction products for the active centres by introducing into the kinetic equations the adsorption equilibrium constant. For example, the kinetics of the vapour-phase dehydration of methanol and ethanol[101], in which two molecules sorbed on the active centres react, are described by the equation

$$r = \frac{k \cdot K_A^2 p_A^2}{(1 + K_A p_A + K_E p_E + K_W p_W)^2}, \qquad (5)$$

where k is the reaction rate constant (mole min^{-1} $mequiv.^{-1}$), K the adsorption equilibrium constant (atm^{-1}), p the partial pressure of the given component, and r the rate of reaction (mole min^{-1} $mequiv.^{-1}$) referred to the alcohol; the subscripts A, E, and W refer respectively to the alcohol, ester, and water. In solving equations of this type for liquid-phase reactions, it is recommended[103] that the concentrations of reactants be replaced by their activities in the condensed phase.

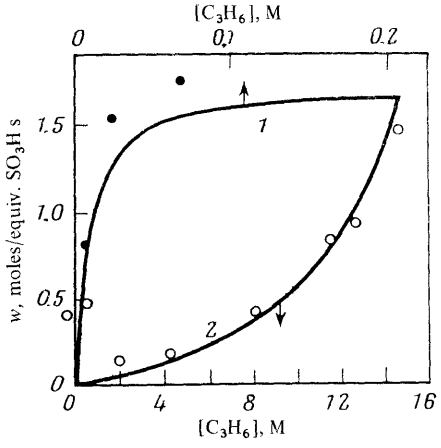


Figure 5. Variation of the rate of alkylation of benzene by propene with the concentrations of the components: 1) propene solution in benzene; 2) benzene–n-heptane mixture saturated with propene.

A possible cause of the inhomogeneity may also be the different states of hydration of the active groups within the bulk of each resin grain. This type of inhomogeneity, caused by the kinetics of the reaction under consideration, was taken into account by Heath and Gates[33] in terms of the "shrinking core" model which they proposed and used to account for the time variation of the efficiency of polystyrene cation exchangers with 8–12% DVB as catalysts of the dehydration of t-butyl alcohol. The anhydrous alcohol does not cause the swelling of the catalyst and the reaction, which begins only on the active surface centres, therefore proceeds very slowly (Fig. 6). Water, formed in the initial stage of the reaction, is partly transferred to the liquid phase and partly combines with the sulpho-groups via hydrogen bonds, causing swelling. This facilitates the transport of alcohol within the grain and accelerates the reaction. During the reaction, the boundary between the hydrated and non-hydrated zones in the grain is displaced inwards and, when each grain has been fully solvated, further absorption of water results in its binding to the active groups, which reduces the activity of the catalyst and hence the reaction rate. The duration of the induction period (see the left-hand branch of the curve in Fig. 6) increases appreciably with decrease of temperature and with increase of the resin grain size, owing to the influence of diffusional inhibition on the kinetics of the given reaction.

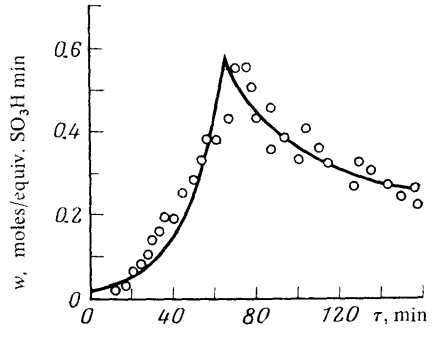


Figure 6. Kinetic curves for the dehydration of t-butyl alcohol.

The fact that the Langmuir–Hinshelwood model could be used to describe many reactions led to ion exchangers being considered as almost ideal catalysts with virtually equivalent active centres. Incidentally, other ideas have been frequently expressed in the literature, whose authors considered the inhomogeneity of the active groups in the steric[105], general chemical[106], and catalytic[43] sense of this term. We believe that this latter view corresponds more accurately to the present state of knowledge about the structure of ion-exchange resins[107], and the results of a direct experiment in which the non-equivalence of the active groups of Amberlyst 15 in the H-form was demonstrated by titrating it with a solution of n-butylamine in cyclohexane using Hammett indicators[108].

The third feature of catalysis by ion-exchange resins, in terms of which resins resemble non-ionogenic solid catalysts of gas- or liquid-phase processes, may be associated with the inhomogeneity of the active centres.

The role of diffusional inhibition, which constitutes a fourth feature of catalysis by ion-exchange resins, is manifested to a greater extent the larger the reactant molecules and the higher the degree of cross linking of the continuous-gel ion-exchange polymer[33,109-111]. Different workers have therefore used, in the kinetic description of catalytic reactions in the presence of ion-exchange resins, Boyd's theory of internal and external diffusion rate control (see pp. 27–30 in Polyanskii's review[11]) and the model of simultaneous diffusion and chemical reaction proposed by Wheeler and Thiele[33,35,112-114]. It is noteworthy that Boyd's theory was proposed for ion-exchange reactions and the Wheeler–Thiele model was designed for gas-phase reactions on the surfaces of solid catalysts. Nevertheless the mathematical apparatus associated with both concepts has been used successfully to investigate catalytic reactions on resins regardless of the phase state of the reactants.

One of the important features of the internal diffusion rate limitation is low activation energies, usually not exceeding 10 kcal mole^{-1}. Thus the activation energy for the hydrogenation of allyl alcohol is 3.4 kcal mole^{-1} [74] and that for the alkylation of phenol by trimeric propene [115] amounts to 9.4 kcal mole^{-1}. Such low activation energies in the presence of diffusional inhibition in no way indicate a high activity of the catalyst: reactions of this kind proceed at a moderate rate. The product of the activation energy and the rate constant for the chemical reaction, which has been called [56] the "power of activation" ("aktivierungsleistung"), is of more general importance as a measure of the activity of the ion exchanger catalyst; for unimolecular reactions, this quantity is expressed in kcal litre mole^{-1} s^{-1}. We believe that the product of the activation energy and the pre-exponential factor can serve as a criterion of catalyst activity.

Using the mathematical apparatus of the theory of absolute reaction rates, some workers [85,116] calculated the activation entropies from the activation energies and rate constants. It was shown that the entropy changes steadily, being a function of the degree of cross-linking of the resin and of the partition coefficients of the reactants between the solid and liquid phases.

The rate constants, expressed in the traditional way or their specific values referred to one milliequivalent of active groups of the ion-exchange resin, are usually employed as a direct characteristic of the reaction kinetics. In those cases where the rate constants do not remain invariant throughout the reaction owing to the influence of the blocking of the active groups or of a change in their solvation state, the kinetics are described by plots of the percentage conversion against time or by the usual kinetic curves.

The influence of various factors on the kinetics of reactions catalysed by ion exchangers has been examined in detail in Polyanskii's monograph [11] (pp. 37–62) and we shall therefore consider here only individual aspects of this problem.

The most important factors on which the reaction kinetics depend are usually thought to be the nature of the resin in a wide sense of this word, including the chemical structure of the matrix, the content of the cross-linking agent, the degree (or constant) of the electrolytic dissociation of the active groups, and the nature of the counterions. The catalytic activity of cation exchangers is correlated with their proton-donating capacity. For example, weakly acidic carboxylic acid cation exchangers hardly catalyse the Prins reaction between formaldehyde and styrene, while in the presence of sulphonated cation exchangers it does proceed [37]. Comparative data on the rates of dehydration of dimethylphenylmethanol and the transesterification of ethyl acetate by methanol in the presence of sulphonic and phosphonic acid cation-exchange resins have been published [102,117] and the considerable advantage of catalysts with strongly acidic active groups has been demonstrated. The activity of ion-exchange resins with active groups of the same type may differ markedly in the presence of matrices with different structures. For example, the KU-2 resin is less active in the dehydration of dimethylphenylmethanol than the sulphonated styrene–butadiene copolymer [117]. On the other hand, the condensation of phenol with acetone in aqueous alcoholic media [118] and the oxidation of ethylmethylphenylmethanol by hydrogen peroxide to a hydroperoxide [119] take place at a much higher rate in the presence of the KU-2 cation-exchange resin than in the presence of sulphophenol-formaldehyde resins with a dense structure of the three-dimensional network.

The problem of the effect of the degree of cross-linking on the reaction kinetics cannot be treated in isolation from the molecular size of the initial reactants and reaction products and sometimes also the degree of swelling of the catalyst on which the bulk-phase concentration of the active groups depends. If one of the components of the reaction mixture has large molecules, comparable to the diameter of the resin micropores, the rate of reaction usually decreases with increased content of the cross-linking agent in the matrix. Such relations have been established for the esterification of 1-butanol by benzoic acid [85], of pentyl alcohol by valeric acid, of isopentyl alcohol by isovaleric acid [52], and of propylene glycol by stearic acid [16], an increase in the degree of cross-linking having a particularly marked influence on the rate of formation of esters with the iso-structure [52]. In some cases even cation exchangers with a moderate DVB content (8%) do not catalyse the reaction, while in the presence of a lower degree of cross-linking it does proceed; such an example has been described in a study [50] devoted to the condensation of phenol with acetone.

If the molecular size of the reaction components is smaller than the size of the resin micropores, an increased degree of cross-linking does not enhance diffusional inhibition or steric hindrance to the formation of the active complex. The corresponding increase in the concentration of active groups or the decrease of the hydration number of the counterions [120], which become more accessible, as a result, to the reactant molecules, can then play the role of the factor accelerating the reaction with increase of the degree of cross linking. Such relations have been observed in studies on the kinetics of the decomposition of formic acid [78] and the dehydration of t-butyl alcohol [121]. However, one should note that Heath and Gates [33], who investigated a large assortment of catalysts in the same dehydration reaction, pointed out the non-monotonic variation of the rate with the degree of cross-linking: the cation exchanger containing 8% DVB proved to be the most active.

In the vapour-phase dehydration of isopropyl alcohol in the presence of homogeneous sulphonated cation-exchange membranes, the relative reaction rates depend on the partial vapour pressure of this substance diluted with nitrogen. At $p < 0.2$ atm, the membrane with 5% DVB was several times more efficient than the analogous catalyst with 2% of the cross-linking agent, but at $p \simeq 0.4$ atm the reaction rates were almost equalised. These differences have been accounted for [70] by a change in the reaction mechanism, but we believe it more likely that they are related to the state of solvation of the active groups.

Even in the presence of a high content of the cross-linking agent, macro-porous cation exchangers exhibit the same and sometimes even a higher catalytic activity [33,52,56] as weakly cross-linked ion-exchange polymers, but are much superior to the latter as regards chemical strength and osmotic stability. Fig. 7 presents the results of a comparative study of the efficiency of cation exchangers with 8% DVB and different porosities as catalysts of the dodecylation of phenol [56]. The porosity of the cation exchangers investigated is regulated by the introduction in the styrene–divinylbenzene copolymerisation stage of 20, 35, and 50% of petrol, which plays the role of an indifferent solvent. The alkylation kinetics in the presence of these catalysts are represented by curves *2*, *3*, and *4* in Fig. 7 respectively. The plots show that the activity of the macroporous ion exchangers falls with decrease in the amount of added indifferent solvent, since the porosity of the catalyst changes in the same direction. In conformity

with the general behaviour, the continuous-gel cation exchanger (curve *1* in Fig. 7) is the least efficient.

The rates of catalytic reactions are naturally influenced by the amount of ion exchanger, but the relations valid under these conditions are inconsistent with the general behaviour. For many reactions (apparently among those whose rate is limited by the chemical interaction step), for example, the esterification of ethyl acrylate[122], the hydrosilylation of unsaturated hydrocarbons[48], or the alkylation of phenols by benzyl alcohol[123], a linear relation has been established between the rate constant and the amount of catalyst. A linear relation between the logarithm of the rate constant and the amount of added catalyst has also been established for the esterification of benzoic acid by methanol[124], whose rate is limited by internal diffusion. An increase of the amount of anion exchanger from 15 to 30% in the aldol condensation of ketones with formaldehyde does not influence the rate of reaction[49]; this finding can be explained by the fact that the formation of hydroxyketones involves only a small proportion of the methylene component—its enolic form.

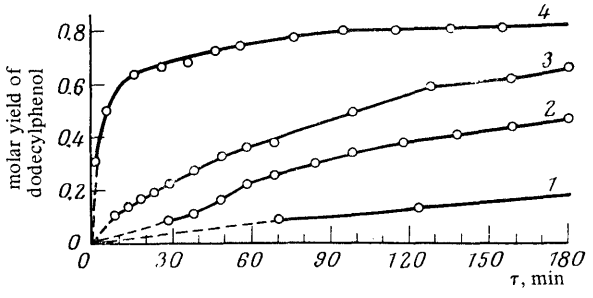


Figure 7. Kinetics of the dodecylation of phenol in the presence of gel (curve *1*) and macroporous (curves *2–4*) sulphonated cation-exchange resins; curves *2–4* correspond to macroporous resins obtained from a copolymer synthesised in the presence of 20, 35, and 50% of petrol respectively.

Since ion-exchange resins exhibit their catalytic functions via the counterions, the nature of the latter has a decisive influence on the reaction kinetics. It has been shown[121] that partial substitution of hydrogen atoms in sulpho-groups by alkali metal atoms leads to a decrease of not only general but also specific (i.e. referred to one milliequivalent of H^+ counterions) rate constants for the dehydration of t-butyl alcohol. The relative decrease of the reaction rate as a result of the substitution of H^+ by Na^+, K^+, or Rb^+ is the same, but in the mixed H–Li-form of the cation exchanger the effect is weaker. The above anomaly is explained by the fact that, in conformity with the laws of ion-exchange equilibrium, lithium substitutes a smaller number of protons in the most active groups than its electronic analogues, or by the involvement of the protons of the water molecules remaining in the cation exchanger after drying[93,121]. The study of the kinetics of the esterification of benzoic acid by 1-butanol led the authors[125] to the conclusion that, with increased degree of substitution of hydrogen ions in the sulphonated cation exchanger by alkali metal or alkaline earth metal cations, the ratio of the numerical partition coefficients changes appreciably and this affects the reaction kinetics, in conformity with Eqn. (3).

The substitution of hydrogen counterions can also lower the proton-donating activity of the sulpho-groups and can hinder the incorporation of the reactant in the three-dimensional polymer network; the change in the rate of propylation of benzene on Amberlyst 15 in accordance with a seventh-degree equation as a function of the fraction of hydrogen atoms converted into protons in relation to the overall content of counterions has been explained[29] by these effects. In reactions involving large molecules, the dependence of the rate constant on the degree of substitution of hydrogen counterions by other cations is influenced by the Thiele modulus, which is determined by the radius of the resin grain and the diffusion coefficient of the reacting substance[112]. Different kinetic relations correspond to different values of this modulus in the sucrose inversion reaction, the rate of which is controlled by internal diffusion.

The instances where the internal-diffusion limitation of the rates of reactions of large molecules and, in the case of a dense structure of the three-dimensional catalyst network, also of molecules of moderate size are fairly common in catalysis by ion exchangers. This cannot be said of external-diffusion rate limitation, since the reaction can be readily achieved in the kinetic region by increasing the rate of stirring of the reaction mixture under static conditions and the flow rates of the reactants under dynamic conditions.

The increase of the reaction rate with decrease of the catalyst grain size does not by itself demonstrate the presence of diffusional inhibition. For example, the rate of esterification of ethanol by propionic acid[126] increased with decrease of the catalyst grain size, but it was found that this was due to the inhomogeneity of the cation exchanger employed, the fine grains of which had a higher exchange capacity than the large grains. It is not therefore surprising that calculation of the specific rate constants referred to one milliequivalent of active catalyst groups yielded identical numerical values for three different fractions, showing that the reaction rate is limited by the chemical interaction step itself.

A reliable criterion of the presence of diffusional inhibition is the inverse proportionality between the reaction rate and the square of the grain radius for internal diffusion rate limitation and to the radius itself for external diffusion rate limitation. However, tests of these simple relations are frequently difficult because of the change in the size of the grains or in their physical state during the reaction itself. Thus a study of the kinetics of the esterification of stearic acid by propylene glycol[127] established for the first time the unexpected increase of the reaction rate with increase in the grain size of the KU-2 cation-exchange resin. It was found that the anomaly is due to the presence of a large number of accumulations of fine particles in the large-grain fraction, which become independent in the reaction mixture, where they act in accordance with their true size. On the other hand, if the aggregates of the cation exchanger grains are ground, screened, and redried, the normal relation is observed between the catalyst grain size and the reaction rate, corresponding to internal diffusion rate limitation.

The rate of formation of isobutene from t-butyl alcohol is higher the smaller the grain size up to the completion of the hydration of the Dowex-50W cation exchanger catalyst grains with the water produced, but, as dehydration proceeds, these differences are smoothed out, i.e. the diffusion-dependent rate limitation is replaced by chemical

rate limitation. All the foregoing considerations emphasise yet again the importance of taking into account and describing exactly the physical state of the ion-exchange resin catalysts employed.

The results of one correct series of experiments are presented in Table 3, which demonstrates the influence of the cation exchanger grain size, the method of drying the cation exchanger, and certain other factors on the kinetics of the esterification of salicylic acid by methanol[80]; analogous data for the inversion of sucrose have been published[79].

It follows from the data in Table 3 that the decrease in grain size, the elimination of water from the reaction mixture, and especially more thorough drying of the cation exchanger *in vacuo* lead to an increase of its catalytic activity. We shall consider in greater detail the last two factors. An increase of the activity of the cation exchanger catalyst with more thorough drying on raising the temperature has also been established in a study of the kinetics of the isomerisation of but-1-ene in the presence of the Na-Fe-form of Amberlyst 15.[43] The observed effects are very appreciable and are manifested by an almost twofold increase of the reaction rate constant with increase of the drying temperature of the resin from 75° to 150°C. In this reaction, they are caused by the more complete elimination of the water blocking the metal ions in the cation exchanger, which act as comparatively strong Lewis acids. The dehydration of the cation exchanger in the H-form in the above esterification reaction (Table 3) leads to the dissociation of the hydrogen bonds and increases the proton-donating activity of the sulpho-groups on formation of the intermediate complexes.

Table 3. The rate of esterification of salicylic acid (w = g h^{-1} per gram of cation-exchange resin) by methanol (M) in the presence of the Zeocarb-225 cation-exchange resin[80].

Grain size, mm	−0,5+0,25					−0,8+0,63	
H_2O in mixture with M, vol.%	2[a]	2	2[b]	0	0[c]	2	0
w	13.39	13.31	13.36	16.81	34.09	10.66	12.66

Note. The amounts of cation exchanger in cases *a* and *b* were 10 and 40 g respectively and in the remaining cases 20 g; the salicylic acid : cation exchanger ratio was 6.90 and 1.73 in cases *a* and *b* and 3.45 in the remaining cases; the cation-exchange resin was usually weighed in the thermostat; it was weighed *in vacuo* only in experiment *c*.

However, cases are also known where thorough drying leads to the loss of the cation exchanger's ability to catalyse the reaction[128]. One should always remember the possible influence of water on the kinetics of the reaction, and one must therefore control rigorously the conditions in the drying of the ion exchangers and follow the changes in their grains (comminution and the formation of cracks); without this, it is impossible to expect reproducible data for the rate of the process investigated.

The purity of the reactants and solvents employed is also of great importance: it has been shown in a study of the kinetics of the dehydration of t-butyl alcohol[33,101], the condensation of phenol with acetone[50], and the esterification of n-butyl alcohol by acetic acids[129] that admixtures of proton-acceptors (water and alcohols) greatly reduce the catalytic activity of cation-exchange resins in the H-form. Admixtures of substances with proton-donating activity should influence in the same way the kinetics of reactions proceeding via intermediate anionic complexes; in both cases, the mechanism of the action of the ingredients reduces to the blocking of the active catalyst centres.

The influence of indifferent solvents on the kinetics of reactions catalysed by ion exchangers has been very little investigated despite the importance of this problem. It is clear, however, that, together with a simple change of the rate of the main process (as in the esterification of benzoic acid by 1-butanol[89]), the addition of solvents may influence the nature of the products formed (as has been noted for the Prins reaction[37]) or can retard parallel reactions (as in the hydration of isoprene[130]). In the esterification of benzoic acid by 1-butanol in n-heptane, benzene, and toluene[89], the logarithm of the reaction rate constant is a linear function of the reciprocal of the dielectric constant. However, one should note that the experimental points exhibit a marked statistical scatter, which may be caused by errors in the estimation of the partition coefficients used for kinetic calculations by Eqn. (3). The influence of the partition of the components of the reaction mixture on the kinetics of the transesterification of ethyl acrylate by 1-butanol in the presence of the KU-2 cation-exchange resin can be inferred from the data of Soviet investigators[131], who established the inverse dependence of the rate constants on the sorbability of solvents whose electronegative atoms are linked by hydrogen bonds to the sulpho-groups of the catalyst, which entails a decrease of the activity of the latter. At the same time there is a possibility of the solvation of the intermediate cationic complex, which also influences the kinetics of the reaction investigated.

The rates of catalytic reactions in the presence of ion exchangers also depend on the size of the solvent molecules and the reacting substances, which determines in many respects the swellability of the catalyst and the possibility of utilising all the reaction centres in the bulk of its grains[109]. The corresponding relations are manifested most clearly in studies on homologues, for which a decrease in the rate constant with increased size of the reactant molecules in the hydrolysis of esters[36] and the oxidation of aliphatic acids by hydrogen peroxide[14] in the presence of cation exchanger catalysts has been established. It has been shown for the last reaction and esterification in the presence of the KU-2 cation-exchange resins that straight-chain molecules react faster than their isomers, since they penetrate more readily into the catalyst grains. Naturally, apart from steric factors, the reactivity of substances is influenced also by inductive factors[132], the main role being attributed to the latter for straight-chain molecules containing not more than five carbon atoms (on the basis of the satisfactory agreement between the experimental data and the familiar correlation equation). For acids with the iso-structure, the correlation is weakened owing to the increasing importance of the role of the steric factor; the same tendency should be observed with increase of molecular size. For a differential assessment of the above factors, it is desirable not to restrict the treatment to the application of methods of correlation analysis and to supplement them by measurements of the efficiency of ion-exchange resins, using Hammett's procedure[1], and of the partition coefficients of the reactants between the solid phase and the external solution. There is no doubt about the usefulness of this combined approach.

The kinetics of reactions in a stream of reactants flowing through a layer of ion-exchange resin depends on the flow rate as well as the factors enumerated above. The fundamental equations derived for ideal plug flow reactors are usually employed in a kinetic description of such reactions[133]. In the integral form, the kinetic equations are

$$k_{\mathrm{I}}\tau = \ln(1-x), \tag{6}$$

$$k_{\mathrm{II}}\tau = \frac{2.3\gamma}{\rho n_0(\gamma-1)} \lg \frac{1-x}{1-\gamma x}, \tag{7}$$

where x is the fractional conversion, k_{I} and k_{II} are the rate constants for first- and second-order reactions respectively, τ is the contact time, γ the molar ratio of the reactants in the second-order reaction, ρ the density of the reaction mass, and n_0 the initial number of moles of one reactant in the second-order reaction. Eqn. (6) describes very accurately the kinetics of the inversion of sucrose[112] and Eqn. (7) describes the kinetics of the alkylation of phenol by higher olefins[134] in the presence of sulphonated cation exchangers with a styrene–divinylbenzene matrix.

IV. A BRIEF DESCRIPTION OF THE APPLICATION OF VARIOUS ION-EXCHANGE RESINS AS CATALYSTS OF REACTIONS OF ORGANIC COMPOUNDS

1. Hydrolytic Reactions

The hydrolysis of esters of aliphatic acids and alcohols[36,83,84,92], sucrose[83,112,135,136], acetals[136,137], ϵ-caprolactone[138], and certain purine nucleosides[66] has been achieved in the presence of sulphonic acid and, in a few instances, phosphonic acid cation exchangers. Carboxylic acid cation exchangers have been shown to be highly specific catalysts of the hydrolysis of insulin[139]; a change in the length of the cross-linking agent molecule influenced the specificity of the action of these catalysts. Studies have been made on the kinetics of the hydrolysis of esters of aliphatic acids and aliphatic or aromatic alcohols[36,83,84] and of sucrose[136] in the presence of cation exchangers, the last report quoting the rate constants for inversion and the diffusion coefficients of the substrate in the sulphophenol-formaldehyde membrane used as the catalyst.

Highly basic anion-exchange resins proved to be effective catalysts of the hydrolysis of acrylonitrile[140] and nicotinonitrile[141]. Nicotinamide has been hydrolysed to nicotinic acid[141], which was sorbed by the catalyst, causing its deactivation. β-Cyanoethoxy-β-propylamide, formed via ethylene cyanohydrin, has been obtained from acrylonitrile instead of acrylamide, which is a product of the hydrolytic reaction in the presence of cation-exchange resins.

Catalytic hydrolysis of esters in the presence of sulphonic acid cation-exchange resins is of greatest promise for industrial applications; this reaction is virtually unaccompanied by side processes.

2. Hydration Reactions

Very few studies have been made on the use of ion exchangers as hydration catalysts. They were devoted to the hydration of 1,2-epoxybutane[142], olefins (propene[143] and isobutene[144]), and isoprene[130] in the presence of sulphonic acid cation-exchange resins and their aim was mainly preparative. In order to improve the conditions of contact of olefins with water and the KU-1 sulphonic acid cation-exchange resin catalysing the hydration reaction, Chaplits[145] and coworkers recommend that the reaction be carried out in the presence of an indifferent solvent. The hydration reactions of unsaturated hydrocarbons are accompanied by their polymerisation, which becomes more pronounced with increased concentration of the monomers in the mixture. In the presence of the carboxylic acid cation-exchange resin Amberlite IRC-84 acrolein and hydracrylaldehyde were hydrated[146]. The hydration of isobutene is used in industry as a method of selective extraction of this olefin[43] from butane–butene cracking fractions.

3. Dehydration Reactions

The dehydration of primary[77,93,94,101], secondary[69,70,147,148], tertiary[33,103,121,149], and dihydric alcohols[61] has been successfully achieved on sulphonic acid cation-exchange resins under comparatively mild conditions (as a rule at $t \leq 150^\circ$C), which rule out significant losses of capacity as a result of desulphonation. Under these conditions primary alcohols give rise to ethers only, while under more severe conditions olefins can be formed together with the ethers, tertiary alcohols yield only olefins, while secondary alcohols are dehydrated in both ways even at 100°C.[147] It has been shown for isopropyl alcohol that sulphuric acid does not catalyse its dehydration at 100°C. The dehydration of castor oil in the presence of the KU-2 cation-exchange resin has been achieved[150] at 180–230°C. Although the process conditions were much milder compared with earlier studies (see Polyanskii[11], p. 122), nevertheless one should note that a prolonged life of the cation-exchange resin cannot be expected under these conditions either, owing to its desulphonation. The more stable salt-forms with alkali metal counterions do not catalyse dehydration[93], but Amberlite-15 saturated with aluminium ions proved to be catalytically active[148].

In addition to the reactions involving the dehydration of alcohols to ethers and olefins, which frequently takes place simultaneously, there is a possibility of the polymerisation of unsaturated hydrocarbons to oligomers[69,117]. The dehydration itself can play the role of a side reaction in the esterification of dihydric alcohols. A cyclic acetal is formed from propylene glycol[151] and not the isomeric 2,4-dimethyldioxan, as suggested previously.

The dehydration of ethanol, which is of practical importance, can be carried out in the absence of parallel reactions and with a considerable displacement of the equilibrium (investigated by Hsu and Kabel[95]) to the right. The dehydration of dimethylphenylmethanol is believed to be irreversible[117]. The kinetics of these reactions have been described[33,70,93,95,121] and their mechanisms have been examined[69,93,121]. The dehydration of ethanol to diethyl ether and of t-butyl alcohol to isobutene is of interest for use on an industrial scale.

4. The Synthesis of Esters

Sulphonic acid cation-exchange resins are the most effective and most frequently used catalysts for the formation of esters from various compounds. The attempt to use phosphonic cation-exchange resins, even macroporous resins, has been unsuccessful[129]. The replacement of soluble acids by sulphonic acid cation exchangers as esterification catalysts sometimes reduces the reaction time[152]

or increases the yield of the desired product[153], apart from the usual advantages.

The main method for the synthesis of esters is esterification in the presence of sulphonic acid cation exchangers, which is achieved by interaction between (1) monohydric alcohols and aliphatic carboxylic[26,52,126,129,153-155], unsaturated[99,109,156], halogenocarboxylic[157], and aromatic acids[80,84,116,124] and (2) between dihydric alcohols and aliphatic monocarboxylic[16,127,158,159] and dicarboxylic acids[160]. In the latter case, the copolycondensation of diethylene glycol with various dibasic acids was carried out and, in order to accelerate the reaction and increase the molecular weight of the polyesters formed, it is recommended that it be performed in the presence of an excess of the alcohol in which the cation exchanger catalyst swells markedly. The favourable influence of the swelling of the cation exchanger in the alcohol on the rate of esterification of acetic acid by 1-butanol was demonstrated in another study[129]. The successful syntheses of esters with t-alkyl radicals and of phosphate esters in non-aqueous media[153,161] as well as the esterification of 20% aqueous solutions of acrylic and methacrylic acids[162] by methanol in the presence of hydroquinone as the polymerisation inhibitor merit particular mention.

In order to accelerate the esterification and displace the reaction equilibrium to the right, the reaction is frequently carried out in the presence of azeotrope-forming solvents, usually aliphatic or aromatic hydrocarbons[110,116]. This is unnecessary in transesterification[102], when anhydrides are made to react with alcohols[160], and when olefins[163] or the corresponding epoxy-derivatives[164] are made to react with acids.

In the presence of cation-exchange resins, there is a possibility of a wide variety of side reactions: dehydration of alcohols, polymerisation of the olefins formed, alkylation of solvents, and dehydration of esters. The kinetics of reactions uncomplicated by side processes have been examined in a number of investigations[89,100,102,124-126] and their mechanisms have been considered in two other studies[52,128].

The reactions between epichlorohydrins and carboxylic acids, leading to formation of monochlorohydrin esters[165] or polyepoxide ester [ether?] resins (see Polyanskii[11], p. 132), proceed via anionic intermediate complexes and are therefore accelerated by anion exchangers.

The synthesis of butyl acetate and other esters in the presence of cation exchangers and the esterification of aqueous solutions of acids are of interest for use on the industrial scale as a method for the utilisation and detoxication of industrial waste.

A continuous method for the manufacture of acrylate and methacrylate esters in the presence of the Dowex-50W cation-exchange resin has been described in a patent[166].

5. Alkylation Reactions

Only sulphonic acid cation-exchange resins are used as alkylation catalysts. Compared with aluminosilicates, they ensure an improved yield of the desired products[63]. In contrast to sulphuric acid, they do not cause the formation of sulphoesters and sulphones[167], are less complicated by side reactions involving the polymerisation of olefins and isomerisation[168] as well as transalkylation[167], and ensure the preferential formation of monoalkylphenols (see Polyanskii[2], p. 518). On kinetic grounds, some authors give preference to gel cation exchangers over macroporous cation-exchange resins[56,63,169], but one should bear in mind that pores absorb liquid having the same composition as tha in the external solution, which can increase the yield of dialkylphenols. Other conditions being equal, the nature of the alkylation products depends on the structure of the cation exchanger matrix[56,62,63,170] and reaction temperature[63].

The majority of studies have been devoted to the alkylation of phenols by alcohols[123,170-174], olefins[56,59,60,62,171,175-177], and cyclic dienes[168,175,178,179]. A few studies have been devoted to the alkylation of β-naphthol by olefins and other hydrocarbons[180], the alkylation of esters by olefins[169,181,182] and alkynes[183], the alkylation of aromatic amines by alcohols[184], and the alkylation of benzene by propene[29]. Apart from the side reactions enumerated above, the alkylation can be accompanied by dealkylation, the isomerisation of alkylphenols and alkyl phenyl ethers[171] as well as alkylating agents[172], and the cyclisation of alkenylphenols to coumarans[176]. In general, the consumption of reactants in side reactions is greater when the reactivity of the substance alkylated in the main reaction is lower. Certain side processes, for example polymerisation, can be reduced to a minimum by promoting the cation exchanger catalyst by sulphur-containing additives[171].

The results of the study of the kinetics of alkylation reactions have been published[29,123,134,185] and a mathematical description of the process has been given[186] whereby one can calculate the degree of conversion of the phenol and the temperature at any point in the reactor. The alkylation mechanism has also been examined[29,63,115,123,170,171].

The studies of Isagulyants and Belov ensured the wide scale industrial application of alkylation reactions in the presence of cation exchangers[167,171]. The alkylation is characterised by high heats of reaction[167,187] and the process is therefore carried out in a cascade of reactors, the heat released being removed in cooling units after each stage. The technological scheme of the alkylation process is described in Kharlambovich and Churkin's monograph[167].

6. Polymerisation and Isomerisation Reactions

Sulphonic acid cation exchangers and, in the case of substances with a high reactivity, phosphonic acid cation exchangers are used as catalysts for the polymerisation of aldehydes and unsaturated hydrocarbons to oligomeric products. This concerns the polymerisation of propene[108], α-methylstyrene[117], the trimerisation of acetaldehyde[188,189], and formaldehyde[190], and the copolymerisation of α-methylstyrene with α-olefins[191]. The polymerisation of dimethylcyclosiloxanes has been achieved in the presence of the macroporous KU-23 sulphonated cation-exchange resin[32]. A carboxylic acid cation exchanger, converted into a peracid, has been used as an initiator of the polymerisation of methyl methacrylate and in the copolymerisation of the same ester with styrene[192]. In the presence of highly basic anion-exchange resins in the Cl-form, obtained by the amination of the chloromethylated styrene–divinylbenzene copolymer by various tertiary amines, acrylamide was polymerised and the polymerisation kinetics were investigated[193]. The kinetics of other polymerisation reactions have also been described[189,192].

Sulphonated cation exchangers have been used as catalysts of the isomerisation of hydrocarbons[43,108,194,195] and of the Beckmann rearrangement of cyclohexanone oxime to caprolactam, the desired rearrangement product being obtained in the highest yield in dimethyl sulphoxide[196]. The isomerisation kinetics have been considered in detail[43,108,194].

The polymerisation and isomerisation reactions are sometimes not accompanied by the formation of side products[189], but they frequently accompany one another or other processes. Such complications occasionally give rise to a whole spectrum of products[195], the nature of which depends on the structure of the catalyst employed. A number of workers have examined the mechanisms of the polymerisation reactions[189,193] and of the isomerisation reactions[43,194].

The trimerisation of acetaldehyde has been carried out on an industrial scale; the polymerisation reactions of dimethylcyclosiloxanes and olefins, forming part of industrial cracking fractions, are promising in this respect.

7. Condensation Reactions

The majority of studies involving the use of ion exchangers as catalysts of condensation reactions had as their aim the preparative synthesis of particular substances. The condensation of 2-mercaptoethanol with hydrogen sulphide[197], of alcohols with phenols[23,198], mesityl oxide[57,199], trioxan[200], and aldehydes[65], of aldehydes with olefins[53,201-203] (the Prins reaction), dioxan derivatives[204], and α-chloromethylstyrene[205], of phenol with acetone[50,206]†, of polycyclic phenols with boric acid[207], of diols with unsaturated aldehydes[208], of tris(hydroxymethyl)ethane with furfural[209], of higher primary aliphatic amines with sulphur-containing dicarboxylic acids[210], of *o*-phenylenediamine with naphthoic or heterocyclic acids[211], and of *o*-aminophenols with monocarboxylic acids[212] has been achieved in the presence of sulphonated cation exchangers. Anion exchangers have been used as catalysts of the aldol condensation of aldehydes[24,111] and ketones[213] and also for the acceleration of the condensation reactions of ketones with aldehydes[49,214], of aldehydes with nitroalkanes[215] and urea[40,216], and of alcohols with acrylonitrile[217]. In the condensation of aldehydes with urea, a strongly basic anion exchanger is much more effective as a catalyst than a moderately basic resin, but this cannot be regarded as a general rule.

The yield of condensation products is frequently reduced by side reactions[20,24,50,111], which hinders the study of the kinetics of the corresponding reactions and shows that it would be unjustified to overestimate the selectivity of ion-exchange resin catalysts. The results of kinetic studies have been described[24,49,50,57] and the reaction mechanisms have been considered[49,217].

The synthesis of cyclic acetals in the presence of ion-exchange resins and, as far as the authors are aware, a method for the synthesis of bis(hydroxyphenyl)propane have been used on an industrial scale. Various types of the Prins reaction and continuous methods for the synthesis of aminoresins are promising for industrial applications[15].

8. Various Reactions

Many reactions, which do not belong to the types considered, are also carried out in the presence of ion-exchange resins. These include various addition reactions, including hydrogenation[49,73,74,218-221], which are carried out in the presence of cation and anion exchangers (containing complex platinum group metal chlorides as the mobile ions), the oxidation of a number of compounds [carboxylic acids[14,222,223], cyclohexanone[224], derivatives of phthalic anhydride[225] (sulphonated cation exchangers are used as oxidation catalysts)], and the decomposition of various aromatic alkyl derivatives of mono- and di-hydroperoxides[13,17,226-228] (also in the presence of sulphonated cation exchangers). It is noteworthy that highly cross-linked gel cation-exchange resins either do not catalyse the disproportionation of hydroperoxides or lose their activity rapidly[17]. The kinetics of these reactions have been investigated[227,228] and two studies have been devoted to the mechanism and kinetics of the oxidation reactions[14,132].

Methods for the decomposition of hydroperoxides and the synthesis of peracids are of interest for incorporation in industrial processes. Recent studies on the thiolysis of 1,3-dioxans are of theoretical interest[229,230].

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The new stage in the development of catalysis by ion-exchange resins considered in this review is characterised by a further improvement of the theoretical level of the relevant research as a result of the wide-scale employment of the kinetic approach. The extensive experimental data obtained reveal in the ion-exchange resin-catalysed reactions features of both homogeneous and heterogeneous catalysis.

Such a general treatment should stimulate the search for a new theoretical model of the catalytic reactions, which takes into account more fully all the aspects of the inter-relations between the ion exchangers and the reacting substances than the Langmuir–Hinshelwood and Wheeler–Thiele models employed at the present time. The necessary preparation for this advance should be ensured by a further development of kinetic studies on a wider basis: this concerns a systematic (and not sporadic, as hitherto) measurement of the partition coefficients and the refinement of their relation to the efficiency of ion-exchange resins using Hammett's method, the study of the influence of the type of solvent on the reaction kinetics, and the regular employment of methods of correlation analysis.

In connection with new theoretical tasks, it is necessary to give more attention to methods for the preparative treatment and investigation of ion-exchange resins as catalysts, in particular it is necessary to justify in greater detail the usefulness of conditioning and to make appropriate recommendations, to elucidate the causes of blocking and to develop regeneration methods, and to synthesise new types of ion exchangers with improved osmotic and thermal stabilities.

While noting the major achievements in catalysis by ion-exchange resins as a method of preparative organic chemistry, one should nevertheless mention the insufficiently wide-scale employment of macroporous, macronetwork, and oleophilic ion-exchange resins. The salt-forms of all resins and the hydroxide-forms of anion-exchange resins have been little used.

Certain advances have been made in the incorporation of ion-exchange resins in industrial processes, but they have still not reached the limit of the existing possibilities.

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While the manuscript was with the Editors, a number of studies devoted to the kinetics of esterification and transesterification[231-234], hydrolysis[235], oxidation[236,237], condensation[238], and alcoholysis[239], catalysed by ion-exchange resins, were published.

† The catalyst is promoted by the addition of 2,2-dimethylthiazolidine.

A series of new studies were devoted to the use of ion exchangers as catalysts of esterification[240-242], hydrolysis[243,244], polymerisation[245,246], condensation[247-251], decomposition[252,253], and alkylation[254-262]. An interesting example of the employment of the catalytic properties of ion-exchange resins for the purification of bisphenols and hydroquinone has been described[263]. A few studies have been devoted to the application in catalysis of cation exchangers[264-266] and anion exchangers[266-269] metallised by Group VIII *d* elements or containing complex transition metal ions as counterions. The use of sulphonated polystyrene on a support consisting of aluminium sheets as a catalyst in a gas–liquid system has been described[270].

The mechanism of the blocking of the catalyst in the hydration of epoxyethane has been considered[271].

Rapid methods for the determination of the properties of ion-exchange resins, which are important for the understanding of their catalytic functions (exchange capacity, total porosity, and ionisation constants), have been described[272-274]. The paper by Polyanskii et al.[275] is devoted to the problem of the inhomogeneity of macroporous ion exchangers and its importance for catalysis, which has not so far been considered in the literature.

A monograph[276] deals with research techniques for ion-exchange resins.

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